ELECTROCHEMISTRY

Electrolyte :	strong	weak
	complete ionization	incomplete ionization

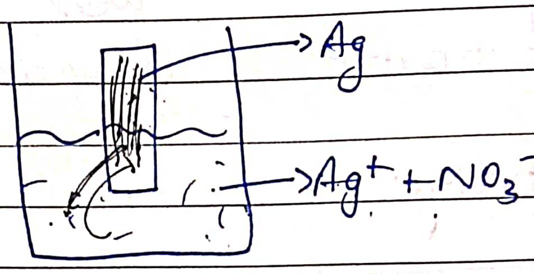
Conduction of electricity :

Metallic conduction (Electronic conduction)	Electrolytic conduction (ionic conductions)
1) It is due to movement of e^-	1) It is due to movement of ions
2) On increasing temp, electronic conduction decreases	2) On increasing temp, electrolytic conduction increase
3) Ohm's law is valid	3) Ohm's law is valid.
4) Depends on nature and structure of metal.	4) Depends on nature of electrolyte
5) It depends on valance e^-/atom.	5) On conc of electrolytes
6) Does not follow Faraday's law	6) Nature of solvent & viscosity.
	7) Size of ions produced & their solvation
	8) Faraday's laws are valid.

Electrochemical cells

Electrolytic cell	Galvanic cell.
Electrical energy → chem energy	Chem energy → electrical energy
	eg Pb storage battery

ELECTRODE POTENTIAL.



Salt must contain the same metal as that in the strip

→ 2 possibilities

1) Ag goes from metal into sol^n.

$Ag \rightarrow Ag^+ + e^-$.

Ag^+ into sol^n, e^- on metal,

Metal gets -ve charge, sol^n gets +ve charge

2) Ag^+ from sol^n goes to metal due to excess e^-

$Ag \rightarrow Ag^+$ only but attracted to metal

+ on metal

− ~~ca~~ in sol^n, (due to NO_3^-)

→ An overall pd develops and ~~ca~~ it is either anode o cathode

- · cell
  - anode : oxidation
  - cathode : reduction

→ A single electrode is half cell

→ We have:

E_{OP}

~~E~~ E_{RP}

E°_{OP}

~~E~~

Current → high RP – low R.P

E°_{RP} :

When a metal is dipped in its electrolytic sol^n, at electrode electrolyte interface, there is a tendency of metal ions from the solution to deposit on the metal electrode, trying to make it +vely charged.

At the same time, metal atom of electrode have a tendency to go into the sol^n as ions, and leave behind the electrons at the electrode trying to make it -vely charged.

At eq^b, there is a seperation of charge, and depending on the tendency of the two opposing reactions, electrode may be +vely or -vely charged with respect to the solution.

A potential difference develops b/w the electrode & electrolyte which is called electrode potential, represented by E.

When conc of all species (active mass) involved in a half cell is unity, then E is known as standard electrode potential.

According to IUPAC convention, standard reduction potentials are called standard electrode potentials.

If at an electrode, oxidation takes place, it is known as anode and potential developed at anode is known as E_{OP} : Electrode Oxidation potential.

E°_{OP} : Standard oxidation potential

If at an electrode, reduction takes place, then it is known as cathode and potential developed is called electrode reduction potential, at std conditions, is known as E^0_{RP}: std reduction potential

All std RP & OP are measured with the help of std hydrogen electrode

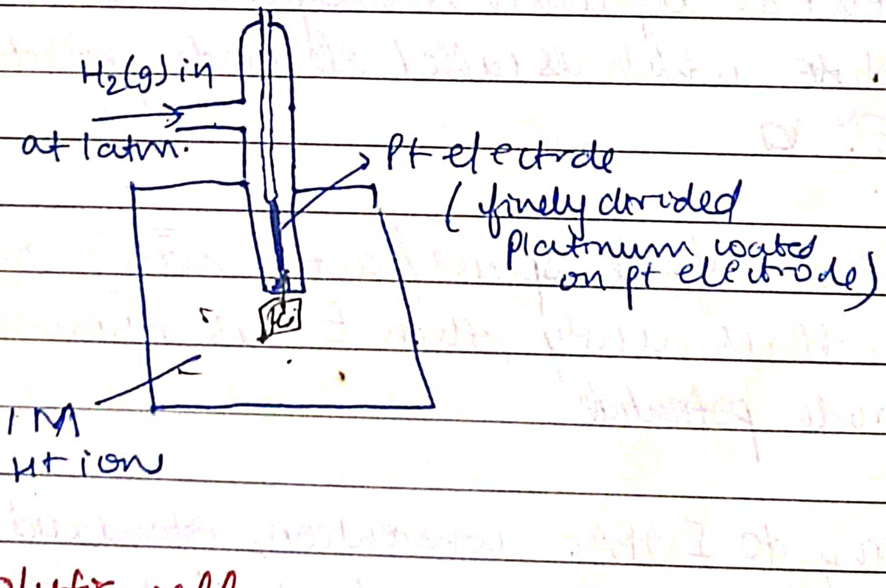
Standard Hydrogen electrode.

OP of SHE: $\underset{1atm}{H_2(g)} \longrightarrow \underset{1M}{2H^+} + 2e^-$. OP = 0.

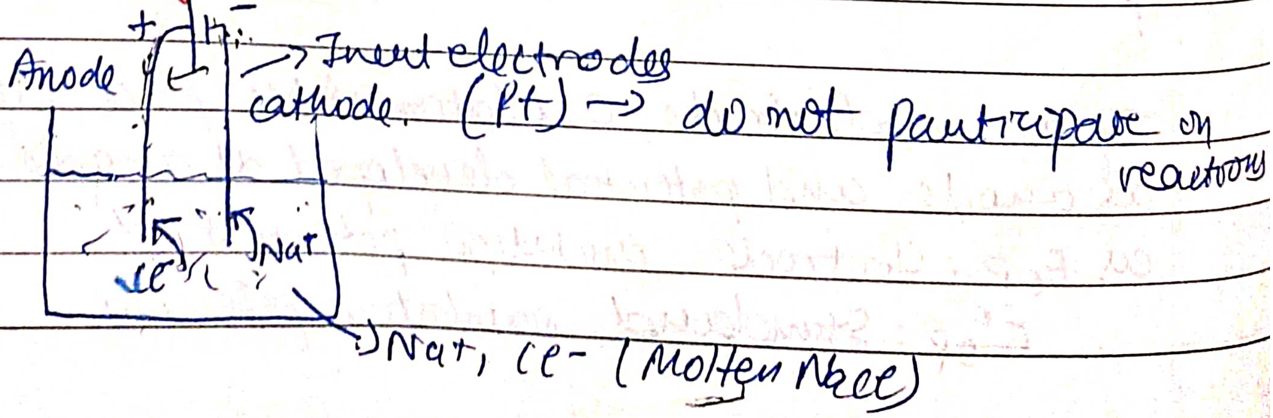
RP of SHE: $\underset{1M}{2H^+} + 2e^- \longrightarrow \underset{1atm}{H_2(g)}$, RP = 0

$\therefore E^0_{H_2(1atm)/H^+(1M)} = 0$

$E^0_{H^+(1M)/H_2(1atm)} = 0.$



Electrolytic cell



Cathode : -ve : $Na^+ + e^- \longrightarrow Na$.
Anode : +ve : $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$.

Deposit = Discharge = product found on electrodes.

Types of ques :

→ Product formed during electrolysis : (Discharge potential theory)
→ Qty of product of electrode (Faraday's law)
→ Conduction - resistance.

Product formed during electrolysis:

Depends on :
1) nature of electrolyte
2) Nature of electrode
3) conc of electrolyte.
4) Charge density
5) Temperature
6) Pressure (if gaseous electrode)

} can be determined experimentally only.

Discharge potential theory.

If more than one type of cation or anion migrate to respective electrode during electrolysis, then that ion discharges first which requires less energy. Potential at which ion is discharged or deposit on electrode is termed as discharge potential. Value of discharge potential is different for different ions.

The ion with lower discharge potential is discharged

Platinum electrode → highly conducting & malleable
Same results for graphite electrode

first (generally). (If over potential is zero)

At cathode, those cation which have more std reduction potential (E°_{RP}) will be first discharged and at anode, those anion with more std oxidation potential (E°_{OP}) are discharged first.

⊛ Only applicable when over potential is zero

Order of discharge potential:

Cation: $Au^{+3} < Ag^{+} < Hg^{+2} < Cu^{+2} < Ni^{+2} < H^{+} < Zn^{2+} < Al^{+3} < Mg^{2+} < Ca^{2+} < Na^{+} < K^{+}$

Anion: $I^{-} < Br^{-} < Cl^{-} < CH_3COO^{-} < OH^{-} < NO_3^{-} < SO_4^{2-}$

Now, discharge potential = −SRP for cation
= −SOP for anion

In aq soln, most electropositive metal cation (s block) will not discharge, but instead, H_2 gas is discharged

$\boxed{2H_2O \longrightarrow H_2 + 2OH^-}$ at cathode.
Na is not reduced

In aqa soln, cation of moderately electropositive metals (Mn, Co, Fe, Zn, etc) and least electropositive metals (Cu, Hg, Ag, Au, Pt) get discharged

→ Using inert electrodes:

$\boxed{\text{Electrolysis of Aq. NaCl}}$:

Cathode: $Na^{+} + e^{-} \longrightarrow Na$
$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-}$ ✓ (Discharge first)

$E_{OP} = - E_{RP}$

$E^0_{H_2O/H_2} > E^0_{Na^+/Na}$.

Anode

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

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$, E_0 OP = − 1.23

This reaction is very slow, to increase rate, extra potential is applied called overpotential.
Due to overpotential rate increases.
But factually, rate of Cl^- increases more than that of O_2
Hence Cl^- is deposited at anode.
So Cl_2 is kinetic product & O_2 is thermodynamic product.
$E^0_{H_2O/O_2} > E^0_{Cl^-/Cl_2}$
so O_2 should be formed but

→ Electrolysis of aq. $CuSO_4$. / $NiSO_4$ with inert electrode

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$ ✓
and $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
as $E^0_{Cu^{2+}/Cu} > E^0_{H_2O/H_2}$.

Anode : $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$ ✓
$SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$
∴ $E^0_{H_2O/O_2} > E^0_{SO_4^{2-}/S_2O_8^{2-}}$
Only when conc of SO_4^{2-} is low.

At higher conc, $S_2O_8^{2-}$ is formed.
If not given, take low conc.

→ Electrolysis of Na_2SO_4 with inert electrode.

At cathode : $2H_2O + 2e^- \longrightarrow H_2\cancel{O} + 2OH^-$ ✓

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

as. $E^\circ_{H_2O/H_2} > E^\circ_{Na^+/Na}$

At anode : $2H_2\cancel{O} \longrightarrow 4H^+ + 2O_2 + 4e^-$ ✓

$SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$

as $E^\circ_{H_2O/O_2} > E^\circ_{SO_4^{2-}/S_2O_8^{2-}}$

Cat : H_2 , An : O_2.

→ Electrolysis of H_2O using inert electrodes :

Cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Anode : $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$.

or. $6H_2O \longrightarrow 2H_2 + 4OH^- + 4H^+ + O_2$.

or $\boxed{2H_2O \longrightarrow 2H_2 + O_2}$

→ Electrolysis of H_2O in acidic medium (H_2SO_4) using inert electrode.

Cathode: $2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O$

Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ ✓

$SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$

→ H_2O in basic medium $(NaOH)$ using inert electrodes

Cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ ✓

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

Anode : $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

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

$\boxed{\text{as } E^\circ_{OH^-/O_2} > E^\circ_{H_2O/O_2}}$

→ Aq $CuSO_4$ using Cu electrodes

Cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$ ✓

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

$E^0_{Cu^{2+}/Cu} > E^0_{H_2O/H_2}$

Anode: $2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$

$2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

$Cu \longrightarrow Cu^{2+} + 2e^-$ ✓

The conc of Cu^{2+} ions remains constant

→ Electrolysis of aq NaCl using Hg as cathode [Castner Kellner's process]

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

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Cathode : $Na^+ + e^- \longrightarrow Na$

$2Na + 2Hg \longrightarrow 2Na-Hg$

(Sodium amalgam)

$2Na-Hg + 2H_2O \longrightarrow 2NaOH + H_2 + 2Hg$

→ Only for high conc of NaCl otherwise water will be reduced

→ Electrolysis of H_2SO_4 using Pt (inert) electrode

1) At normal or high current density

Anode: $SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$ ← (high current density)

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ ← (normal current)

Cathode : $2H_3O^+ + 2e^- \longrightarrow 2H_2O + H_2$. ✓

→ $AgNO_3$, using Ag electrodes

Cathode : $Ag^+ + e^- \longrightarrow Ag$. ✓
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$
$3NO_3^- \longrightarrow 3NO + 3O_2 + 3e^-$
$Ag \longrightarrow Ag^+ + e^-$ ✓

→ Aqueous NaOH : H_2 at cathode, O_2 at anode (from OH
→ fused NaOH : Na at the cathode, O_2 at anode
→ dil HCl : H_2 at cathode, Cl_2 at anode

Calculations

We define: charge on 1 mol of e^-
$1.6 \times 10^{-19} C \times 6.022 \times 10^{23}$
$\cong 96500 C$
$\simeq 1F$, (1 Faraday)

$Cu^{2+} + 2e^- \longrightarrow Cu$
1 mol   2 mol e^- 1 mol
2F

$2F \longrightarrow 63.5 g$
$1F \longrightarrow \frac{63.5}{2} g = E_{Cu}$ (Eq^v weight of Cu)

$Al^{+3} + 3e^- \longrightarrow Al$
1 mol   3 mol   1 mol

$3F \longrightarrow 27$
$1F \longrightarrow \frac{27}{3} = 9 =$ Eq^v weight of Al.

1 Faraday is that charge which produces that weight of a substance which is equal to its equivalent weight.

Or charge on one mole of electron is called 1 Faraday.

In these ques, treat electron as a reactant, apply mole concept on it, & select limiting reagent for these reaction from electron or other reactants

Faraday's Laws

Ist law:

Mass is deposited on electrodes as long as charge is supplied. Or

$m \propto q$

$m = zq$, z is electrochemical eqv

$m = zit$

we have $96500\ C \longrightarrow 1$ eqv weight.

$1C \longrightarrow \frac{E}{F}$

$q \longrightarrow \frac{qE}{F}$ weight

$\therefore W_{dep} = \frac{qE}{F}$

$\frac{W}{E} = (eq)_{deposit} = \frac{q}{F}$

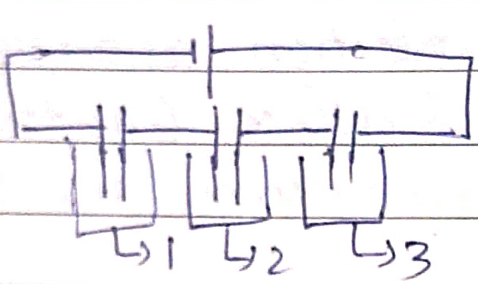
Also $W = \frac{q}{F} \cdot \frac{M}{P}$ → Molecular weight, P → n factor.

$\frac{W}{M} = \left(\frac{q}{F}\right)\frac{1}{P} = n$ (moles deposited) or $n = \frac{it}{Fp}$.

IInd law

For cells in series

$q = \text{const}$



we have, $W = \underbrace{\left(\frac{q}{F}\right)}_{\text{const}} E = Zq$

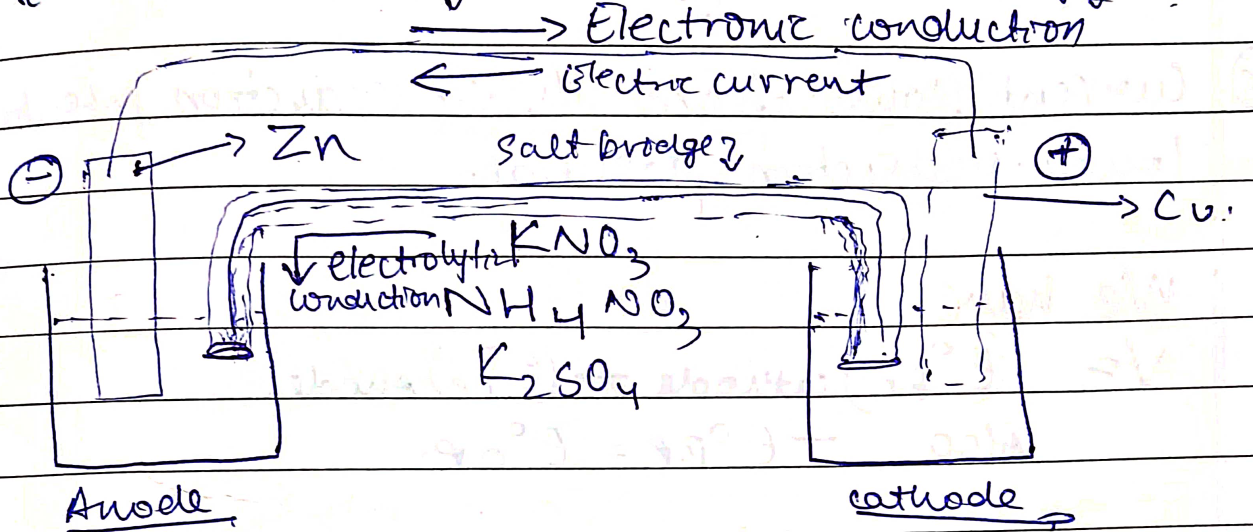
$Z = \frac{E}{F}$

$W \propto E \propto Z$

$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$

Galvanic cell with salt bridge

(Chemical energy → electrical energy)



We know, $E^{\circ}_{Zn/Zn^{2+}} > E^{\circ}_{Cu/Cu^{2+}}$ } oxidation

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

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

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

function of salt bridge

1) completes the circuit
2) It maintains electrical neutrality in the electrodes
3) It minimizes liquid junction potential

If any half cell containing H^+, Ag^+, Hg^+, Hg^{2+}, then KCl not used as electrolytes as they form ppt at mouth of glass tube. In this case, KNO_3, NH_4NO_3 is used.
~~Although, cat & anion don't have same transport no.~~

→ But it is not necessary to have salt bridge in Galvanic cell, but in **NCERT** → it is written that it is necessary

Condition for salt bridge material:

1) The material used in salt bridge must not make ppt at electrode
2) Transport no of cation = transport no. of anion (Generally, radius of cation = radius of anion).
3) Although few do not have equal transport no. can also be used eg NH_4NO_3
4) Salt bridge should be changed from time to time

→ The ions of electrolytes also transport through salt bridge for neutrality.

⊛ Current flows from Higher reduction potential to lower reduction potential.

We have.

$$V = (E^\circ_{RP})_{cathode} - (E^\circ_{RP})_{Anode}.$$

Also, $-E^\circ_{RP} = E^\circ_{OP}$.

$$\therefore V = (E^\circ_{RP})_{cathode} + (E^\circ_{OP})_{Anode}$$: in std condition

EMF: Electromotive force:
It is the maximum potential difference across the electrodes that exists when the cell is not working

→ EMF of cell is not an additive property, it is an intensive property.
But
Gibb's energy is an additive property.

So, we have

Electrical energy = qV.

$(EE)_{max} = qE = nFE$

Now EE is electrical (non mechanical energy)

and ΔG = max non mechanical work done

$\Delta G = -nE^\circ F$, − as out of system

$$\boxed{\Delta G^\circ = -nE^\circ F}$$

Eg:

$Zn \longrightarrow Zn^{2+} + 2e^-$, $\Delta G_1^\circ = -2E^\circ_{Zn/Zn^{2+}}F$

$Cu^{2+} + 2e^- \longrightarrow Cu$, $\Delta G_2^\circ = -2E^\circ_{Cu^{2+}/Cu}F$

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$, ΔG_3.

We have $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$.

$-2E^\circ F = -2E^\circ_{Zn/Zn^{2+}}F - 2E^\circ_{Cu^{2+}/Cu}F$

$E^\circ = E^\circ_{OP} + E^\circ_{RP}$

But: $Fe^{3+} + 3e^- \longrightarrow Fe$, $E^\circ_{Fe^{3+}/Fe} = a$.

$Fe^{2+} + 2e^- \longrightarrow Fe$, $E^\circ_{Fe^{2+}/Fe} = b$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$, $E^\circ_{Fe^{3+}/Fe^{2+}} = ?$

We can not do a−b directly as n is not const

So $Fe^{3+} + 3e^- \longrightarrow Fe$; ΔG_1°

$Fe \longrightarrow Fe^{2+} + 2e^-$, ΔG_2°.

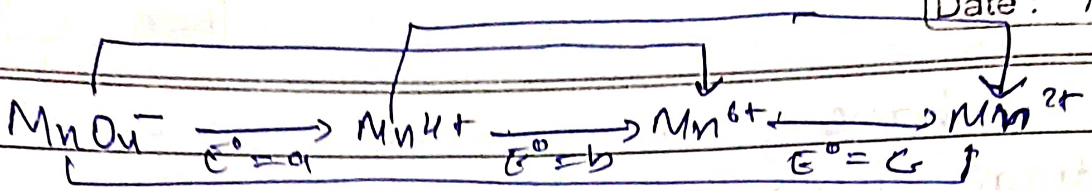
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$, ΔG_3.

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

$\therefore -FE^\circ_{Fe^{3+}/Fe^{2+}} = -3FE^\circ_{Fe^{3+}/Fe} - 2FE^\circ_{Fe^{2+}/Fe}$

$= -3aF + 2bF$

$\therefore E^\circ_{Fe^{3+}/Fe^{2+}} = 3a - 2b$



Find if cell reaction is correct

IUPAC: Anode || Cathode

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

But this is not always given in correct order. We need to first find which is actually anode & cathode

∴ Assume Zn to be anode & Cu cathode

Anode: $\therefore Zn \longrightarrow Zn^{2+} + 2e^-$, $E^\circ_{OP} = a$

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$, $E^\circ_{RP} = b$

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

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

We have, for this rxn to be feasible, $\Delta G < 0$

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

$\Rightarrow E^\circ_{cell} > 0$

$$\boxed{E_{cell} > 0}$$

If it comes less than zero, then assumed anode becomes cathode & same for cathode

Like if $Cu | Cu^{2+} || Zn^{2+} | Zn$ not feasible

then $Zn | Zn^{2+} || Cu^{2+} | Cu$ is feasible

Also eg $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

We have $Q = \dfrac{P_{H_2}\,[Zn^{2+}]}{[H^+]^2}$

$\longrightarrow$

NERNST EQ^N

We have $\Delta G^\circ = -nE^\circ F$

~~ΔG~~ $-nEF = -nE^\circ F + RT\ln Q$

$\therefore E = E^\circ - \dfrac{RT}{nF}\ln Q$

Thus is Nernst eq^n (it is derived for half cell).

at 25°C, $E = E^\circ - \dfrac{0.059}{n}\log Q$.
at 30°C
$E = E^\circ - \dfrac{0.06}{n}\log Q$.

For anode,

ode: $E_{Zn|Zn^{2+}} = E^\circ_{Zn|Zn^{2+}} - \dfrac{0.059}{2}\log[Zn^{2+}]$

ode: ~~Eother~~ $E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \dfrac{0.059}{2}\log\dfrac{1}{[Cu^{2+}]}$

$E_{cell} = E_{OP} + E_{RP}$

$= E^\circ_{Zn/Zn^{2+}} + E^\circ_{Cu^{2+}/Cu} - \dfrac{0.059}{2}\log\left[\dfrac{Zn^{2+}}{Cu^{2+}}\right]$

$$\boxed{E_{cell} = E^\circ_{cell} - \dfrac{0.059}{n}\log Q.}$$

→ If cell is at eq^n $\Longrightarrow$ $\overset{\Delta G = 0}{E_{cell} = 0}$

$$\therefore E^\circ_{cell} = \frac{0.059}{n} \log K_{eq}$$

→ Concentration cell

Anode and cathode are made of the same material

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

∴ Current flows due to conc or pressure difference b/w anode and cathode.

$$\therefore E_{cell} = -\frac{RT}{nF} \ln Q$$

$$= -\frac{0.059}{n} \log Q.$$

~~Ex~~ Eg of conc cell

$Pt, H_2 | H^+ || H^+ | H_2, Pt$

$Pt, Cl_2 | Cl^- || Cl^- | Cl_2, Pt$

$Ag | Ag^+ || Ag^+, Ag$

We have.

$\underset{(P_1)}{Pt\ H_2} | H^+(C_1) || C_2\ H^+ | \underset{(P_2)}{H_2}\ Pt$

Assume Anode

Assum cathode

At Anode: $\underset{P_1}{H_2} \longrightarrow \underset{C_1}{2H^+} + 2e^-$

At cathode: $2H^+ + 2e^- \longrightarrow H$

Overall: $H_2 + 2H^+ \longrightarrow 2H^+ + H_2$
$P_1 \quad C_2 \qquad\qquad C_1 \quad P_2.$

$$Q = \left(\frac{C_1}{C_2}\right)^2 \frac{P_2}{P_1}$$

∴ We have, $E^\circ_{cell} = 0$

$$\therefore E_{cell} = -\frac{0.059}{2} \log Q = -\frac{0.059}{2} \log\left(\frac{P_2}{P_1}\right)\left(\frac{C_1}{C_2}\right)^2$$

Case 1, $P_1 = P_2$

$$E_{cell} = -0.059 \log \frac{C_1}{C_2}.$$

For feasible, $C_2 > C_1$, $\Longrightarrow$ current from high → low con

Case 2, $C_1 = C_2$

$$E_{cell} = -\frac{0.059}{2} \log \frac{P_2}{P_1}$$

For feasible, $P_1 > P_2 \Longrightarrow$ current from low P to high P.

<u>For half-cell, we have,</u>

$$E_{H_2/H^+} = E^\circ_{H_2/H^+} - \frac{0.059}{2} \log \frac{C_1}{P_1}$$

If $P_1 = 1$ atm

$$E_{H_2/H^+} = 0 - \frac{0.059}{2} \log [H^+] = \frac{0.059}{2} \text{ pH}$$

Types of ques:

1) $H_2 \mid HCl \mid H_2 \Longrightarrow$ Conc of H^+ is same
2) $H_2 \mid 0.1N\ H^+ \parallel 0.2N\ H^+ \mid H_2 \Longrightarrow$ pressure is same

3) Pt $H_2 \,|\, 0.1\,M\,H^+ \,||\, 0.2\,M\,H^+ \,|\, H_2$ ... Pt
$\quad$ 2 atm $\qquad\qquad$ 4 atm

4) $H_2 / 0.1\,M\,H_2SO_4 \,||\, 0.2\,N\,H_2SO_4 / H_2$
$= H_2 / 0.2\,M\,H^+ \,||\, 0.2\,M\,H^+ / H_2$

5) $H_2 \,|\, 0.1\,M\,HCl_2 \,||\, 0.2\,M\,H_2SO_4 \,|\, H_2$
$= H_2 \,|\, 0.1\,M\,H^+ \,||\, 0.4\,M\,H^+ / H_2$

~~6 H_2~~

6) $H_2 \,|\, 0.1\,M\,NaOH \,||\, 0.1\,M\,HCl / H_2$
or $H_2 \,|\, K_w/[OH^-]\;H^+ \,||\, 0.1\,M\,H^+ \,|\, H_2$

7) $H_2 / 0.1\,M\,CH_3COOH \,//\, 0.1\,M\,H_2SO_4 / H_2$
$\sqrt{K_aC}\;M\;[H^+]$

8) $H_2 / 0.1\,M\,CH_3COOH \,//\, 0.1\,M\,NH_4OH / H_2$
$\sqrt{K_aC}\;M\;H^+ \,//\, K_w/\sqrt{K_bC}\;H^+$

9) $H_2 / 0.1\,M\,\underbrace{CH_3COOH + 0.1\,M\,HCl}_{100\,ml} \,//\, 0.1\,M\,CH_3COOH / H_2$
$0.1\,M\,H^+ \qquad \sqrt{K_aC}\;H^+$

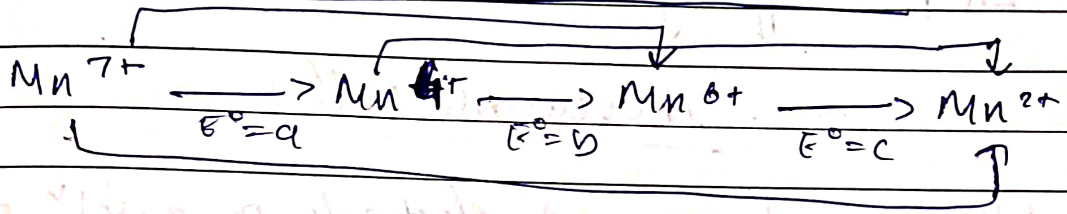
10) $H_2 / 0.1\,M\,CH_3COONa \,||\, 0.1\,M\,NH_4Cl / H_2$
hydrolysis $\qquad$ Hydrolys
$\downarrow 0.1\,M\,NaOH \qquad \downarrow 0.1\,M\,HCl$

Q $H_2 \,|\, 0.1\,M\,H_3PO_4 \,||\, 0.1\,M\,NH_4OH \,/\, H_2$
$K_1 = 10^{-5}$ $\qquad$ $V = 100\,ml$
$K_2 = 10^{-8}$ $\qquad$ $K_b = 1.8\times10^{-5}$
$K_3 = 10^{-12}$
$V = 100\,ml$

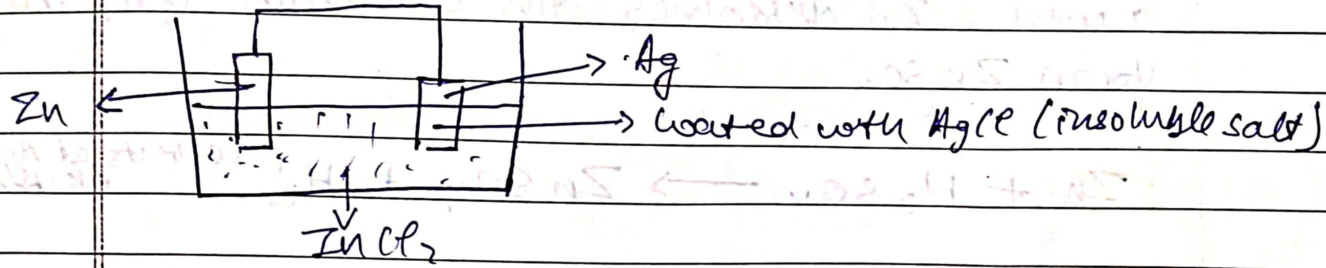
Find E_{cell} for

V_{NaOH}	V_{HCl}	V_{NaOH}	V_{HCl}
0	0	100	100
10	10	150	100
20	20	150	150
50	50	200	200

V_{NaOH}	V_{HCl}	V_{NaOH}	V_{HCl}
250	200	350	200
300	200	400	200



Galvanic cell without salt bridge



$$Zn(s) + 2AgCl \longrightarrow 2Ag(s) + Zn^{2+} + 2Cl^-$$

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

at cathode : $2AgCl + 2e^- \longrightarrow 2Ag(s) + 2Cl^-$

Ag(s) is formed, which does not enter solⁿ, Cl^- enters solution which maintains electrical neutrality.

Reversible cell

Conditions :

- Driving force & opposition force differ by a small amt
- It should be possible to reverse any change by applying a force infinitesimally greater than the acting one

→ If $E_{ext} < E_{cell}$, e^- from anode to cathode

→ $E_{ext} = E_{cell}$, no e^- flow

→ $E_{ext} > E_{cell}$, cathode becomes anode & anode becomes cathode

e^- still from anode to cathode

Eg 1) $Zn / Zn^{2+} \parallel Cu^{2+} / Cu$
2) $Zn \mid Zn^{2+} \parallel AgCl / 2Ag(s) + 2Cl^-$

Irreversible cell

Cell composed of Zn & Ag electrode in a soln of H_2SO_4. When 2 electrodes are connected externally by a wire, Zn dissolves with evolution of H_2 to form $ZnSO_4$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$ ↗ evolves at Ag electrode

When this cell is connected ext source of potential slightly greater than its own, Ag dissolves at one electrode, and H_2 evolves at other.

$$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2$$

Standard cell

→ It should be such that its potential is reproducible constant with time, and it should be irreversible.
→ It should not suffer permanent damage due to passage of current & should preferably have low temp. coefficient of E.M.F.

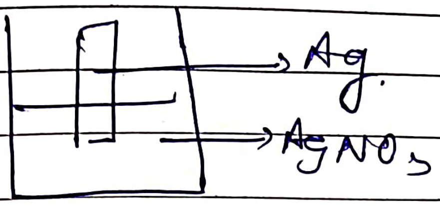
Eg. Weston unsaturated & saturated cell

Types of electrodes

1) Metal-metal ion electrode

Eg M/M^+ , Anode
M^+/M, Cathode

Eg Ag^+/Ag is cathode, Ag/Ag^+ is anode.



Other Eg:
Cu/Cu^{2+}
$Na(Hg)/Na^+(a)$
as $Na(Hg) \longrightarrow Na^+ + e^-$

~~Other eg~~ At anode: $Ag \longrightarrow Ag^+ + e^-$

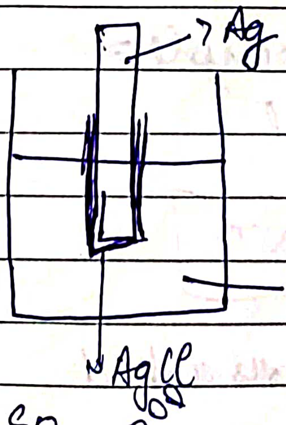
$$E_{Ag/Ag^+} = E^0_{Ag/Ag^+} - \frac{0.059}{n} \log [Ag^+]$$

At cathode: $Ag^+ + e^- \longrightarrow Ag$

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - \frac{0.059}{n} \log \frac{1}{[Ag^+]}$$

VVIMP 2) Metal-metal ~~form~~ insoluble salt - anion electrode

Representation: Anode $\{ Ag/AgCl/Cl^-$ or $Ag/AgCl, Cl^-$
Cathode $\{ AgCl/Cl^-/Ag$, $AgCl, Cl^-/Ag$



We have $Ag \longrightarrow Ag^+ + e^-, \Delta G_1^0$
$Ag^+ + Cl^- \rightleftharpoons AgCl, \Delta G_2^0$

$Ag + Cl^- \longrightarrow AgCl + e^-, \Delta G_3^0$

So

$$E_{Ag/AgCl, Cl^-} = E^0_{Ag/AgCl, Cl^-} - \frac{0.059}{1} \log \frac{1}{[Cl^-]}$$

Also, we have $K_{sp} = [Ag^+][Cl^-]$ or $[Cl^-] = \frac{K_{sp}}{[Ag^+]}$

$-E^0_{Ag/Ag^+} - \frac{0.059}{1}\log[Ag^+]$

$E_{Ag/AgCl, Cl^-} = E^0_{Ag/AgCl, Cl^-} - \frac{0.059}{1}\log\frac{[Ag^+]}{K_{sp}}$

$= E^0_{Ag/AgCl, Cl^-} + 0.059\log K_{sp} - 0.059\log[Ag^+]$ — ②

And, we have

$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$

$\Delta G_1^0 = -FE^0_{Ag/Ag^+}$

$\Delta G_2^0 = -RT\ln K_{eq} = -RT\ln\frac{1}{K_{sp}} = RT\ln K_{sp}$

$\Delta G_3^0 = -E^0_{Ag/AgCl, Cl^-}$

$\therefore -FE^0_{Ag/Ag^+} + RT\ln K_{sp} = -E^0_{Ag/AgCl, Cl^-}\times F$

$\therefore E^0_{Ag/AgCl} + \frac{RT\ln K_{sp}}{F} = E^0_{Ag/Ag^+}$ — ①

Putting ① in ②

$E_{Ag/AgCl, Cl^-} = E^0_{Ag/Ag^+} - 0.059\log[Ag^+]$

$= \boxed{E_{Ag/Ag^+}}$ → use this and $[Ag^+]$ by K_{sp} and $[Cl^-]$ conc etc

⟹ E of metal-metal insoluble = E metal only electrode

BUT, E^0 IS DIFFERENT

Whenever metal metal insoluble ans asked

$E^0_{\cancel{Ag/AgCl}}$ $E^0_{AgCl/Ag} = E^0_{Ag^+/Ag} - \log K_{sp}\times\frac{0.059}{1}$

⑤ Hg_2Cl_2 $\uparrow$

II Calomel Electrode

Anode : $Hg(l) \,|\, Hg_2Cl_{2(s)}, Cl^-_{(aq)}$

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

Cathode : $Cl^-, Hg_2Cl_{2(s)} \,|\, Hg(l)$

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg(l) + 2Cl^-_{(aq)}$$

we have,

$$\frac{1}{2} Hg_2Cl_2 \rightleftharpoons Hg^+ + Cl^-$$
$$Hg^+ + e^- \longrightarrow Hg$$
$$\frac{1}{2} Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$$

RP

$$\therefore E = E^0 - \frac{0.059}{2} \log [Cl^-]^2$$
$$= E^0 - 0.059 \log [Cl^-]$$

→ Electrode is generally made with chloride soln of 0.1M or 1M KCl, or saturated KCl

→ 3 types of calomel electrodes are used:

1) Most common : Standard calomel electrode:
$[KCl] = 3.5M$, $E_{cell} = 0.24V$, w.r.t SHE

2) Normal calomel electrode,
$[KCl] = 1M$, $E_{cell} = 0.268V$, w.r.t SHE

3) Decinormal calomel electrode
$[KCl] = 0.1M$, $E_{cell} = 0.338V$, w.r.t SHE

Hg_2Cl_2 is known as calomel.

⑥

extra

III) Antimony - antimony trioxide electrode

$Sb(s) \,|\, Sb_2O_3(s), OH^-$ or $OH^-, Sb_2O_3(s) \,|\, Sb$

$$2Sb + 6OH^- \underset{[H]}{\xrightarrow{[O]}} Sb_2O_3 + 3H_2O + 6e^-$$

IV) Mercury - mercury oxide electrode

$Hg(l) \,|\, HgO(s), OH^-$ or $OH^-, HgO(s) \,|\, Hg(l)$

$Hg(l) + 2OH^- \rightleftharpoons HgO + H_2O + 2e^-$

V) $Cu(s) \,|\, Cu(OH)_2, OH^-$ or $OH^-, Cu(OH)_2(s) \,|\, Cu(s)$

$Cu(s) + 2OH^- \rightleftharpoons Cu(OH)_2(s) + 2e^-$

VI) $Zn \,|\, ZnSO_4, SO_4^{2-}$ or $SO_4^{2-}, ZnSO_4(s) \,|\, Zn(s)$

If anion also written ⇒ insoluble salt

$Zn(s) + SO_4^{2-} \rightleftharpoons ZnSO_4 + 2e^-$

VII $Pb(s) \,|\, PbSO_4(s), SO_4^{2-}(aq)$ or $SO_4^{2-}(aq), PbSO_4(s) \,|\, Pb(s$

$Pb(s) + SO_4^{2-} \rightleftharpoons PbSO_4(s) + 2e^-$

③ Gas - gas ion electrode

I) Hydrogen electrode:

$Pt, H_2(g) \,|\, H^+(aq)$ or $H^+(aq) \,|\, H_2(g)\, Pt$

$2H^+ + 2e^- \longrightarrow H_2$, $Q = \dfrac{P_{H_2}}{[H^+]^2}$

2) Chlorine electrode

reversible wrt Cl^-

$Pt, Cl_2(g) \,|\, Cl^-(aq)$ or $Cl^-(aq) \,|\, Cl_2(g)\, Pt$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$, $Q = \dfrac{[Cl^-]^2}{P_{Cl_2}}$

3) Oxygen electrode

$Pt, O_2(g) \,|\, OH^-(aq)$ or $OH^-(aq), O_2, Pt$

$O_2 + 2H^+ + 4e^- \rightleftharpoons 2OH^-$

$$a = \frac{[OH^-]^2}{P_{O_2}\,[H^+]^2}$$

Oxygen gas at a given pressure is bubbled through a sol^n containing OH^-

But as eq^b b/w O_2 & OH^- can't be established quickly, O_2 electrode doesn't behaves as a truly reversible electrode

also represented as:

$Pt, O_2(g) \,|\, H_2O(l)$ or $H_2O(l) \,|\, O_2(g), Pt$

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O(l)$

4) Hydrogen gas bubbling in a sol^n of acid (eg HCl) forms an electrolyte of the type $H^+ + e^- \rightarrow \frac{1}{2} H_2$

The electrode is reversible wrt H^+ ions. ∵ H_2 is non conducting, Pt or a metal which is not attacked by acid and easily comes in contact with H_2 is used to make electric contact

④ Oxidation-reduction electrode:

In this, 2 ions of same metal in different oxidation states are present in sol^n and an inert metal like Pt is immersed in sol^n.

1) $Fe^{3+}(aq) \,|\, Fe^{2+}(aq), Pt$: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

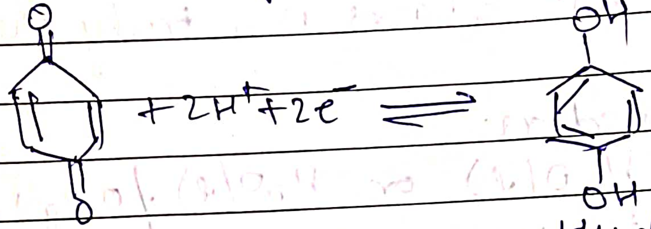
2) $Cr_2O_7^{2-}(aq) \,/\, Cr^{3+}(aq), H^+(aq), Pt$: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

3) $MnO_4^-(aq) \,|\, Mn^{2+}(aq), H^+(aq), Pt$: $MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

(8)

4) $Co^{3+}(aq) | Co^{2+}(aq), Pt$, $Co^{3+}(aq) + e^- \longrightarrow Co^{2+}$

5) **Quin Hydrone electrode:** Oxid^n - Red^n electrodes can also be made using organic molecules that can exist in 2 diff oxid^n states. A generally used material of this type is related to important biochemical oxid^n, red^n rx^{n}s, as the system of hydroquinone, which can form the oxid^n, red^n sys b/w quinone (Q) & hydroquinone (QH_2)



Quinone Hydroquinone

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

Presence of a Pt electrode in a sol^n containing these 2 species provides an electrode that can donate or accept e^-. If hydro-quinone (QH_2) and quinone (Q) : $Pt | QH_2, Q, H^+$

electrode: $Pt, QH_2 | Q, H^+$

This electrode is the Quin-hydrone electrode coz of charge complex that is formed b/w QH_2 & Q.

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

$$Q = \frac{1}{[H^+]^2} \quad (\text{rx}^n \text{ coefficient})$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log\left(\frac{1}{[H^+]^2}\right)$$

$$= E^0_{cell} - 0.059(pH)$$

$$\hookrightarrow 0.699V.$$

limitations:

It cannot be used for sol^n with pH > 8. In more alkali sol^n, QH_2 ionizes appreciably as an acid & also gets parti oxidized by atmospheric oxygen. This alters the normal eq^b b/w Q & QH_2 which form the basis of the electrode

Quin-hydrone electrode is combined with a saturated calomel electrode to form a cell.

$Hg, Hg_2Cl_2(s), KCl(\text{saturated}) \, || \, H^+_{(\text{unknown conc})} \, Q, QH_2 / Pt$
$\rightarrow$ RP

$E_{Q;2H^+/H_2Q} = E^\circ_{Q;2H^+/H_2Q} - 0.059\,pH$
$= 0.699 - 0.059\,pH$

$E_{calomel} = 0.24V \leftarrow$ RP.

$\therefore E_{cell} = 0.699 - 0.059\,pH - 0.24$

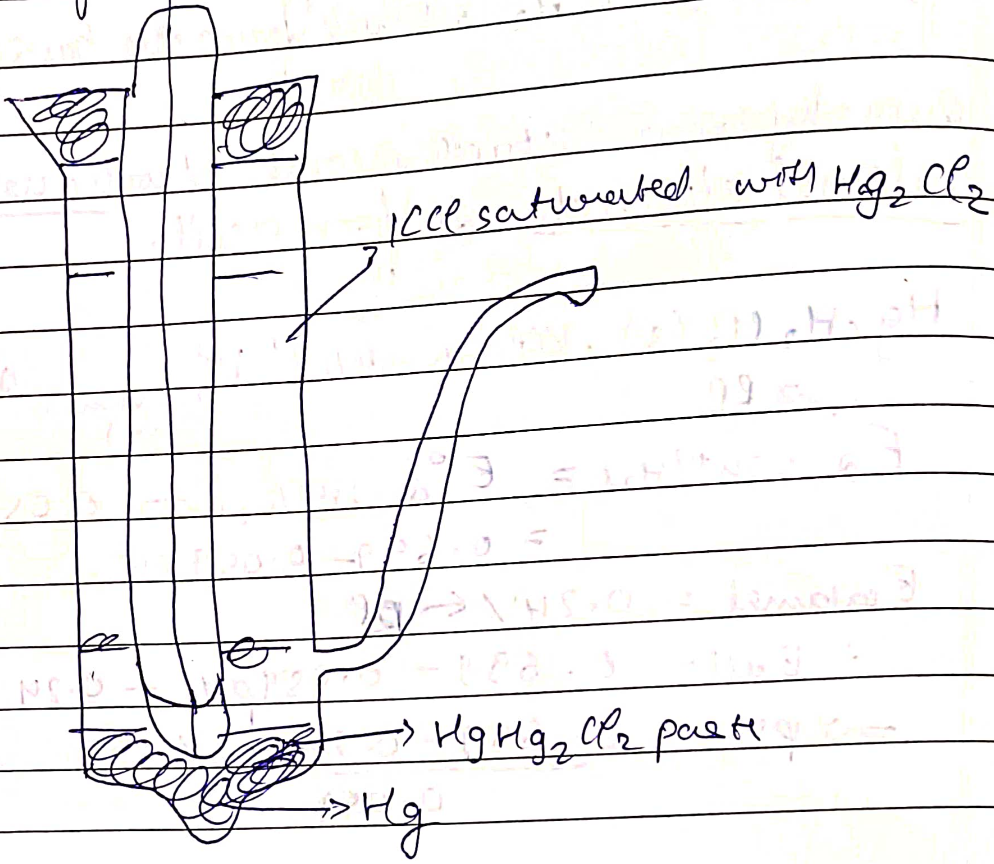
$\Rightarrow pH = \dfrac{0.699 - 0.24 - E_{cell}}{0.059}$

- **Mercury - mercurous sulphate electrode** (metal-metal insoluble)
It consist of Hg covered with sparingly soluble Hg_2SO_4 in contact with $H_2SO_4 | K_2SO_4$
$Hg(l), Hg_2SO_4(s) | SO_4^{2-}(aq)$
Cathode : $Hg_2SO_4 + 2e^- \longrightarrow 2Hg(l) + SO_4^{2-}(aq)$
$Q = [SO_4^{2-}]$, $n = 2$

- **Mercury - mercuric sulphate** ($Hg-HgSO_4$) **electrode**

$Hg(l), HgSO_4(s) / SO_4^{2-}(aq)$
$Q = [SO_4^{2-}]$, $n = 2$.

Diagram of standard calomel electrode:



BATTERIES

- Are basically galvanic cells that convert chemical energy of redox rxn into electrical energy
- For practical ~~use~~ use, battery should be light, compact and its voltage shouldn't vary appreciably during use.

Two types of batteries:

I Primary batteries:

- Rxn occurs only once and gets used over a prd of time, battery becomes dead & can't be reused.

1) Lechlanche / Dry cell

Anode: Zn (Zn container)
Cathode: Graphite rod surrounded by MnO_2 & carbon
Electylte: NH_4Cl, $ZnCl_2$

Rxns:
Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$
Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

- NH_3 produced forms complex with Zn^{2+}: $[Zn(NH_3)_4]^{2+}$
- Cell has a potential ~1.5V
- Used in transistors and clocks.

ii) Mercury cell

Anode: Zn / Hg amalgam
Cathode: paste of HgO & carbon
Electrolyte: paste of KOH & ZnO

Rxns:

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$
Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$
Ovr: $Zn(Hg)_{(s)} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

- Cell potential ~1.35V
- Suitable for low current devices like hearing aids, watches
- Cell potential remains const throughout life as ovr rxn does not involve any ion in soln whose conc changes.

II Secondary batteries

1) Lead storage battery:

Anode: Pb (Pb grids filled with spongy Pb)
Cathode: grid of Pb packed with PbO_2
Electrolyte: 38% sol^n of H_2SO_4

Rxns:

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$
Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$
Ovr: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

- On charging, rx^n is reversed and $PbSO_4$ is converted to Pb & PbO_2 at anode & cathode respectively
- Used in automobiles and inverters

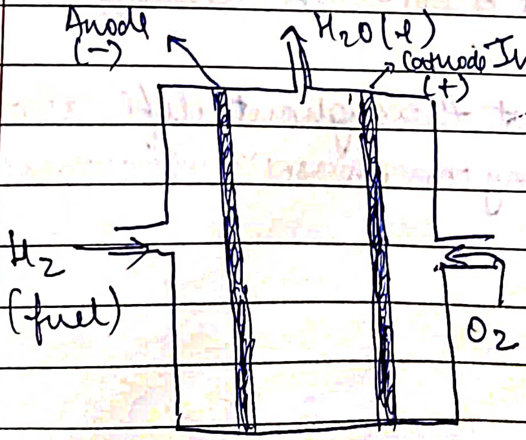
ii) Nickel-cadmium cells

- has longer life than lead storage battery
- but is more expensive

Rx^n: $Cd(s) + 2Ni(OH)_3 \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

FUEL CELLS

Are Galvanic cells that are designed to convert energy of combustion of fuels like H_2, CH_4, CH_3OH directly to electrical energy.



In the cell,
H_2 & O_2 are bubbled through porous carbon electrodes into conc aq NaOH sol^n.
Catalysts like finely divided Pt/Pd are incorporated in the electrodes to increase rate of rx^n

Rxn's (4)

Cathode : $O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-$

Anode: $2H_2 + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Ovr: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

- The cell runs continuously as long as reactants are supplied.
- They produce energy at 70% efficiency as compare to thermal plants of 40% efficiency

CORROSION

- Corrosion coats metal surfaces with oxides or salts.
- eg. Rusting of iron, tarnishing of silver, green coating on Cu and Bronze.

Rusting:

→ **Anode**: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$ $(E^\circ_{Fe^{2+}/Fe} = -0.44V$

These e^- released move through metal and go to another spot to reduce O_2 in presence of H_2.
H^+ obtained from i) dissolution of CO_2 into H_2O to form H_2CO_3,
ii) dissolution of other acidic oxides from atmosphe
This spot behaves like cathode.

→ **Cathode**: $O_2(g) + 4H^+(aq)$ ~~→ 2Fe²⁺~~ $+ 4e^- \longrightarrow 2H_2O(l$
$E^\circ(H^+, O_2 | H_2O = 1.23)$

→ Ovr: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l$
$E^\circ = 1.67V$

The Fe^{2+} is further oxidised to Fe^{3+} which comes out as rust as hydrated oxides. $(Fe_2O_3 \cdot xH_2O)$

Atmospheric oxidation:

$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$

→ **Methods to prevent corrosion:**

1) covering surface with paint or chemicals like bisphenol
2) cover metals with other metals (Sn, Zn, etc) that are reactive than metal, to save the object
3) Electrochemical method: provide a sacrificial electrode of other metal (like Mg, Zn) which gets corroded itself but saves the object

Conduction in electrolytic cells

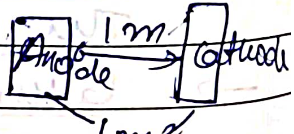
It depends on:

1) Interionic attraction (depends on solute - solute interaction)
2) Solvation of ions (solute - solvent interactions)
3) Viscosity of solvent (solvent - solvent interaction)

Conductance

We have $R = \frac{\rho l}{A}$, ρ is resistivity (Ωm) (IUPAC name) or specific resistance

If $l = 1$ unit, ~~A~~ $A = 1$ unit, $\boxed{R = \rho}$



Also, we define G (conductance) $= \frac{1}{R}$

unit: Ω^{-1} = mho = siemen (S)

and $\frac{l}{A}$ is cell constant

Also, we have, $\frac{1}{\rho} = \frac{1}{R}\frac{l}{A}$

$K = G\frac{l}{A}$

↳ Kappa, specific conductance ~~[illegible]~~
conductivity (IUPAC naming)

$l = 1$, ~~A~~ $A = 1$ then $K = G$

Specific conductance is the conductance of a conductor which is observed when it is one cm in length and 1 cm^2 in area of C.S. Mag depends on T, P, nature.

Equivalent conductance

Conducting power of all ions produced by 1 g equivalent of a substance.

It may be defined as conductance which is observed when 2 sufficiently large electrodes are dipped into a solution at such a distance so as to enclose in between them the entire volume of solution containing 1 g eq of electrolyte

Λ_{eq} (capital λ) is defined as the product of specific conductance & volume (ml) of solution which contain 1 g eq of electrolyte, ~~A~~ $\lambda_{eq} = KV$, If conc $= 1g/L$ then $\lambda_{eq} = \frac{K \times 1000}{N}$

unit of Siemen $m^2 \, eq^{-1}$, $[S \, m^2 \, eq^{-1}]$

$[\Omega^{-1} \, cm^2 eq^{-1}]$

Λ_{eq} = conductance of V ml sol^n containing 1 eq^v electrolyte

= conductance of 1 ml $\times$ V

$= KV$

Also, we have, $N = \frac{1}{V(L)} \xrightarrow{1\,eq^{N}} = \frac{1000}{V_{ml}}$

$$\therefore \Lambda_{eq} = \frac{1000 \times K}{N}$$

Molar conductance

Conducting power of all ions produced by 1 mol of a substance

Λ_m = conductance of V ml of sol

$\Lambda_m =$ conductance of V ml of solⁿ with 1 mol electrolyte
= Conductance of 1 ml × V
$= KV$

also, $M = \frac{1 \rightarrow 1\,mol}{V(L)} = \frac{1000}{V(ml)}$

$V_{ml} = \frac{1000}{M}$

$\therefore \Lambda_m = \frac{1000K}{M} = [S\ m^2\ mol^{-1}]$

$R = \frac{\rho l}{A}$ is applicable to all conductors: electronic or electrolytic and for uniform conductors of any CS, not necessarily rectangular

we have, $\Lambda_m = n\Lambda_{eq}$

Now, calc ~~[illegible]~~ λ_{eq} of salt ws λ_m of ions given

Eg. $K_2SO_4 \cdot Al_2(SO_4) \cdot 24H_2O$

$\lambda^\circ_m = 2\lambda^\circ_{m(K^+)} + \lambda^\circ_{m(SO_4^{2-})} + 2\lambda^\circ_{(Al^{3+})} + 3\lambda^\circ_{(SO_4^{2-})}$

$\lambda^\circ_m = 2\lambda^\circ_{K^+} + 2\lambda_{Al^{3+}} + 4\lambda^\circ_{SO_4^{2-}}$

$\frac{\lambda_m^\circ}{n} = \lambda_{eq}^\circ = \frac{1}{4} \times \lambda_{m\,K^+} + \frac{1}{4}\lambda_{m\,Al^{3+}} + \frac{1}{2}\lambda_{m\,SO_4^{2-}}$

If λ_{eq} of ions given

$= \frac{1}{4} \times 1 \times \lambda_{eq\,K^+} + \frac{1}{4} \times 3 \times \lambda^\circ_{eq\,Al^{3+}}$
$+ \frac{1}{2} \times 2 \times \lambda^\circ_{eq\,SO_4^{2-}}$

Effect of temperature and pressure on molar ionic conductance

For most of ions in water, the value Λ^{∞} increases with temp and this increase is about 2% per degree rise in temp. The temp dependence is expressed as :-

$$\Lambda^{\infty} = \Lambda^{\infty}_{25^\circ C}\left[1 + a\left(\underset{(\text{in } ^\circ C)}{t} - 25\right)\right]$$

where a is a constant (known as temp coefficient) and it is temp. For most of the ions, the temperature coefficient has a value of 0.02. (Exception for H^+, it is 0.014 and for OH^-, the value is 0.016). This is probably due to the difference in the conductance mechanism. The temp dependence results ~~from~~ from the decrease in viscosity of water with temp which amounts to 2% per degree. The value of Λ^{∞} decreases with increase of pressure which again is a consequence of increase of viscosity of water with pressure

Variation of conductance with dilution

Upon dilution, i.e. lowering conc, specific conduction decreases, while equivalent and molar conductance increases.

i.e as $C\downarrow$, $K\downarrow$, $\Lambda_m\uparrow$, $\Lambda_e\uparrow$

At infinite dilution or almost 0 conc,

Λ_{eq} and Λ_m attain their respective limiting values called equivalent / molar conductance at infinite dilution (Λ^{∞}) or zero conc (Λ°) resp.

For weak electrolyte :

Λ: Λ_{eq} or Λ_m ↑ with dilution as degree of dissociation ↑ resulting in more no. of ions in solⁿ. These ions are carriers of electricity. $\alpha \longrightarrow 1$ $\therefore$ Λ & Λ_m attain their respective max value.

K: Though no. of ions ↑, vol of solⁿ also ↑, ↑ in vol is in greater proportion than ↑ in no. of ions [illegible] resulting in decrease in no. of ions per c.c solⁿ. K being conductivity of 1 cc solⁿ ↓.

Strong electrolytes

Λ: These remain completely ionised at all concentrations Λ and Λ_m increase as ionic mobilities of ions ↑ due to ↓ in inter ionic attraction.
At ∞ dilution, inter-ionic attraction ceases to exist completely.

K: Volume ↑ ⟹ conductance / cc solⁿ ↓.

The variation of molar conductance of a strong electrolyte with concentration is theoretically given by Debye-Hückel-Onsager equation: $\Lambda_m = \underline{\Lambda_m^{\circ} - A\sqrt{C}}$

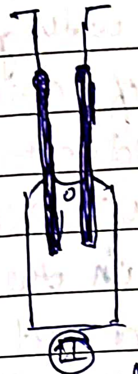
or $\underline{\Lambda_m^{0} - (A + B\Lambda_m^{\circ})\sqrt{C}}$

CONDUCTANCE CELL

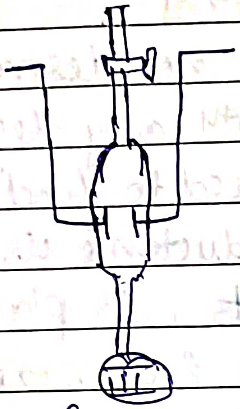
The cells for electrolytic conductance measurements are made of highly insoluble pyrex glass or of quartz

③

For general lab use, Ostwald cell is used



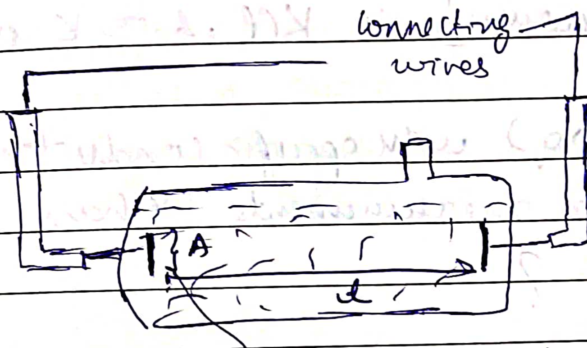
Dipping cell

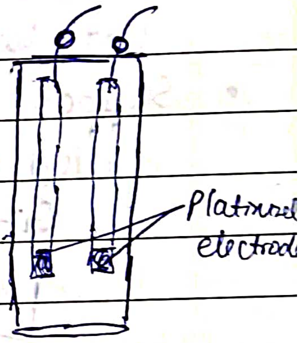


Pipette cell

Industrial purposes.

Ostwald cell.
For lab.





We know that a wheatstone bridge can be used for measuring unknown resistance.

- But if in ionic sol^{n}s, we pass D.C, the composition of the sol^n will change.
- Also, the sol^n cannot be connected to the bridge like a metallic wire.

→ For first problem, use AC.

→ For second problem, we use conductance cell.

conductimetric titration
Appⁿ of electrochem series
KL Kapoor.

Pg 75 Read ncert
Pg 76, Pg 79 formula
$\Lambda_m = \Lambda^0_m - A\,C^{1/2}$
and types of electrolytes pu

④

Determining cell constant.

- It is neither convenient nor desirable with general cells to measure l and A with any degree of accuracy, & an indirect method is used to find conductivity. If a solⁿ, whose spec conductance is known accurately from other measurements, is placed in the experimental cell, and its resistance R is measured, it is possible to obtain cell const $\frac{l}{A} = \frac{K}{C}$

- The electrolyte (known) is KCl, & its K is known with high precision
- Suppose C M KCl (aq) with specific conductance K is filled in conductance measurements, we have

$$\underbrace{G}_{\text{Conductance}} = \frac{1}{R} = \frac{I}{V}\ ?$$

Factors affecting conductivity of electrolytes

a) Inter ionic attraction
- If inter ionic attraction b/w solute is more, then conductivity will be less

b) Polarity of solvent:
If the solvent is greater polarized then the ionization and conductivity will be more.

c) Viscosity of medium:
By increasing the viscosity of medium, the conductivity decreases.

d) Temperature
As the temp of electrolyte solution is increased, the conductivity increases because K.E ions increases and all type of attraction forces decreases and the viscosity of medium decreases.

e) **Dilution**

i) The degree of ionization of weak electrolytes increases with the increase of dilution of the solution . The conductivity is increased due to the increasing no. of ions.

ii) Effect of dilution on specific conductance
Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in $1\ cm^3$ soln. decreases conductance also decrease on dilution.

iii) Effect of dilution on equivalent/molar conductivity
The equivalent / molar conductivity increases with dilution. For strong electrolyte, λ_m, λ_{eq} increases very slowly but for weak electrolytes, λ_m & λ_{eq} increase sharply

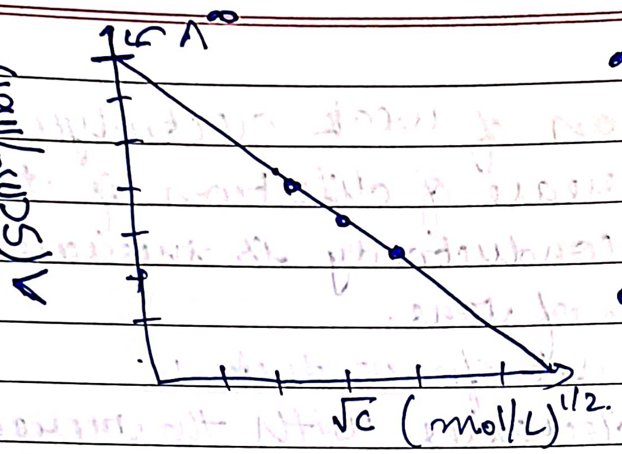
- When the whole of the electrolyte has ionized, further addition of the water brings a small change in the value of equivalent or molar conductance. This stage is called infinite dilution

- The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called conductivity ratio or degree of dissociation of solute.

$$\alpha = \frac{\Lambda_{eq}}{\Lambda^0_{eq}} = \frac{\Lambda_m}{\Lambda^0 m}$$

STRONG ELECTROLYTES

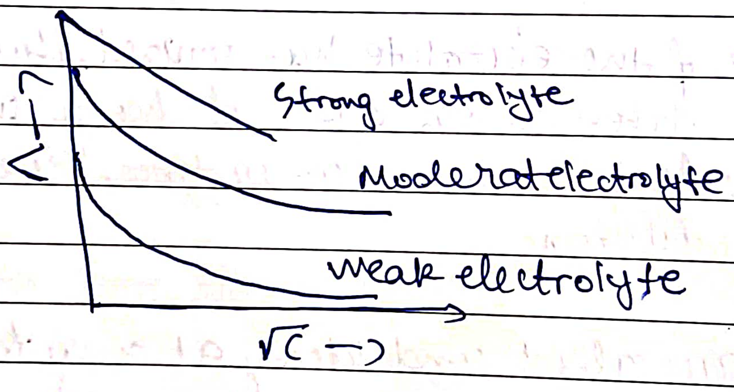
- For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation
$\Lambda = \Lambda^0 - A\sqrt{C}$, where A is a constant



- on dilution, interionic seperatio increases causing free movement and less hindrance. Thus increases Λ_m & Λ_{eq}
- for strong electrolytes, Λ^∞ or Λ^0 can be calculated from the y intercept

WEAK ELECTROLYTES

- Weak electrolytes have lower κ at higher conc and ∴ for such electrolytes, the change in Λ with dilution is due to increase in the no. of ions in a solⁿ containing a given amount of electrolyte.



- Weaker the electrolyte, more sharp is the increase of Λ_m or Λ_{eq} on dilution

KOHLRAUSH'S LAW of independent migration of ions

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte, irrespective of the nature of the other ion with which it is associated, and the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions ∴

$\Lambda^0_m = \Lambda^0_+ + \Lambda^0_-$ for AB type salt

For A_xB_y type salt, $\Lambda^\circ_m = x\Lambda^\circ_{A^{y+}} + y\Lambda^\circ_{B^{x-}}$

Applications of Kohlrausch's law

- To calculate Λ°_m of a weak electrolyte, say CH_3COOH, we can use Λ°_m of : a SE having cation like HCl
  " " " anion like CH_3COONa
  " " " both cat & anion like NaCl

$$\therefore \Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COO^-} + \Lambda^\circ_{H^+}$$
$$= \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl} + \Lambda^\circ_{CH_3COONa}$$

- To determine degree of dissociation α

$$\alpha = \frac{\text{no. of molecules ionized}}{\text{Total dissolved molecules}} = \frac{\Lambda_m}{\Lambda^\infty_m} = \frac{\Lambda_m}{\Lambda^\circ_m}$$

- Determination of solubility of sparingly soluble salts

→ The conductance (K) of an electrolyte is found using the conductivity cell. If required, the conductivity of water is subtracted from it. As sol^n of sparingly soluble salts are very dilute, we assume $\Lambda^\circ_m = \frac{1000\,K}{C} \Rightarrow \boxed{C = \frac{1000\,K}{\Lambda^\circ_m}}$

C is the molarity and hence the solubility.

- Determining the Ionic product of water

From Kohlrausch's law, we find Λ°_m of H_2O where Λ°_m is the molar conductance of water at infinite dilution when one mole of water is completely ionized to give one mole of H^+ and one mole of OH^- ions $\Rightarrow \Lambda^\circ_{m(H_2O)} = \Lambda^\circ_{H^+} + \Lambda^\circ_{OH^-}$

And also, $\Lambda_m = \frac{1000K}{C}$,

we know that $\Lambda_m = \Lambda^\circ_m$ as dissociation of water is low

∴ $\Lambda^\circ_m = \frac{1000K}{C}$, $C = \frac{1000K}{\Lambda^\circ_m}$

K is found experimentally, & molar conc is determined by the above formula. As $C = [H^+] = [OH^-]$, we have $\boxed{K_w = C^2}$.

- Ionic mobility u ($m^2/(\text{volt sec})$)

  $uF = \lambda^\infty$

  Velocity of ions : $\boxed{u.\frac{V \to Pd}{l \to dist}}$ or $u\overset{E.F}{\overset{\uparrow}{E}}$

Ionic mobility

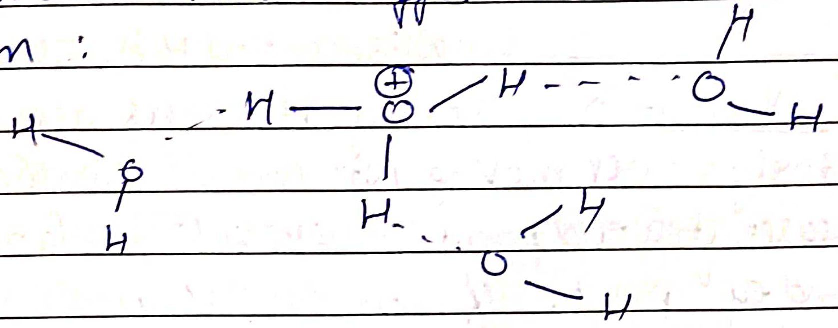
Distance travelled by an ion / second under a potential gradient of 1 V/m.

Potential gradient is given by $\frac{\text{P.D b/w electrodes}}{\text{Dist b/w electrodes}}$.

- Ionic mobility is extremely small as compared to speed of gaseous molecules which is about 10^2 m/s.
- Low mobility of ions is due to the fact that there are frequent collisions b/w ions and solvent molecules.
- Mean free path of molecules in water is very less.
- Li^+, Na^+ have comparatively low ionic mobility due to their higher charge density because of their small radii. Hence they are heavily hydrated by ion-dipole interaction than larger ions. Since the hydrated ion has to drag along a shell of H_2O as it moves along with the soln, its mobility is naturally less.

(*) Ionic mobility of H^+ is found to be 5 to 10 times more than other ions except OH^-. H^+ ion, due to its small size, has high charge density and highly hydrated.

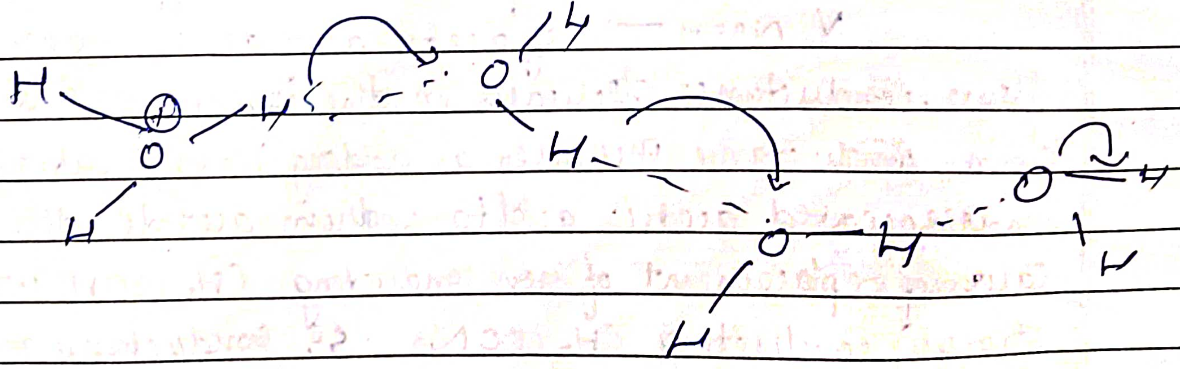
Experimental evidence suggest that H^+ ions are hydrated to form :



This ~~[illegible]~~ is a large structure, suggesting ionic mobility should be low. But actually, ionic mobility of H^+ in water is very high- this is explained by -Grotthus mechanism.

GROTTHUS MECHANISM :→

In Grotthus mechanism, a proton moves rapidly from H_3O^+ ion to a H.B H_2O molecule and is transferred further along a series of H.B. H_2O molecules, by a rearrangement of Hydrogen bonds.

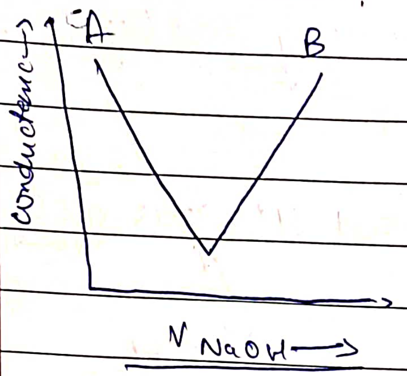


This model also explains why H^+ ion moves around 50 times ~~of~~ more rapidly through ice than through water

CONDUCTOMETRIC TITRATION

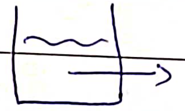
1) Strong acid v/s strong base.

HCl v/s NaOH ← add.

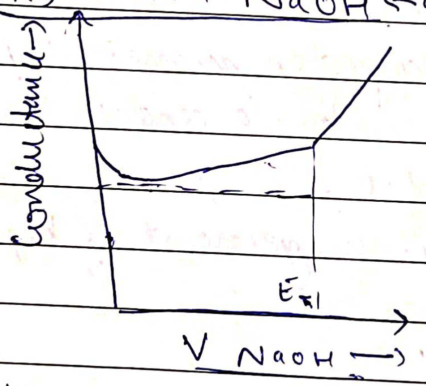


Before NaOH is added, conductivity of HCl has higher value due to highly mobile H^+ ions. As $NaOH^-$ is added, H^+ combines with OH^- to form undissociated H_2O. Thus faster moving H^+ ions are replaced by relatively slower moving Na^+ ion. So conductance decreases till end point, when solⁿ contains only NaCl. Beyond eqⁿ point, if more NaOH is added, then solⁿ contains an excess of fast moving OH^- ions which results in increasing conductance, and it continues increasing as more NaOH is added.

ii) Weak acid v/s strong base.



CH_3COOH + NaOH ← add



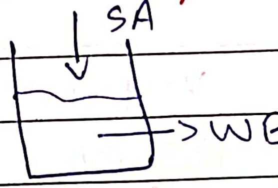
Before adding NaOH solⁿ, solⁿ shows poor conductance due to low ionization of weak acid. Initially, addⁿ of ~~NaOH~~ NaOH causes not only replacement of H^+, but also suppresses dissociation of acetic acid as CH_3COONa forms. Hence, conductance decreases in the beginning. But very soon, conductance increases as adding NaOH neutralizes undissociated acetic acid to sodium acetate, thus causing replacement of non conducting CH_3COOH with strongly conducting CH_3COONa. So, conductance increases till end points, and further addition of NaOH, due to OH^- ion, conductance highly increases. Graph near the equivalent point is curved due to hydrolysis of sodium acetate. Actual equivalent pt

④

can be ~~of~~ obtained by extrapolation method.

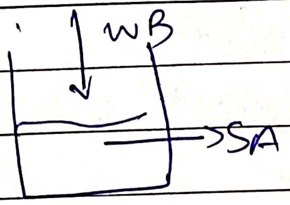
iii) Strong acid v/s weak base : $NH_4OH + HCl$

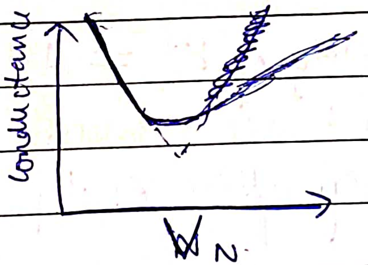
1)



, same as above.

2)



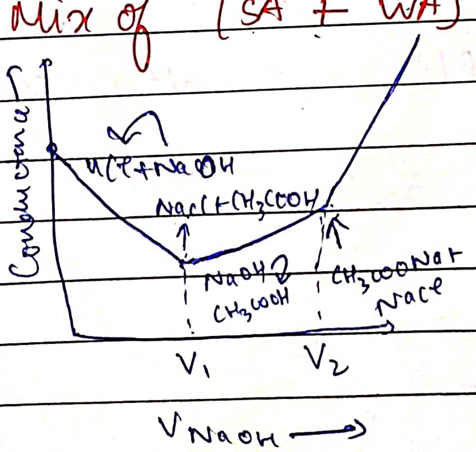


There is replacement of fast moving H^+ ion by slow NH_4^+ ion, so conductivity decreases till end pt. After eq pt, conductivity remains practically constant as NH_4OH has very slow conductivity against NH_4Cl or HCl. A slight curvature is noticed near the end point, this is explained on the basis of the following reaction:

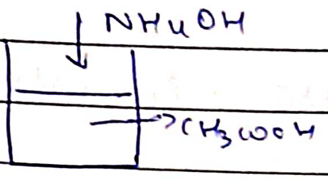
$$NH_4^+ + 2H_2O \longrightarrow NH_4OH + H_3O^+.$$

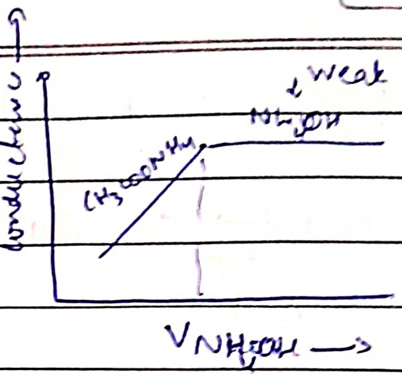
This generates fast H_3O^+. It is due to the H_3O^+ ions produced by hydrolysis in the system that the fall in the conductivity of sol^n is arrested and a curvature on the plot is observed.

iv) Mix of (SA + WA) v/s S.B



v) WB v/s SA

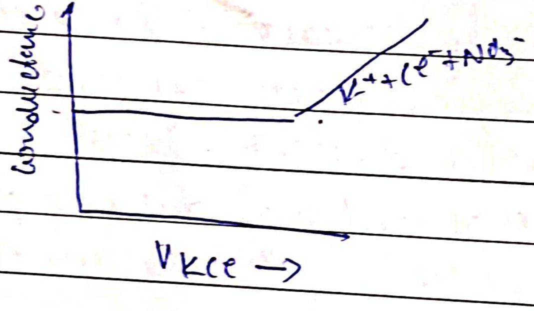




vi) PPT rxn

Ionic mobility of $K^+ = Ag^+$ (almost) experimentally which it replac
The conductance remains almost same, and it wi
increase only after end points.

$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow K^+NO_3^- + AgCl(s)$



$$\boxed{G_{total} = \sum_{i=1}^{n} G_i + G_{water}}$$

conductivity is additive

Other formulae.

- $\Delta H = nF\left(T\frac{dE}{dT} - E\right)$, where $\frac{dE}{dT}$ is called as temperature coefficient of EMF i.e rate of change of E with temperature.
- $\Delta S = nF\left(\frac{dE}{dT}\right)_P$

Contd after qualitative

Electrochemical series application

Use of E°

Higher reduction potential (E°_{RP}) $\propto$ oxidizing power. In electrochemical series, as we move down, the oxidizing power decreases

Q1 Write order of O.P : $Ag^+ > Cu^+ > H^+ > Ni^{2+} > Zn^{2+}$ (aq)

2 Write Reducing power: $Ag < Cu < H_2 < Ni < Zn$. (s)

Given E°_{RP} : $H^+/H_2 : 0$, $Zn^{2+}/Zn : -0.76$, $Ag^+/Ag : +0.8$

$Cu^+/Cu : 0.34$, $Ni^{2+}/Ni : -0.25$

Q2 Why among alkali metals, lithium is strongest R.A.

$Li \longrightarrow Li^+ + e^-$; $E^\circ_{RP} = -3.0$

$Na \longrightarrow Na^+ + e^-$; $E^\circ_{RP} = -2.7$

Q Order of Reducing ~~power~~ Potential of $\underset{-2.37}{Mg}, \underset{-2.87}{Ca}, Ba \rightarrow -2.90$

R.P : $Ba > Ca > Mg$

Q Determine relative order of oxidizing power of halogens (X_2) and reducing power of halide ions (X^-) in aq sol^n.

$F_2 > Cl_2 > Br_2 > I_2$: O.Power.

$F^- < Cl^- < Br^- < I^-$: R.Power.

E° : $F_2/F^- : +2.7$, $Cl_2/Cl^- : +1.4$, $Br_2/Br^- : 1.09$

$I_2/I^- : 0.54$

Ni, Zn, Cu, Ag

Q 1) Name metal that can be oxidized by Ag^+. Ni, Zn, Cu

2) Cannot be oxidized by Ni^{2+} : Ag, Cu

3) Can be oxidized by Zn^{2+} : —

4) Can't be reduced by Cu : Ni, Zn

5) Can be reduced by Ag : —

Cannot be reduced
↑

6) Cannot be displaced from their salt by Ni : Zn

7) That Zn can displace ; Ag, Cu, Ni
↳ can reduce

Q Why H_2O_2 is better OA than H_2O ?

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ E_0 : +1.77 V

H_2O is less.

Q Zn and not Cu is used for recovery of Ag from $[Ag(CN)_2]^-$:

Ans Zn is more reactive $2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag\downarrow$

$[Ag(CN)_2]^- + Cu \longrightarrow [Cu(CN)_4]^{2-} + Ag$

$E_0\ Zn/Zn^{2+} > E^\circ\ Cu/Cu^{2+}$

Zn is more powerful RA than copper, and is cheaper than Cu.

Pd : 3

Q

	E°RP	w.r.t H
$Sc^{3+} + 3e^- \rightarrow Sc$	−2.010	RA
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.6	RA
$V^{2+} + 2e^- \rightarrow V$	−1.20	RA
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18	RA
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44	RA
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	RA
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.24	RA
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	OA
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76	RA

1) State whether they act as OA or RA

2) Predict order of R. Power : Sc > Ti > V > Mn > Zn > Fe > Co > Ni > Cu

RA