Electro Chemistry

Part - I

Electrolytic Cells.

Electrical energy converts in to chemical energy

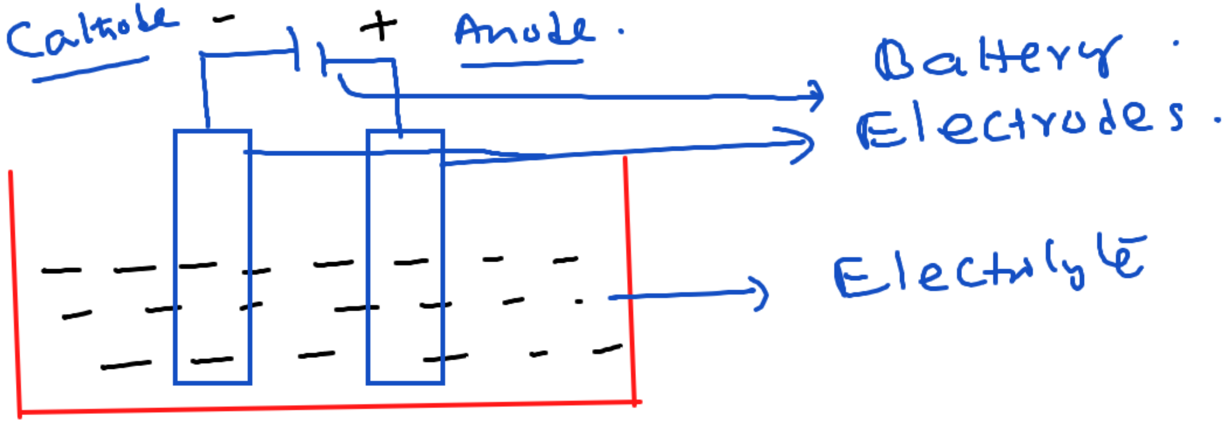
Part - II

Electro chemical cell.

Chemical energy converts in to Electrical energy.

Electrolytic Cells

In this cell E.E converts into C.E.



Conductors

"allows Electricity"

Electronic/metallic Conductors

- Conductivity due to free $\bar{e}$
- matter flow does not takes place.
- Conductivity $\propto 1/\text{Temp}$
- No Chemical Change

ex: metals

Electrolytic Conductors

- free ions.
- flow of matter takes place.
- Conductivity $\propto$ Temp.
- Chemical change occur.

Ex: water.

Electrolytes .

Ions $\propto$ conductivity

Strong Electrolytes

α is more $> 70\%$.

stong acids :-

$HClO_4$ HCl, H_2SO_4 HNO_3 etc

Stong Bases :

$NaOH$, KOH

Salt (SA+SB):- Na_2SO_4 $NaCl$ KBr

Weak Electrolytes

$\alpha < 30\%$

Weak acid.

CH_3COOH, $HCOOH$

weak Bases.

$Ca(OH)_2$

$Al(OH)_2$

Non- Electrolytes .

No Ions .

Glucose

fructose

Sucrose

urea .

Electrodes

Anode

+ve.

1. oxidation Takes place
2. Loosing of e^-

Cathode.

−ve.

1. Reduction Takes place.
2. Gaining of e^-.

Electrodes

Active Electrodes

Electrodes participates in Reactions

Ex: Cu.

Inert electrodes

Electrodes not participates in Reactions

Ex: Pt.

Electrolysis:-

"The Decomposition of electrolytes by passing electricity in its aqueos State (or). molten State called Electrolysis."

has Ions. conductors { aq^{d} NaOH. ⇒ NaOH + water.
molten NaOH ⇒ NaOH$_{(l)}$.

NaOH$_{(solid)}$ ⇒ Insulator - no Ions.

NEET

Cell Condition

$\Delta G > 0$ $\Delta G = +ve$

$E < 0$ $E_{cell} = -ve$

anode (+) :- anion will Reaches.

Oxidation Takes place.

loosing of $\bar{e}$s.

Order for Oxidation potential :-

$$NO_3^- < \overset{\checkmark}{SO_4^{-2}} < \underline{OH^-} < F^- < \underline{Cl^-} < Br^- < I^-$$

Cathode (–) :- 1. Cations are Reaches.

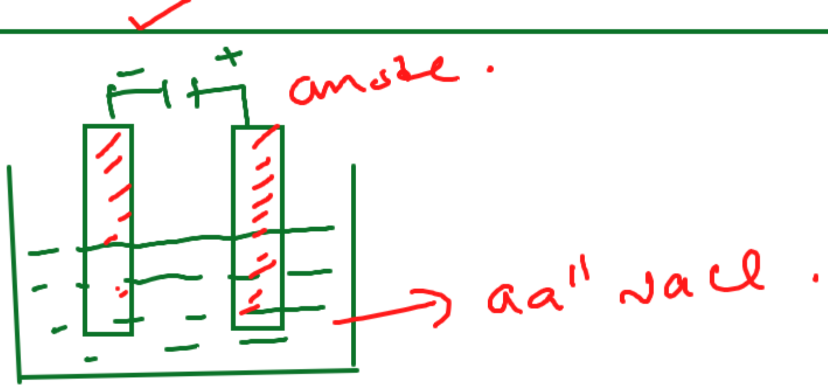
2. Reduction takes place.

3. Gaining of e^-

Order of Reduction Potential :-

$Li^+ < K^+ < Ca^{+2} < \underline{Na^+} < mg^{+2} < Al^{+3} < Zn^{+2} < Fe^{+2}$

$< \underline{\underline{H^+}} < Cu^{+2} < Fe^{+3} < Ag^+ < Pt^{+2} < Au^{+3}$.



$NaCl \rightarrow Na^+ + Cl^-$

$H_2O \rightarrow OH^- + H^+$

anode (+) :- anions Reached

Oxidation

$Cl^- > OH^-$

$2Cl^- + 2e^- \longrightarrow \underline{\underline{Cl_2 \uparrow}}$

Cathode :- (−) Cations Reached.

Reduction

$Na^+ < H^+$.

$2H^+ \longrightarrow H_2 \uparrow + 2e^-$.

anode: $Cl_2 \uparrow$

Cathode: $H_2 \uparrow$.

$OH^{\ominus}$

$4OH^- \rightarrow 2H_2O + 4e^- + \boxed{O_2}\uparrow$

② Electrolysis of Na_2SO_4

anode: (+)

(Oxidation)

[Loosing of e^-]

● $OH^- > SO_4^{-2}$.

$4OH^- \rightarrow 2H_2O + 4e^- + \boxed{O_2}$.

Na^+ SO_4^{-2}

H^+ OH^-

Cathode: − (−).

(Reduction)

[gaining of e^-]

$Na^+ < H^+$

$2H^+ + 2e^- \rightarrow H_2\uparrow$.

aq'' $AgNO_3$ Electrolysis

anode :- (+)

$NO_3^- < OH^-$

$4OH^- \longrightarrow 2H_2O + 4e^- + O_2\uparrow$

Cathode (−).

$Ag^+ > H^+$.

$Ag^+ + 1e^- \rightarrow Ag\downarrow$

anode : O_2.

Cathode :- Ag.

aq'' NaOH Electrolysis.

anode (+)

OH^-

$4OH^- \rightarrow 2H_2O + 4e^- + O_2$

Cathode (−).

$Na^+ < H^+$.

$2H^+ + 2e^- \rightarrow H_2\uparrow$

anode :- O_2

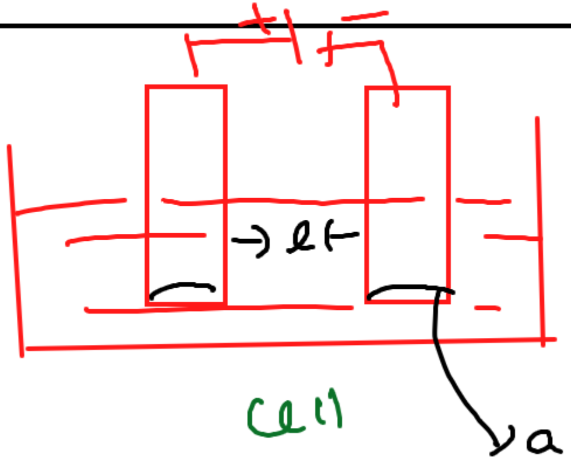
Cathode :- H_2

Conductance :- (C). Opposite to Resistance.
allows the Electricity.

$C = 1/R$. Ohm^{-1} Ω^{-1} mho siemen.

Resistance: (R) :- Opposite to Conductance.
Stop the Electricity.

$R = \frac{1}{C}$ Ohm | Ω (omega).



l = length b/w two electrode (cm).

a = cross sectional area. (cm²)

"The Ratio b/w l & a Called cell constant

$$\text{cell constant} = \frac{l}{a} = \frac{cm}{cm^2} = cm^{-1}$$

(cm)

m^{-1}.

Ohm's law :-

$R \propto l$ —①

$R \propto 1/a$ —②

Resistivity (or) Specific Resistance.

$$R \propto \frac{l}{a}$$

$$R = \rho \cdot l/a$$

$$\rho = \frac{R}{(l/a)} = \frac{\text{Resistance}}{\text{Cell constant}}$$

$$\text{Units} = \frac{\text{ohm}}{\text{cm}^{-1}} = \text{Ohm cm.}$$

$$= \underline{\text{Ohm m.}}$$

$$\rho = \frac{R}{(l/a)}$$

$$\frac{1}{\rho} = \frac{1}{R} \times (l/a)$$

Conductivity. $K = C \times l/a$.

(or) Specific Conductance = Conductance × cell const.

$\Omega^{-1}\ cm^{-1}$ mho cm^{-1}.

$ohm^{-1}\ cm^{-1}$ $S\ cm^{-1}$.

Specific Conductance:- (κ) kappa.

"The sum of conductance of all ions present in specific area in electrolytes" called specific conductance.

$$\boxed{\kappa = C \times l/a}$$

Units = $Ohm^{-1}\, cm^{-1}$ $\qquad \mho\, cm^{-1}$

$mho\, cm^{-1}$

$S\, cm^{-1}$

Equivalent Conductance :- λ (or) Λ (Lamda)

"The Sum of all ions Conductance present in one Equivalent Electrolyte"

$$\lambda^{eq} = \frac{\text{Sp-conductance} \times 1000}{\text{Normality}}$$

$$\boxed{\lambda^{eq} = \frac{K \times 1000}{N}}$$

$$\frac{ohm^{-1}\,cm^{-1} \times}{\frac{gream}{cm^{3}}} = ohm^{-1}\,cm^{2}\,gream^{-1}$$

$$= ohm^{-1}\,m^{2}\,gream^{-1}.$$

molar conductance :-

"The Sum of conductance of all ions present in 1mole Electrolytes" called molar Conductane.

$$\lambda^m = \frac{\text{Sp. conductanc} \times 1000}{\text{molarity}}$$

$$\boxed{\lambda^m = \frac{K \times 1000}{m.}}$$

$Ohm^{-1}\ cm^{2}\ mole^{-1}$

$Ohm^{-1}\ cm^{2}\ mole^{-1}.$

Electrochemistry

$C = 1/R$

$R = 1/C$

$\rho = R/(l/a)$

$K = C \times l/a$

$\lambda^{ea} = \frac{K \times 1000}{\text{Normality}}$

$\lambda^{m} = \frac{K \times 1000}{\text{molarity}}$

K = Specific Conductance.

λ^{ea} = ea" Conductance

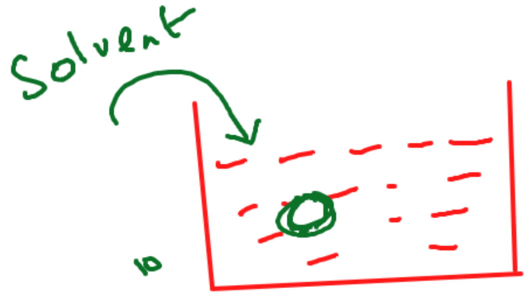
λ^{m} = molar conductance.

l/a = cell const

R = Resistance

C = conductance

ρ = Specific Resistance.



Dilution

Conductivity $\propto$ no. of ions.

Up on Dilution Total ions increases.

but a particular area ions decreases.

NEET:- Up on Dilution

Specific Conductance (K) :- ↓es

eq. Conductance (Λ_{eq}) :- ↑es

molar Conductance (Λ_m) :- ↑es.

Conductivity of a cell is 2 $\Omega^{-1}\,cm^{-1}$, So Calculate Equivalent conductance & molar conductance of 0.1 M H_2SO_4 Electrolyte is —?

$K = 2$

$M = 0.1$ molar

$N = n\,factor \times M$

$= 0.2$ molar

$$\lambda_m = \frac{K \times 1000}{M} = \frac{2 \times 1000}{0.1} = 2 \times 10^4$$

$$\lambda_{eq} = \frac{K \times 1000}{N} = \frac{\cancel{2} \times 1000}{0.\cancel{2}} = 10^4$$

0.02 M $Ca(OH)_2$ eq conductance $5\times10^{-3}\ \Omega^{-1}\,cm^{2}\,geq^{-1}$.

So its sp-conductance is.

$Ca(OH)_2 = n = 2$

$N = 2\times0.2$

$= 0.40$

$$\lambda^{eq} = \frac{K\times1000}{N}$$

$$K = \frac{\lambda eq\times N}{1000} = \frac{5\times10^{-3}\times 0.4}{1000} = 2\times10^{-6}$$

the distance b/w two electrodes are 10^{-2} cm.

Resistance is $\underline{20\ \Omega}$ so calculate specific conductance!

C cross sectional area is = 10^{-4} cm^2).

$K = C \times l/a.$

$K = \frac{1}{R} \times \text{cell const } (l/a).$

$$K = \frac{1}{20} \times \left(\frac{10^{-2}}{10^{-4}}\right) = \frac{1}{20} \times 10^{2} = 0.5 \times 10 = \underline{\underline{5}}.$$

$\Omega^{-1}\,\text{cm}^{-1}.$

Ex

$n=1$

λ_m NaOH $= 10^{-2}$

λ_{eq} NaOH $= ?$

$$\lambda_{eq} = \frac{\lambda_m}{n} = \frac{10^{-2}}{1} = \underline{\underline{10^{-2}}}$$

Ex $n=2$

λ_m $Ca(OH)_2 = 10^{-2}$

λ_{eq} $Ca(OH)_2 = ?$

$$\lambda_{eq} = \lambda_m / n$$
$$= 10^{-2}/2$$
$$= \underline{\underline{5\times10^{-3}}}$$

$$\frac{\lambda_{eq}}{\lambda_m} = \frac{\frac{K\times1000}{N}}{\frac{K\times1000}{M}}$$

$$\boxed{\frac{\lambda_{eq}}{\lambda_m} = \frac{M}{N}}$$

$$\boxed{\frac{\lambda_{eq}}{\lambda_m} = 1/n}$$

Ex $n=2$

λ_{eq} $H_2SO_4 = 10^{-2}$

λ_m $H_2SO_4 =$

$$\lambda_m = n\cdot\lambda_{eq}$$
$$= 2\times10^{-2}$$

$n=1.$

λ_{eq} $HNO_3 = 10^{-4}$

λ_m $HNO_3 = ?$

$$\lambda_m = n\times\lambda_{eq}$$
$$= \underline{\underline{10^{-4}}}$$

Faraday laws

1st of Faraday

product Deposited at electrode.

$W \propto Q$

$W = ZQ$

$W = Z \times C \times t$

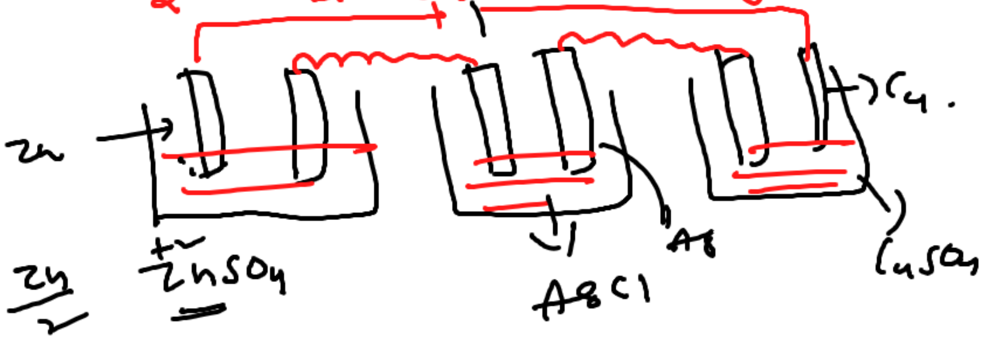
W = deposited mass

Z = Electro Chemical Equivalent

Q = charge
= C × t
= current × time.

C = amp
t = sec.

2nd law of Faraday



$\boxed{W \propto E}$

$W_1 : W_2 : W_3 = E_1 : E_2 : E_3.$

$= M/n_1 : M/n_2 : M/n_3.$

1mole = 1 GMW.

1 Faraday = 1 GEW.

$\underline{\underline{27}}$ g of Al = 1mole.

9g of Al = 1 Faraday.

27 g of Al = 3 Faraday.

* $Fe^{+2} \longrightarrow Fe^{+3} + 1e^-$

"1 F" Required.

$\boxed{1F = 96500 \text{ Columbs}}$

* $\overset{+7}{KMnO_4} \longrightarrow \overset{+4}{MnO_2}$

3F required

(3×96500 = 289500 columb.

* $\overset{+6}{Cr_2}\overset{-2}{O_7} \longrightarrow 2Cr^{+3}$.

3F requird. (for 1Cr)

6F requid (for 2Cr).

$\underline{\underline{\text{eg}}}$ · 2F of Oxygen = $\underline{\underline{16}}$ $\underline{\underline{g}}$

1F = 8 grams

Combined Eq^n

From Faraday 1st & 2nd law.

NEET.

$$Z = E/F. \quad — ①$$

F ① law

$$W = Z \cdot Q \quad — ②$$

① Sub^n in ②

$$W = \frac{E}{F} \cdot Q.$$

$$Q = Ct$$

$$W = \frac{E\,Ct}{F}$$

$$E = \text{Eq}^n\ \text{wt} = m/n.$$

$$\boxed{W = \frac{mCt}{nF}}$$

W = deposited mass
m = molar mass
n = charge
C = current in amp.
t = time in sec.
F =

Ex A Solution of $\overset{+2}{Cu}\overset{-2}{SO_4}$ is electrolysed for 10min with a Current 1.5 amp. What is the mass of Copper deposited at Cathode is ——

$m_{Cu^{+2}} = 63.$

$n = 2$

$c = 1.5\ \text{amp.}$

$t = 10\ \text{min}$

$= 10 \times 60\ \text{sec.}$

$$W = \frac{Mct}{nF}.$$

$$W = \frac{63 \times 1.5 \times \overset{5}{\cancel{10}} \times 60}{\cancel{2} \times F} = \frac{28350}{F}$$

$$W = \frac{2835}{96500} = \underline{\underline{0.029}}$$

A Solution of $CuSO_4$ is Elecrolysed for half an hour with a Current 6 amp. So mass of Copper deposited?

$t = 30\,\text{min} = 30 \times 60\ \text{sec}$

$c = 6$

$M_{Cu} = 63$

$n = 2$

$$w = \frac{MCt}{nF} = \frac{63 \times \overset{3}{\cancel{6}} \times 30 \times 60}{\cancel{2} \times F}$$

$$= \frac{340200}{F} = \frac{340200}{96500}$$

$$w = 3.52\ \text{grams}$$

*n What is the weight of $\underline{\underline{Al}}$ deposited by a current of 965 amp for 10 sec —

$\underline{\underline{Al^{+3}}}$

$$W = \frac{MCt}{nF} = \frac{27 \times \cancel{965} \times 10}{3 \times \underset{100}{\cancel{96500}}}$$

$$= \frac{27}{30} = \underline{0.99}.$$

a) 2.99

b) 0.99

c) 3.99

d) 0.55

When same Quantity of Current is passed through $CuSO_4$, $AgNO_3$. If 3.175 gm of Cu is deposited what is the "Ag" deposited. weight!

$M_{Cu} = 63$ $W_{Cu} = \underline{\underline{3.175}}\ g.$

$M_{Ag} = 108.$ $W_{Ag} = ?$

$E^{+2}_{Cu} = \frac{63}{2} = 31.5$

$E^{+}_{Ag} = \frac{108}{1} = 108$

$$\frac{W_{Cu}}{W_{Ag}} = \frac{E_{Cu}}{E_{Ag}}.$$

$$\frac{3.175}{W_{Ag}} = \frac{31.5}{108}.$$

$$W_{Ag} = \frac{\overset{0.1}{\cancel{3.175}} \times 108}{\cancel{31.5}} = \underline{\underline{10.8g}}$$

a) 9.8 g

~~b)~~ 10.8 g

c) 11.8 g

d) 12.8 g.

Electro Chemistry

Kohlrauschls Law :- $y = c - mx$.

NEET pyq Ea''

$$\boxed{\lambda_m = \lambda_m^{0} - K\sqrt{c}}$$

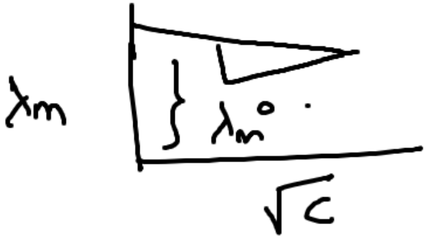
1. $y = -mx + c$

negative slope.

intercept = c.

Graphs

λ_m vs $\sqrt{c}$.



slope = K.

" The Limitining molar conductance of a Electrolyte is equals to Sum of molar conductance of anion and cation called Kohlrasuch's law"

$${}^{\infty}_{m}\lambda_{\underline{\underline{AB}}} = {}^{\infty}_{m}\lambda_{A^{+}} + {}^{\infty}_{m}\lambda_{B^{-}}$$

$${}^{\infty}_{m}\lambda_{\underline{CH_3COOH}} = {}^{\infty}_{m}\lambda_{CH_3COO^{-}} + {}^{\infty}_{m}\lambda_{H^{+}}$$

$${}^{\infty}_{m}\lambda_{NH_4OH} = {}^{\infty}_{m}\lambda_{NH_4^{\oplus}} + {}^{\infty}_{m}\lambda_{OH^{\ominus}}$$

$$ {}_{m}\lambda^{\infty}_{\underline{A}B_2} = 1 \cdot {}_{m}\lambda^{\infty}_{A^{+2}} + 2 \cdot {}_{m}\lambda^{\infty}_{B^{+1}} $$

$$ \lambda_{A_2B_3} = 2\,{}_{m}\lambda^{\infty}_{A^{+3}} + 3\,{}_{m}\lambda^{\infty}_{B^{+2}} $$

$$ {}^{\infty}\lambda^{e\omega}_{AB_2} = {}^{\infty}\lambda^{e\omega}_{A^{+2}} + {}^{\infty}\lambda^{e\omega.}_{\bar{B}^{2}} $$

$$ \lambda_{A_2B_3} = {}_{\infty}\lambda^{e\omega}_{A} + {}_{\infty}\lambda^{e\omega.}_{B}. $$

Applications:-

① To Determine weak Electrolyte molar conductance by using Strong Electrolyte

NEET

$$\lambda_{CH_3COOH} = {}_m\lambda^\infty_{CH_3COO^\ominus} + {}_m\lambda^\infty_{H^\oplus}$$

$$= \underbrace{{}_m\lambda^\infty_{CH_3COO^\ominus} + {}_m\lambda^\infty_{Na^\oplus}} + \underbrace{{}_m\lambda^\infty_{H^\oplus} + {}_m\lambda^\infty_{Cl^\ominus}} \underbrace{- {}_m\lambda^\infty_{Na^+} - {}_m\lambda^\infty_{Cl^-}}$$

$$\lambda_{CH_3COOH} = {}_m\lambda^\infty_{\underline{CH_3COONa}} + {}_m\lambda^\infty_{\underline{HCl}} - {}_m\lambda^\infty_{\underline{\underline{NaCl}}}$$

Ex :-

$${}_m\lambda^{\infty}_{CH_3COONa} = 190 \quad S\,cm^2\,mol^{-1}$$

$${}_m\lambda^{\infty}_{NaCl} = 90 \qquad "$$

$${}_m\lambda^{\infty}_{HCl} = 20 \qquad "$$

$${}_m\lambda^{\infty}_{CH_3COOH} = ? \qquad 190+20-90 = \underline{\underline{120}} \quad S\,cm^2\,mol^{-1}$$

20

$\lambda_{NH_4Cl} = x$

$\lambda_{NaOH} = y$

$\lambda_{NaCl} = z$

$\lambda_{NH_4OH} = ?$

$\lambda^{+}_{NH_4} + \lambda_{OH^{\ominus}}$.

$\lambda_{NH_4Cl} + \lambda_{NaOH} - \lambda_{NaCl}$.

$\underline{\underline{x + y - z}}$.

a) $x + y + z$

[✓ b) $x + y - z$]

c) $x + 2 - y$

d) $x - y - z$

③ $\overset{\infty}{\lambda}_{HCOOH} = ?$

$\overset{\infty}{\lambda}_{CH_3COONa} = 120 \ S\,cm^2\,mol^{-1}$

$\overset{\infty}{\lambda}_{NaCl} = 80 \ S\,cm^2\,mol^{-1}$

$\overset{\infty}{\lambda}_{HCl} = 40 \ S\,cm^2\,mol^{-1}$

$$\lambda_{CH_3COOH} = \lambda_{CH_3COONa} + \lambda_{HCl} - \lambda_{NaCl}$$

$$= 120 + 40 - 80 = \underline{\underline{80}}.$$

49

$\lambda\, CH_3COOH = {}_{\infty}\lambda\, CH_3COOK + {}_{\infty}\lambda\, H_2SO_4 - {}_{\infty}\lambda\, K_2SO_4 .$

(2) To Determine Degree of dissociation (α) of Weak Electrolytes:-

$$\alpha = \frac{{}_m\Lambda_c}{{}_m\Lambda_0}$$

$$\alpha = \frac{{}_m\Lambda_c}{{}_m\Lambda^\infty}$$

${}_m\Lambda_c$ = molar conductance at concentration "C"

Λ_0 = molar conductance. at zero concⁿ.

Λ_∞ = molar conductance at "∞" Dilution.

molar conductance of CH_3COOH at 0.1M concn is 180 $ohm^{-1}\ cm^2\ mol^{-1}$ and at infinity dilution is 360 $ohm^{-1}\ cm^2\ mol^{-1}$ so its degree of dissociation is?

$${}_m\lambda_c = 180.$$

$${}_m\lambda_\infty = 360$$

$$\alpha = \frac{{}^m\lambda_c}{{}^m\Lambda_\infty} = \frac{180}{360} = 0.5$$

50% acetic acid ionised.

$_m\lambda_c = 240 \cdot \text{Ohm}^{-1}\,\text{cm}^2\,\text{mole}^{-1}$ for NH_4OH so its.

$_m\lambda_o = 2400 \cdot$ " Degree of ionisation is.

Sol:

$$\alpha = \frac{m\lambda_c}{m\lambda_o} = \frac{240}{2400} = \underline{\underline{0.1}}$$

10% ionised

③ To determine acid dissociation constant for weak electrolyte.

①
$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C \cdot \left(\frac{{}_m\Lambda_c}{{}_m\Lambda_\infty}\right)^2}{1 - \frac{\Lambda_c}{\Lambda_\infty}}.$$

very dilute Electrolyte

②
$$K_a = C\alpha^2 = C\left(\frac{{}_m\Lambda_c}{{}_m\Lambda_\infty}\right)^2.$$

for formic acid at $\underline{\infty}$ dilution it's molar
Conductanc 240 ohm^{-1} cm^{2} mole^{-1} at $\underline{0.01m}$ is.
$\underline{60}$ ohm^{-1} cm^{2} mole^{-1} So find out acid dissociation.
const for formic acid !

$\lambda^{\infty} = 240.$

$\Lambda^{c} = 60$

$$K_a = c\left(\frac{\Lambda^{c}}{\Lambda^{\infty}}\right)^2$$

$$K_a = 0.01\left(\frac{\cancel{60}}{\underset{4}{\cancel{240}}}\right)^2 = 0.01\times(0.25)^2$$

$$= 10^{-2}\,(25\times10^{-2})^2$$

$$= 10^{-2}\,(625)\times10^{-4}$$

$$= 625\times10^{-6} \;//$$

(4) To determine the Solubilities of Sparingly Soluble Salts

$$\lambda_m = \frac{K \times 1000}{\text{molarity}} \Rightarrow$$

molarity = solubility (s).

Normality = s

$$\lambda_{ea} = \frac{K \times 1000}{\text{normality}}$$

$$\lambda_m = \frac{K \times 1000}{s} \Rightarrow \boxed{s = \frac{K \times 1000}{\lambda_m}}$$

$$\lambda_{ea} = \frac{K \times 1000}{s} \Rightarrow \boxed{s = \frac{K \times 1000}{\lambda_{ea}}}$$

λ_m :

molar conductance of AgBr is 5×10^{-4} $\text{ohm}^{-1}\,\text{cm}^{2}\,\text{mole}^{-1}$

So its solubility ? (specific cond : 10^{-2} · $\text{ohm}^{-1}\,\text{cm}^{-1}$)

K

$$\boxed{S = \frac{K\times1000}{\lambda_m}} = \frac{10^{-2}\times10^{3}}{5\times10^{-4}} = 0.1\times10^{+5}$$

$$= \underline{\underline{10^{4}}}$$

* ✓ $\overset{\lambda eq.}{\text{Eq}^{n}\ \text{cond}^{n}}$ of $BaSO_4$ is 2×10^{-4} $\text{ohm}^{-1}\,\text{cm}^{2}\,\text{geq}^{-1}$.

✓ $\underset{K.}{\text{Specific cond}^{n}}$ of $BaSO_4$ is 4×10^{-2} So find out

its Solubility ?

$$S = \frac{K\times10^{3}}{\lambda eq} = \frac{\overset{2}{\cancel{4}}\times10^{-2}\times10^{3}}{\cancel{2}\times10^{-4}} = \frac{2\times10}{10^{-4}} = \underline{\underline{2\times10^{5}}}.$$

1. $\lambda = \lambda^{\circ} - K\sqrt{C}$.

2. $\lambda_{CH_3COOH} = \lambda_{CH_3COONa} + \lambda_{HCl} - \lambda_{NaCl}$.

$\lambda_{CH_3COOH} = \lambda_{CH_3COOK} + \lambda_{H_2SO_4} - \lambda_{K_2SO_4}$

$\lambda_{HCOOH} = \lambda_{HCOONa} + \lambda_{HCl} - \lambda_{NaCl}$

$\lambda_{NH_4OH} = \lambda_{NH_4Cl} + \lambda_{NaOH} - \lambda_{NaCl}$.

③

$$\alpha = \frac{{}^{m}\Lambda^{c}}{{}^{m}\Lambda^{0}}$$

$$\alpha = \frac{{}^{m}\Lambda^{c}}{{}^{m}\Lambda^{\infty}}$$

④ $$K_a = \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{C\left(\frac{\Lambda^c}{\Lambda^0}\right)^2}{1-\frac{\Lambda^c}{\Lambda^0}}$$

$$K_a = C\alpha^2 = C\left(\Lambda^c/\Lambda^0\right)^2$$

⑤ $$S = \frac{K \times 1000}{\lambda m} = \frac{K \times 1000}{\lambda eq}.$$

Limitations:-

→ it is applicable only for weak electrolytes.

Debye- huckel onsager Equation:-

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{\eta(DT)^{1/2}} + \frac{8.2\times10^5}{(DT)^{3/2}}\Lambda_0\right]\sqrt{C}.$$

$$\boxed{\Lambda_c = \Lambda_0 - K\sqrt{C}}$$

η = viscosity co-efficient.

D = Dielectric const

T = Temp.

C = Conductance.

Stong electrolyte.

$$\lambda^{eq}_{CaCl_2} = ?$$

$$\lambda^{eq}_{MgSO_4} = ?$$

$$\lambda^{eq}_{Ca^{+2}} = 119 \quad S\,cm^2\,geq^{-1}$$

$$\lambda^{eq}_{Cl^-} = 76.3 \quad ''$$

$$\lambda^{eq}_{Mg^{+2}} = 106 \quad ''$$

$$\lambda^{eq}_{SO_4^{-}} = 160 \quad ''$$

$$\lambda^{eq}_{CaCl_2} = 1\cdot\lambda^{eq}_{Ca^{+2}} + 1\cdot\lambda^{eq}_{Cl^-}$$

$$= 119 + \underline{76.3}$$

$$= \underline{\underline{195.3}} \quad S\,cm^2\,geq^{-1}$$

$$\lambda^{eq}_{MgSO_4} = \lambda^{eq}_{Mg^{+2}} + \lambda^{eq}_{SO_4^{-2}}$$

$$= 106 + 160$$

$$= \underline{\underline{266}} \quad S\,cm^2\,geq^{-1}$$

$= {}^{m}\lambda_{Ca^{+2}} = 119 \ S\,cm^2\,mol^{-1}$

$= {}^{m}\lambda_{SO_4^{-2}} = 160$ "

$= {}^{m}\lambda_{\overline{Cl}} = 76$ "

$= {}^{m}\lambda_{Mg^{+2}} = 106$ "

① $${}^{m}\lambda_{CaCl_{\underline{2}}} = {}^{m}\lambda_{Ca^{+2}} + \underline{2}\,{}^{m}\lambda_{Cl^-}$$

$$= 119 + 2(76)$$

$$= 119 + 152$$

$$= \underline{271} \ S\,cm^2\,mol^{-1}$$

② $$\lambda_{MgSO_4} = 1\cdot\lambda_{Mg^{+2}} + 1\cdot\lambda_{SO_4^{-2}}$$

$$= 106 + 160 = \underline{\underline{266}}$$

Electro Chemistry

Part -2

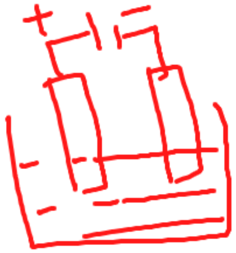
Electro Chemical cell :- (or) Galvanic cells.

" in this cell "Chemical Energy converts into Electrical Energy "

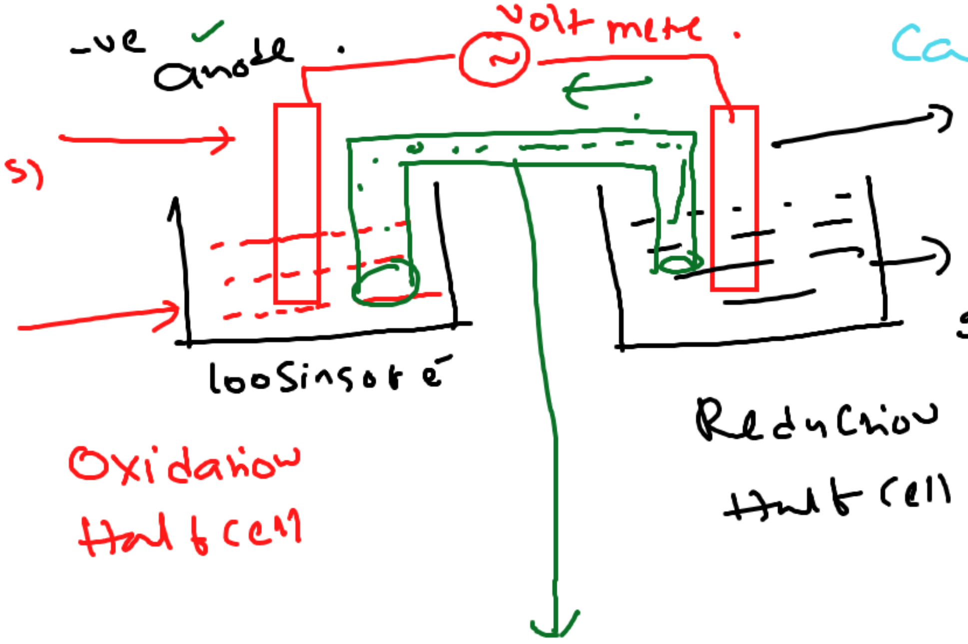
Ex: Daniel cell.

1. Battery
2. watch cell.

Daniel cell :-



Electrolytic cell



NEET ⇒ $\bar{e}$ flow from <u>anode</u> to <u>Cathode</u> .

⇒ Current flow from <u>Cathode</u> to <u>anode</u> .

Salt Bridge :-

KNO_3 Salt + agar-agar gum .

it balance the both half cell .

anode :-

Oxidation takes places.

loosing of e^-

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

cathode.

Reduction takes place.

gains of e^-.

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

over all cell Reaction

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}.$$

$E_{cell} = 1.1$ volts

	Electrolytic cell :-	Electro chemical cell
anode :-	(+)	(−)
cathode :-	(−)	(+).

Electricity consumed

Electricity Generated.

Volt cells

Anode : Oxid" Takes place.

Cathode :- Reduction Takes place.

NEET V. Imp

Which one act as anode :-

Which one act as Cathode :-

Electro Chemical Series.

✓

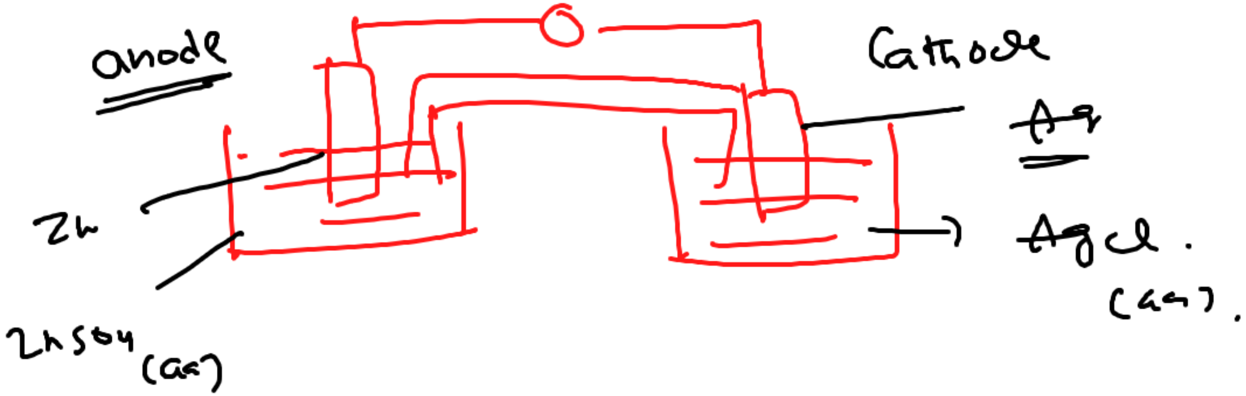
Upper Element : anode.

Down Elements : Cathode.

Zn → anode :- Oxidation
loosing of e^-

Cu → Cathode :- Reduction
gaining of e^-

② .



E.C. Series

Zn

↓

Ag

Anode: Zn – Oxid : $Zn \rightarrow Zn^{+2} + 2e^-$

Cathod: Ag – Red : $2Ag^+ + 2e^- \rightarrow 2Ag$

Cell Rxn

$$Zn + 2Ag^+ \rightarrow Zn^{+2} + 2Ag.$$

Cell

made upon

㊴.

Ag - AgCl . - Cathode - $2Ag^+ + 2e^- \rightarrow 2Ag$.

Cu - CuSO$_4$ - anode - $Cu \rightarrow Cu^{+2} + 2e^-$

$Cu + 2Ag^+ \rightarrow Cu^{+2} + 2Ag$

Cu

Ag $\downarrow$.

㊵

Ag — cathode.

H_2|Pt — anode.

H

Ag $\downarrow$.

Electro Chemical Series

low

metals.

↓

H

↓

non metals

high

increasing of Reduction potential of Elements.

metal - looses $\bar{e}$ - Oxid" - anode - low Reduction potential

non metal - gains $\bar{e}$ - Red" - Cathode - high Reduction potential.

Reduction potential increases.

Reduction potential.

−3.045 low

Li

K

Cs

Ba

Ca

Na

Mg

Al

Zn

Fe

Cd

Pb

Co

Ni

Sn

Pb

Fe

H_2

Cu

S

I_2

Ag

Hg

Br_2

O_2

Cl_2

Au

Mn

F_2 +2.870 high.

Daniel cell:

$$\boxed{\mathrm{Zn}_{(s)}} + \mathrm{Cu}^{+2}_{(aq)} \longrightarrow \mathrm{Zn}^{+2}_{(aq)} + \mathrm{Cu}_{(s)}$$

loosing of $\bar{e}$

Oxidation.

Reduction.

gaining of $\bar{e}$

Reducing agent

(or)

Reductant

Oxidising agent

(or) oxidant.

Cell notation IUPAC· Rule :-

→ Salt bridge.

Anode || Cathode.

(oxidation) (Reduction).

Daniel cell

$Zn \mid Zn^{+2} \parallel Cu^{+2} \mid Cu.$

Oxidation Reduction.

Electro Chemistry

E_{cell} :- Cell potential.

E°_{cell} :- Standard cell potential. S.T.P conditions.

$$E^{oxid} = E^{oxid.}_{Zn|Zn^{+2}}$$ (Loosing ē)

$$E^{Red} = E^{Red.}_{Cu^{+2}|Cu}$$ (gaining of ē)

$$E_{cell} = E^{oxid} + E^{Red}.$$

① model

NEET PYQ

Reduction

$$\mathrm{Zn}_{(s)} + \mathrm{Cu}^{+2}_{(aq)} \rightarrow \mathrm{Zn}^{+2}_{(aq)} + \mathrm{Cu}_{(s)}$$

Oxidation

$$E^{oxid}_{Zn|Zn^{+2}} = 0.4 \text{ volts}$$

$$E^{Red}_{Cu^{+2}|Cu} = -0.2 \text{ volts}$$

$$E^{cell} = E^{oxid} + E^{Red}.$$

$$E^{cell} = 0.4 - 0.2 = 0.2 \text{ volts}$$

$$\boxed{\begin{aligned} E^{oxid} &= -E^{Red}. \\ E^{Red} &= -E^{oxid} \end{aligned}}$$

(2Q)

✓ $E^{Oxid}_{Zn|Zn^{+2}} = 0.4$ Volts

$E^{oxid}_{Cu|Cu^{+2}} = -0.2$ volts $E^{Red} = 0.2$ volts

"Zn-oxid"

"Cu-Red"

$E^{Cell} = E^{oxid} + E^{Red}$

$= 0.4 + 0.2 = 0.6$ Volts

(3Q)

$E^{Red}_{Zn^{+2}/Zn} = 0.4$ Volts

$E^{Red}_{Cu^{+2}/Cu} = -0.2$ volts

$E^{Cell} = -0.4 - 0.2 = -0.6$ Volts

(4Q)

✓ $E^{Red}_{Zn^{+2}/Zn} = 0.4$ Volts

✓ $E^{oxid}_{Cu|Cu^{+2}} = -0.2$ volts

$E^{Cell} = -0.4 + 0.2$

$= -0.2$ Volts.

② Cell notation:-

✓

Oxid" $Zn | Zn^{+2} || Cu^{+2} | Cu$ Red".

Anode Cathode

both Reduction potentials of Zn & Cu are +0.4 V & -0.2 volts Respectively so $E^{cell} = ?$

Sol: $E^{Red} = 0.4$ $E^{oxid} = -0.4$

$E^{oxid} = -0.2$

$E^{cell} = -0.4 - 0.2 = \underline{\underline{-0.6 \text{ Volts}}}$

$Zn | Zn^{+2} || Cu^{+2} | Cu$

(1Q) both Zn & Cu oxid' potential +0.4 V & −0.2 volts So E^{cell} = 0.6 Volts

(2Q) both Zn & Cu Red" potential +0.4 V & −0.2 volts So E^{cell} = −0.6 volts

(3Q) Zn oxid pot" +0.4 V
Cu Red pot" −0.2 V
So E^{cell} = 0.2 volts

(4Q) Zn Red pot" +0.4 volts
Cu oxid pot" −0.2 volt
So E^{cell} = −0.2 volts

II. ΔG & E cell Relation :-

ΔG = Gibb's free energy Change

E_{cell} = Cell potential.

Std. Conditions.

$$\boxed{\Delta G = -nFE_{cell}}$$

$$\boxed{\Delta G^\circ = -nFE^\circ_{cell}}$$

F = Faraday = 96500 columbs.

n = Change in Electrons.

(Q) $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$ $E_{cell} = +0.4$ volts

So calculate ΔG ?

Sol:

$n = 2.$

$F = 96500$

$E_{cell} = +0.4$ volts

$\Delta G = ?$

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

$$\Delta G = -2 \times 96500 \times 0.4$$

$$\Delta G = -0.8F$$

$$\Delta G = \underline{\underline{-77200}}.$$

(2Q) $\overset{\text{oxid''.}}{Zn} + Cu^{+2} \rightarrow Zn^{+2} + Cu$ both <u>Reduction</u> potential of Zn & Cu −0.4 v & +0.2 V so its change in Gibb's free energy is — ?

$$\Delta G = -nF\, E_{cell}$$

$$E_{cell} = E^{oxid} + E^{Red}.$$

Step1

$$E^{Red}_{Zn} = -0.4\,V \Rightarrow \overset{E^{oxid}.}{+0.4}$$

$$E^{Red}_{Cu} = +0.2\,V$$

$$E^{cell} = 0.6\,\text{Volts}$$

Step2

$$\Delta G = -2 \times F \times 0.6$$

$$\Delta G = \underline{\underline{-1.2\,F}}$$

Q³

$Zn|Zn^{+2}||Ag^{+}|Ag$

both oxid" potential of Zn & Ag are -0.4 & $+0.2$ volts ✓

So $\Delta G = ?$

1. Rxn:-

Oxid".

$$Zn_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + 2Ag_{(s)}.$$

Red.

$E^{cell} = -0.4 - 0.2$

$= -0.6\,V$

2. E^{cell} :-

3. $\Delta G = -nFE^{\circ}$

$= -2 \times F \times -0.6 = 1.2F$

a cell is made up of with Ag & Cu

and both Reduction potentials are -0.4 & 0.2 V.

So find out its E_{cell} :-

ΔG :-

oxid.

$Cu \rightarrow$ anode

$Ag \rightarrow$ cathode.

Sol:-

1. anode: Cu (oxid)
   Cathode:- Ag (Red)

$$Cu + 2Ag^{+1} \longrightarrow Cu^{+2} + 2Ag.$$

$$\boxed{n=2}$$

2. write the Rxn

3. $E^{cell} = -0.4 - 0.2 = -0.6$ volts

4. $\Delta G = -2 \cdot F \; -0.6 = \underline{\underline{+1.2F}}$

$X + Y^{+2} \longrightarrow X^{+2} + Y \qquad \Delta G^{\circ} = 9.650$ volts .

So its $^{\circ}E^{cell} = ?$

Sol:-

$$\Delta G^{\circ} = -nF\overset{\circ}{E}^{cell}$$

$$E^{cell} = \frac{-\Delta G^{\circ}}{nF} = \frac{-9.650}{2\times 96500} = -\frac{\cancel{9650}\times 10^{-3}}{2\times \cancel{96500}_{10}}$$

$$E^{cell} = 0.5\times 10^{-4} \text{ volts}$$

$H_2 + 2Ag^{+1} \longrightarrow 2H^{+} + 2Ag$ $\Delta G = 0.9650.$

So E_{cell} is ?

$$\Delta G = -nF\,E^{cell}$$

$$E^{cell} = \frac{-\Delta G}{nF} = \frac{0.9650}{2\times 96500} = \frac{\cancel{9650}\times 10^{-4}}{2\times \underset{10}{\cancel{96500}}}$$

$$= 0.5\times 10^{-5}$$

$$= \underline{\underline{5\times 10^{-6}}}.$$

Nernst Equation:-

Acc^{n} Td.

1. $\Delta G = -nF E_{cell}$.

2. $\Delta G = \Delta G^{\circ} + RT \ln_e K$.

$$-nF E_{cell} = -nF E^{\circ}_{cell} + RT \ln_e K.$$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln_e K.$$ Nersent Eq^{n}

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log_{10} K.}$$

at 25°C

298K

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

at 25° Nernst Eq'n

$$\boxed{E^{cell} = E^\circ_{cell} - \frac{0.059}{n} \log K.}$$

$$\boxed{K = \frac{[P]}{[R]}.}$$

at 25°C $\quad Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

(0.1) $\qquad (0.001M)$

$E^{\circ}_{cell} = 0.6$ volts

$E_{cell} = ?$

Sol

$$K = \frac{[Zn^{+2}]}{[Cu^{+2}]} = \frac{0.001}{0.1} = \frac{10^{-3}}{10^{-1}} = \underline{\underline{10^{-2}}}.$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log K.$$

$$= 0.6 - \frac{0.059}{2} \log 10^{-2}$$

$$E_{cell} = 0.6 + \frac{0.059 \times \cancel{2}}{\cancel{2}} = \underline{\underline{0.659}} \text{ volts}$$

$$\underset{(0.1m)}{x^{+1}} + y \longrightarrow \underset{(0.01m).}{y^{+1}} + x \qquad E^{\circ}_{cell} = 0.8 \text{ volts}$$

at 25° ① $E^{cell} = ?$

② $\Delta G = ?$

1. $K = \dfrac{[y^{+1}]}{[x^{+1}]} = \dfrac{0.01}{0.1} = \dfrac{10^{-2}}{10^{-1}} = \underline{\underline{10^{-1}}}.$

2. $E = 0.8 - \dfrac{0.059}{1}\log 10^{-1} = 0.8 + 0.059$

$= 0.859.$

3. $\Delta G = -1 \times F \times 0.859 = \underline{\underline{-0.859\,F}}$

Formula

1. $E^{cell} = E^{oxid} + E^{Red}$

2. $E^{oxid} = - E^{Red}$

3. $\Delta G = -nF\ E_{cell}$

$\Delta G^{\circ} = -nF\ E^{\circ}_{cell}$

4. $\Delta G = \Delta G^{\circ} + RT \ln_e K$

5. $E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF} \log K$.

6. $E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log K$ at 25°C.

Electro Chemistry

Nernst Eq^n :-

$$E_{cell} = E^{o}_{cell} - \frac{2.303\,RT}{nF} \log K.$$

at 25°C

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n} \log K.$$

25°C

$$\underset{(0.1)}{X^{+2}} + y \longrightarrow \underset{(0.001)}{y^{+2}} + X$$

for this both Standard Red" potential of X & y are -0.6 & $\underset{-0.2}{0.2}$ Volts so Calculet. its $E_{cell} = ?$

① $E^0 = -0.6 - 0.2$

$= -0.8$

② $K = \dfrac{[y^{+2}]}{[x^{+2}]} = \dfrac{10^{-3}}{10^{-1}} = 10^{-2}.$

② $E = E^0 - \dfrac{0.059}{n} \log K.$

$E = -0.8 - \dfrac{0.059}{2} \log 10^{-2}$

$E = -0.8 + \dfrac{0.059 \times \cancel{2}}{\cancel{2}}$

$E = -0.8 + 0.059 = 0.741$

The Std. Red^{n} potential of Cu is 0.34V than. Calculate $\underline{\text{Oxid}^{n}}$ $\underline{\text{potential}}$ of Cu in $\boxed{0.01M}$ $CuSO_4$ Sol^{n} at 25°C.

$$Cu^{+2} + 2\bar{e} \rightarrow Cu \quad . E = 0.34.$$

$$E^{Red}_{Cu^{+2}/Cu} = +0.34$$

$$\underset{(s)}{Cu} \rightarrow \underset{(aq)}{Cu^{+2}} + 2\bar{e} \qquad E^{oxid}_{Cu|Cu^{+2}} = -0.34$$

$$K = [Cu^{+2}] = 0.01 = 10^{-2}$$

$$E^{oxid} = E^{0}_{oxid} - \frac{0.059}{n}\log K.$$

$$E^{oxid} = -0.34 - \frac{0.059}{2}\log 10^{-2}$$

$$E^{oxid} = -0.34 + 0.059$$

$$E^{oxid} = -0.281$$

Std. Red. potential of Ag & Zn are 0.80 & −0.76 V. respectively. So calculate Ecell for

+0.76.

oxid $Zn|Zn^{+2} \,||\, Ag^{++}|Ag$ ✓

(0.01m) (0.1m) ✓

$Zn + 2Ag^{+} \rightarrow 2Ag + Zn^{+2}$

① $E^{\circ}_{cell} = E_{Zn|Zn^{+2}} + E_{Ag^{+}|Ag} = 0.76 + 0.80 = 1.56$ Volts

② $E_{cell} = 1.56 - \frac{0.059}{2}\log\frac{[0.1]}{[0.01]}\;\frac{10^{-1}}{10^{-2}}$

$= 1.56 + 0.029 = \underline{\underline{1.589}}$ Volts

$$A + B \longrightarrow C + D \qquad \Delta G_1 = -n_1 F E_1$$

$$(+) \quad C + D \longrightarrow E + F \qquad \Delta G_2 = -n_2 F E_2$$

$$A + B \longrightarrow E + F \qquad \Delta G_3 = -n_3 F E_3 .$$

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-n_3 \cancel{F} E_3 = -n_1 \cancel{F} E_1 - n_2 \cancel{F} E_2$$

$$n_3 E_3 = n_1 E_1 + n_2 E_2$$

$$\boxed{E_3 = \frac{n_1 E_1 + n_2 E_2}{n_3}}$$

①

$Cu^{+} \longrightarrow Cu^{\cancel{+2}} + e^{-}$ $\Delta G_1 = x$

$\cancel{Cu^{+2}} + 2e^{-} \longrightarrow Cu$ $\Delta G_2 = y$

$Cu^{+} + e^{-} \longrightarrow Cu$ $\Delta G_3 = ?$ $\underline{\underline{x + y}}$

---

②

✓ $Cu^{+} \longrightarrow Cu^{+2} + e^{-}$ $\Delta G_1 = x$

✓ $Cu \longrightarrow Cu^{+2} + 2e^{-}$ $\Delta G_2 = y$.

$Cu^{+} + e^{-} \longrightarrow Cu$ $\Delta G_3 = ?$

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

$\cancel{Cu^{+2}} + 2e^{-} \longrightarrow Cu$ $-y$

$Cu^{+} + 1e^{-} \longrightarrow Cu$ $\underline{\underline{\Delta G_3 = x - y}}$

$Cu^{+1} \longrightarrow Cu^{+2} + e^{-}$ $n_1 = 1e^-$ $E_1 = -0.15V$

$Cu^{+2} + 2e^{-} \longrightarrow Cu$ $n_2 = 2e^-$ $E_2 = 0.34V$

$Cu^{+1} + 1e^{-} \longrightarrow Cu$ $n_3 = 1e^-$ $E_3 = ?$

$$E_3 = \frac{n_1E_1 + n_2E_2}{n_3} = 0.53V.$$

$Fe^{+3} + e^- \rightarrow Fe^{+2}$ $\quad E_1 = 0.77\,V \quad n_1 = 1$

$Fe^{+2} + 2e^- \rightarrow Fe$ $\quad E_2 = -0.44\,V \quad n_2 = 2$

$Fe^{+3} + 3e^- \rightarrow Fe.$ $\quad E_3 = ? \quad n_3 = 3$

$$E_3 = \frac{n_1E_1 + n_2E_2}{n_3} = \frac{(1 \times 0.77) + (2 \times -0.44)}{3} = \underline{\underline{-0.04\,V}}\ (\approx).$$

$Mn^{+7} + 5\bar{e} \longrightarrow Mn^{+2}$ E_1 1.51 Volts

$Mn^{+4} + 2\bar{e} \longrightarrow Mn^{+2}$ E_2 1.23 Volt

$Mn^{+7} + 3\bar{e} \longrightarrow Mn^{+4}$ $E_3 = ?$

$Mn^{+7} + 5\bar{e} \rightarrow Mn^{+2}$ 1.51

$Mn^{+2} + \longrightarrow Mn^{+4} + 2e$ -1.23.

$Mn^{+7} + 3\bar{e} \rightarrow Mn^{+4}$ E_3

$$E_3 = \frac{(5 \times 1.51) + (2 \times -1.23)}{3} = \underline{\underline{+1.63}}.$$

$$Fe \longrightarrow \cancel{Fe^{+2}} + 2e^- \qquad E_1 = 0.2$$

$$\cancel{Fe^{+2}} \longrightarrow \cancel{Fe^{+1}} + 1e^- \qquad E_2 = 0.3$$

$$\cancel{Fe^{+1}} \longrightarrow Fe + 1e^- \qquad E_3 = 0.4$$

$$Fe \longrightarrow Fe^{+3} + 3e^- \qquad E_4 = ?$$

$$= \frac{0.4 + 0.3 + 0.4}{1}$$

$$E_4 = \underline{1.1} \text{ Volts}$$

:- IV :-

at Equilibrium :-

$$\underset{BWD}{\overset{FWD}{\rightleftharpoons}}$$

FWD = E_{cell} +ve.

BWD - E_{cell} -ve.

at Eq^{n} over all $E_{cell} = 0$

Nerst Eq^{n}

$$0 = E^\circ_{cell} - \frac{2.303RT}{nF}\log K_{eq}$$

$$E^\circ_{cell} = \frac{2.303RT}{nF}\log_{10} K_{eq}.$$

NEET

$$\boxed{K_{eq} = 10^{\frac{nFE^\circ_{cell}}{2.303RT}}}$$

25°C

$$0 = E^\circ_{cell} - \frac{0.059}{n}\log_{10} K_{eq}$$

$$E^\circ_{cell} = \frac{0.059}{n}\log_{10} K_{eq}$$

$$\boxed{K_{eq} = 10^{\frac{nE^\circ_{cell}}{0.059}}}$$

at 25° at fa''

$Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$ $E^{\circ}_{cell} = 0.0059$:

So Calculate Equilibrium Constant.

$$K_{eq} = 10^{\frac{nE_{cell}}{0.059}} = 10^{\frac{2 \times 0.00\cancel{59}}{0.0\cancel{59}}} \; 10 = \underline{\underline{10^{0.2}}}$$

at 25°C $Zn|Zn^{+2} || Cu^{+2}|Cu$

both Standard Reduction potentials are.

Zn & Cu are -0.5 volts & 0.09 volts.

So Calculate Equilibrium constant?

$$E^\circ = E^{oxid}_{Zn|Zn^{+2}} + E^{Red}_{Cu^{+2}|Cu}$$

$$= 0.5 + 0.09$$

$$= 0.59 \text{ volts}$$

$$K_{eq} = 10^{\frac{nE^\circ}{0.059}}$$

$$K_{eq} = 10^{\frac{2\times\overset{10}{\cancel{0.59}}}{\cancel{0.059}}}$$

$$\underline{\underline{K_{eq} = 10^{20}}}$$

Electro Chemistry

*Q

$$Fe^{+2} + 1\bar{e} \rightarrow Fe^{+1} \qquad E^{cell} = 1.1 \text{ volts.}$$

$$Fe^{+1} + 1\bar{e} \rightarrow Fe \qquad E^{cell} = 2.2 \text{ volts}$$

$$\overline{Fe^{+2} + 2\bar{e} \rightarrow Fe} \qquad E^{cell} = ?$$

$$E^{cell} = \frac{1.1 + 2.2}{2} = \frac{3.3}{2} = 1.65 \, \underline{\underline{\text{volts}}}.$$

at Ea" $E_{cell} = 0$.

$$E^\circ_{cell} = \frac{2.303RT}{nF}\log_{10}K_{ea}.$$

$$K_{ea} = 10^{\frac{nFE^\circ_{cell}}{2.303RT}}$$

at 25°C

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_{ea}.$$

$$K_{ea} = 10^{\frac{nE^\circ_{cell}}{0.059}}.$$

at 25°C. Stand. Red. potential Ag & Zn are 0.80 & −0.76 V respectively. calculate Eq" Const for

$$Zn_{(s)} + 2Ag^{+}_{(aq)} \rightleftharpoons Zn^{+2}_{(aq)} + 2Ag_{(s)}.$$

(1) $E^{o}_{cell} = 0.80 + 0.76 = 1.56$ volts.

/ (2) $K_{eq} = 10^{\frac{nE^{o}_{cell}}{0.059}} = 10^{\frac{\overset{52}{\cancel{2\times 1.56}}}{\underset{0.03}{\cancel{0.059}}}} = 10^{52}$

The Eq^{n} const for

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+2} + Sn^{+4}$$

$$+6 \xleftrightarrow{2\bar{e}} +4$$

a) 10^{10}.

[✓ b) 10^{20}.]

c) 10^{30}.

d) 10^{40}.

$E^{\circ}_{Fe^{+3}/Fe^{+2}} = 0.75$ volts

$E^{\circ}_{Sn^{+4}/Sn^{+2}} = 0.15$ volts

$\left(\frac{2.303RT}{F} = 0.06 \right)$

$E_{cell} = 0.6$.

$\underline{\underline{K_{eq}}} = ?$ $\quad 10^{\frac{n \times E}{0.06}}$

$$= 10^{\frac{2 \times \overset{10}{\cancel{0.6}}}{\cancel{0.06}}} = \underline{\underline{10^{20}}}$$

Daniel cell is

a) $Zn|Zn^{+2} || Ag^{+}|Ag$

b) $Zn|Zn^{+2} || Cu|Cu^{+2}$

[✓ c)] $Zn|Zn^{+2} || Cu^{+2}/Cu$

d) $Cu^{+2}|Cu || Zn|Zn^{+2}$

$Zn \mid Zn^{+2}\,(0.01)\,10^{-1} \parallel Fe^{+2}\,(0.001)\,10^{-3} / Fe^{+3}\,(0.01)\,10^{-2} \mid Pt$

$E_{cell} = 1.71$ volts.

at 25°C

Kea = ?

1. $E^{o}_{cell} = ?$

2. Kea = ? $10^{\frac{nE}{0.059}}$

$Kea = 10^{\frac{2\times1.71}{0.059}}$

$= 10^{\frac{342}{0.059}} =$

$Zn + 2Fe^{+2} \rightleftharpoons Zn^{+2} + 2Fe^{+3}$ so

$(0.001)\,10^{-3}$ $(0.01)\,10^{-2}$ $(0.01)\,10^{-2}$

✓ $E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log K$

$1.71 = E^{o}_{cell} - \frac{0.0591}{2}\log 1$

$$\boxed{E^{o}_{cell} = 1.71}$$

$10^{5.79}$

$K = \frac{[Fe^{+2}][Zn^{+2}]}{[Fe^{+2}]}$

$K = \frac{10^{-1}\times10^{-2}}{10^{-3}}$

$K = \frac{\cancel{10^{-3}}}{\cancel{10^{-3}}}$

$K = 1$

Ex at 25°C

oxid. Red.

$Zn|Zn^{+2}$ (0.01M) || $Cu^{+2}|Cu$ (0.001M)

$E^\circ_{cell} = ?$

oxid $E^\circ_{Zn|Zn^{+2}} = 0.5$ volts

Red. $E^\circ_{Cu^{+2}|Cu} = 0.4$ volts.

0.9 volts

1. $E_{cell} = ?$ 0.9 V.

2. Kea = ? 10^{30}.

3. $\Delta G^\circ = ?$

$$Kea = 10^{\frac{nE}{0.06}} = 10^{\frac{2\times \overset{\overset{15}{\cancel{3}0}}{0.\cancel{9}}}{\underset{02}{0.\cancel{06}}}} = 10^{30}$$

$$\Delta G^\circ = -nF E^\circ_{cell}$$

$$= -2 \times 96500 \times 0.9$$

$$= -1.8F$$

$\Delta G^\circ = \cdot 173700$ J.

Types of Electrodes. : 5 types.

1. metal-metal ion Electrodes ($Zn|Zn^{+2}$)
2. Gas Electrode - $H_{2(g)}$ $Cl_{2(g)}$. ($H_2|Pt$, $Cl_2|Pt$).
3. metal-amalgum electrodes. M(Hg). Na(Hg) Zn(Hg).
4. Redox electrodes. ($Fe^{+2}|Fe^{+3}$), Quinhydridine electrode.
5. metal-metal in Soluble Salt ($Ag|AgCl$) $Hg|Hg_2Cl_2$

Electro Chemistry

Types of Galvanic Cell

- Chemical Cells. (Emf produced due to Chemical Reactions)
  - ✓ Chemical cell Without Transferance
  - With Transferance. ✓
- Conc^{n} Cell [Emf produced to Transfer of matter]
  - Electrode Conc^{n} Cell
  - Electrolyte Conc^{n} Cell
    - with Trans.
    - without Trans.

Chemical cell without Transfearance:-

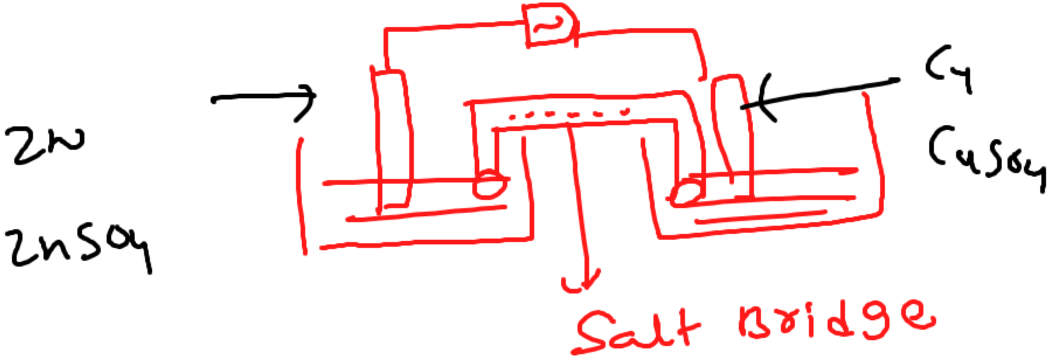
$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{Zn^{+2}}{Cu^{+2}}.$$

Daniel Cell:-

- Salt Bride present.

$Zn | Zn^{+2} || Cu^{+2} | Cu.$

- anode half cell. - oxid" - loosing of e^-
- cathodic half cell. - Red" - gaining of e^-



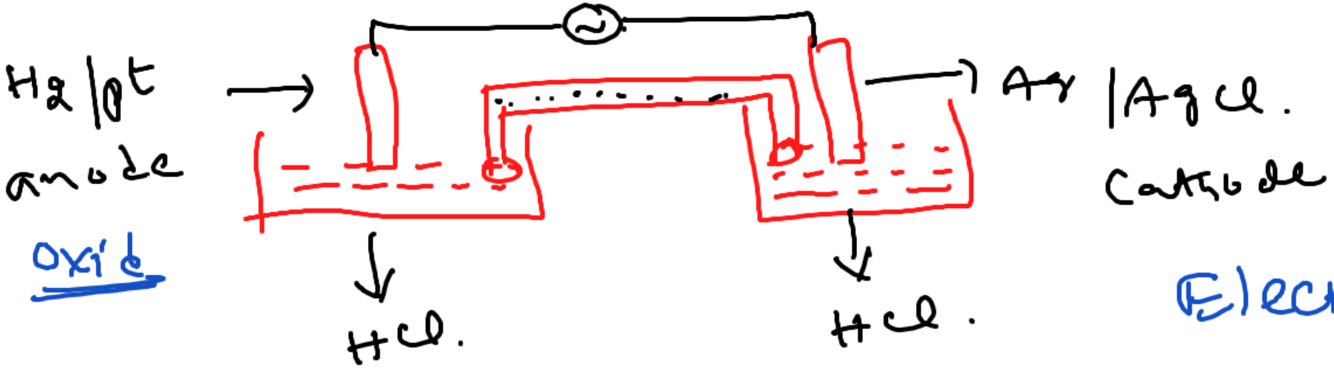
$$Zn \rightarrow Zn^{+2} + 2e^-$$

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

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

$$E = E^{oxid} + E^{Red}.$$

Ex: ②



Electrolyte common.

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

Reduction Cathode :- $AgCl + e^- \rightarrow Ag + Cl^{\ominus}$.

Cell Reaction :- $\frac{1}{2}\underset{(p_1)}{H_2} + \underset{(s)}{AgCl} \rightarrow \underset{(s)}{Ag} + \overset{\text{(conc)}}{HCl\,(a)}$.

$K = a/p_1$

Cell notation :- $\boxed{Pt\,H_2 \,|\, HCl \,|\, AgCl, Ag}$

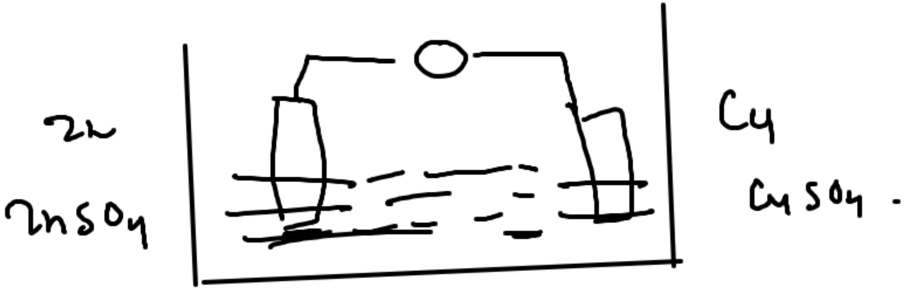
Nerest Eqn :- $E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{a_{HCl}}{P_{H_2}}$

II Chemical cell with Transfearnce:-

— Transfer of ions Takes place. One cell to another cell.

Ex'. Daniel cell with out Salt Bridge.

$$E_{cell} = E^{oxid} + E^{Red} + E_{Junction\ potential}.$$



No Salt Bridge.

Salt bridge – No Juction potential. E_J

No salt brisse – Juction potential present.

Cell notation $Zn \mid ZnSO_4 \,\vdots\, CuSO_4 \mid Cu$.

$$E = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{a_{Zn^{+2}}}{a_{Cu^{+2}}} + \underline{\underline{E_J}}.$$

V.V. Imp

Concentration cell

✓ Electrode . Conc^n cell.

✓ 1. Same electrodes

2. Diff Concentration.

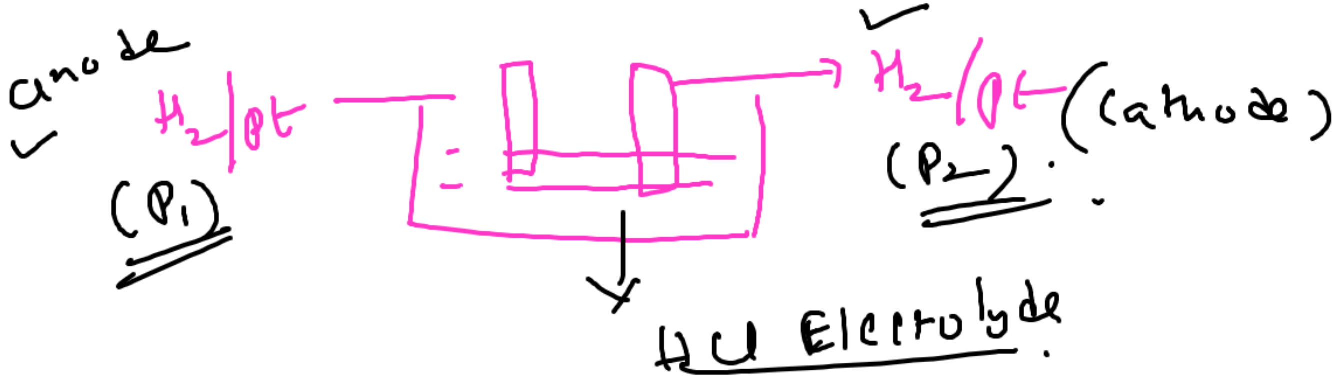
✓ Electrolyte .

1. Same eltrolyte

2. Diff electrode .

Electrode Concⁿ cell

- Same Electrode
- Diff Concⁿ of Electrolyte



$$K = \frac{[P_2]^{1/2}}{[P_1]^{1/2}}$$

anode :- Oxid^n $\frac{1}{2}H_2(P_1) \rightarrow H^+ + e^-$

cathode :- Red^n $H^+ + e^- \rightarrow \frac{1}{2}H_2(P_2)$.

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

Cell notation. $Pt, H_2(P_1) \,|\, HCl \,|\, H_2(P_2) \,|\, Pt$.

anode. common. cathode.

Nernst Eq":—

$$E = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{(P_2)^{1/2}}{(P_1)^{1/2}}$$

$\boxed{E^\circ_{cell} = 0.}$ Common Electrolyte.

$$E = \frac{-RT}{nF} \ln \left(\frac{P_2}{P_1}\right)^{1/2}$$

$\boxed{P_1 > P_2}$

$$E = \frac{RT}{nF} \ln \left(\frac{\checkmark P_1}{\underline{P_2}}\right)^{1/2}$$

$E_{cell} = \underline{+ve}.$

$\Delta G = \underline{-ve}.$

<u>Spanataneous.</u>

anode		Cathode
$Pt\ Cl_2\ (P_1)$	HCl	$Cl_2\ (P_2),\ Pt$.

Spataneous condition

1) $P_1 > P_2$

2) $P_2 > P_1$

3) $P_1 = P_2$

4) none.

anode :- $Cl^- \longrightarrow \frac{1}{2} Cl_{2\,(P_1)} + 1e^-$.

Caltode :- $\frac{1}{2} Cl_{2\,(P_2)} + e^- \longrightarrow Cl^{\ominus}$.

---

cell Reaction. $\frac{1}{2} Cl_{2\,(P_2)} \longrightarrow \frac{1}{2} Cl_{2\,(P_1)}$.

Nenst Eq^n :- $E = -\frac{RT}{nF} \ln k = -\frac{RT}{F} \ln \frac{(P_1)^{1/2}}{(P_2)^{1/2}}$

$\underline{\underline{E^\circ_{cell} = 0}}$

$E = \frac{RT}{F} \ln \left(\frac{P_2}{P_1}\right)^{1/2}$

$P_2 > P_1$ E +ve

$\Delta G = -ve$

Electrolyte Conc" Cell

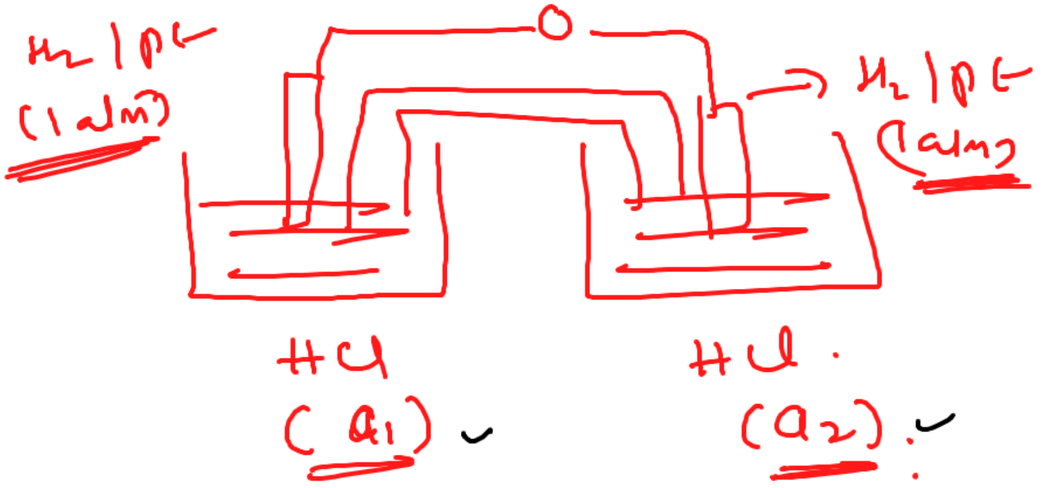
* Conc" Cell $E^{\circ}_{cell} = 0\,V$

* at Eq" $E_{cell} = 0$.

Same Electrolyte
but diff conc"

1 Conc" $E = -\frac{RT}{nF}\ln K$.

2 at Eq" $0 = E^{\circ}_{cell} - \frac{RT}{nF}\ln K$.



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

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

$a_2 > a_1$ $E_{cell} = +ve$

$\Delta G = -ve$.

Spatanaous

$$Pt, H_{2\,(g, 1\,atm)} \,|\, HCl_{(a_1)} \,||\, HCl_{(a_2)} \,|\, H_{2\,(g, 1\,atm)} \,|\, Pt.$$

Anode :- $\frac{1}{2} H_2 \longrightarrow \underset{a_1}{H^+} + e^-$

Cathode :- $\underset{a_2}{H^+} + e^- \longrightarrow \frac{1}{2} H_2$ $K = \frac{a_1}{a_2}$

$$H^+_{a_2} \longrightarrow H^+_{a_1}$$

$$Cu \mid \underset{(a_1)}{CuSO_4} \parallel \underset{(a_2)}{CuSO_4} \mid Cu.$$

oxid

Anode :- $Cu \rightarrow Cu^{+2}_{a_1} + 2e^-$

Red^n Cathode :- $Cu^{+2}_{a_2} + 1e^- \rightarrow Cu$

Net Rxn $\underset{(a_2)}{Cu^{+2}} \longrightarrow \underset{(a_1)}{Cu^{+2}}$

Nernst Eq^n :- $E = -\frac{RT}{F} \ln a_1/a_2 = \frac{RT}{F} \ln \frac{a_2}{a_1}$

Spontaneous Cond^n : $\boxed{a_1 < a_2}$

$E_{cell} = +ve$

$\Delta G = -ve.$

anode || Cathode.

Pt, Cl_2 (5 1atm) | HCl a_1 || HCl a_2 | Cl_2 (81 atm).

Spontaneous.

1. $a_2 > a_1$
2. $a_1 > a_2$
3. $a_1 = a_2$
4. None.

anode – oxidⁿ :– $Cl^-_{a_1} \rightarrow \frac{1}{2} Cl_2 + e^-$

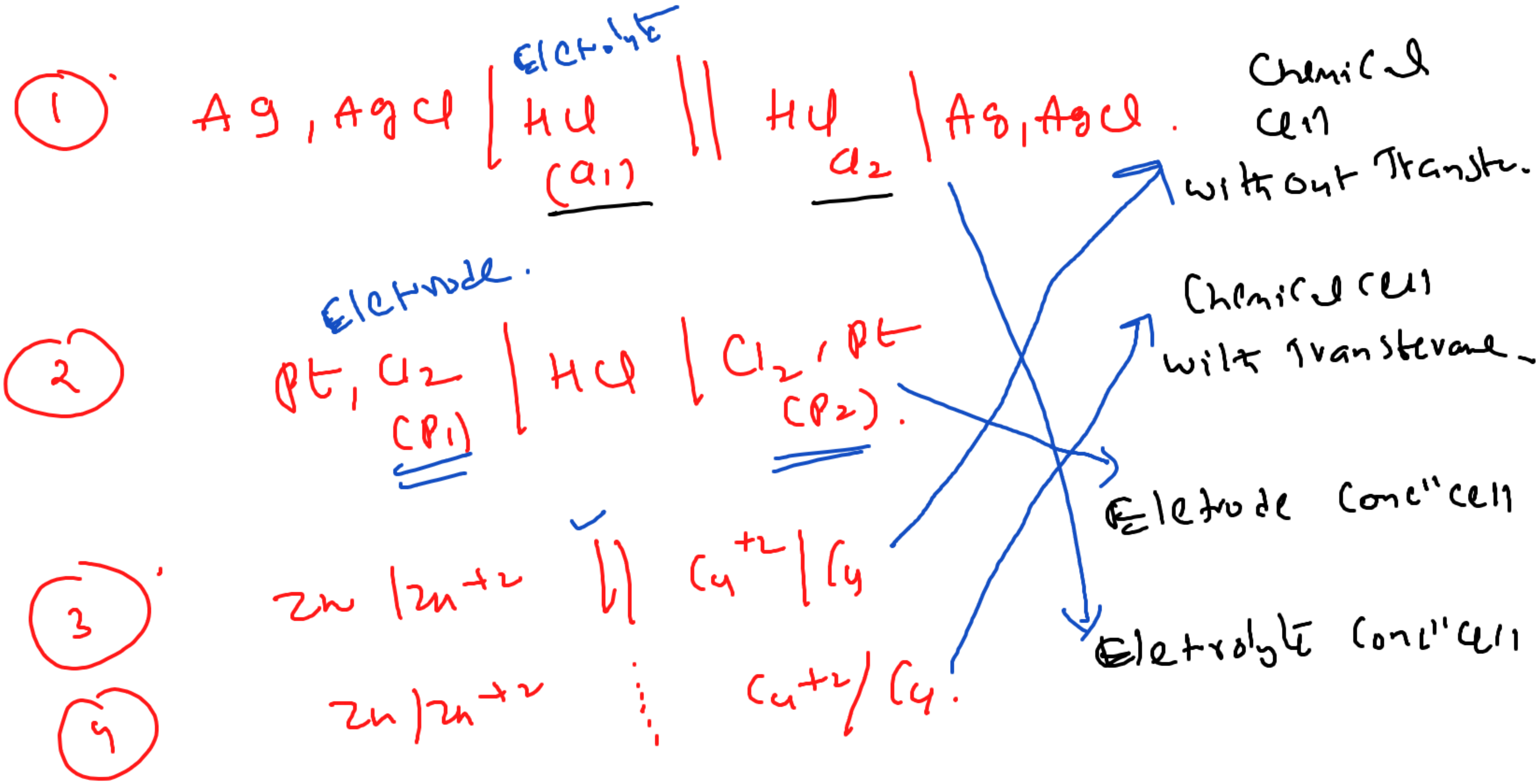
cathode – Redⁿ :– $\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-_{a_2}$

net Rxn :– $Cl^-_{a_1} \longrightarrow Cl^-_{a_2}$

$a_1 > a_2$

Nernst Eqⁿ : $E = -\frac{RT}{nF} \ln \frac{a_2}{a_1} = \frac{RT}{nF} \ln \frac{a_1}{a_2}$

spatn



Electrolyte

① $Ag, AgCl \mid \underset{(a_1)}{HCl} \parallel \underset{a_2}{HCl} \mid Ag, AgCl$.

Electrode.

② $Pt, \underset{(P_1)}{Cl_2} \mid HCl \mid \underset{(P_2)}{Cl_2}, Pt$.

③ $Zn \mid Zn^{+2} \parallel Cu^{+2} \mid Cu$

④ $Zn \mid Zn^{+2} \vdots Cu^{+2} / Cu$.

Chemical cell without Transfer.

Chemical cell with Transferance.

Electrode Conc" cell

Electrolyte Conc" cell

Electro Chemistry

Battery

Electro Chemical Cell.

Chemical energy convert into E.E.

Primary Cell

one use only.

① Leclanche cell.
(Dry cell)

② Mercury cell

Secondary Cell

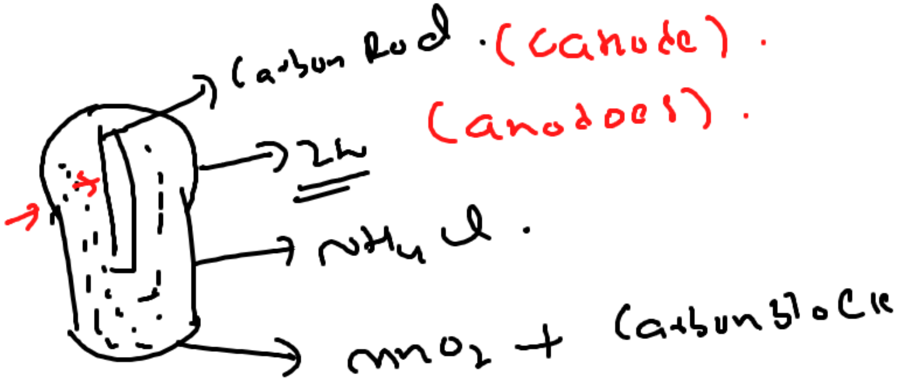
uses many times

Rechargable.

1. Lead Storage Batteries
2. Ni-Cd cell.

$$\left.\begin{array}{l}\text{Leclanche cell (Dry cell).}\\ \text{mercury cell}\end{array}\right\} 1^\circ \text{ Batteries}$$

$$\left.\begin{array}{l}\text{Pb - Storage cell.}\\ \text{Ni-Cd cell}\end{array}\right\} 2^\circ \text{ Battries}$$



Zn | anode

C | cathode

anode:-

oxidation

$Zn \rightarrow Zn^{+2} + 2\bar{e}$

Cathode:-

Reduction.

$MnO_2 + NH_4^+ + \bar{e} \rightarrow MnO(OH) + NH_3$.

(or)

$MnO_2 + H_2O + \bar{e} \rightarrow MnO(OH) + \bar{OH}$

$NH_4Cl + \bar{OH} \rightarrow NH_3 + \bar{Cl} + H_2O$

$Zn^{+2} + 2Cl + 2NH_3 \rightarrow ZnCl_2 \cdot 2NH_3$

$\boxed{1.5\ \text{volts}}$.

anode :- Zinc

Cathode :- Carbon.

paste :- $MnO_2 + C$.

Separate :- $NH_4Cl + ZnCl_2$

complex :- $ZnCl_2 \cdot 2NH_3 \simeq [Zn(NH_3)_2]Cl_2$

E_c :- 1.5 volts

not Rechargable

Mercury cell:-

anode :- Zn-Hg

Cathode :- C + HgO.

Paste :- ZnO + potash.

anode: oxidation

$$Zn\text{-}Hg + 2\bar{OH} \rightarrow ZnO + Hg + H_2O + 2e^-$$

Cathode: Reduction.

$$HgO + H_2O + 2\bar{e} \rightarrow \underset{(l)}{Hg} + 2\bar{OH}$$

Over all: $Zn\text{-}Hg + HgO \rightarrow ZnO + Hg$

$\boxed{1.35V.}$

$$\boxed{\begin{array}{ccc} \text{Leclanche} & > & \text{mercury cell} \\ \text{1.5 volts} & > & \text{1.35 V} \end{array}}$$

not Rechargable.

Secondary Cell

Lead Storage Battery

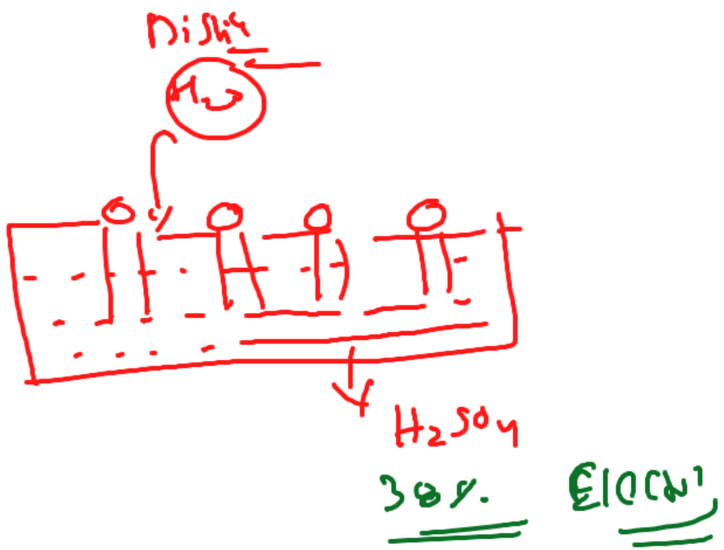
Rechargeble

1. Charging
2. Discharging.

⇒ Lead Electrode.

Sponge lead — anode.

Grid lead + PbO — Cathod



$$* \quad \underline{Pb} + \underline{PbO_2} + 2H_2SO_4 \underset{\text{Charging.}}{\overset{\text{discharging.}}{\rightleftarrows}} 2PbSO_4 + 2\underline{H_2O}. \qquad \underline{\underline{2.15\text{volts}}}$$

at anode:- $PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{-2} + 4H^+ + 2e^-$

at Cathode:- $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{-2}$

- 5% H_2SO_4 1.88V
- 40% H_2SO_4 2.15V

Cell Notation:-

$$Pb \mid PbSO_4 , \mid H_2SO_4 \mid PbSO_4 , PbO_2 \mid Pb.$$

② Ni - Cd

Nickel - Cadmium Cell :- Expensive.

$$Cd + 2Ni(OH)_3 \underset{\text{Charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2Ni(OH)_2 + CdO + H_2O$$

Fuel Cell

Fuel energy converts into E.E.

Ex: H_2-O_2 fuel cell.

Anode :

Oxidation

$H_2 + 2OH^- \rightarrow 2e^- + 2H_2O$

Cathode.

Reduction.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

overall

$$\boxed{2H_2 + O_2 \rightarrow 2H_2O}$$

-: Corrosine :-

Natural process.

metal → metal oxide
(mineral).

Ex:. Rusting of Iron.

Gradual decreasing of mass of metal.

Gradual destruction of metal.

① Rusting of Iron $Fe \longrightarrow Fe_2O_3 \cdot xH_2O$.

② Tarnishing of Silver. $Ag \longrightarrow Ag_2S$.

③ green Coating of Cu $Cu \longrightarrow CuCO_3$.

anode:

$Fe \rightarrow Fe^{+2} + 2e^-$.

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

Over all $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{+2} + 2H_2O$

$E_{cell} = +ve$

$E_{cell} = 1.67V$.

$\Delta G = -ve$ Spantaneous.

Preventive methods of corrosion:-

$\longrightarrow \underline{\underline{\textcircled{X}}} + \textcircled{Fe}$

1. paint the objects.
2. alloying with more anodic metal.
3. Galvanisation.

$\textcircled{Zn} + Fe$

(Sacrificial anode)

$\underline{25^\circ C}$

Zn $E^0_{cell} = -0.762$ Volts

E_{cell} Zn in $ZnSO_4$? $(0.1\,M)$. $\frac{1}{10}$

E

$$E = E^0_{cell} - \frac{0.059}{n} \log [Zn^{+2}]$$

$$Zn_{s} \rightarrow Zn^{+2}_{aq}$$

$$K = \frac{[Zn^{+2}]}{[Zn]} = [Zn^{+}]$$

$$= -0.762 - \frac{0.059}{2} \log\left(\frac{1}{10}\right)$$

$$= -0.762 + 0.0295$$

$$= -0.7915 \text{ volts}$$

At what Conc^n Cu^{+2} become Cu

$E^\circ_{Cu^{+2}} = 0.34$ Volts. E_{cell} = zero.

$\log 2 = 0.3$
$\log 2.8 = 0.43$
$\log 3 = 0.47$

$Cu^{+2} \to Cu$ $n=2$

Sol:

$$E = E^\circ - \frac{0.059}{2}\log\frac{1}{[Cu^{+2}]}.$$

$$0 = 0.34 - 0.0295 \log\frac{1}{[Cu^{+2}]}$$

$$\log\frac{1}{[Cu^{+2}]} = \frac{0.34}{0.0295} = 11.57.$$

$$\log_{10}[Cu^{+}] = -11.57 \Rightarrow [Cu^{+}] = 10^{-11.57}$$

$$= 10^{-12+0.43} = 2.8\times10^{-12}$$

Calculate the Std. Gibbs energy change for the redox reaction of Daniel cell. ?

$Zn + Cu^{+2} \Rightarrow Cu + Zn^{+2}$

$E^{\circ} = 1.1$ Volts.

$n-2$

$F = 96500$

$\Delta G^{\circ} = -nFE^{\circ}_{cell}$

$\Delta G^{\circ} = -2 \times 96500 \times 1.1 = -21300$ Joules

$= \underline{\underline{-21.3 \text{ kJ}}}$.

25 E^{o}_{cell} for Reaction

$2Ag^{+} + Cu \longrightarrow Cu^{+2} + 2Ag$ is 0.46V.

So Eq" const (Keq) = ?

$n = 2$

$E^{o} = 0.46$.

$\log 2 = 0.3$

$2 = 10^{0.3}$

$$K_{eq} = 10^{\frac{-nE^{o}_{cell}}{0.06}}.$$

$$K_{eq} = 10^{\frac{-\cancel{2} \times 0.\cancel{46}^{15.3}}{\cancel{0.06}_{3}}} = 10^{-15.3} = 10^{-15} \times 10^{0.3}$$

$$= 2 \times 10^{-15}$$

$\underline{\underline{25^\circ C}}$

$$\underset{}{Mg} + \underset{(0.0001M)}{\overset{\checkmark}{2Ag^+}} \longrightarrow 2Ag + \underset{(0.13M)}{Mg^{+2}} . \quad E^\circ_{cell} = 3.17V$$

$E_{cell} = ?$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Mg^{+2}]}{[Ag^+]^2}$$

$$E_{cell} = 3.17 - 0.0295 \log \frac{0.13}{(\underset{10^{-4}}{0.0001})^2}$$

$$= 3.17 - \left(0.0295 \left(\log 0.13 - \log 10^{-8}\right)\right).$$

$$= 3.17 - \left(0.0295 \left(-0.88 + 8\right)\right).$$

$$= 3.17 - 0.26 = 2.94 \text{ volts}$$ //.