

11/05/2022

## UNIT - 1

# ELECTRODICS & ITS APPLICATIONS

Kinetics

Electrochemistry

### \* Electrodics:

Conversion of electrical energy to chemical energy (or) vice versa is done with the help of electrochemistry.

Thermodynamics

### \* CHEMICAL ENERGY to ELECTRICAL ENERGY:

#### Sub-Topics:

- 1) Conductance
- 2) Electrodes & related applications
- 3) Applications in chemical analysis.

### \* CONDUCTANCE:

Materials can be classified into 4 types based on conductivity:

- 1) Conductors: conducts electricity
- 2) Insulators: do not conduct electricity
- 3) Super conductors: conducts at curie temp.
- 4) Semiconductors: conduction takes place when it is doped.

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### Types of conductors:



→ Metallic (electronic): - solids.  
Ex: metals.

→ Electrolytic (Ionic): - liquids.  
ions are responsible.

\* Metallic conductors } obeys Ohm's Law.  
& electrolytic      }  
conductors            }  $V = IR$ : ~~IDEAS~~

- \* When temp ↑ses in metallic conductors, resistance ↑ses and conductance ↓ses
- \* When temp ↑ses in electrolytic conductors degree of dissociation ↑ses; ions for conduction ↑ses; hence conduction ↑ses.

⇒ Electrolyte : A substance which gives ions on dissociation (in a suitable solvent) are called electrolytes.

TYPES: Strong and Weak electrolyte.

Strong electrolyte: Degree of dissociation is almost equal to 1. Ex: strong acids majority

Weak electrolyte: Degree of dissociation is smaller than 1

Ex: Weak acids.

\*\* already written

\* Differentiate between Metallic and Electrolytic conductors.

\* Resistance: Opposition to the flow of e<sup>-</sup>s in a material  
[Units =  $\Omega$  (ohm)]

\* Conductance: Allows the flow of e<sup>-</sup>s in a material

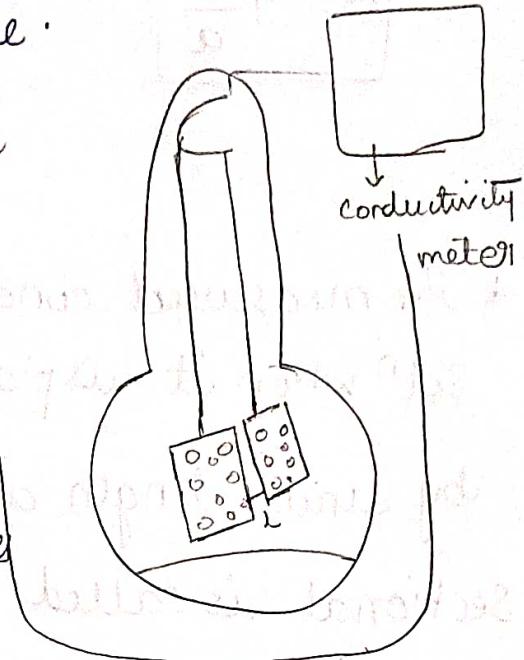
[Units = mho ( $\text{ohm}^{-1}$ )]

\* Electrodes are generally made up of platinum; since it is inert in nature.

→ Top surface of electrolytic plates is coated with platinum black.

to avoid reaction with other elements/molecules

Platinum black also increases its sensitivity.



let  $l$  = distance between the plates.

$A$  = area of cross section of plates.

$$\text{cell constant} = \frac{l}{A}$$

units:  $\text{cm}^{-1}$

$$R = \frac{\rho l}{a}$$

### Molar Specific Conductance ( $K$ )

• conductance offered by 1 cc sol<sup>n</sup>.

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

$R$  = resistance offered by sol<sup>n</sup>.

$$R \propto l$$

$$\propto \frac{1}{a}$$

$$R = \frac{\rho l}{a}$$

where

$\rho$  = resistivity

$$K = \frac{1}{\rho l/a} = \text{conductivity}$$

$$\frac{l}{a} \frac{1}{K} = R \quad \text{units of } R = \Omega$$

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

units of  $K = \Omega^{-1} \text{cm}^2 \text{mol}^n$

= Seiman,  $(\text{Sm})$

= S/m.

$$k = G \frac{l}{a}$$

at  $\frac{l}{a} = 1 \text{ cm}^{-1}$

$$\begin{aligned} k &= G \\ P &= R \end{aligned}$$

\* The measured conductance of an electrolytic sol<sup>n</sup> when it is placed b/w 2 electrodes separated by unit length and are unit ~~across~~<sup>of</sup> cross-sectional area called specific conductance.

- Molar Conductance: ( $\lambda_M$ )

- Conductance is measured with respect to molarity.  $[S \cdot \text{cm}^2 \cdot \text{mole}^{-1}]$

$$\lambda_M = \frac{1000 \times k}{M}$$

Equivalent Conductance:

Conductance is measured with respect to normality.  $[S \cdot \text{cm}^2 \cdot \text{eq}^{-1}]$

$$\lambda_{eq} = \frac{1000 \times k}{N}$$

With dilution  $\uparrow$  conductance, volume  $\uparrow$ es, conc.  $\downarrow$ es.

$1 \text{ mole} \Rightarrow$  electrolytic conductance offered by 1 M solution is molar conductance.

conductance offered by 1 N electrolytic solution placed between 2 electrodes is called equivalent conductance.

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$$\boxed{\text{Molarity} = \text{Normality}} \quad \text{if } n\text{-factor} = 1$$

\* Calculate cell constant  $\alpha$  cell which is used to measure conductance of KCl soln. Resistance found to be  $150\Omega$  and conductivity is

$$1.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

$$\Rightarrow K = 1.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

$$R = 150\Omega$$

$$K = \frac{1}{R} \frac{l}{a}$$

$$\text{cell constant} = 15 \times 10^{-3}$$

$$\frac{l}{a} = 200 \times 10^{-3} \text{cm}^{-1}$$

\*  $A = 5 \text{cm}^2$  and they are separated by 10cm apart in a conductivity cell that offered  $125\Omega$  resistance for KCl soln at  $25^\circ\text{C}$ . Calculate conductivity.

$$K = \frac{1}{R} \frac{l}{a} \cdot M^2$$

$$= \frac{1}{125} \times \frac{10}{5} \text{m}^{-3} \text{cm}^2 \text{mol}^2$$

$$\boxed{K = 16 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}}$$

\* Specific conductivity of 0.1M NaCl sol<sup>n</sup> is  $3.4 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ . Resistance offered by the same sol<sup>n</sup> is 80 $\Omega$  at 25°C. The same cell is used for KCl sol<sup>n</sup> which offered 50 $\Omega$  resistance. Calculate specific conductance of sol<sup>n</sup>.

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

$$K_1 = 3.4 \times 10^{-2} \quad K_2 = ?$$

$$R_1 = 80 \Omega \quad R_2 = 50 \Omega$$

$$K \propto \frac{1}{R}$$

$$\frac{K_1}{K_2} = \frac{R_2}{R_1} \quad K_2 = \frac{K_1 R_1}{R_2} = 5.44 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$$

\* Calculate molar conductance & equivalent conductance of AgCl sol<sup>n</sup> of 0.1M at 25°C. Cell constant is 1.0 cm<sup>-1</sup> and resistance is 20 $\Omega$ .

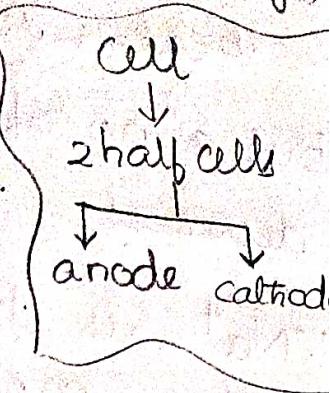
$$\lambda_M = \frac{1000}{M} \times \frac{1}{R} \times \frac{l}{a}$$

$$= \frac{1000}{0.1} \times \frac{1}{20} \times 1.0 = 500 \text{ S cm}^2 \text{ mole}^{-1}$$

$\lambda_{eq} = \lambda_M$	$\therefore M = N$	$n_f = 1$
		$= 500 \text{ S cm}^2 \text{ mole}^{-1}$

# \*CONDUCTOMETRIC TITRATION (only electrolytes)

- 1) Strong acid vs Strong Base  
(HCl) (NaOH)
- 2) Weak acid vs Strong Base.  
(CH<sub>3</sub>COOH) (NaOH)
- 3) Mix. of acids vs Strong Base.  
(HCl + CH<sub>3</sub>COOH) (NaOH)



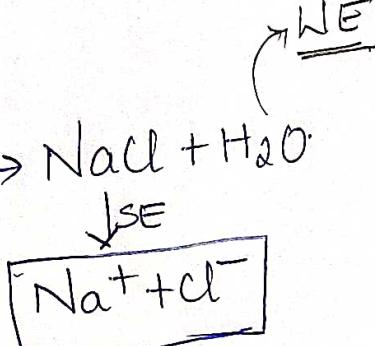
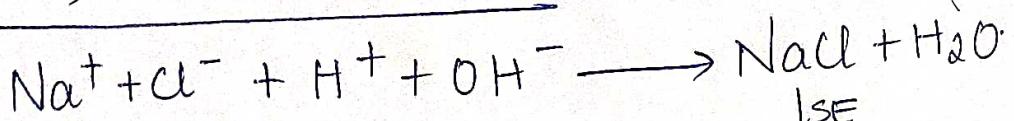
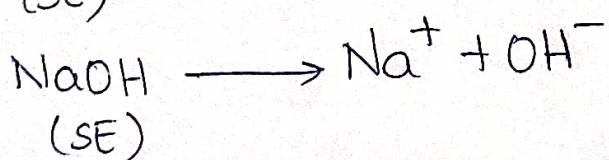
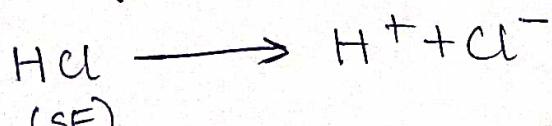
\* Factors affecting titrations / conductance of soln.

- 1) Nature of electrolyte → S.E ( $\alpha \approx 1$ )
  - 2) Solvent - viscosity → W.E ( $\alpha \ll 1$ )
  - 3) Temperature
  - 4) Concentration/ no. of ions
  - 5) Mobility of ions.
- Once the exp started these remain constant.

viscous soln = resistance to mobility of ions unless flow.

Galvanic cell	electrolytic cell	
		anode (+)
		cathode (-)

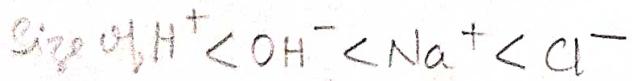
1) Strong Acid vs Strong Base:



No. of ions in the beaker remains same  
 But no. of  $H^+$  ions  $\text{NaOH}$   
 decreases.

$\because \text{Na}^+$  is heavier than  $H^+$ .  
 Mobility of ions decreases; thereby conductance is decreased.

by the time titration is completed : it becomes minimum.  
 Till the point at which  $\text{HCl}$  is completely neutralised no. of ions decreases but after that no. of ions increases and hence conductance increases.



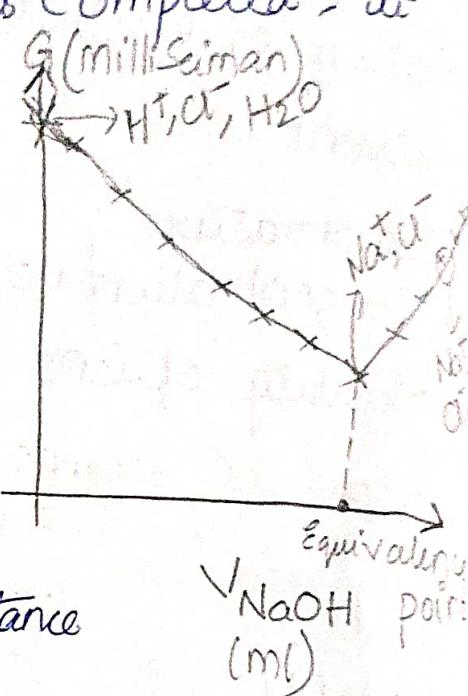
Conductance offered :  $H^+ > OH^- > Na^+ > Cl^-$

The volume at which the standard solution is neutralised, <sup>by a base</sup> is at the equivalence point.

$$V_{\text{NaOH}} = e \cdot P$$

$$N_{\text{NaOH}} V_{\text{NaOH}} = N_{\text{HCl}} V_{\text{HCl}}$$

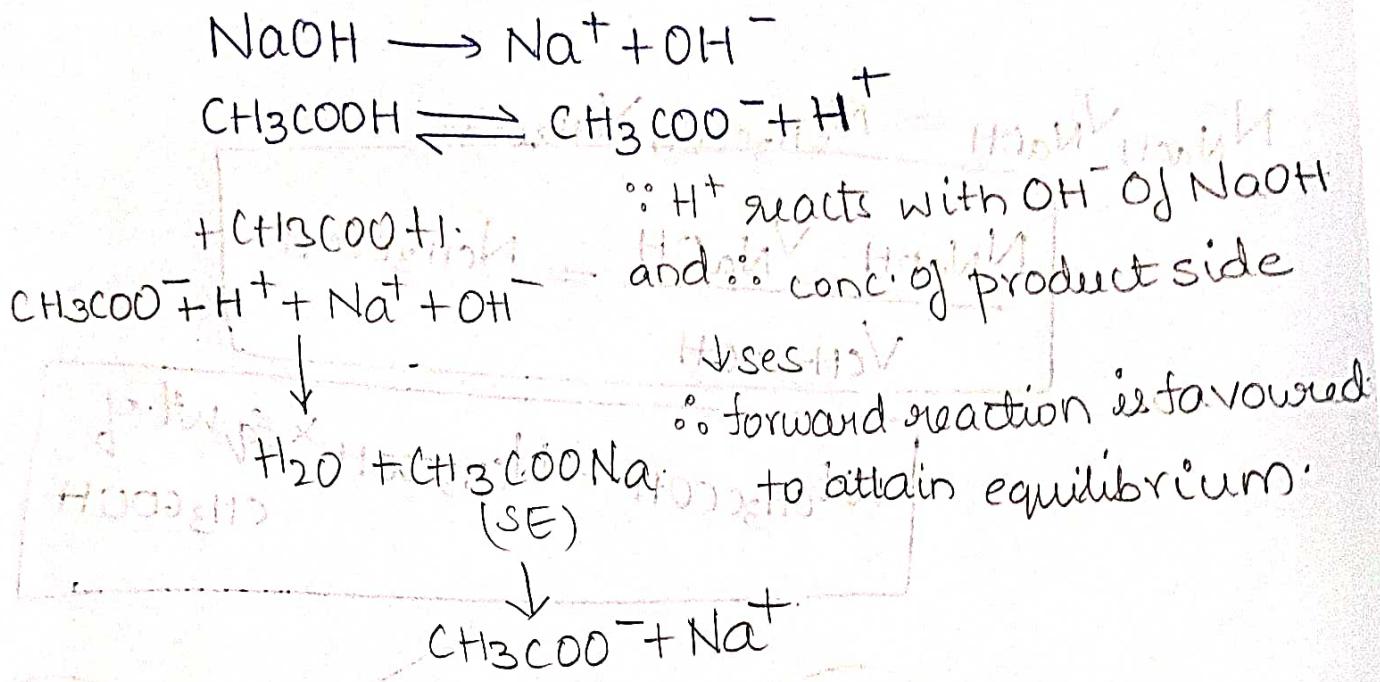
$$N_{\text{HCl}} = \frac{N_{\text{NaOH}} V_{\text{NaOH}}}{V_{\text{HCl}}}$$



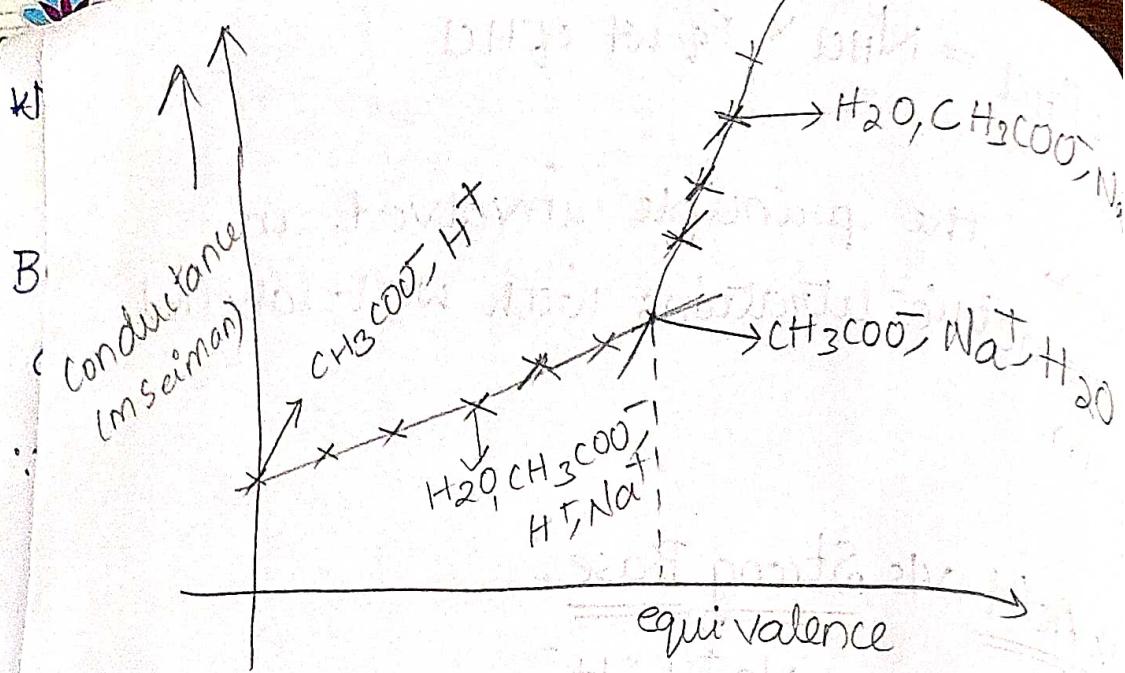
$$W_{HCl} = N_{HCl} \times \text{Eq. wt of HCl}$$

\* Describe the principle involved in conductometric titrations with well-labelled diagram.

## 2) Weak Acid vs Strong Base:



After the neutralisation of  $\text{CH}_3\text{COOH}$ , there are only  $\text{Na}^+$  &  $\text{OH}^-$ ; where  $\text{OH}^-$  will cause a steep increase in conductance. Before neutralisation is attained, the salt  $\text{CH}_3\text{COONa}$  (SE) formed dissociates into  $\text{CH}_3\text{COO}^-$  &  $\text{Na}^+$  and also the molecule  $\text{CH}_3\text{COOH}$  favours forward reaction ~~does~~ so as to attain equilibrium.



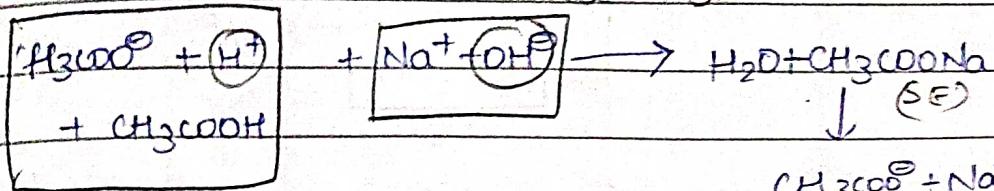
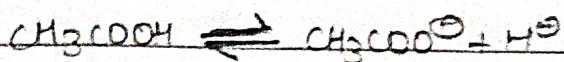
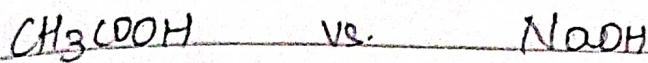
$$N_{\text{NaOH}} \sqrt{\text{NaOH}} = N_{\text{CH}_3\text{COOH}} \sqrt{\text{CH}_3\text{COOH}}$$

$$\frac{N_{\text{NaOH}} \sqrt{\text{NaOH}}}{\sqrt{\text{CH}_3\text{COOH}}} = N_{\text{CH}_3\text{COOH}}$$

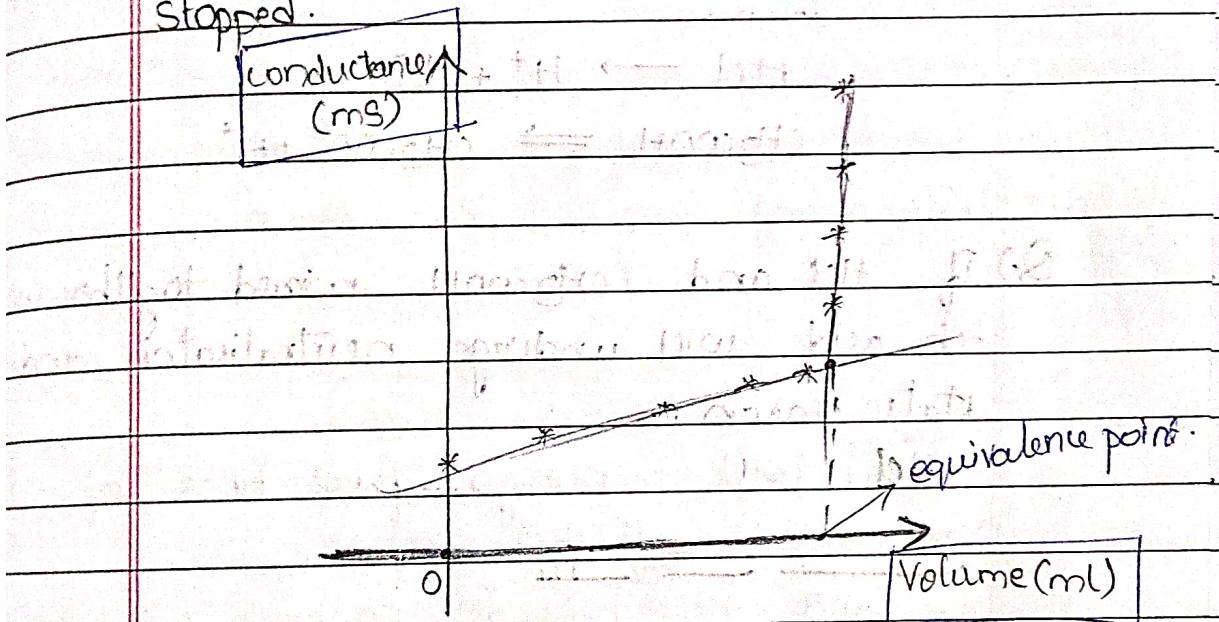
$$W_{\text{CH}_3\text{COOH}} = N_{\text{CH}_3\text{COOH}} \times \text{Eq wt of } \text{CH}_3\text{COO}^-$$

3) Mixture of acids v/s strong Base:

\* Weak Acid      vs      Strong Base:-



In  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ , concn decreases so forward rxn is favoured to get equilibrium. Once equilibrium is achieved rxn is stopped.



$$\frac{(\text{N.V})}{\text{NaOH}} = \frac{(\text{N.V})}{\text{CH}_3\text{COOH}}$$

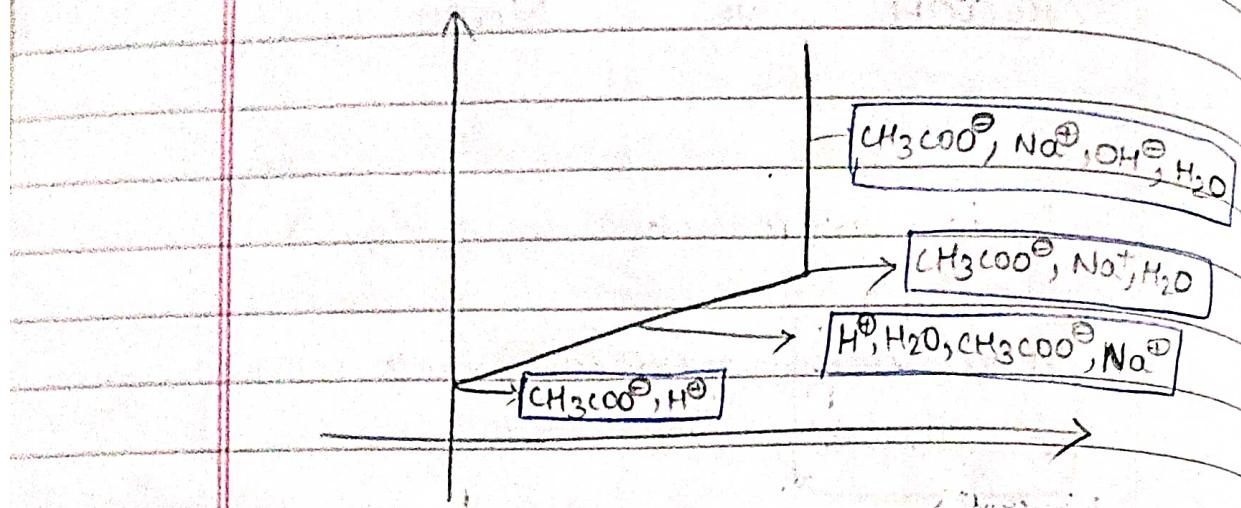
$N_{\text{NaOH}}$  = known

$V_{\text{NaOH}}$  = equivalence point

$N_{\text{CH}_3\text{COOH}}$  = ?

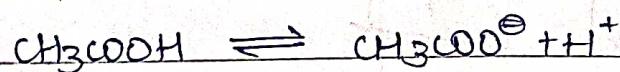
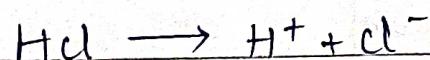
$V_{\text{CH}_3\text{COOH}}$  = known.

$$N_{\text{CH}_3\text{COOH}} \times \frac{\text{Eq. wt of } \text{CH}_3\text{COOH}}{60} = \text{wt of } \text{CH}_3\text{COOH per litre}$$



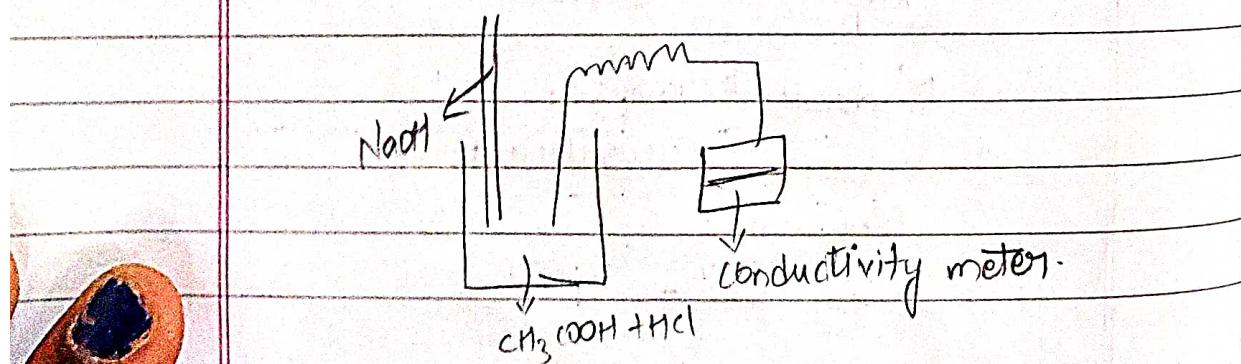
\* Mixture of Acid vs Strong base.

⇒ Common ion effect:-

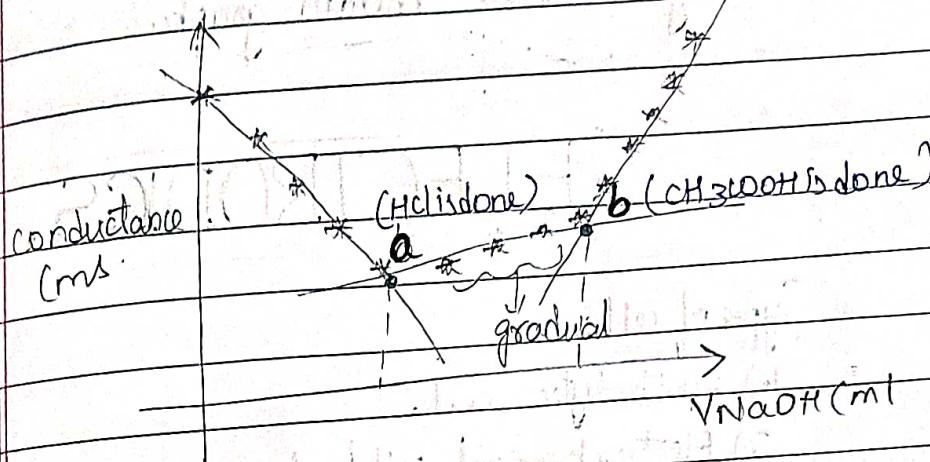


Q.) If HCl and CH<sub>3</sub>COOH mixed together, which acid will undergo neutralisation and state reason.

**HCl** will undergo first bcoz of common ion effect and **t<sub>1</sub>Cl** bcoz of - no back rxn is poss.



\* Due to common ion effect when two electrolytes ( $SE + WE$ ) are mixed and they produce a common ion<sup>by both</sup>, then common ion of  $SE$  is responsible for the  $WE$ . common ion is suppressed i.e. dissociation of  $WE$  is suppressed by common ion of  $SE$ .



$a = V_{NaOH}$  req. for neutralisation of  $HCl$  soln.

$b = V_{NaOH}$  req. for neutralisation mixture.

$b - a = V_{NaOH}$  req. for neutralisation of mixture.

$$\frac{NV}{NaOH} = \frac{NV}{HCl}$$

$N_{NaOH}$  = known

$V_{NaOH} = a \text{ ml}$

$N_{HCl} = ?$

$V_{HCl}$  = known.

$$N_{HCl} \times (36.5) = \text{wt of HCl (g/L)}$$

↓  
equiv of HCl.

$$\frac{NV}{NaOH} = \frac{NV}{CH_3COOH}$$

$V_{CH_3COOH}$  = known.

$N_{NaOH}$  = known

$V_{NaOH} = (b-a) \text{ ml}$

$N_{CH_3COOH} = ?$

$$\text{N} \text{CH}_3\text{COOH} \times \frac{60}{\text{Gm eq wt of CH}_3\text{COOH}} = \text{wt of CH}_3\text{COOH in g/L}$$

(Q) Describe and discuss principle involved in any two conductometric titration with a neatly labelled model graph.

## ELECTRODICS

\* Types of cell:-

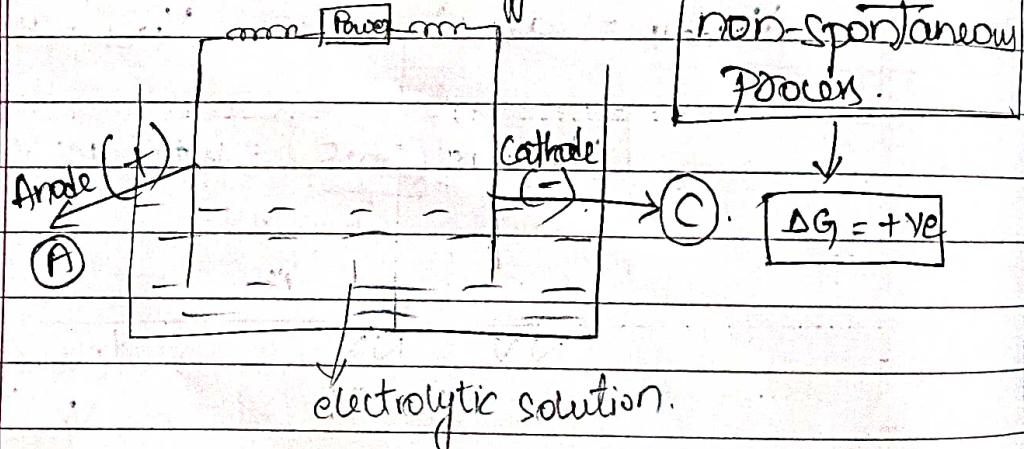
1.) Electrolytic cell.

2) Electrochemical cell / galvanic cell.

\* Cell is a device which converts CE to EE and vice versa.  
 $\text{CE} \rightarrow \text{chemical energy}$   
 $\text{EE} \rightarrow \text{electrical energy}$

\* Electrolytic cell :- using current to occur chemical change.  
 \* (rechargeable battery)

A  $\xrightarrow{\text{current}}$  B (chemical change takes place)  
 Electrical energy.



\* non spontaneous redox rxn.  $\rightarrow$  electrolytic cell.

### \* Electrochemical cell / galvanic cell :-

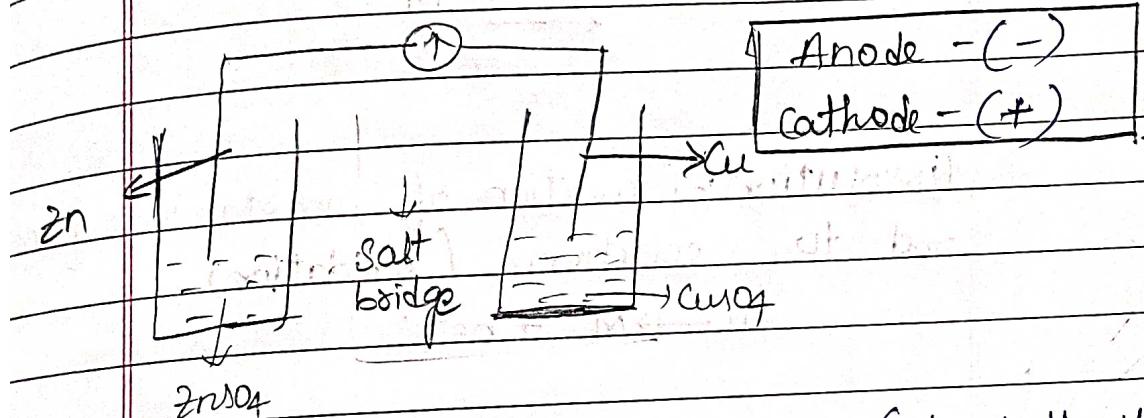
\* chemical energy  $\rightarrow$  Electrical energy

\* (non rechargeable battery)

\* Spontaneous redox rxn takes place. (redox rxn)

$$\Delta G_f = -ve$$

, change in gibbs free energy



\* cell contains two electrodes (two half cells namely anode and cathode) and in this device chemical energy is converted into electrical energy and vice versa

\* There are two types 1.) Electrolytic cell  
2.) Galvanic cell.

Q.) Differentiate b/w galvanic and electrolytic cell.

Galvanic (non rechargeable)

Electrolytic (rechargeable)

\* Spontaneous

\* Non-spontaneous

\*  $\Delta G_f = -ve$

\*  $\Delta G_f = +ve$

\* Anode (-ve), cathode (+ve)

\* Anode (+ve), cathode (-ve)

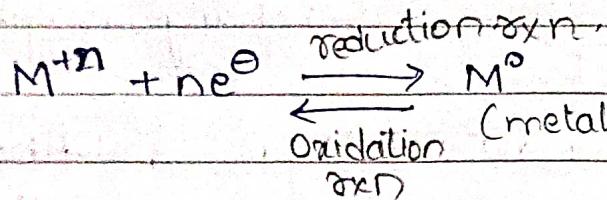
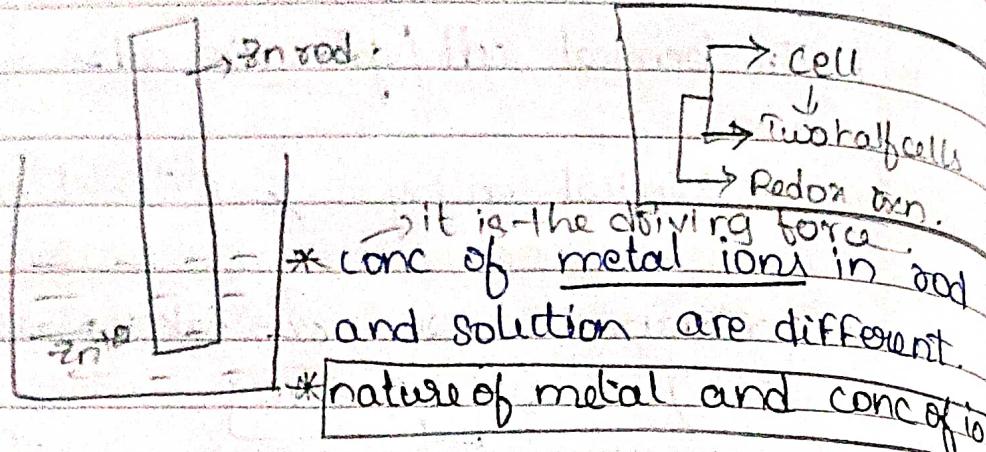
\* chemical energy  $\rightarrow$  electrical energy

\* electrical  $\rightarrow$  chemical energy

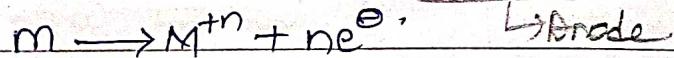
\* Two diff electrolytic solutions

\* Same electrolytic solutions

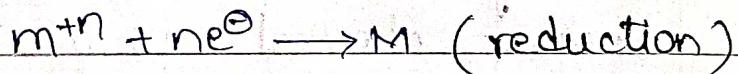
## ELECTRODE POTENTIAL:-



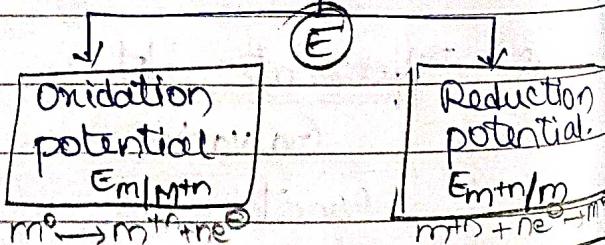
\* dissolution:- Production of metal ions from rod to solution. (Oxidation)



\* deposition:- metal ions of solution are deposited on metal rod.



\* measure of tendency of to undergo dissolution or deposition is known as electrode potential.



\* Standard electrode potential.

$E^\circ$

↳ 1 molar, 25°C

Standard Oxidation potential

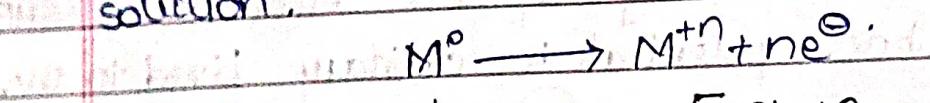
$E^\circ_{m^0/M^{+n}}$

Standard reduction potential

$E^\circ_{M^{+n}/m}$

- \* Electrode potentials: It is a measure of tendency of metal rod to undergo either dissolution or deposition when it is in contact with corresponding ionic solution. ( $E$ )
- \* Based on the nature of the metal and of electrolytic solution initially, it will prefer to undergo oxdn or redn but after some time equilibrium is established at which rate of dissolution = rate of deposition (rate of oxidation = rate of reduction)
- \* Hence, oxidation & reduction potential values are same but their sign is opposite.

- \* Oxidation potential: Measure of tendency of metal rod to undergo oxidation when it is in contact with corresponding ionic solution.



represented as  $E_m^{\circ}/m^{+n}$

- \* Standard electrode potential :- (Electrode potential definition) when it is in contact with 1 molar solution at  $25^{\circ}\text{C}$  ( $E_s^{\circ}$ )

- \* SOP :- Measure of tendency of metal rod to undergo oxidation when it is placed in corresponding 1 molar solution at  $25^{\circ}\text{C}$ . ( $E_m^{\circ}/m^{+n}$ )

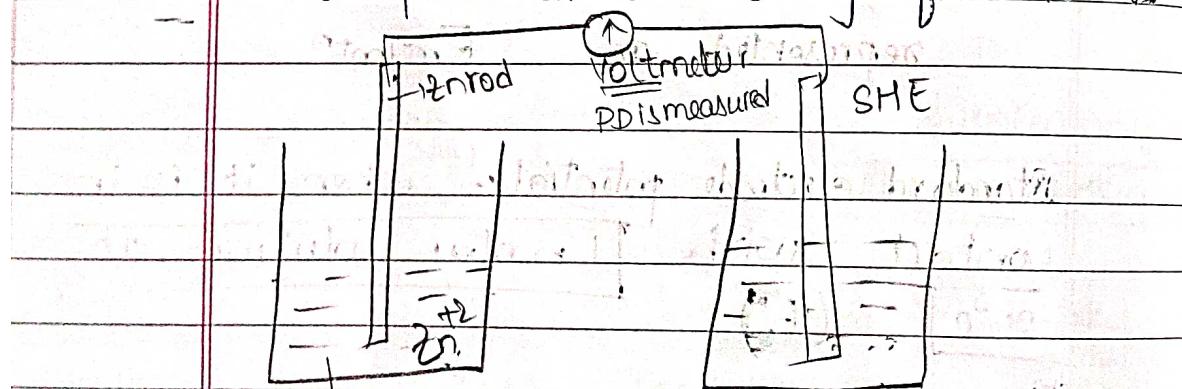
## \* Standard electrode potential ( $E^\circ$ ):-

(Q.) Can we determine single electrode potential?  
Ans:- potential difference can be measured in the absolute potential.

\* primary reference electrode  $\rightarrow$  SHE  $\rightarrow$  standard hydrogen electrode ( $E = 0V$ ) ( $25^\circ C$ , 1 molar)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{right}} - E_{\text{left}} \end{aligned}$$

\* To determine standard electrode potential of any given electrode, it is connected with primary reference electrode to complete the construction of cell. The measured potential difference of cell is standard electrode potential.  
Since primary reference electrode is SHE whose potential is arbitrary fixed to 0V.



↓  
electrode whose

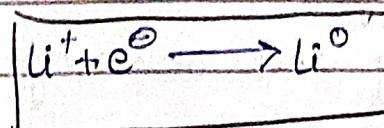
P.D. to be  
determined.

\*

## ELECTRO CHEMICAL SERIES:-

Standard electrode potential values are arranged in increasing or decreasing order.

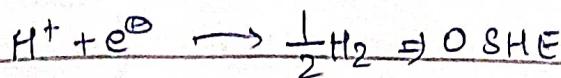
more S.E.P.  $\rightarrow$  cathode.  $\rightarrow$  reduction.  $\rightarrow$  oxidising agents



$\Rightarrow$  S.E.P. is low

Anode (Powerful reducing agent)  
Oxidation

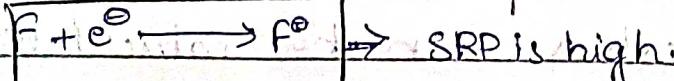
-ve  
S.E.P.



S.E.P.

Cathodes (Powerful oxidising agent)  
Reduction

+ve  
S.E.P.



\* at anode oxidation.

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

\* at cathode reduction.

$$\text{EMF} = +\text{ve}$$

feasible.

\* In this E.C.S. standard electrode potential values are arranged in increasing or decreasing order.

\* In general S.E.P. values of the electrodes are arranged in increasing order.

\* lower S.R.P value decrease  
 its ability to undergo reduction is less  
 reduction  $\rightarrow$  protected (deposition)

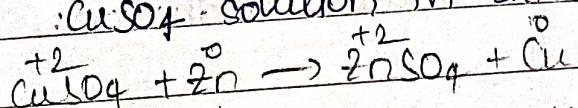
so powerful reducing agent.

### Applications:-

- \* ECS is used to construct a feasible cell to select proper anode or cathode to construct a cell of +ve Emf.
- \* ECS is going to help us to know their chemical reactivity.
- \* Nature of oxidising and reducing tendency can be predicted.  
 It can predict feasibility of a reaction.  
 Eg:  $Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$  ✓  
 $E^\circ_{Zn^{+2}/Zn} = -0.76 V$  (anode)  
 $E^\circ_{H^+/H_2} = 0.0V$  (cathode)  
 $E_{cell} = +ve$ ,  
 $Ag + HCl \rightarrow AgCl + H_2$  X
- \*  $E^\circ_{cell}$  values can be calculated.

### Cell Notation:

Q.) Can I store  $CuSO_4$  solution in zinc container?



$$E^\circ_{Zn/Zn^{+2}} = +0.76 V. (SOP) \Rightarrow S.R.P = -0.76 \text{ (anode)}$$

$$E^\circ_{Cu/Cu^{+2}} = -0.34 V (SOP) \Rightarrow S.R.P = 0.34 \text{ (cathode)}$$

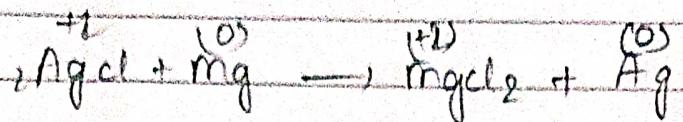
$$E_{cell} = E_a - E_o$$

= +ve.

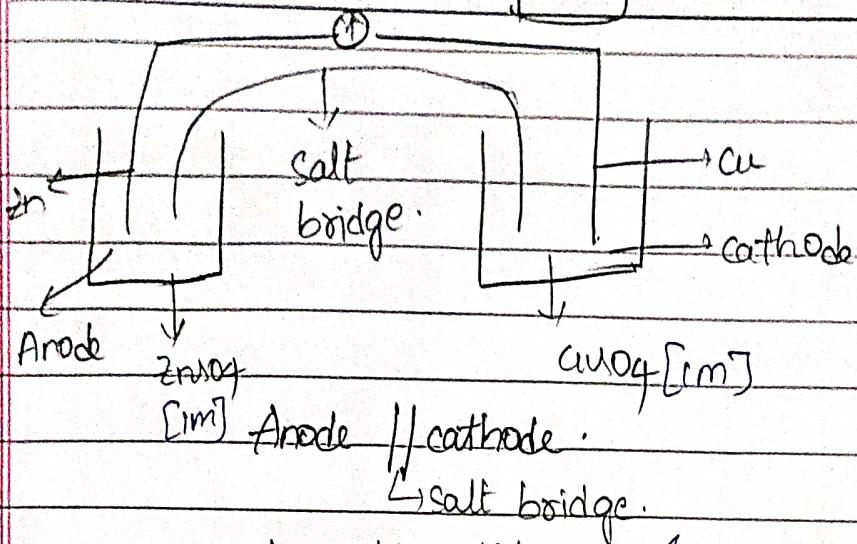


rxn happens  
we cannot store

Q.7) Can we use: Mg spatula to stir AgCl sol.



[No]



\*  $\text{Zn} | \text{Zn}^{+2} \text{ [1m]} || \text{Cu}^{+2} | \text{Cu} \checkmark$  at  $25^\circ\text{C}$  and at 1 atm.

$\text{Zn}^{+2} | \text{Zn} || \text{Cu} | \text{Cu}^{+2} \times$ .

→ phase separation.

\*  $\text{Mg} | \text{Mg}^{+2} \text{ [1m]} || \text{Cu}^{+2} | \text{Cu} \text{ at } 25^\circ\text{C} \text{ and at 1 atm.}$

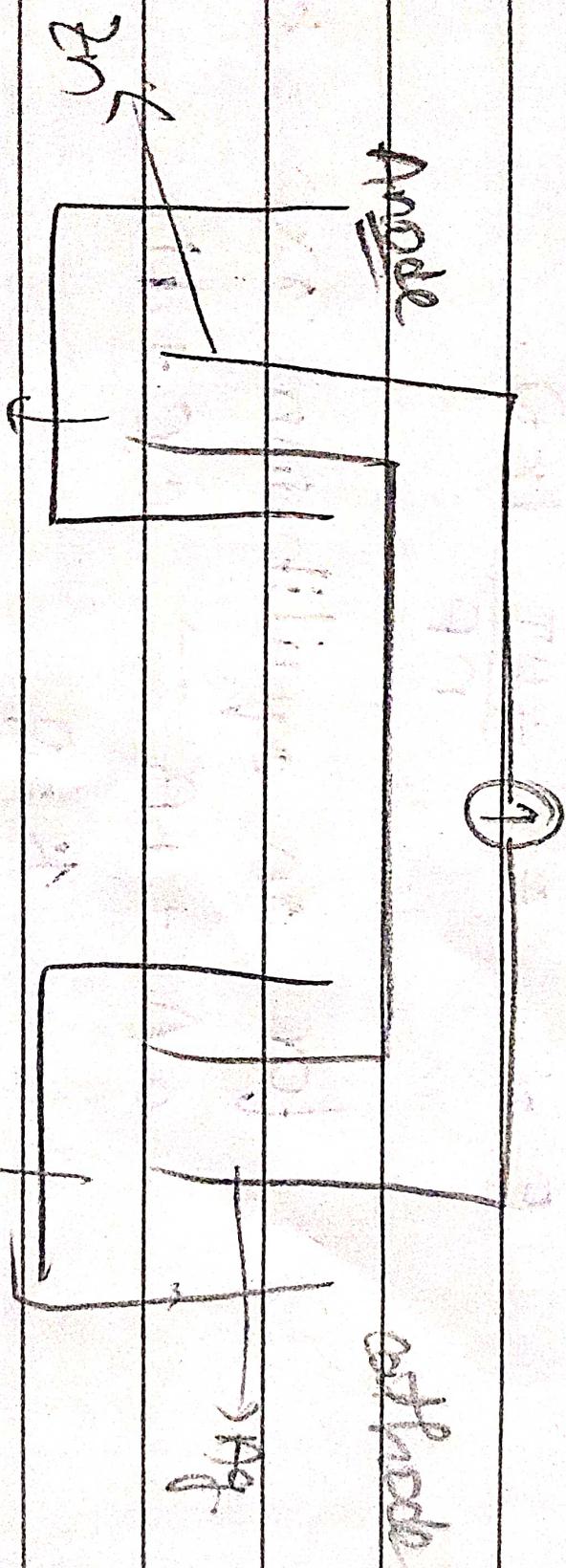
\*  $\text{Mg} | \text{Mg}^{+2} \text{ [1m]} || \text{Ag}^+ | \text{Ag} \text{ at } 25^\circ\text{C} \text{ and at 1 atm.}$

Nearst Equation:-

\*  $Mg | Mg^{+2} | | 2Ag^{+} / Ag$  at  $25^{\circ}C$  and at 1 atm.

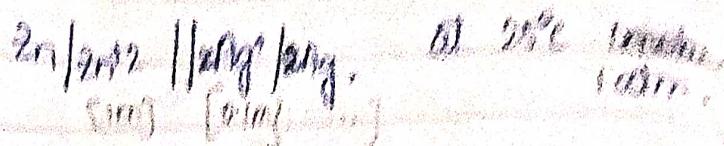
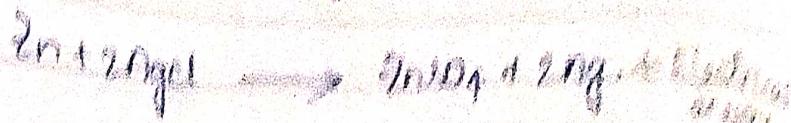
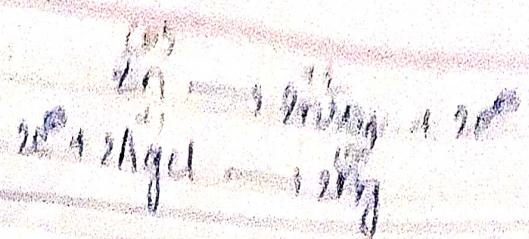
[1.m] [0.m]

\* Nernst Equation:-



$2\text{M}\text{O}_{(\text{m})}$

$\text{AgCl} (0.\text{m})$



NERNST EQUATION:

$E^\circ \rightarrow$  Standard electrode potential.  
 $[\text{Irr}] \text{ and } 298\text{K}$

$E \rightarrow$  electrode potential.

chemical energy $\Rightarrow$	Sporstaneous Redox rxn.	$\Rightarrow$ electrical energy
-------------------------------	----------------------------	---------------------------------

$\hat{=} \Delta G = \text{work}$

work = electrical energy =  $nFE$

$$\Delta G = -nFE \quad \text{---(1)}$$

$$\Delta G^\circ = -nFE^\circ \quad \text{---(2)}$$

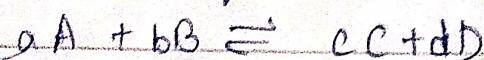
Vonthoff's Diagrams

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{---(3)}$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ + \frac{RT}{nF} \ln Q$$

for an equilibrium rxn :  $k=1$ .



$$K = Q$$

$$[Zn] = 1$$

VACUUM  
Dust  
Pump

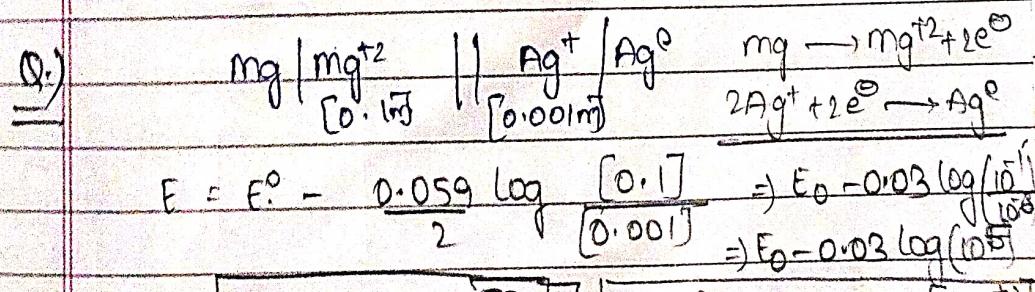
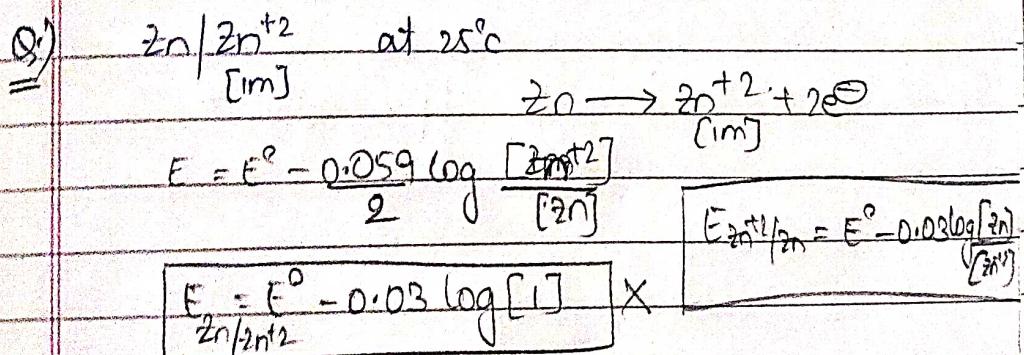
$$E - E^{\circ} = \frac{RT}{4F} \ln (2.303) \log K_{10}$$

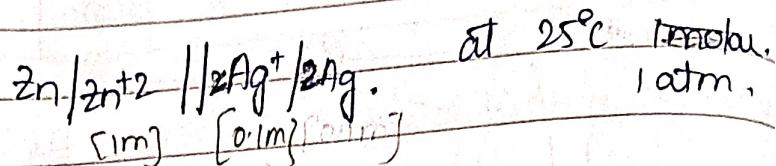
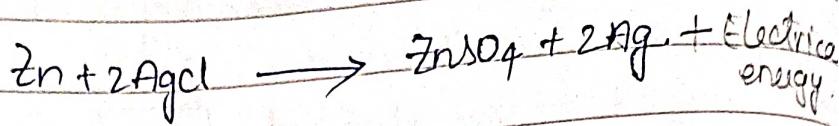
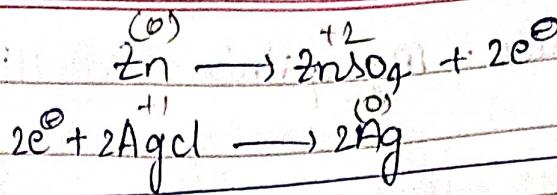
$$E - E^{\circ} = \frac{RT}{4F} \times 2.303 \log \frac{[c]^a [d]^b}{[n]^a [o]^b}$$

$$E = E^{\circ} - \frac{0.0591}{R} \log \frac{[P]}{[P_0]}$$

#### Applications:-

- \* To calculate electrode potential or cell emf at any given condn (other than standard condition)
- \* To determine equilibrium const.
- \* To calculate free energy change of galvanic cell
- \* To check feasible of cell.
- \* We can find the conc ratio (or) conc of any one of the electrolyte.





\* **NERNST EQUATION:** (work concept)

$E^\circ \rightarrow$  standard electrode potential.  
 $[1\text{M}]$  and  $273\text{K}$ .

$E \rightarrow$  electrode potential.

$\Delta G \rightarrow$  other than  
 $(P, \Delta V)$  work

chemical energy  $\Rightarrow$  Spontaneous Redox rxn.  $\Rightarrow$  Electrical energy

$$\Delta G = \text{work.}$$

$$\text{work : electrical energy} = nFE$$

$$\Delta G = -nFE \quad \text{--- (1)}$$

$$\Delta G^\circ = -nFE^\circ \quad \text{--- (2)}$$

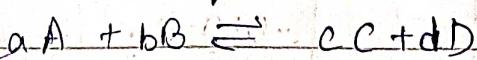
Vanthoff's Isotherm

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{--- (3)}$$

$$-nFE = -nFE^\circ + RT \ln Q$$

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

for an equilibrium rxn  $= K = Q$ .



$$K = Q.$$

$$[Zn] = 1$$

classmate

Date \_\_\_\_\_

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$$E - E^{\circ} = \frac{RT}{nF} \cdot (2.303) \log \frac{K}{10}$$

$$E = E^{\circ} - \frac{RT}{nF} \times 2.303 \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

\*

### Applications:-

\* To calculate electrode potential or cell emf at any given condn (other than standard condition)

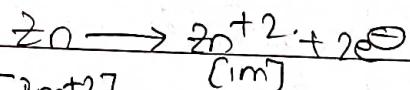
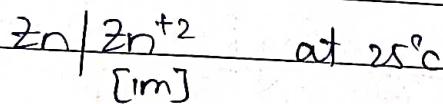
\* To determine equilibrium const.

\* To calculate free energy change of galvanic cell

\* To check feasible of cell.

\* We can find the conc ratio (or) conc of any one of the electrolyte.

Q.)

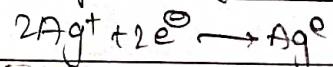
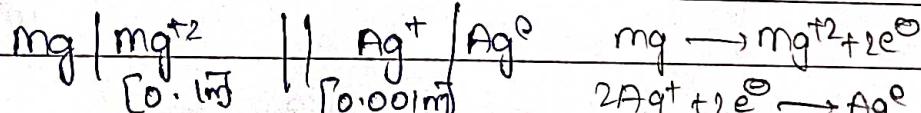


$$E = E^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}]}$$

$$E_{\text{Zn}^{+2}/\text{Zn}} = E^{\circ} - 0.03 \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}]}$$

$$E_{\text{Zn}/\text{Zn}^{+2}} = E^{\circ} - 0.03 \log \frac{1}{[\text{Zn}^{+2}]}$$

Q.)



$$E = E^{\circ} - \frac{0.059}{2} \log \frac{[0.1]}{[0.001]} \Rightarrow E_0 - 0.03 \log \frac{(10)^2}{(10)^3}$$

$$\Rightarrow E_0 - 0.03 \log (10^5)$$

$$E = E_0 - 0.059 \times \frac{1}{2} \quad | \quad E = E^{\circ} - \frac{0.059}{2} \log \frac{[\text{mg}^{+2}]}{[\text{mg}^{+2} + 1]}$$

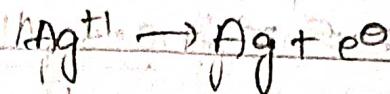
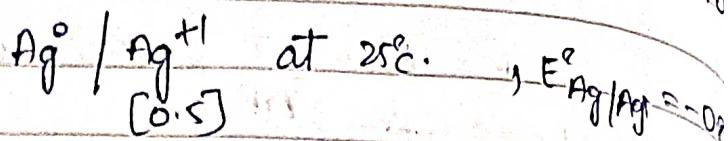
Always consider SRP

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Date \_\_\_\_\_  
Page \_\_\_\_\_

i.e Reduction rxn.

Q.) Calculate Electrode potential for the electrode at 25°C

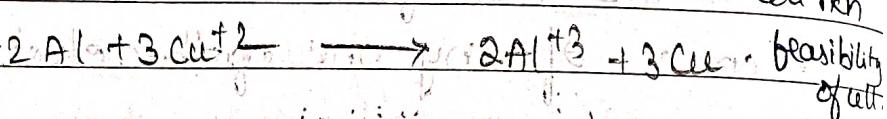
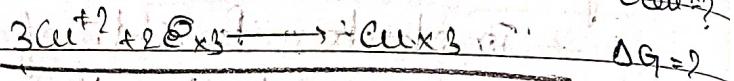
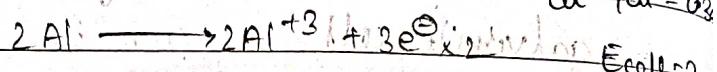
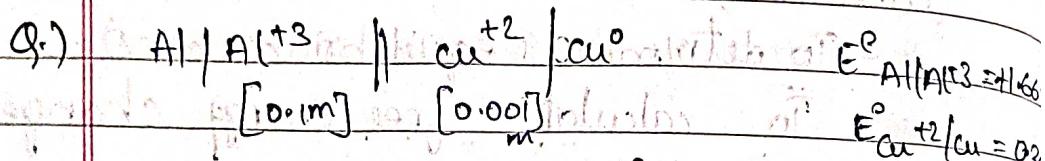


$$E_{\text{Ag}^\circ/\text{Ag}} = E_{\text{Ag}^{+1}/\text{Ag}^\circ} - 0.059 \log(2)$$

$$E = 0.8 - 0.059(2)$$

$$0.8 - 0.0177$$

$$\boxed{E = 0.7823 \text{ V}}$$



$$E = E^\circ - \frac{0.059}{6} \log \frac{[\text{Al}^{+3}]^2}{[\text{Cu}^{+2}]^3} \quad (a)$$

$$E_{\text{cell}} = E^\circ - E_A \\ = 0.34 + 1.66$$

$$E_{\text{cell}} = 2$$

$$E = 2 - 9.8 \times 10^{-3} \log \frac{10^{-2}}{10^{-9}} \quad (b)$$

$$E = 2 - 9.8 \times 7 \times 10^{-3} \quad \Delta G = -nFE$$

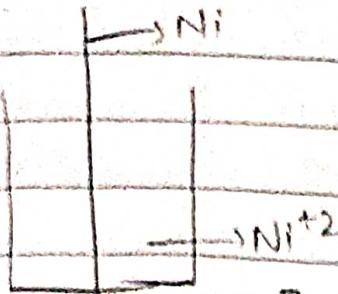
$$E = 2 - 0.0686 \quad = -6 \times 96500 \times 1.93$$

$$\boxed{E = 1.9314 \text{ V}}$$

$$\boxed{\Delta G = -1118280.6 \text{ J}}$$

Cell is feasible

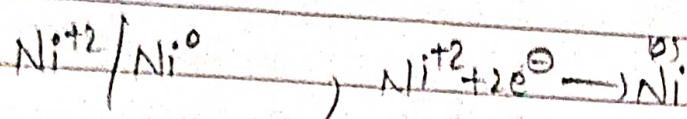
Q.)



$$E^\circ_{\text{Ni}/\text{Ni}^{+2}} = +0.23 \text{ V}$$

$$E_{\text{Ni}^{+2}/\text{Ni}} = ?$$

$$[\text{O}_2] = 1 \text{ atm}, \Delta G_1 = ?, \text{ Notation is ok.}$$



$$E = E^\circ - \frac{0.059}{n} \log \frac{P_{\text{O}_2}}{[{\text{Ni}^{+2}}]}$$

$$E = -0.23 - \frac{0.059}{2} \log_{10}.$$

$$E_{\text{Ni}^{+2}/\text{Ni}^{\circ}} = -0.23 - 0.0295.$$

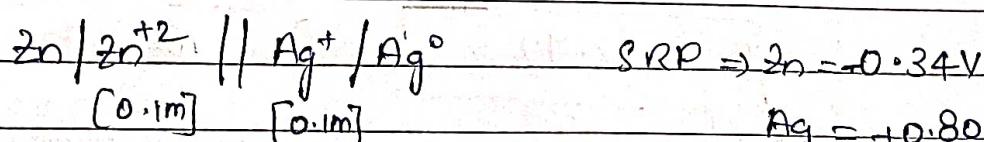
$$E_{\text{Ni}^{+2}/\text{Ni}} = -0.2595 \text{ V}$$

$$\Delta G_f = -nFE$$

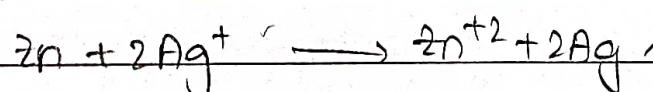
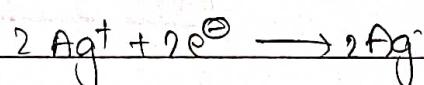
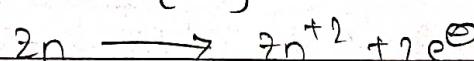
$$= -2 \times 96500 \times (-0.2595) \text{ J}$$

$$\Delta G_f = 50083.5 \text{ J}$$

Q.)



$$\text{Ag} = +0.80 \text{ V}$$



$$E_{\text{cell}}^\circ = E_c - E_A = 0.8 + 0.34 = 1.14 \text{ V}$$

$$E = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Ag}^+]^2}$$

$$E = 1.14 - \frac{0.059}{2} \log 10,$$

$$E = 1.14 - 0.0295$$

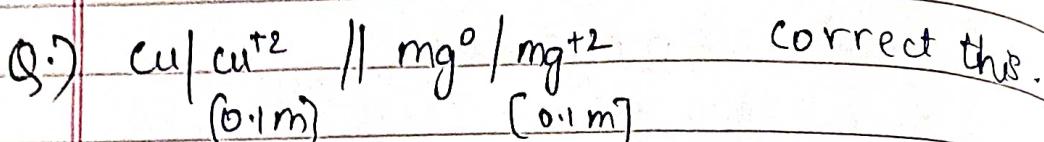
$$\Delta G = -nFE$$

$$E = 1.1105 V$$

$$= -2 \times 96500 \times 1.1$$

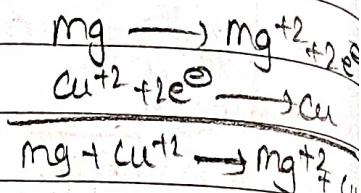
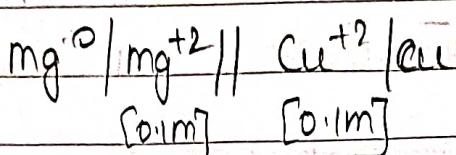
$$\Delta G = -214326.5$$

Feasible



$$E_{Cu/Cu^{+2}} = -0.34 V$$

$$E^{\circ}_{Mg^{+2}/Mg^{\circ}} = -2.38 V.$$



$$E_{cell} = E_C - E_A = 0.34 - (-2.38)$$

$$= 2.72.$$

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

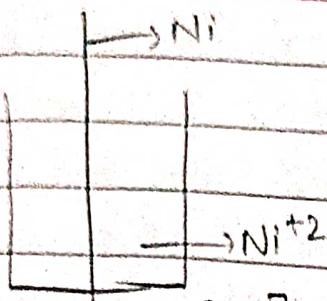
$$E = 2.72 V \quad || \quad \Delta G = -nFE^{\circ} \quad (0.059/2) \times 2 \times 96500 \times 2.72$$

Feasible

$$\Delta G = -524960$$



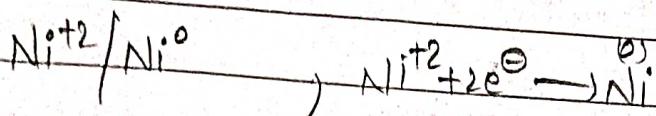
(8.)



$$\epsilon^\circ_{Ni/Ni^{+2}} = +0.23 V$$

$$\epsilon^\circ_{Ni^{+2}/Ni} = ?$$

$[0.1]m$ ,  $\Delta G_f = ?$ , Notation & rxn.



$$\epsilon = \epsilon^\circ - \frac{0.059}{n} \log \frac{P_{Ni^{+2}}}{[Ni^{+2}]}$$

$$\epsilon = -0.23 - \frac{0.059}{n} \log 10$$

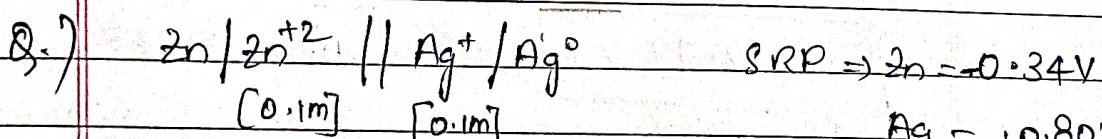
$$E_{Ni^{+2}/Ni^0} = -0.23 - 0.0295$$

$$\boxed{E_{Ni^{+2}/Ni^0} = -0.2595 V}$$

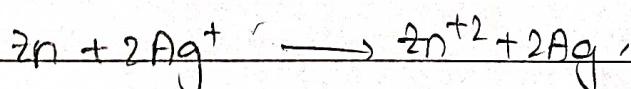
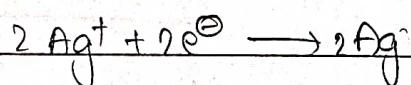
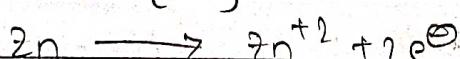
$$\Delta G_f = -nFE$$

$$= -2 \times 96500 \times (-0.2595)$$

$$\boxed{\Delta G_f = 50083.5}$$



$$Ag = +0.80 V$$



$$\epsilon_{cell}^\circ = E_c - E_A = 0.8 + 0.34 = 1.14$$

$$E = \epsilon_{cell}^\circ - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Ag^+]^2}$$

$$E = 1.14 - \frac{0.059}{2} \log 10.$$

$$E = 1.14 - 0.0295$$

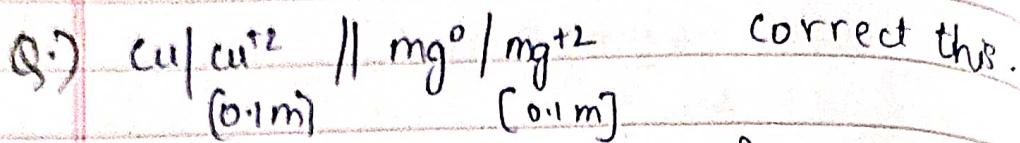
$$\Delta G = -nFE$$

$$E = 1.1105 V$$

$$= -2 \times 96500 \times 1.11$$

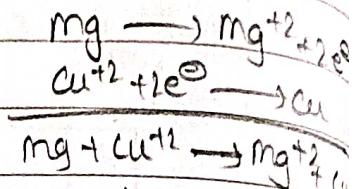
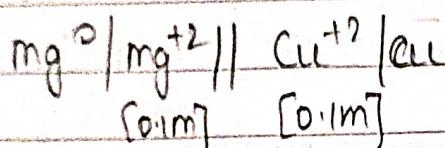
$$\Delta G = -214326.5$$

feasible



$$E_{Cu/Cu^{+2}} = -0.34 V$$

$$E^{\circ}_{Mg^{+2}/Mg} = -2.38 V$$



$$E_{cell} = E_C - E_A = 0.34 - (-2.38)$$

$$= 2.72$$

$$E = E^{\circ}_{cell} - \frac{0.059}{2} \log \frac{[Mg^{+2}]}{[Cu^{+2}]}$$

$$E = 2.72 V \quad \Delta G^{\circ} = -nFE^{\circ}$$

$$= -2 \times 96500 \times 2.72$$

feasible

$$\Delta G = -524960$$

→ used in designing sensors.

## TYPES OF ELECTRODES:-

Electrode → System of halfcells.

Electrode (or) halfcells.

1.) Gas - ion electrode

2.) metal - metal ion electrode ] not in syllabus.

3.) metal - metal insoluble salt electrode

4.) Redox electrode

5.) Ion-selective electrode.

\* 1.) Gas - ion electrode - Hydrogen electrode (SHE)

\* 2.) metal - metal ion - electrode -  $m^{+n}/m$ .

\* 3.) metal - metal insoluble salt electrode :-

\* Calomel electrode. → toxic materials used,  $\text{Hg}^{2+}$  issued

\* Ag - AgCl electrode.

\* 4.) Redox electrode :- \* Quinhydrone

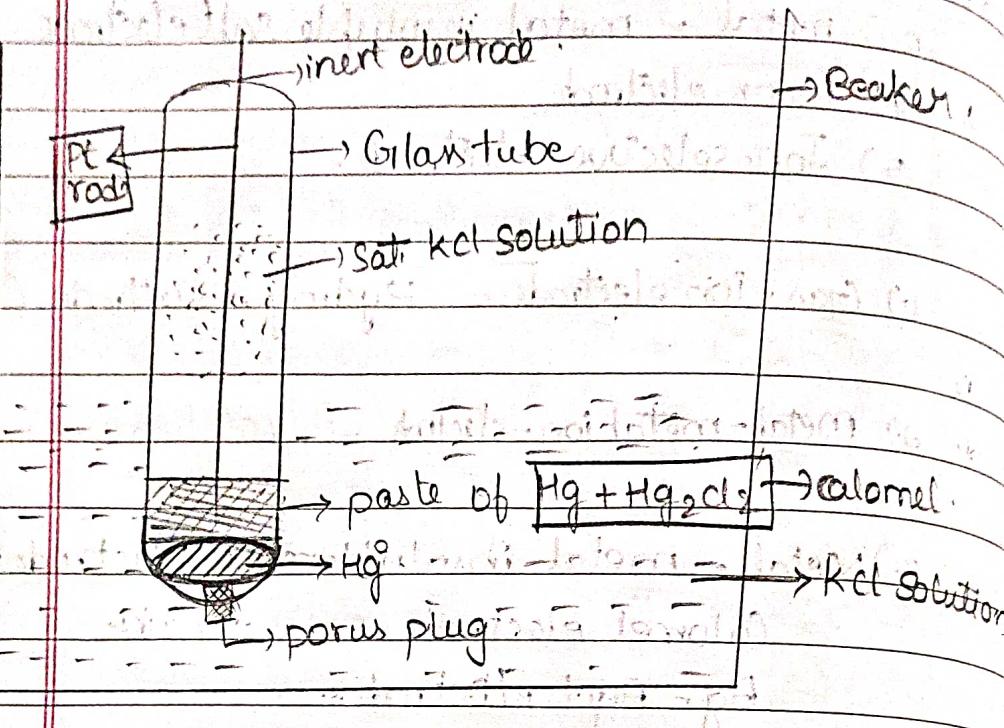
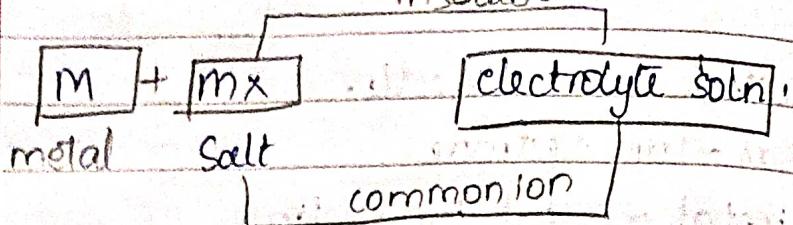
\*  $\text{Fe}^{+3}/\text{Fe}^{+2}$

\* 5.) Ion - selective :- \* Glass electrode

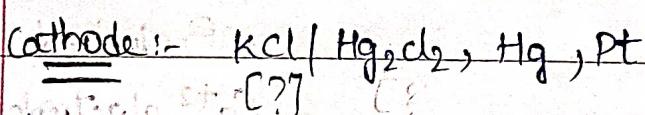
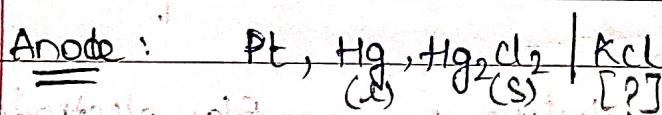
\*  $\text{F}^-$  electrode

\*  $\text{Ca}^{+2}$  electrode.

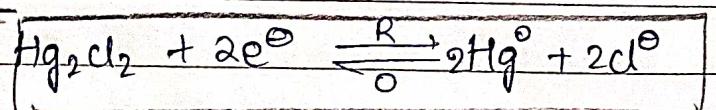
Metal - metal insoluble salt;  
insoluble



\* Electrode notation:-



\* Electrode rxn:-



\* Nernst eqn:-

$$E = E^\ominus - \frac{0.059}{n} \log \frac{P}{R}$$

$$E_{\text{calomel electrode}} = E_{\text{calomel electrode}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Hg}^{\circ}]^2 [\text{Cl}^{\circ}]^2}{[\text{Hg}_2\text{Cl}_2]} \quad (1)$$

$$* E_{\text{CE}} = E_{\text{CE}}^{\circ} - 0.0591 \log [\text{Cl}^{\circ}]$$

\* electrode potential always depends on concn of electrolytic solution.

\*  $[\text{KCl}] = \text{saturated soln} \Rightarrow \text{saturated calomel electrode}$

\*  $[\text{KCl}] = [1\text{N}] \Rightarrow \text{Normal calomel electrode.}$

\*  $[\text{KCl}] = [1\text{N}] \Rightarrow \text{Decinormal calomel electrode.}$

KCl soln.

SEE	$\rightarrow 0.242\text{V}$	
NCE	$\rightarrow 0.282\text{V}$	SRP values.
DNCE	$\rightarrow 0.33\text{V}$	

\* limitation:

\* We have to use this electrode only below  $50^{\circ}\text{C}$  as  $\text{Hg}_2\text{Cl}_2$  is not stable beyond  $50^{\circ}\text{C}$ ,  $\text{Hg}_2\text{Cl}_2$  decomposes so equilibrium is disturbed.

\* Tonic materials are used. ( $\text{Hg}$ ), ( $\text{Hg}_2\text{Cl}_2$ )

\* Impurities like oxidising agent; reducing agent will effect electrode rxn. There by alters the developed electrode potential.

### \* Advantages

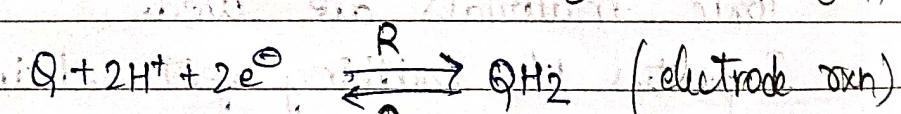
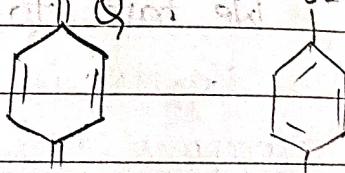
\* Easy to construct and economical.  
 \* This more accurate, reliable, reproducible  
 \* Hence, Saturated calomel electrode is used  
 as reference electrode (secondary reference  
 electrode instead of SHE (primary reference  
 electrode)).

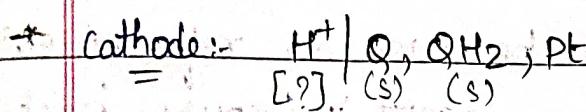
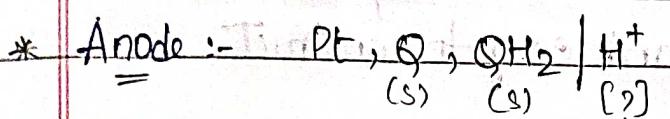
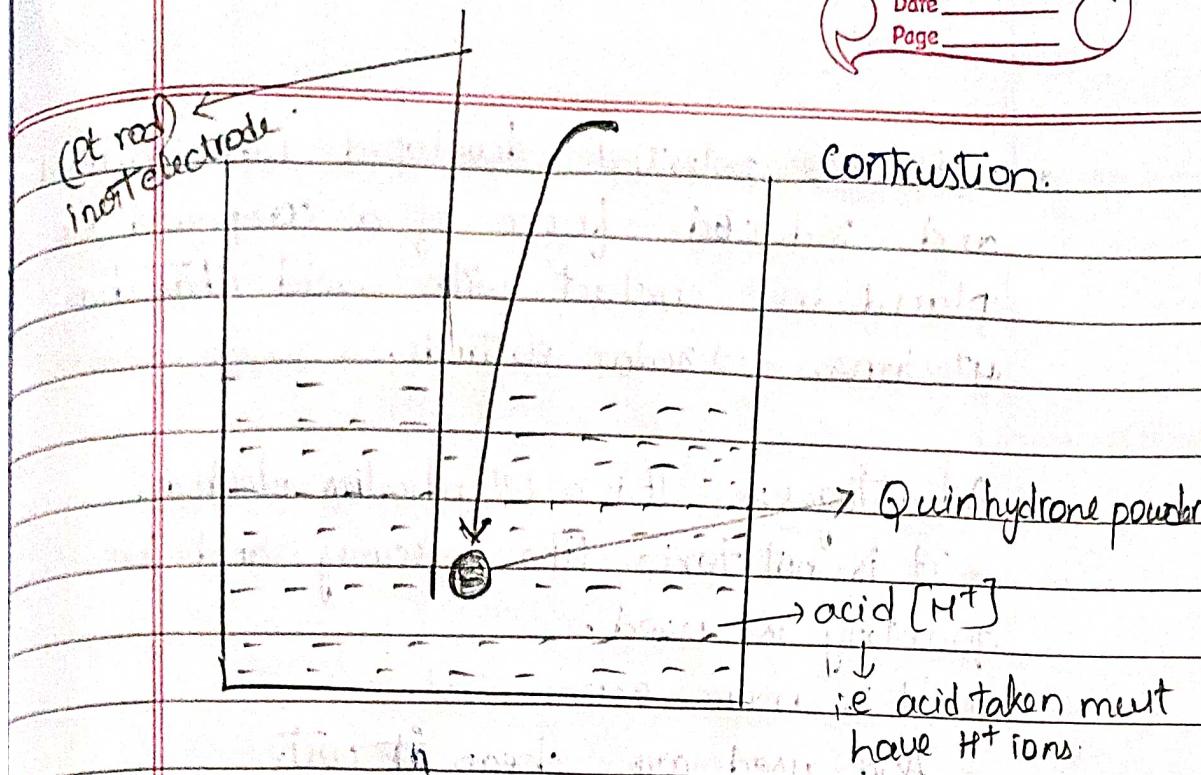
\* Ag | AgCl electrode is also good example of  
 metal-metal insoluble electrode.  
 \* Ecofriendly (or) less toxic materials are  
 used so this electrodes are preferred over  
 SCE.

### \* Redox electrode:-

#### \* Quinhydrone Electrode :-

Quinhydrone powder = Quinone + hydroquinone





\* Nerst eqn:-

$$E_{QE} = E_{Q,C}^{\circ} - \frac{0.0591}{2} \log \frac{[QH_2]^2}{[Q][H^+]^2}$$

Indicates  $\rightarrow 0.6994 \text{ V.}$

$$\text{But } E_{QE} = E_{Q,C}^{\circ} + 0.0591 \log [H^+]$$

$$E_{QE} = 0.699 + 0.0591 P_H$$

\*  $E = 0.699 + 0.0591 P_H$

Q.) Describe the construction of quinhydrone electrode and mention its limitation.

Q.) Discuss the construction, electrode representation, electrode rxn, nerst eqn for a redox electrode

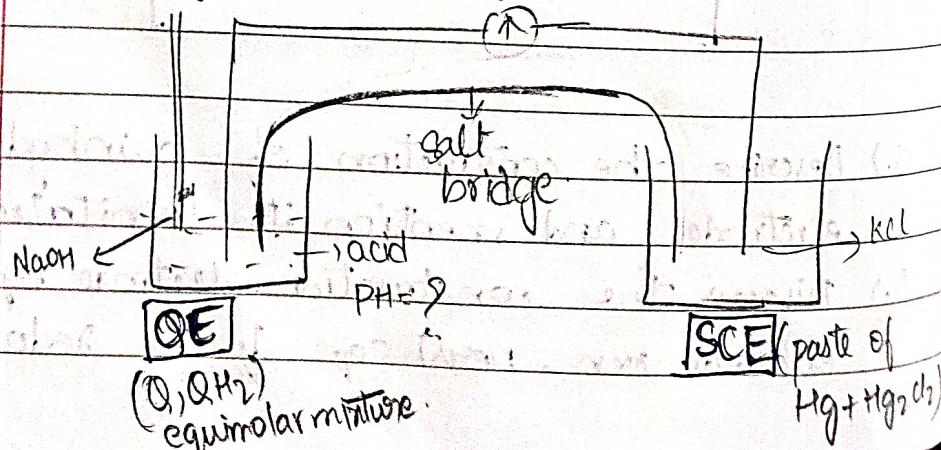
\* Electrode potential developed when oxidized and reduced form of a compound placed in contact with acid that has  $H^+$  ions.  $\rightarrow$  redox electrode. (it cannot be used as reference electrode)

- \* Advantages :- \* It is a pH indicator electrode.
- \* It is not toxic like mercury and less quantity is used.
- \* It is more economical.
- \* Acid used are cheap at cost.
- \* Simple and easy to construct.

#### \* Limitations :-

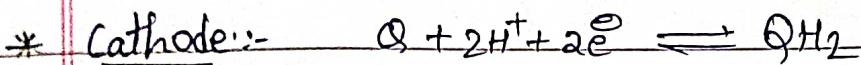
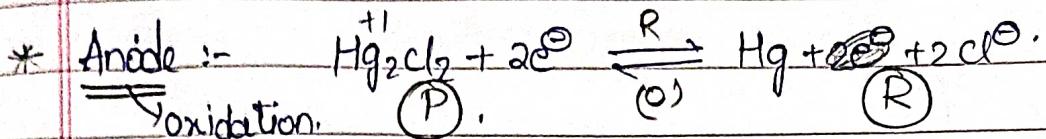
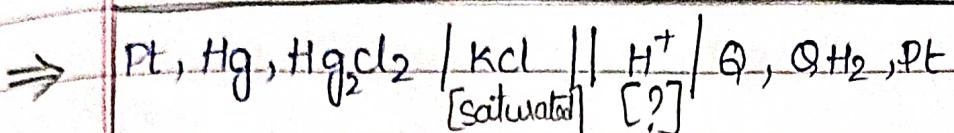
- \* It cannot be used as reference electrode.
- \* If oxidizing agent is impure back reaction is favoured so the compound taken must be pure.
- \* Presence of oxidising or reducing agent impurities alters electrode potential.
- \* Conversion of  $O_2$  to  $OH^-$  is affected pH of the solution,

#### \* Determination of pH of a solution using Quinhydrone electrode.



- \* Q.E  $\rightarrow$  SRP = 0.69 V  $\rightarrow$  cathode - working electrode
- \* SCE  $\rightarrow$  SRP = 0.24 V  $\rightarrow$  anode - reference electrode.

\* A || C  
Saturated calomel electrode || Quinhydrone electrode



$$E_{cell} = E_C - E_A \quad (\text{Anode \& cathode potentials are represented as SRP values})$$

$$E_{cell} = E_{QE} - E_{SCE} \quad (E_{QE} = 0.699 - 0.0591 \text{ pH})$$

$$E_{SCE} = 0.242 \text{ V}$$

$$E_{cell} = 0.699 - 0.0591 \text{ pH} - 0.242$$

$$= 0.45 - 0.0591 \text{ pH}$$

$$E_{cell} = 0.45 - 0.0591 \text{ pH}$$

~~for 100% eff.~~  
~~for 100% eff.~~  
~~for 100% eff.~~

$$pH = \frac{0.45 - E_{cell}}{0.0591}$$

$E_{cell}$  value  
is known  
in the  
experiment.

\* Ion-selective Electrode :- Glass electrode.

Q.) Calculate pH of a solution when a cell constructed using Quinhydrone and SCE, Cell value observed 0.42 volts.

$$\text{pH} = \frac{0.45 - 0.42}{0.0591} = \frac{0.45 - E_{\text{cell}}}{0.0591}$$

$$\boxed{\text{pH} = 0.5}$$

\* **Ion-selective Electrode** :- Glass electrode

Q.) Calculate pH of a solution when a cell constructed using Quinhydrone and SCE, Cell value observed 0.42 volts.

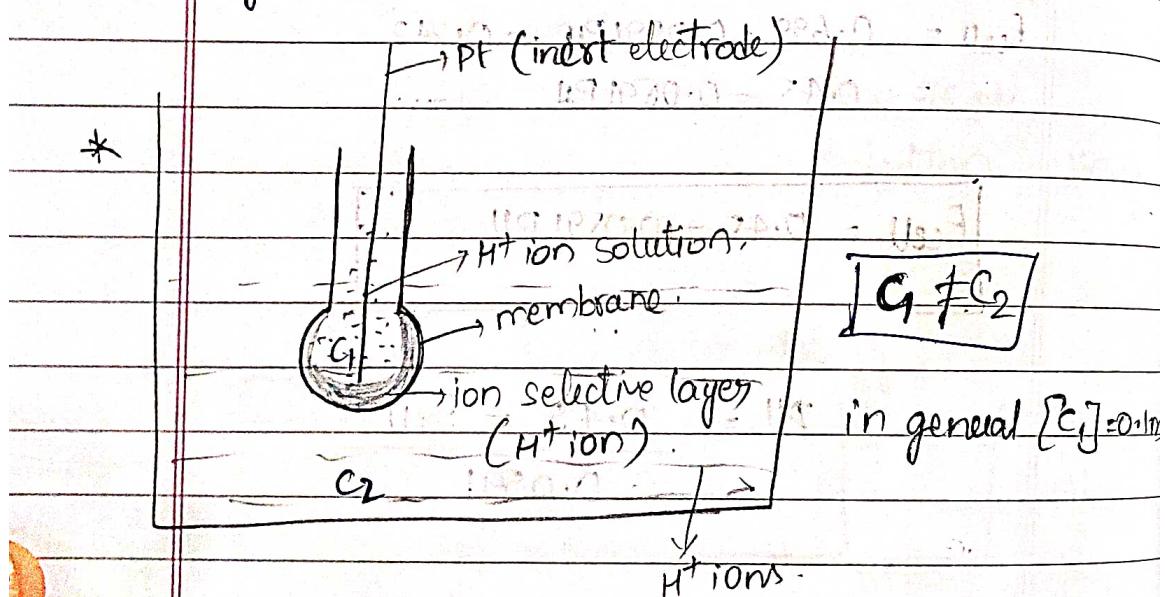
$$\text{pH} = \frac{0.45 - 0.42}{0.0591} = \frac{0.45 - E_{\text{cell}}}{0.0591}$$

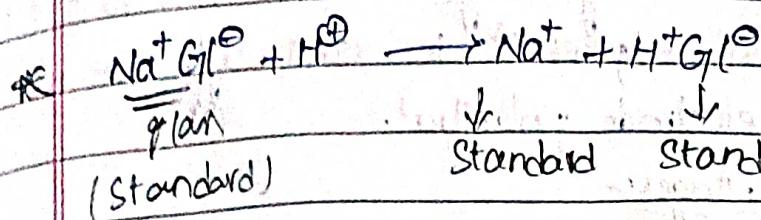
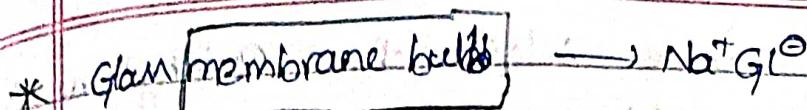
$$\boxed{\text{pH} = 0.5}$$

# **Electrochemical sensors**

Glass electrode, fluoride ion selective electrode, calcium ion selective electrode.

\* **Glass Electrode** :- It is selective for  $\text{H}^+$  ion.  
 ↳ amorphous sodium silicate / borate.  
 Here we select a glass with thin layer and higher conductance.





\* here  $\text{Na}^+$  is replaced with  $\text{H}^+$  which is responsible for electrode potential.

$$E = E^\ominus - \frac{0.059}{n} \log \frac{P}{P_0}$$

$$E_{\text{GE}} = E_{\text{G}}^\ominus - 0.059 \log \frac{[\text{H}^+]}{[\text{H}_0^+]}$$

$$E_{\text{GE}} = E_{\text{G}}^\ominus - 0.059 \text{pH}$$

$$= E_{\text{G}}^\ominus + 0.059 (\log [\text{H}^+])$$

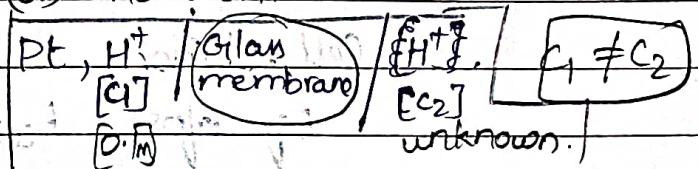
, It varies based on chemical composition

\* It is a pH indicator electrode (hydrogen electrode)

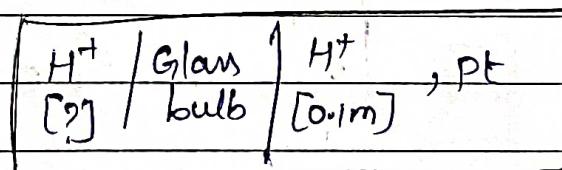
\* Used for determining  $\text{H}^+$  ion concentration.

\* Electrode symbol (or) notation:-

Anode :-



Cathode :-



Advantages:-

\* Portable

\* PH indicator electrode

\* Only HCl is used ie easy and economical and simple to construct.

- \* It is more selective than Quinhydrone electrode.
- \* Its working range is upto pH = 11.5 to 12 pH.
- \* Impurities present in electrolyte soln will alter electrode potential.

\* Disadvantages:-

- \* Cannot use upto pH = 14
- \* we need a special glass for constructing glass electrode

\* Application:-

Determination of pH of a solution using glass electrode.

Q.) Discuss the pH of given unknown soln using a cell which is constructed with glass and SCE electrodes.

Hint:- construct a cell using these electrode.

\* decide anode & cathode.

\* write possible halfcell reactions.

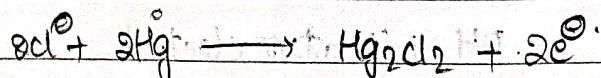
\* Cell notation:

\* Eqn of  $E_{cell}$ .

If  $E_{G.E}^{\circ} > E_{SCE}^{\circ}$  then  $SCE \rightarrow$  Anode  
 $G.E \rightarrow$  cathode.

SCE || G.E.

Pt, Hg,  $Hg_2Cl_2 | KCl$  ||  $H^+ |$  Glass bulb,  $[0.1M]$ , Pt.



- \* It is more selective than Quinhydrone electrode.
- \* Its working range is upto 1.5 to 12 pH.
- \* Impurities present in electrolyte soln will alter electrode potential.

\* Disadvantages:-

- \* Cannot use upto pH = 14.
- \* we need a special glass for constructing glass electrode.

\* Application:-

Determination of pH of a solution using glass electrode.

Q) Discuss the pH of given unknown soln using a cell which is constructed with glass and SCE electrodes.

Hint:- \* construct a cell using these electrode.

\* decide anode & cathode.

\* write possible halfcell reactions.

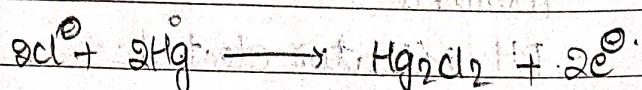
Cell notation:-

\* Egn for  $E_{cell}$ .

If  $E^{\circ}_{G.E} > E^{\circ}_{SCE}$  then: SCE  $\rightarrow$  Anode  
 $G.E \rightarrow$  cathode.

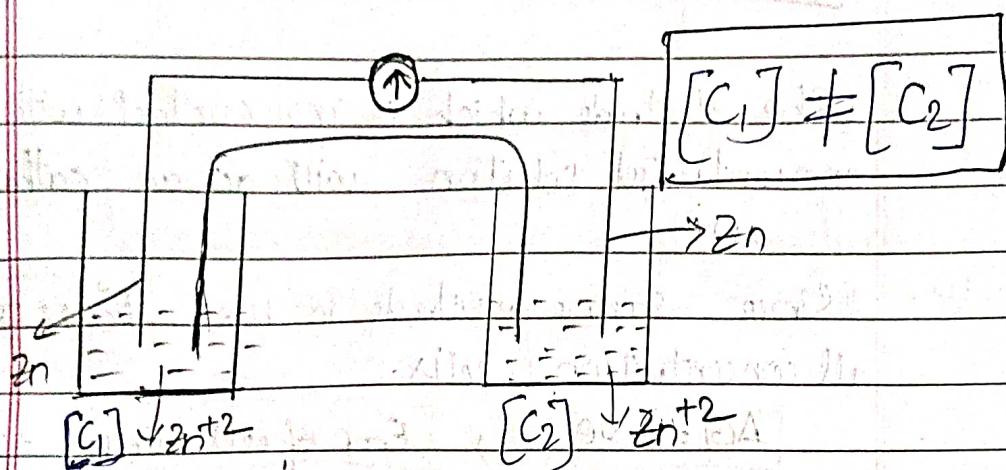
SCE || G.E.

Pt, Hg,  $Hg_2Cl_2$  | KCl ||  $H^+$  | Glass |  $H^+$ , Pt.

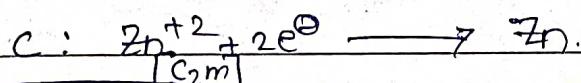


$$E_{\text{cell}} = E_C - E_A \\ = E_{C,E}^{\circ} - 0.0591 \text{ pH} - 0.2422$$

## \* CONCENTRATION CELLS :-



(C.M) COMPARISON POTENTIAL



$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}$$

for concentration cells,  $E_{\text{cell}}^{\circ} = 0$

$$\text{then } E_{\text{cell}}^{\circ} = E_C - E_A \\ = -0.76 - (-0.76) = 0 \text{ V}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}$$

$$E = -\frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}$$

$$[C_1] \neq [C_2]$$

→ Spontaneous redox rxn

to produce electricity

\* Concentration cell is a type of galvanic cell where electrodes are same and electrolyte solution is also but their respective electrolyte concentration is different.

\* The electrode which is in contact with low concentrated solution will act as anode.

\* The electrode which is in contact with high concentrated solution will act as cathode.

\* Since same electrode is used  $E_{\text{cell}}^{\circ} = 0$  for all concentration cells.

$$\Delta G = -ve$$

$$\rightarrow E_{\text{emf}} \text{ of cell} = E_{\text{cell}} = +ve$$

## POTENTIOMETRY TITRATIONS:

→ It is the application of electrode.

\* These are applications of electrodes.

\* In this chemical analysis, cell is constituted in that one reference electrode and other is working electrode.

\* Working electrode is selected based on analyte (test solution)

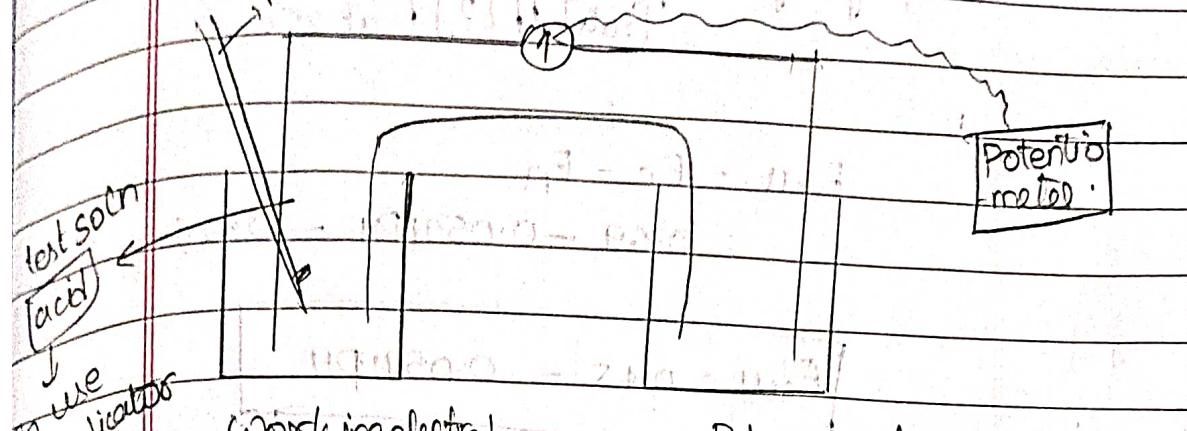
\* The selected electrode potential depends inversely on concentration of test solution.

SHE → standard hydrogen electrode  
SCE → saturated calomel electrode

CLASSMATE  
Date \_\_\_\_\_  
Page \_\_\_\_\_

## \* Acid - Base Titrations

AIM : Determine the strength of a given acid sample.



Working electrode. Reference electrode

Pt electrode or indicator electrode (Quinhydrone) SCE (0.24 V)

pH indicator electrode :-

1.) Quinhydrone electrode :

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

2.) Glass electrode :

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

3.) Hydrogen electrode :

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

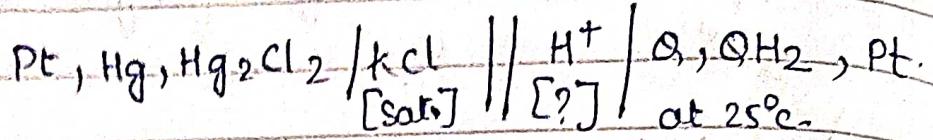
(Q.) Why calomel electrode is not selected as working electrode in potentiometry acid-base titration  
Ans. CO<sub>2</sub> in its electrode potential is not dependent of  $[H^+]$  to know the conc of acid.

$$E_{SCE} = E^{\circ}_{SCE} - 0.0591 \log [Cl^-]$$

p84K

Cell Notation:-

SCE || Quinhydron



$$E_{\text{cell}} = E_c - E_A$$

$$= 0.69 - 0.0591 \text{ pH} - 0.24$$

$$E_{\text{cell}} = 0.45 - 0.0591 \text{ pH}$$

S.N.O	$\text{V NaOH (ml)}$	$E_{\text{cell}}$	$\Delta E / \Delta V$
1.	0.0	300	-
2.	0.5	275	50
3.			
			due to change in electrolyte solution concn $E_{\text{cell}}$ values are changing

as we go on adding  $\text{NaOH}$  then  $\text{H}^+$  ion decreased i.e. pH increases as a whole.  $E_{\text{cell}}$  decreases and at some time it becomes ( $= 0$ ),

$$\frac{N V}{\text{NaOH}} = \frac{N V}{\text{HCl}}$$

$$\frac{N_{\text{HCl}}}{V_{\text{HCl}}} = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}}}{V_{\text{HCl}}}$$

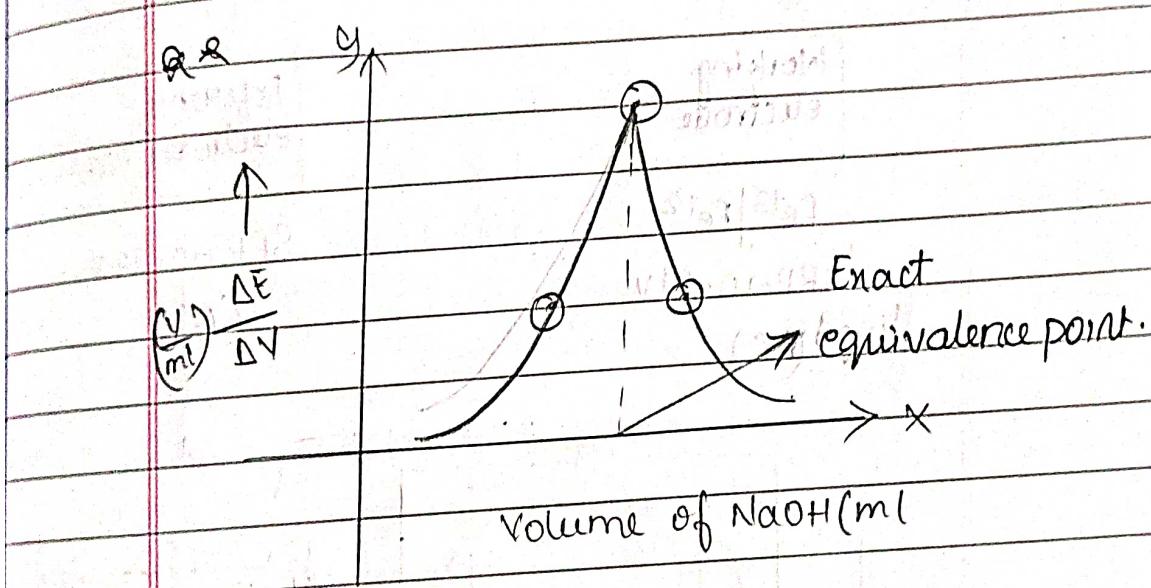
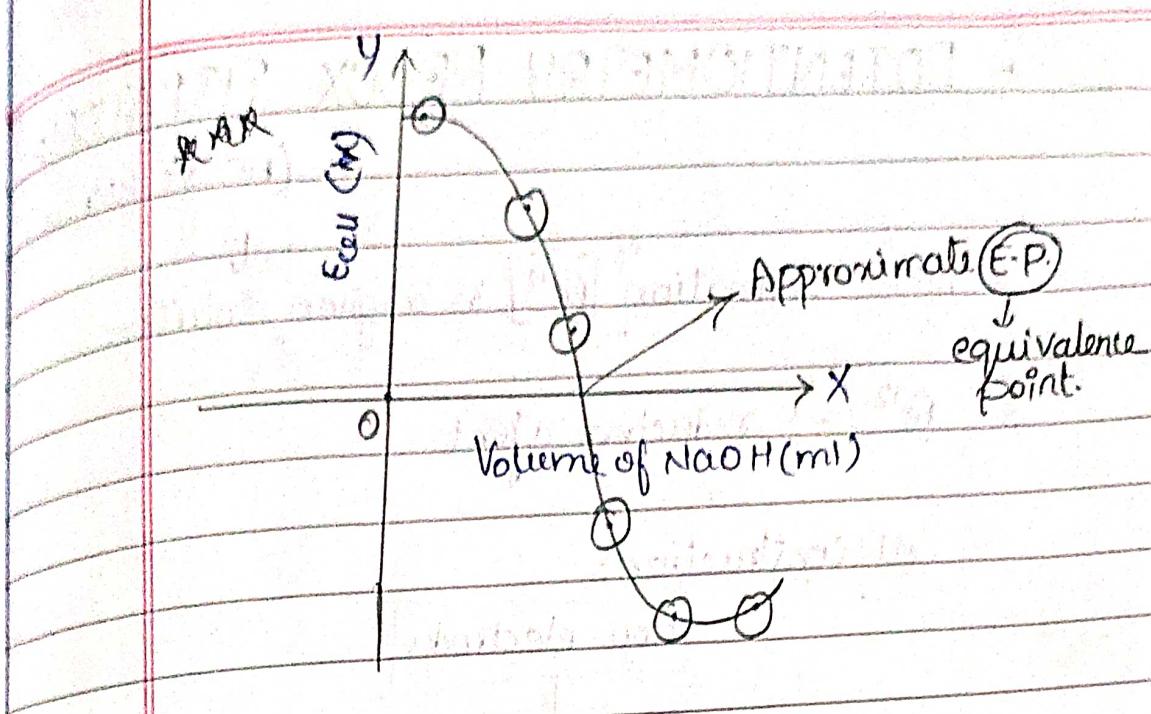
$$N_{\text{NaOH}} = \text{known}$$

$$N_{\text{HCl}} = E.P \left( \frac{\Delta E}{\Delta V} \right)$$

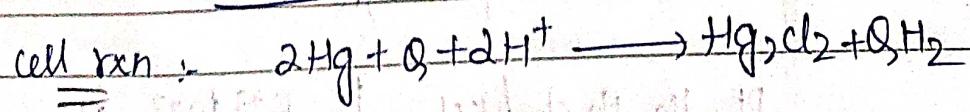
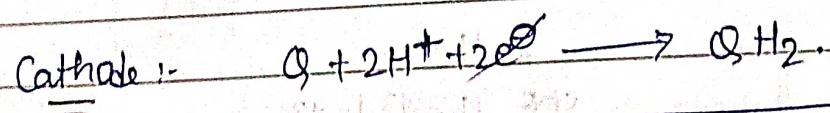
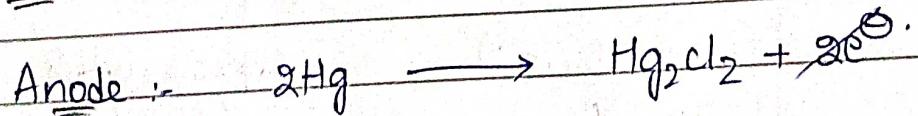
$$N_{\text{HCl}} = ?$$

$$V_{\text{HCl}} = \text{known.}$$

$$N_{\text{HCl}} \times 36.5 = (\text{m.wt. of HCl})$$



~~Ques~~ Half cell rxns:-



in g/L.

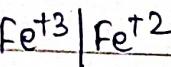
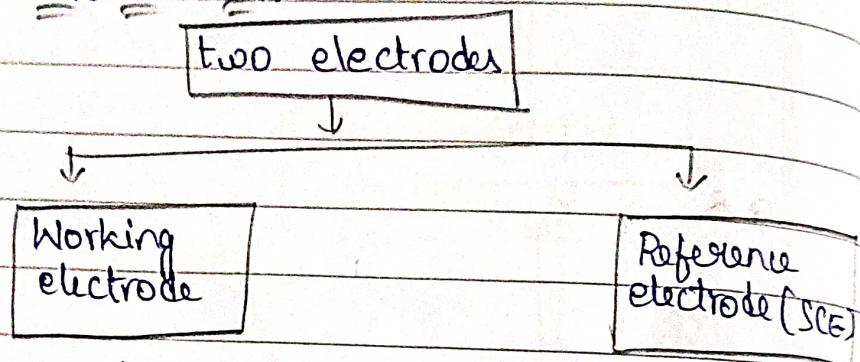
# POTENTIOMETRY REDOX TITRATION

( $\text{Fe}^{+2}$  vs  $\text{KMnO}_4$ )

\* AIM: Estimation of  $[\text{Fe}^{+2}]$  in a given solution

\*  $\text{Fe}^{+2} \rightarrow$  reducing agent.

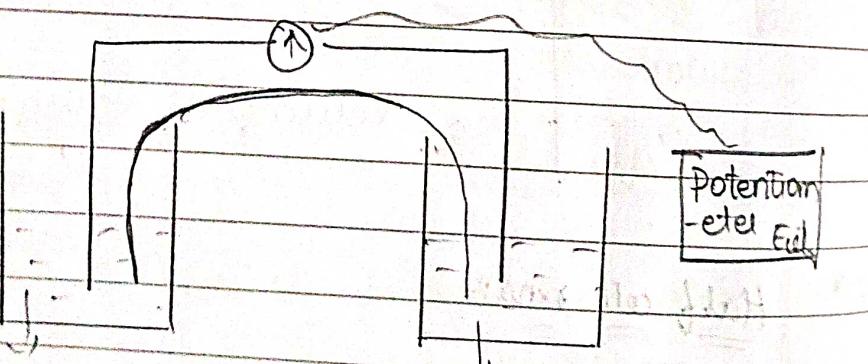
\* Cell construction:-



(A)

SRP  $\rightarrow 0.77\text{ V}$

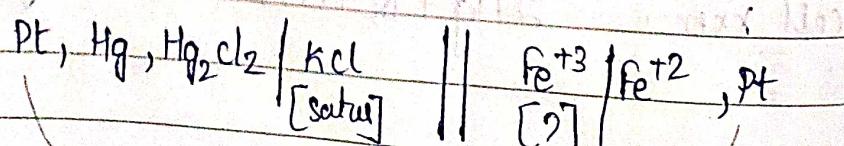
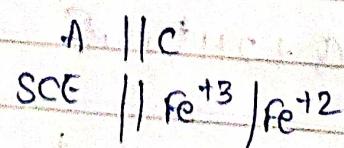
(C)

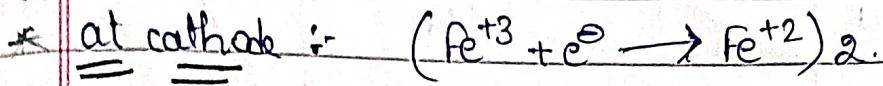
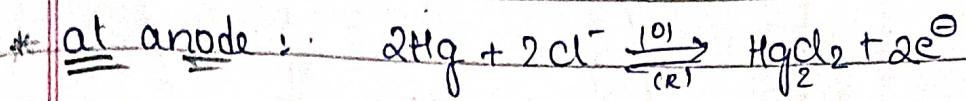


cathode

Reference electrode (SCE)

Anode





$$E_{\text{cell}} = E_C - E_A$$

$$E_{\text{Fe}^{+3}/\text{Fe}^{+2}} = E^{\circ}_{\text{Fe}^{+3}/\text{Fe}^{+2}} - 0.0591 \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]}$$

$$E_{\text{cell}} = E_{\text{Fe}^{+3}/\text{Fe}^{+2}} - E_{\text{cath}}$$

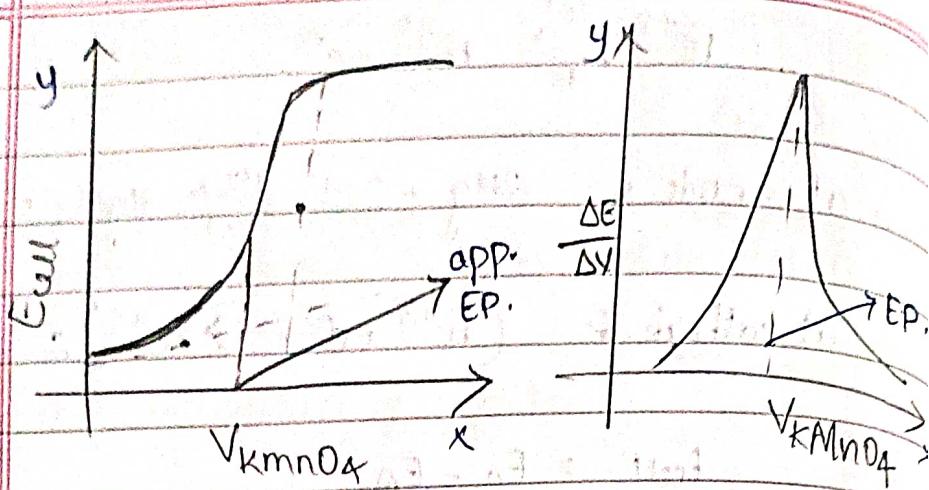
$$E_{\text{cell}} = 0.77 - 0.0591 \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]} - 0.24 \text{ V}$$

$$E_{\text{cell}} = 0.53 - 0.0591 \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]}$$

SNo	V mmol/l	$E_{\text{cell}}$	$\Delta E/\text{mV}$

↓ Increase  
in  
 $E_{\text{cell}}$ .

\* During titration,  $[\text{Fe}^{+2}]$  is decreasing &  $[\text{Fe}^{+3}]$  is increasing as a whole  $E_{\text{cell}}$  value is increasing.



$$\frac{NV}{\text{KMnO}_4} = \frac{NV}{\text{Fe}^{+2}}$$

$$N_{\text{Fe}^{+2}} = ?$$

$N_{\text{Fe}^{+2}}$  = known

$N_{\text{KMnO}_4}$  = known

$V_{\text{KMnO}_4}$  = E.P.

$$N_{\text{Fe}^{+2}} = N_{\text{KMnO}_4} \times V_{\text{KMnO}_4}$$

$$N_{\text{Fe}^{+2}} = \frac{V_{\text{Fe}^{+2}} \times 2.0}{V_{\text{KMnO}_4}}$$

$$N_{\text{Fe}^{+2}} \times 56 = W_{\text{Fe}^{+2}} (\text{g/L}) \rightarrow \text{Quantitative analysis.}$$