

# **Analytical Techniques and Instrumentations**

**Module – 2**

**(Part-1)**

## Cell

The cell which is considered in Electrochemistry  
is called Electrochemical cell.

(i) It is a device.

(ii) Capable of generating or converting electrical energy from chemical energy or vice versa.

### Classification:-

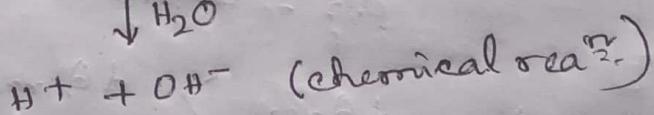
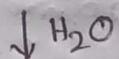
(A) Galvanic cell or voltaic cell:-

(i) name generated L. Galvani or A. Volta.

(ii) An electrochemical cell that derives electrical energy from chemical energy (spontaneous reactions taking place within the cell).

(B) Electrolytic cell:-

Electrolysis:- passage of electricity



⇒ An electrochemical cell that converts electrical energy into chemical energy is called electrolytic cell.

### Components:-

(i) Electrodes      (ii) Anode      (iii) Electrolyte.

                        (iv) Cathode      (v) Separator.

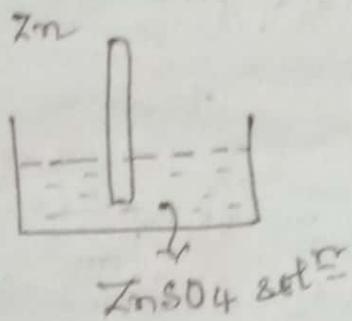
## Electrodes:-

Anode :- It is an electrode where the oxidation reaction takes place.

Basically, an electrode is a metal conductor, the chemically active materials are coated on the electrode surface.

e.g: For a zinc electrode, the active material is Zn and Zn metal is coated on a metal conductor surface.

Here the active material undergoes chemical reaction.



To function Zn as an electrode  
→ it must be dipped into its own ionic solution.

ZnSO<sub>4</sub> soln contains Zn<sup>2+</sup> ions.

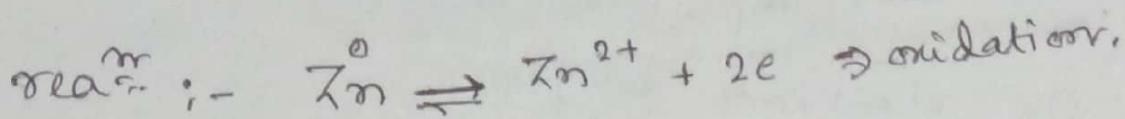
~~Electrode consider as an interface between two phases.~~

Generally, when an electrode comes in contact with its known ion, it shows possibility to gain e<sup>-</sup>. As a result, electron surface gain charge ⇒ thus potential is generated.

Let us consider,  $\text{ZnSO}_4$  conc<sup>m</sup> is less.

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To gain equilibrium, Zn metal loose  $e^-$  to come into the solution.

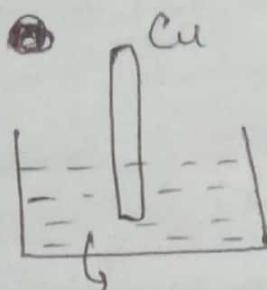


The lost electron resides on the metal or electrode surface  $\Rightarrow$  thus Anode negatively charged.

ANODE  $\rightarrow$  Left Cathode.

Oxidation Anode Negative.

Cathode:- It is an electrode where the reduction reaction take place.



~~CuSO<sub>4</sub> soln~~

Let us consider  $\text{CuSO}_4$  solution conc<sup>m</sup> is more.

To gain equilibrium,  $\text{Cu}^{2+}$  accept  $2e^-$  to and deposit as Cu in the electrode.

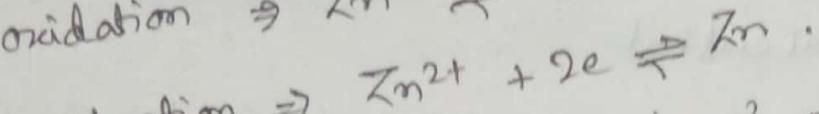
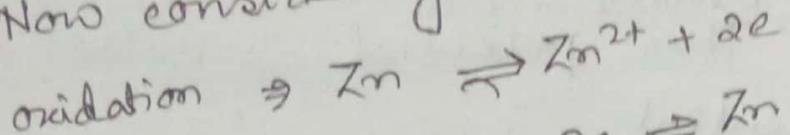
The electrons are taken from electrode surface  $\Rightarrow e^-$  deficient center  $\Rightarrow$  positively charged.  $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}^{\circ} \Rightarrow \text{reduction.}$

generally, reduction.

reduce in what?  $\Rightarrow$  oxidation state  
oxidation state of  $\text{Cu}^{2+}$  decrease from +2 to 0.  
(decrease in oxidation state)

Now if two electrode solution connected by salt bridge and two terminals of electrode connected by electrical wire  $\Rightarrow$  there will be flow of  $e^-$  from electron rich  $\Rightarrow$  Anode to  $e^-$  deficient cathode  $\Rightarrow$  ie flow of electricity.

Now considering two reaction of Zn.



Question is which one '+ve' potential and which one '-ve' potential?

Answer:- Consider reduction reac<sup>n</sup>. to be '+ve'.

So, we always remember  $\Rightarrow$  reduction potential.  
 $\therefore$  Oxidation potential will be '-ve' of reduction potential.

For writing particular reac<sup>n</sup>.  $\Rightarrow$  we will always write in its reduction form.

## Cell potential

The potential difference between the <sup>24</sup> cathode and anode is called cell potential.

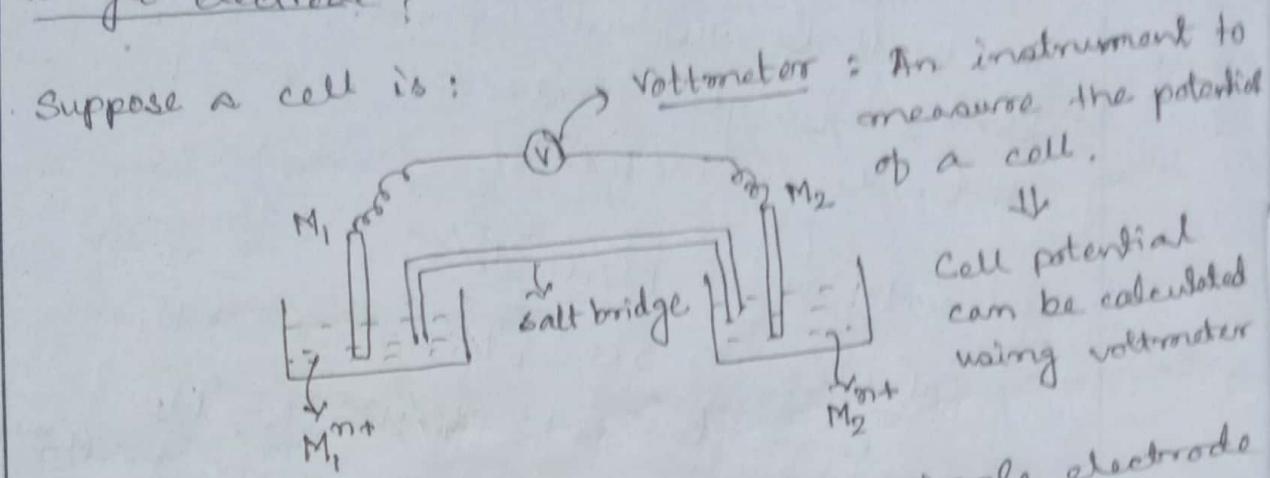
## Single electrode potential

When a metal is in ~~boards~~ contact with its own ionic solution, there is the a possibility of electron exchange between the metal ~~ion~~ and ions present in the solution. As a result, there is a generation of potential <sup>on electrode surface</sup>. This potential is called single electrode potential.

## Standard Electrode Potential ( $E^\circ$ )

- The measured reduction potential of an electrode, when the conc<sup>n</sup> of solution is kept at 1(M); temp. and pressure is kept at 298 K and 1 atm is called Standard Electrode Potential.
- ~~so it's~~ standard electrode potential talks about its reduction behavior.
- Highly positive ~~is~~  $E^\circ \Rightarrow$  more prompt towards red<sup>n</sup>.
- Less positive  $E^\circ \Rightarrow$  more prompt towards oxid<sup>n</sup>.  
 $E_M^\circ > E_N^\circ \therefore M \Rightarrow$  act as cathode.  
 $N \Rightarrow$  act as anode.

Q. How to measure a potential of a cell and a single electrode?



Doubt :- If it is asked to calculate single electrode potential ( $M_1$  or  $M_2$ )  $\Rightarrow$  it's practically impossible.

Way out :- If we choose  $M_2$  electrode as standard electrode  $\Rightarrow$  means whose potential is known.

From the cell potential and the standard electrode potential we can derive the or calculate the potential of  $M_1$  electrode.

### Reference electrode

(i) They are the electrodes with reference to those, the electrode potential of any electrode can be measured.

(ii) They are of two types :

Why R?  
H<sub>2</sub> activates  
H<sub>2</sub> gas.

(a) Primary Electrode :-

Standard electrode whose potential is arbitrarily taken as zero at all temperatures. e.g: standard hydrogen electrode (SHE).

(b) Secondary Electrode :-

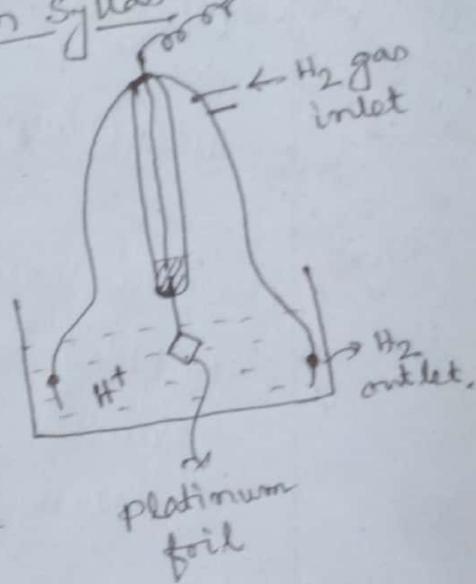
The electrode whose potential is known with respect to standard hydrogen electrode. e.g: calomel electrode.

Hydrogen Electrode (SHE)

(not included in Syllabus)

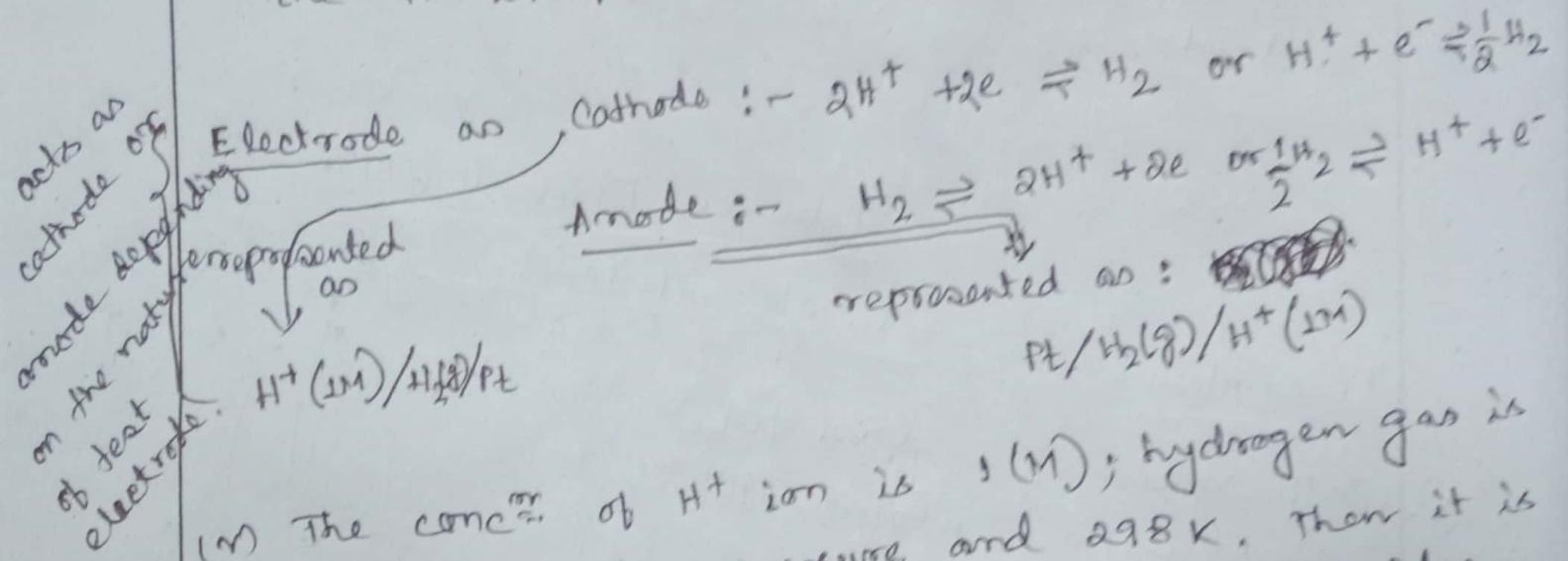
Description :-

- NH<sub>4</sub> Pt<sup>2+</sup>. H<sub>2</sub> activates H<sub>2</sub> gas.
- (1) It consists of a glass tube fused with a platinum (Pt) foil at the bottom.
  - (2) Mercury is placed at the bottom of the tube and copper wire is dipped into it to provide external electrical contact.
  - (3) The glass tube is surrounded by a bell-shaped glass jacket fused at the top of the glass tube.
  - (4) There is a H<sub>2</sub> gas inlet ~~on top~~ at the top and H<sub>2</sub> gas outlet at the bottom.



(iii) The platinum foil is dipped into the solution containing  $H^+$  ion and  $H_2$  gas is bubbled <sup>32</sup> about the electrode (Pt) through gas inlet.

(iv) The hydrogen gas gets absorbed at the platinum foil and establishes equilibrium with the  $H^+$  ions.



(v) The conc<sup>n</sup> of  $H^+$  ion is 1(m); hydrogen gas is bubbled at 1 atm pressure and 298 K. Then it is termed as SHE. Its potential arbitrarily chosen as zero.

(vi) The test electrode is coupled with a SHE and the emf of the cell is determined to calculate the potential of test electrode.

Limitations:-

(i) Maintaining the conc<sup>n</sup> of  $H^+$  ion at unity is difficult.

(ii) Difficulty is there to maintain pressure of  $H_2$  to be 1 atm.

(iii) Pt is highly susceptible for poisoning by the impurities in the gas.

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(iv) In presence of oxidizing agents, it can't be used.

### Calomel Electrode

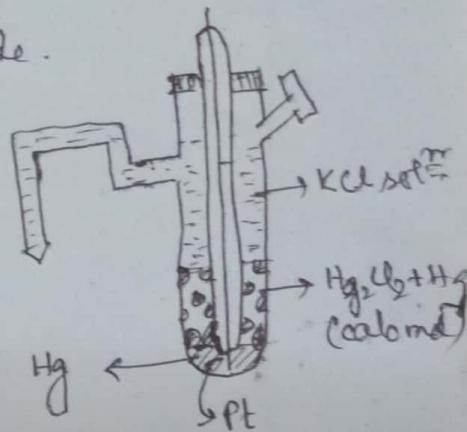
(i) Secondary

~~reference~~ reference electrode.

(ii) It is a metal-metal salt ion electrode. The components are mercury, mercurous chloride ( $Hg_2Cl_2$ ) and solution of potassium chloride.

(iii) Mercury is placed at the bottom of a glass tube having a side tube on each side.

(iv) Mercury is covered by a paste of  $Hg_2Cl_2$  and mercury (calomel)



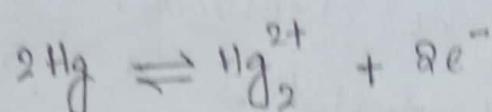
(v) A solution of KCl is introduced above the paste through the side tube.

(vi) A platinum wire sealed into the glass tube is dipped into the mercury to provide external electrical contact.

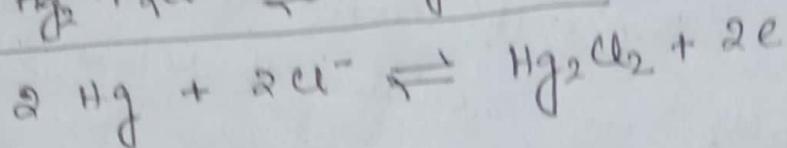
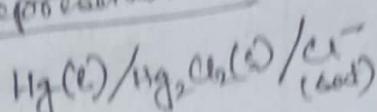
(vii) The conc.<sup>n</sup> used for KCl sol<sup>n</sup> is normal (N), deci-normal (N/10) or saturated sol<sup>n</sup> of KCl.

(viii) The calomel electrode can act as cathode or anode depending on the nature of other electrode of the cell.

(ix) (a) Anode :- in calomel electrode  $\Rightarrow$  oxidation take place.



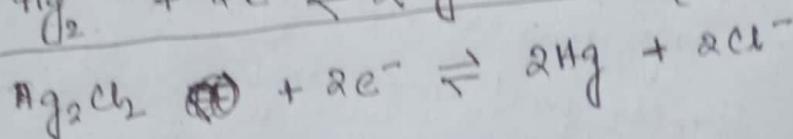
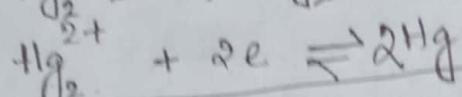
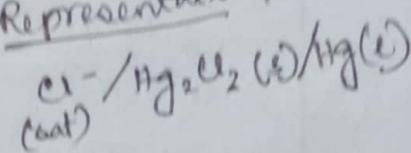
Representation :-



(b) Cathode :- in calomel electrode  $\Rightarrow$  reduction take place.



Representation :-



Electrode potential :- For this calculation  $\Rightarrow$  focus on the reduction reaction,

$$K = \frac{[\text{Hg}]^2 [\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

$$[\text{Hg}_2\text{Cl}_2] = 1. \quad [\text{Hg}] = 1.$$

$$\therefore K = [\text{Cl}^-]^2$$

$$\therefore E = E^\circ - \frac{0.0591}{2} \log [\text{Cl}^-]^2$$

Vant Hoff's eqn:

$$\Delta G_r = \Delta H^\circ + RT \ln K$$

$$\therefore E = E^\circ - \frac{0.0591}{m} \log K$$

$$m=2$$

$$\therefore E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

at 298K.

(x) Electrode potential is decided by the conc.<sup>n</sup> of  $\text{Cl}^-$  ions. Thus it is said that electrode is reversible with respect to  $\text{Cl}^-$  ions.

At 298K the potentials are:

deionized 0.1 (N)  $\text{KCl}$  electrode ( $0.334\text{V}$ )

1 (N)  $\text{KCl}$  " ( $0.281\text{V}$ )

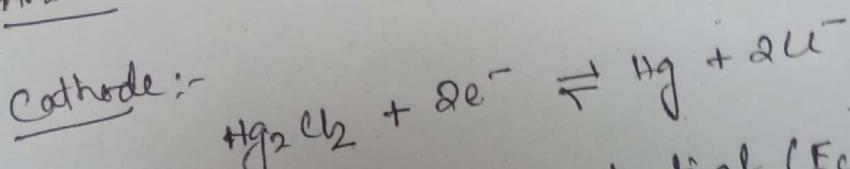
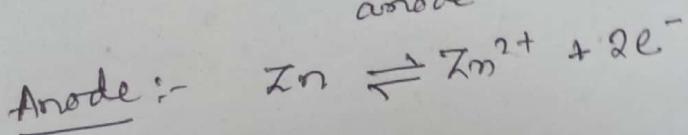
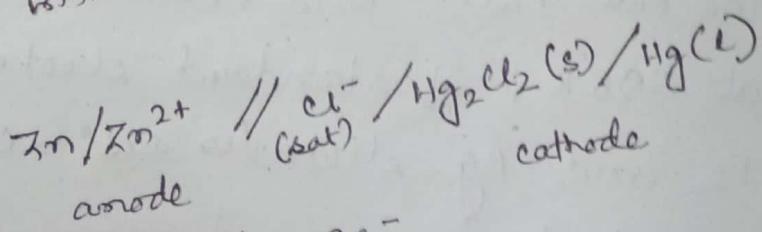
Saturation  $\text{KCl}$  sol<sup>n</sup> " ( $0.2422$ )

Uses:- (a) Act as secondary electrode in the measurement of other electrode.

(b) Most commonly used reference electrode in all potentiometric determinations.

Determination of single electrode potential :-

Suppose suppose the test electrode &  $\text{Zn/Zn}^{2+}$  coupled with a saturated calomel electrode.



Voltmeter gives cell potential ( $E_{\text{cell}}$ )

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{anode}} = (0.2422 - E_{\text{cell}}) \rightarrow \text{known quantity.}$$

Problems:-

- ① Standard electrode potential of 20 Cadmium and Copper are  $-0.44\text{V}$  and  $0.34\text{V}$ . Write the cell representation with cell reaction.
- ② Standard electrode potential of Ag and Ni are  $0.8\text{V}$  and  $-0.25$ . Calculate standard electrode potential cell emf with cell representation.
- ③ The standard In electrode potential is  $-0.76\text{V}$ .  
in contact with  $\text{ZnSO}_4$  sol<sup>n</sup>. The concn. of  $\text{ZnSO}_4$  is  $0.05\text{M}$  and its degree of dissociation is  $0.6$ . Calculate the potential of the electrode.
- ④ For the cell,  $\text{Fe}/\text{Fe}^{2+}(0.01) \parallel \text{Ag}^+(0.1)/\text{Ag}$  write the cell reac<sup>n</sup>. and calculate the emf of the cell at  $298\text{K}$ , if standard electrode potentials of Fe and Ag electrodes are  $-0.44\text{V}$  and  $0.8\text{V}$  respectively.

## Ion selective Electrode

- (a) It is the one which selectively responds to a <sup>26</sup> specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution.  
e.g: glass electrode.
- (b) The electrode generally consist of a membrane which is capable of exchanging the specific ions with solution with which it is in contact with.

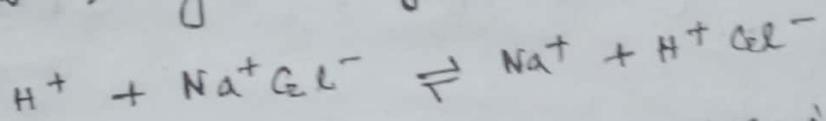
## Glass electrode

- (a) sensitive towards  $H^+$  ion or pH sensitive electrode; most widely used for pH determination.
- (b) Construction:-
- (i) The electrode consists of a glass ~~bulb~~ bulb made up of a special type of glass with high electrical conductance.
  - (ii) The glass bulb is filled with a solution of constant pH (0.1M HCl), and is inserted with Ag-AgCl electrode, which is internal reference electrode and also serves for external electrical contact.
  - (iii) glass contains  $Na_2O - 22\%$ ,  $CaO - 6\%$  and  $SiO_2 - 72\%$

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### (c) Working principle :-

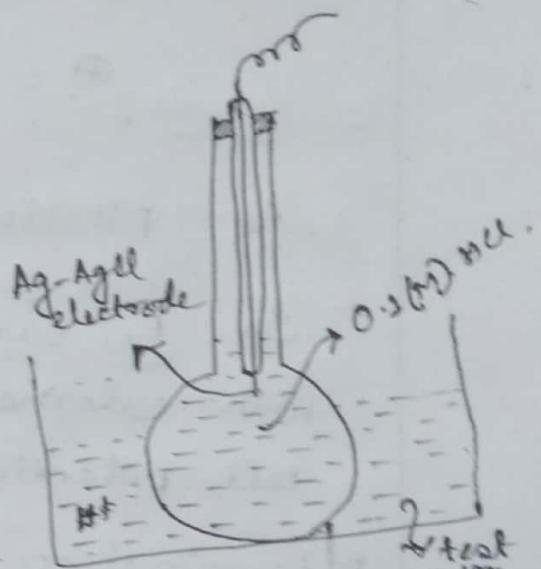
- (i) The electrode is dipped in a solution containing  $H^+$  ions, whose pH should be determined.
- (ii) The  $Na^+$  ions in the glass membrane are exchanged for  $H^+$  ion of the test solution.
- (iii) Due to this exchange there is a generation of boundary potential ( $E_b$ ). The glass electrode potential is given by  $E_G = E_b + E_{Ag/AgCl}$ .



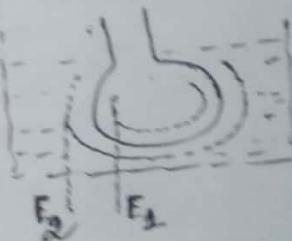
(iv)  $E_b = 0$ , if there is no difference in  $H^+$  ion inside and outside the membrane. However,

it is observed that a small potential is developed, called to asymmetry or asymmetric potential at the surface ( $E_{asy}$ ). Hence

$$E_G = E_b + E_{Ag/AgCl} + E_{asy}$$



(v) When the conc. of  $H^+$  ion inside and outside the membrane is different, then considering {  
 bulb internal soln. conc.  $c_1 (M)$   
 bulb external soln. conc.  $c_2 (M)$



(1)  $E_b = E_a - E_g$        $\left\{ \begin{array}{l} E_a = \text{anode outside potential of bulb} \\ E_g = \text{cathode potential of bulb} \\ C_1 = 0.1 \text{ M} \end{array} \right.$

$$= \frac{RT}{F} (\ln c_2 - \ln c_1)$$

(2)  $E_b = L + \frac{RT}{F} \ln c_2$        $\therefore 0.0591 \log c_2 = L$

$$\textcircled{2} \quad = L + \frac{\{RT \times 2.303\}}{F} \log c_2$$

Again,  $\text{pH} = -\log [\text{H}^+]$ ; hence  $[\text{H}^+] = c_2$

$$\therefore E_b = L - 0.0591 \text{ pH} \quad \left[ \because 2.303 \times \frac{RT}{F} = 0.0591 \right]$$

at 298K,

$\therefore E_{cr} = L - 0.0591 \text{ pH} + \underbrace{E_g / \text{Agce}}_{\text{corr.}} + E_{\text{easy}}$

$$\textcircled{2} \quad = L_1 - 0.0591 \text{ pH} \quad \left[ \because L_1 = L + E_g / \text{Agce} + E_{\text{easy}} \right]$$

$= \text{constant}$ .

As pH is unknown, thus  $E_{cr}$  = unknown.

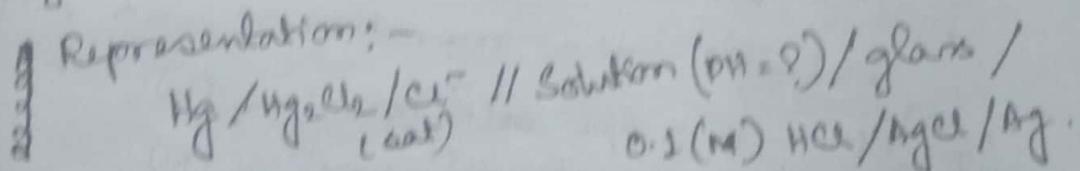
So  $E_{cr}$  can be calculated by coupling with calomel electrode and calculating the cell potential.

(2). Determination of glass electrode potential and pH:-

Anode: Calomel electrode

Cathode: glass electrode

Representation:-



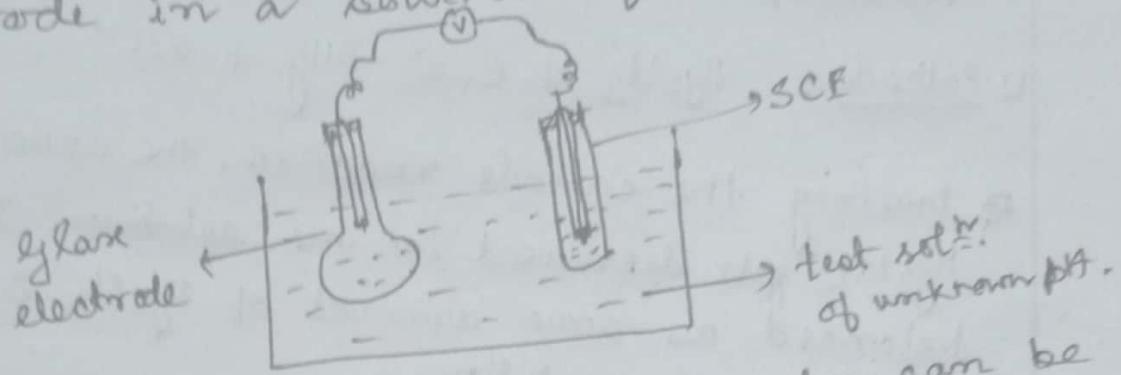
$$E_{\text{cell}} = E_{\text{O}_2} - E_{\text{cal}}$$

$$= \{L_1 - 0.0591 \text{ pH}\} - E_{\text{cal}}$$

$$\therefore \text{pH} = \frac{L_1 - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$

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$L_1$  can be measured by dipping the glass electrode in a solution of known pH.



~~Potentiometer~~ Instead of voltmeter, pH meter can be used directly to calculate pH directly.

#### Advantage:-

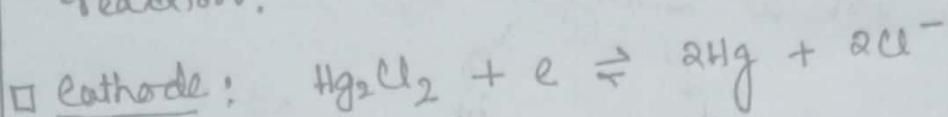
- (i) Glass electrode can be used in the presence of strong oxidizing or reducing substances and metal ions.
- (ii) can be used in measurement with very small quantities of solution.

#### Limitations:-

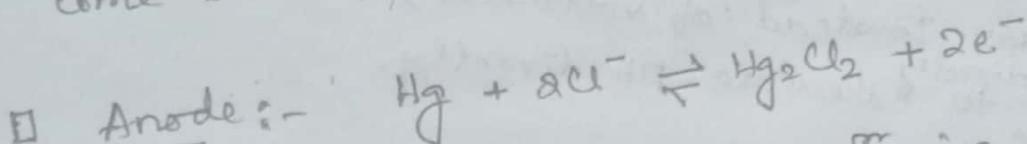
- (i) can be used up to a pH 13 but becomes sensitive to  $\text{H}^+$  ions above pH 9 resulting in an alkaline error.
- (ii) It does not function satisfactorily in pure alcohol.

Q. How is the potential of calomel electrode remains constant?

According to Nernst equation, the potential of a calomel electrode depends on <sup>30</sup> the concn. of  $\text{Cl}^-$  ion. But in absence of  $\text{Cl}^-$  ion, the potential may depend on mercury ions, as these ions participate in electrode reaction.



During the cathode reaction, the concn. of mercury  $\text{Hg}_2\text{Cl}_2$  gets decreased in the solution. It is getting balanced as some amount of  $\text{Hg}_2\text{Cl}_2$  from ppt precipitate come into the solution.



During this reac<sup>n</sup>,  $\text{Hg}_2\text{Cl}_2$  concn. in solution increases. But due to common ion effect of  $\text{Cl}^-$  the  $\text{Hg}_2\text{Cl}_2$  salt gets precipitated out.

⇒ Maintaining the  $\text{Hg}_2\text{Cl}_2$  concn. in the solution, the  $\text{Cl}^-$  ion has taken a very good responsibility.

□ The advantage of KCl is that  $[\text{Cl}^-]$  does not change if some liquid evaporates.

Q. Why we write  $\text{Hg}_2^{2+}$  instead of  $\text{Hg}^+$ ?

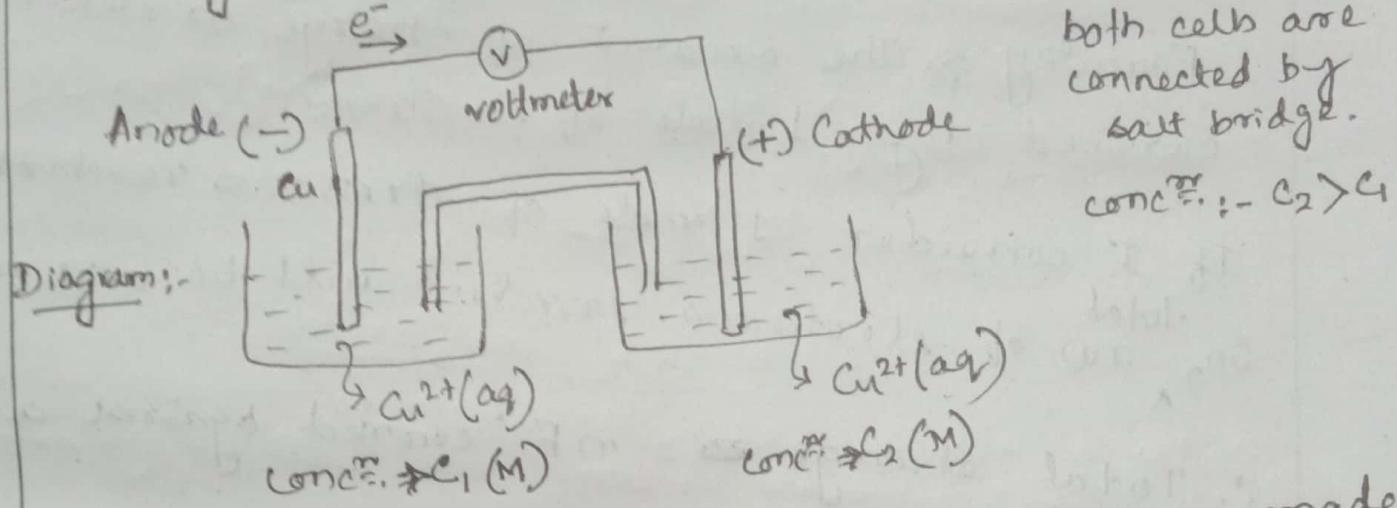
$\text{Hg}^+ \Rightarrow 5d^{10} 6s^1$  (unstable)  $\Rightarrow$  two  $\text{Hg}^+$  combine together to form  $\text{Hg}_2^{2+}$ . That's why we write  $\text{Hg}_2^{2+}$ .

## Concentration Cells

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- (i) It is an electrochemical cell.
- (ii) The anode and cathode are made up of the same element (metal or non-metal) in contact with solutions of the same electrolyte, but of different concentration.

⇒ They are called concentration cells with transference.

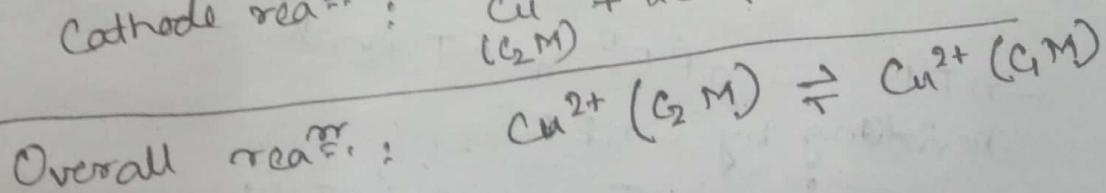
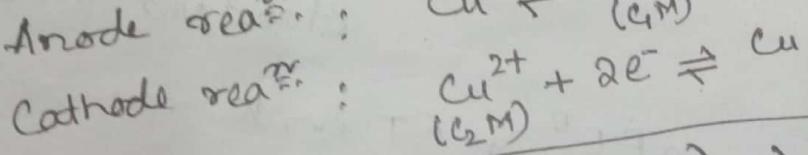
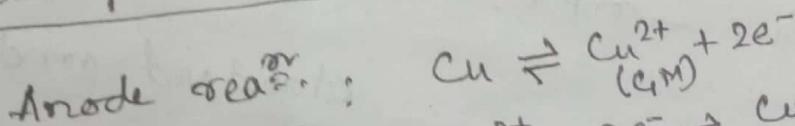


both cells are connected by salt bridge.

$$\text{conc.} : - C_2 > C_1$$

E.g: A cell in which both the electrodes are made of copper metal dipped in  $CuSO_4$  solution of different conc<sup>??</sup>.

cell representation:-  $Cu(s)/Cu^{2+}(C_1 M) // Cu^{2+}(C_2 M)/Cu(s)$



Derivation of Nernst equation:-

Here we are going to consider the overall reac<sup>m</sup>. Equilibrium constant ( $K$ ) =  $\frac{[Cu^{2+}]_{(C_1 M)}}{[Cu^{2+}]_{(C_2 M)}} = \frac{C_1}{C_2}$

## Vant Hoff's eqn. :-

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$$\Delta G_r = \Delta G_r^\circ + RT \ln K$$

$$\Delta G_r = -nFV_m$$

$$= -nFE_{\text{cell}}$$

$E_{\text{cell}}$  is the cell potential.

$n$  = no. of electrons involved in reaction.

$$F = 1 \text{ Faraday.}$$

1 Faraday  $\Rightarrow$  The amount of charge or electricity carried by 1 mole of electrons.

If I consider 1 mole of reactants.

So, total no. of electrons involved will be =  $n$  mole.

$\therefore$  Total charge  $= nF$  carried against a potential of  $E_{\text{cell}}$ .

$$\therefore V_m = (\text{Potential} \times \text{total charge}) \\ = nFE.$$

$$\therefore \Delta G_r = -nFE. \quad \therefore \Delta G_r^\circ = -nFE_{\text{cell}}^{\circ} \text{ for standard conditions.}$$

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

Dividing by  $-nF$  :

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \times 2.303 \log \frac{C_1}{C_2}$$

$$\left( 2.303 \times \frac{RT}{F} \right) = \left( \frac{2.303 \times 8.303 \times 298}{96500} \right) = 0.0591$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

$$= E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

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

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

$$= 0$$

$$\therefore E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$= \frac{0.0591}{2} \log \frac{C_2}{C_1} \quad [\text{For the present Cu-system } n=2]$$

$$\text{As } C_2 > C_1 \quad \therefore E_{\text{cell}} = +\text{ve}$$

$$\therefore \Delta G_r = -nFE = -\text{ve}$$

So the cell react. is spontaneous.

Concentration cell without transference

~~no salt bridge.~~

(i) In this cells, the two half cells are not connected through a salt bridge.  $\Rightarrow$  connected by porous membrane

(ii) ~~Electrode~~ Here electrolyte ~~concentrations~~ concentration are same.

(iii) ~~Electrode~~ Generally use metal amalgam as electrode. In both the electrodes certain different quantities of metal in mercury.

# Conductometric Titration

## Concepts:

### Conductance:

The ability of an ion to conduct electricity is called conductance. The unit of conductance is mho. It is inversely proportional to resistance.

### Factors affecting conductance of a solution:

- Concentration of ion in the solution
- Size of the ion
- Charge of the ion

### Definition:

The titration, which involves the determination of equivalence point of a solution by the measurement of conductance of the solution are called **conductometric titrations**.

# Conductometric Titration

Conductance is ease with which current flows through the solution. It is reciprocal of resistance.

$$C=1/R = \Omega^{-1} \text{ or mho or Siemens}$$

## Theory:

The Conductance of the solution is explained by considering ohm's law.

According to ohm's law the current flowing through the conductor is directly proportional to voltage and inversely proportional to the resistance.

$$I = \frac{E}{R} \quad \text{or} \quad E = IR$$

The resistance of the any conductor is directly proportional to the length of inversely proportional to the area of cross section of the conductor

Therefore  $R = S (l/a)$  where S is specific resistance

Therefore  $C = 1/R = 1/S (a/l)$ ,  $K (a/l)$ ,  $K$ = specific conductance

It is defined as the conductance of the solution which is place between two electrodes of area  $1\text{cm}^2$  and  $1\text{cm}$  apart

The conductance of the solution is depends on mobility of the ion and number of the ion

**Types of conductance:** There are three type's namely specific conductance, equivalence conductance, and molar conductance.

**Specific conductance (K)** is conductance of the solution which are placed between two electrodes of area  $1\text{cm}^2$  and at  $1\text{cm}$  apart

$$K = 1/R \text{ (l/a)} \quad K = \text{Siemen m}^{-1}$$

# Conductivity meter

## Instrumentation:

- An electronic conductivity meter measures the electrical conductivity in a solution.
- It has two electrodes, they are made of platinum. The electrodes are cylindrical and arranged concentrically.
- Conductivity could in principle be determined using the distance between the electrodes and their surface area using Ohm's law but generally, for accuracy, a calibration is employed using electrolytes of well-known conductivity.
- Conductivity may be measured by applying an alternating electrical current ( $I$ ) to two electrodes immersed in a solution and measuring the resulting voltage ( $V$ ). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor.
- The specific conductance of a solution is measured with this instrument.

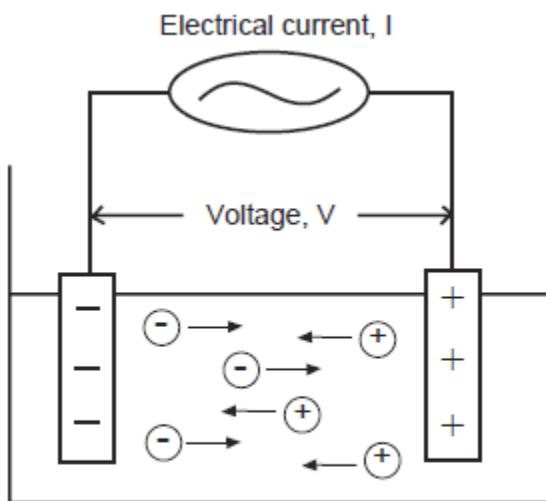


Fig. 1: Migration of ions in solution

## Procedure for the titration of mixture of acids vs strong base:

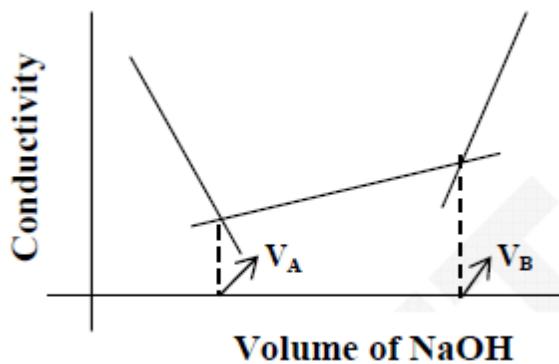
**Microburette:** 1N NaOH

**Accessories:** conductivity cell connected to a digital conductivity meter.

**Beaker:** Pipetted out 25cc of the given acid mixture and dip the conductivity cell. Pipette out 25 ml of acid mixture in to a beaker. Immerse the conductivity cell in to it & connect it to conductivity meter and measure the conductance. Add NaOH from the burette in the increments of 0.5 ml and measure the conductance after

## Conductivity meter

each addition. Plot a graph of conductance against volume of NaOH & determine the equivalence point. Calculate the normality & weight of HCl & CH<sub>3</sub>COOH in the given solution.



Where,  $V_A$  = Volume of NaOH required to neutralize HCl.  $(V_B - V_A)$  = Volume of NaOH required to neutralize acetic acid.

# Conductometric Titration

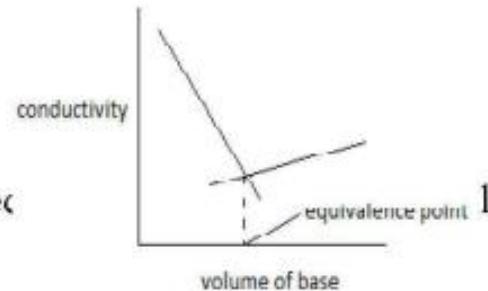
## Strong acid v/s weak base

HCl v/s NH<sub>4</sub>OH

Conductivity of the solution decreases due to the replacement of fast moving H<sup>+</sup> ions by NH<sub>4</sub><sup>+</sup> ions but after equivalence point, conductivity almost remains constant, since NH<sub>4</sub>OH is weak electrolyte giving very small conductivity.



A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



## Weak acid v/s Strong base

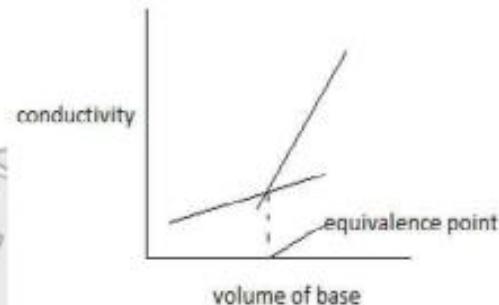
Consider the titration of acetic acid against NaOH.

The conductance of the acid will be initially low since acetic

acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH<sup>-</sup> ions. Hence the conductance increases sharply.



A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



# Conductometric Titration

## Weak acid v/s weak base

Consider the titration of acetic acid against  $\text{NH}_4\text{OH}$ . The conductance of acid will be initially low since acetic acid is a weak electrolyte.

When  $\text{NH}_4\text{OH}$  is added to acid salt is formed and the conductance of the solution increases. On complete neutralization of acid conductance does not change rapidly since  $\text{NH}_4\text{OH}$  is a weak base.

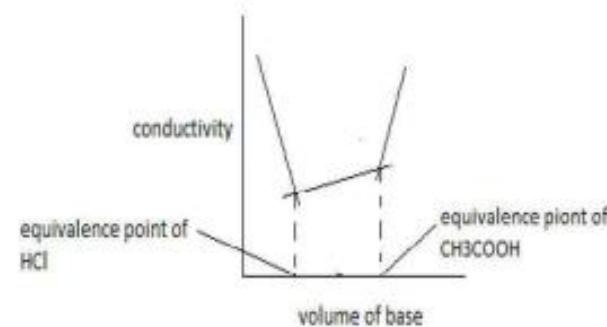
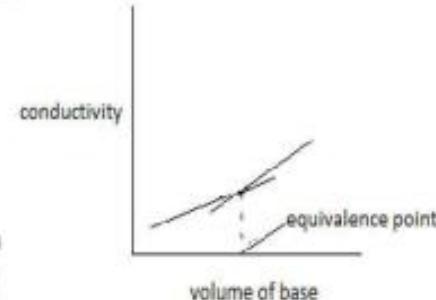


A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

## Mixture of strong acid and weak acid v/s strong base

$\text{HCl}$ ,  $\text{CH}_3\text{COOH}$  v/s  $\text{NaOH}$

the strong acid like  $\text{HCl}$  is titrated against a strong base such as  $\text{NaOH}$ , the conductance first decreases due to replacement of fast moving  $\text{H}^+$  ions by slow moving  $\text{Na}^+$  ions



# Conductometric Titration

The weak acid do not get neutralized initially because of the well known common ion effect.

In the presence of excess of  $H^+$  ions, the ionization of the weak acid is suppressed and hence, weak acid like  $CH_3COOH$  ionizes gradually after the first end point and the available  $H^+$  ions are neutralized giving the second end point. Because of common ion effect dissolution of acetic acid is suppressed. Hence it does not provide  $H^+$  ions which required for neutralization.

After the neutralization point of HCl,  $CH_3COOH$ , conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving  $OH^-$  ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

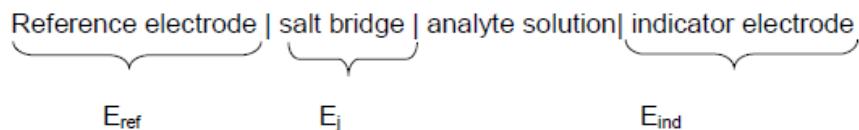
## Advantages:

- Mixture of acid can be titrated
- Indicators are not used
- Very weak acids can be titrated
- Can be used with colored solution.



# Potentiometer

A typical cell for potentiometric analysis consists of a reference electrode, an indicator electrode and a salt bridge. This cell can be represented as



A **reference electrode**,  $E_{ref}$ , is a half-cell having a known potential that remains constant at constant temperature and independent of the composition of the analyte solution. The reference electrode is always treated as the left-hand electrode in potentiometric measurements. Calomel electrodes and silver/silver chloride electrodes are types of reference electrodes.

An **indicator electrode** has a potential that varies with variations in the concentration of an analyte. Most indicator electrodes used in potentiometry are selective in their responses. Metallic indicator electrode and membrane electrodes are types of indicator electrodes.

The third component of a potentiometric cell is a **salt bridge** that prevents the components of the analyte solution from mixing with those reference electrode. A potential develops across the liquid junctions at each end of the salt bridge. The junctions potential across the salt bridge,  $E_j$ , is small enough to be neglected.

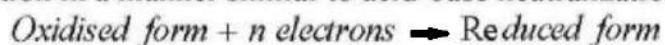
The potential of the cell is given by the equation;

$$E_{cell} = E_{ind} - E_{ref} + E_j$$

As an indicator electrode Pt metal is used.

# Potentiometric Titration

**Principle:** Redox titrations can be carried out potentiometrically using platinum calomel electrode combination in a manner similar to acid-base neutralizations. For the reaction



The potential is given by Nernst equation

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

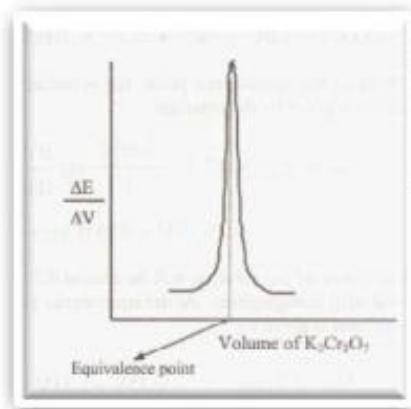
Where  $E^{\circ}$  is the standard potential of the system. The potential of the system is thus controlled by the ratio of concentration of the oxidized to that of the reduced species present. As the reactions proceed the ratio increases and hence the potential also increases more rapidly in the vicinity of the end point of titration. A plot of change in potential against volume is characterized by a sudden change of potential at the equivalent point. At the end point potential is determined by a large increase in potential at the end point.

**Procedure:** Pipette out 25.0 cm<sup>3</sup> of ferrous ammonium sulphate solution into a beaker. Add a test tube of dilute sulphuric acid. Immerse the platinum-calomel electrode assembly into the beaker containing the solution. Connect the electrodes to the potentiometer. Note down the emf of the cell before the addition of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Now add 0.5 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> from the semi micro burette. Allow the solution to mix well and measure the potential. Continue the procedure till a sudden rise in emf of the cell is observed. Take about 5-6 more readings.

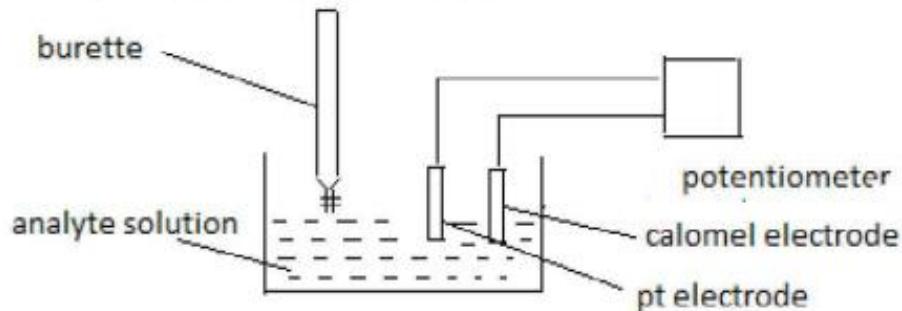
# Potentiometric Titration

**Instrumentation :** A potentiometer consists of an indicator electrode (e.g.: Platinum), A standard reference electrode (E.g.: Calomel electrode), & potentiometer to read the values directly as change in potential

Vol. of $\text{K}_2\text{Cr}_2\text{O}_7$ (V) ml	Emf E (mv)	$\Delta V$ ( $V_2-V_1$ ) ml	$\Delta E$ ( $E_2-E_1$ )	$\Delta E / \Delta V$ (mv/ml)



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Determine the end point by plotting  $\frac{\Delta E}{\Delta V}$  against the volume as shown in the figure.

$$N_{\text{FAS}} = \frac{(N V)_{\text{K}_2\text{Cr}_2\text{O}_7}}{V_{\text{FAS}}}$$

# Potentiometric Titration

$$\begin{aligned}\text{Amount of FAS per liter} &= N_{\text{FAS}} \times \text{Eq. Wt. of FAS (392)} \\ &= \dots\dots\dots g \text{ (say 'a')} \end{aligned}$$

392 g of FAS contains 55.85 g Fe

$$a \text{ g of FAS contains } \frac{55.85 \times a}{392}$$
$$= \dots\dots\dots g$$

**Result:** Normality of the given FAS solution = \_\_\_\_\_ N  
Weight of FAS / ltr = \_\_\_\_\_ g/ltr.  
Weight of Fe present in one liter = \_\_\_\_\_ g/ltr.

## Applications:

1. Coloured solution can also be titrated.
2. Acid-base titration can also be done in this method.
3. In this method Oxidation-reduction titrations can also be carried out.
4. Precipitation reactions can also be carried out potentiometrically.

# Colorimetric Method

## COLORIMETRIC DETERMINATION OF COPPER

Principle: When a monochromatic light of intensity  $I_0$  is incident on a transparent medium, a part,  $I_a$  of it is absorbed, a part,  $I_r$  is reflected and the remaining part,  $I_t$  is transmitted.

$$I_0 = I_a + I_r + I_t$$

For a glass-air interface  $I_r$  is negligible and therefore,

$$I_0 = I_a + I_t$$

$I_t / I_0 = T$  called the transmittance,  $\log 1/T = \log I_0 / I_t$  is called the absorbance or optical density. The relation between absorbance, A, concentration, c (expressed in mol/dm<sup>3</sup>) and path length, t (expressed in cm) is given by Beer-Lambert's law,

$$A = \log I_0 / I_t = \epsilon ct$$

where  $\epsilon$  is the molar extinction coefficient, t is the path length and is a constant for a given substance at a given wavelength. If t, the path length is kept constant, then, A Vs C. Hence a plot of absorbance against concentration gives a straight line.

### Procedure

A series of standard solutions of copper sulphate penta hydrate is treated with ammonia to get blue cuprammonium complex, and is diluted to a definite volume. The absorbance of each of these solutions is measured at 590 nm since the complex shows maximum absorbance at this wavelength. The absorbance values are plotted against concentration to get a calibration curve. The given test solution is treated with strong ammonia and diluted to the same volume as above. The absorbance of this solution at 620 nm is measured and its concentration is determined from the calibration curve.

# Colorimetric Method

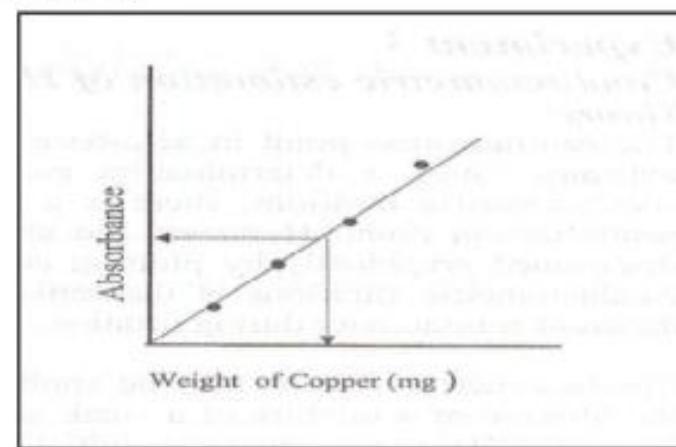
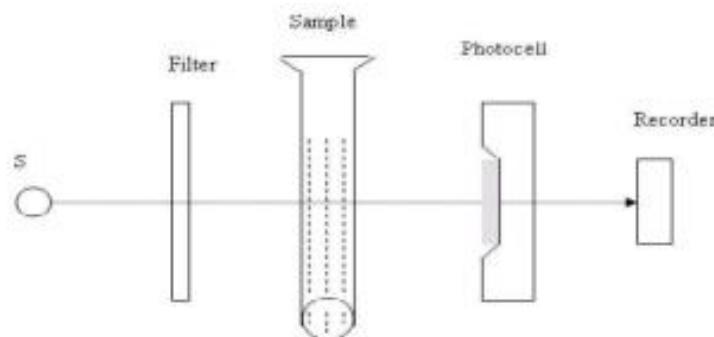
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Source: tungsten bulb is used as a light source.

Filter: It is a device for isolating monochromatic light.

Sample: sample is held in glass cell.

Photocell: Converts the emitted light into electrical signal.



Vol. of CuSO <sub>4</sub>	Vol. of NH <sub>3</sub>	Wt. of Cu in mg	Optical Density
Blank	5		
2	5		
4	5		
6	5		
8	5		
10	5		

# Instrumentation

- Light source: A tungsten lamp is used as a light source for wavelength in the visible range (300-700 nm).
- Monochromators: It is a device for isolating monochromatic light.
- Lens: Instruments using filters as wavelength selectors require lenses to focus correctly the light from the source through the filter and cuvette to the detector.
- Cuvette: For accurate and precise reading, cuvette must be transparent , clean and devoid of any scratch. It is made of quartz, to minimize reflection of light.
- Photosensitive detector: It is made of photovoltaic cell, which receives the transmitted and convert it into electric signal. A digital device is there, which is capable of converting electric signal into absorbance value.

# Colorimetric Method

Draw a calibration curve by plotting absorbance against volume of copper sulphate solution. Using the calibration curve, find out the volume of copper sulphate solution given i.e., the volume of test solution and calculate the amount of copper in the given solution.

From the graph

Volume of  $\text{CuSO}_4$  in test solution  $= \underline{\hspace{2cm}}$  ml (say  $V$  ml)

Working solution concentration  $= 4 \text{ mg/cc}$

249.6 mg of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains 63.55 mg of  $\text{Cu}^{2+}$

Therefore 4 mg of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains  $\frac{63.55 \times 4}{249.6}$   
 $= \dots 1.02 \text{ mg}$

1 ml of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains 1.02 mg of  $\text{Cu}^{2+}$

$V$  ml of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains  $V \times 1.02 \text{ mg of Cu}^{2+}$

Since the stock solution is diluted to 50 times

$\text{Cu}^{2+}$  present in test solution  $\frac{V \times a}{50}$   
 $= \underline{\hspace{2cm}} \text{ mg}$

Result: Concentration of  $\text{Cu}^{2+}$  in test solution  $= \underline{\hspace{2cm}} \text{ mg}$

# Colorimetric Method

## **Applications:**

- In quantitative analysis: large number of metal ions, anions and cations compounds can be determined by in this method
- Photometric Titration i.e. equivalence point can also be determined
- Determination of the composition of colored complex

## **Advantages:**

- Can be determine the concentration of the colored solution
- It is very simple method
- Colorimeter gives most accurate value
- Used for lower concentration

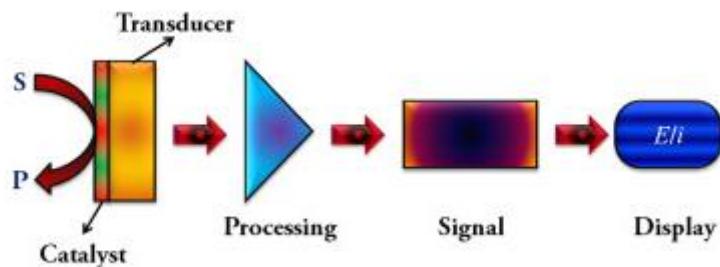
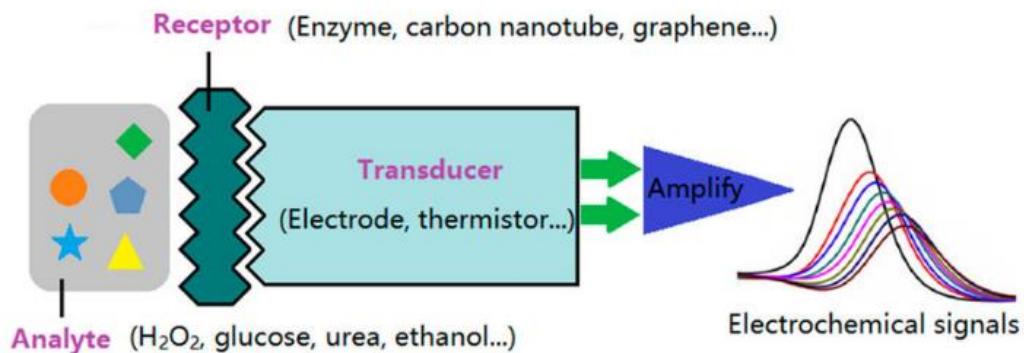
## ELECTROCHEMICAL SENSORS

### Definition:

Electrochemical sensors are the devices that provide information about the composition of a system in real time by coupling with a chemically selective layer (the recognition element) to an electrochemical transducer. In presence of the recognition element, the analyte undergoes electrochemical reactions and the transducer converts the associated information into an applicable qualitative or quantitative signal.

### **Principle of electrochemical sensor**

The electrochemical sensor consists of transducer component covered by recognizer component (receptor). The recognizer element chemically interacts with analyte and signal is generated. The electrochemical transducers transform the chemical signal into electrical signals. The increase/decrease in current/potential/resistance will be directly proportional to the concentration of analyte.



## **CLASSIFICATION**

The electrochemical sensors are mainly divided into three types: potentiometric, conductometric, and amperometric/voltammetric

### **Potentiometric sensors:**

The potentiometric sensor measures the potential of a working or indicator electrode (Pt) by coupling with secondary reference electrode (SCE or Ag/AgCl). The potential of the working electrode will be dictated by particular analyte and its concentration in the solution.  
e.g.: Potentiometers used in potentiometric titrations (Potentiometric titration of FAS versus K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>).

### **Conductometric sensors:**

The conductometric sensor measures the conductivity of the medium, which is directly related to the number of particular ions in the medium.  
e.g.: Conductivity meters used in conductometric titrations (e.g., Conductometric titration of Acid mixture versus strong base).

### **Amperometric/voltammetric sensors:**

These sensors measures the current between working/indicator and reference electrode which will be directly proportional to the concentration of the species, which are being electrochemically transformed (that is, reduced or oxidized) at the electrode.

e.g., O<sub>2</sub> gas sensors allows the measurement of dissolved O<sub>2</sub> gas in blood (<https://www.youtube.com/watch?v=y7zumlEaPAs>).