# UNIT-II Instrumental Method of Analysis

In-SEM Exam = 15 Marks

* Question Paper Pattern - (No Numericals)

| | | OR | | |
|---|---|---|---|---|
| Que. 3 | (a) — 5 Marks | | Que. 4 (a) | — 5 Marks |
| | (b) — 4 Marks | | (b) | — 4 Marks |
| | (c) — 3 Marks | | (c) | — 3 Marks |
| | (d) — 3 Marks | | (d) | — 3 Marks |

Only Theory Questions.

* Reference books for Unit-II :-

(i) Analytical Chemistry - S.M. Khopkar
(ii) Engg. Chemistry - O.G. Palana
(iii) Engg. Chemistry - Shashi Chawla



Course Objective -

To acuire the knowledge of electro-analytical techniques that facilitates rapid & precise understanding of material

Index / Mind Map of Unit- II :-

- Prerequisit of Electrochemistry -
  - Electrochemical & Electrolytic cell.
  - Electrode Potential, Nernst Eqⁿ.

- Introduction -
- Reference Electrode - Types
- Calomel Electrode - Principle, Diag., Construction, Advantages.

- Ion selective Electrodes -
  - Glass Electrode / Indicator
  - Solid Membrane
  - Enzyme based membrane
  - Gas sensing membrane

- Conductometry -
  - Importent teens - Defⁿ, Units, formula
  - Conductivity Cell - Diag., Construction, Working
  - Conductometric Titrations - (i) WA vs WB (ii) SA vs SB, (iii) SA vs WB (iv) WA vs SB
  Reⁿ, Titraⁿ curve, Explanation.

- pH metry -
  - Buffer solⁿ - Defⁿ, Types, Examples
  - pH metric measurement of strong acid vs strong base
  Reⁿ, Procedure (Calibration of pH meter), 3 steps of titration, Titration curve, Calculation formula.

## * Reference Electrode :→

Definition -

The electrode which has stable & reproducible electrode potential & acts as half cell, there by completing the cell is known as 'reference electrode'.

Types :-

Ref. Electrode

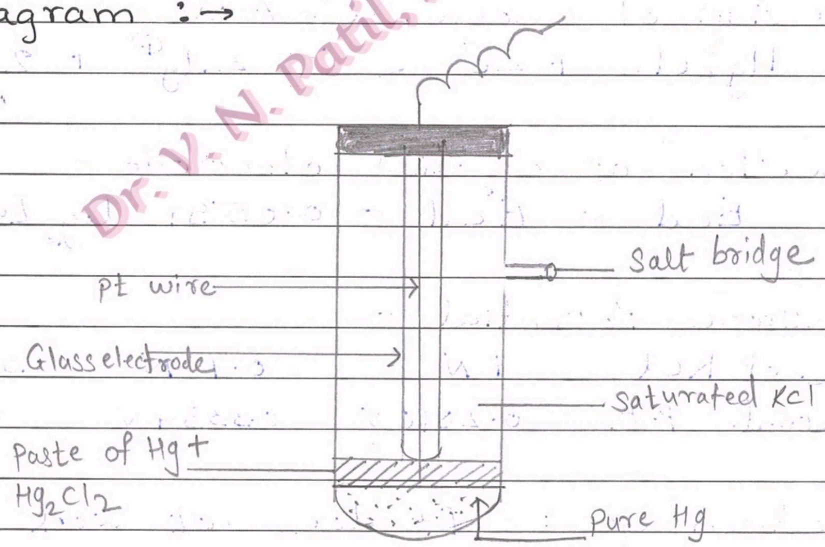
Primary → eg SHE

Secondary → eg. Calomel, Ag-Ag, Quinn hydrone,



### Calomel Electrode :→

Diagram :→




Principle :- It works as an secondary reference electrode whose electrode potential is stable & reproducible. It acts a half cell & consists of Hg, $Hg_2Cl_2$, KCl, etc.

Construction of a calomel electrode :-

- It consists of a thick glass tube.
- At the bottom of the tube pure Hg is placed, above which paste of $Hg + Hg_2Cl_2$ is placed.
- In which a Pt wire is fitted in a thin glass tube, & the wire is connected to electrometer.
- Remaining glass tube is filled with saturated KCl $sol^n$.
- The electrode is connected to salt bridge & whole assemble is sealed.



Representation of Calomel Electrode -

$$Hg \mid Hg_2Cl_2 , Cl^{\ominus}$$

Reaction of calomel electrode -

$$Hg_2Cl_2 + 2\bar{e} \rightleftharpoons 2Hg^{\oplus} + 2Cl^{\ominus}$$

Equation of calomel electrode -

$$E_{cal} = E^{\circ}_{cal} - 0.0591 \log_{10} [Cl^-]$$

Electrode Potential -

| | | | |
|---|---|---|---|
| Conc. of KCl | 1 N | 0.1 N | Saturated |
| Electrode Pot. | 0.2810 V | 0.3334 V | 0.2422 V |

Disadvantages :- It does not work in the $sol^n$ having temp. more than 50-80°c because paste of $Hg + Hg_2Cl_2$ decomposes in pure Hg, thereby disturbing the whole assembly.
Advantages :- Portable, easy to handle, simple equipment, compact.

* Ion selective electrodes (ISE) :-

Definition / Principle :- The electrode which responds to specific ions ~~to~~of ~~t~~he solution, thereby showing particular potential is called as 'ion selective electrodes' or 'chemico sensors'.

Types of ISE →

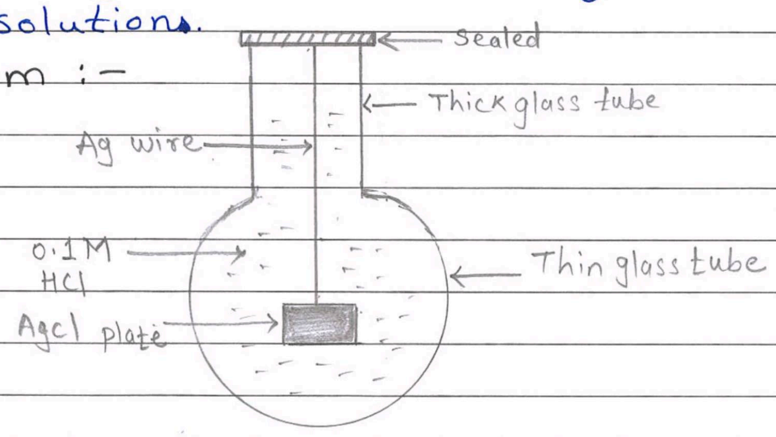
i) Glass membrane electrode / Glass electrode
ii) Solid state memb. electrode.
iii) Liquid - Liquid membrane electrode.
iv) Enzyme based membrane / Biochemical electr
v) Gas sensing electrodes.

i) Glass Membrane / Glass electrode :-
(Indicator Electrode) →

Principle :- When two solutions of different $H^{\oplus}$ ions are separated by thin glass membran a potential difference is developed on the surface of membrane.

Glass membrane acts as an ion exchange i.e. exchange of $Na^{\oplus}$ from glass with $H^{\oplus}$ from solutions.

Diagram :-



Representation :-

$Ag, AgCl \mid 0.1\,M\,HCl \mid H^{\oplus}$

Equation :- $E_G = E_G^{o} + 0.0591\,pH$

Construction :-

- It consists of a thick glass tube.
- At the bottom of glass tube, there is a thin glass bulb.(thin walled).
- ~~At Pt or~~ Ag coated wire.
- A Pt wire or Ag coated Ag wire is dipped in 0.1 M HCl $sol^n$ filled in the bulb.
- The whole assembly is sealed.

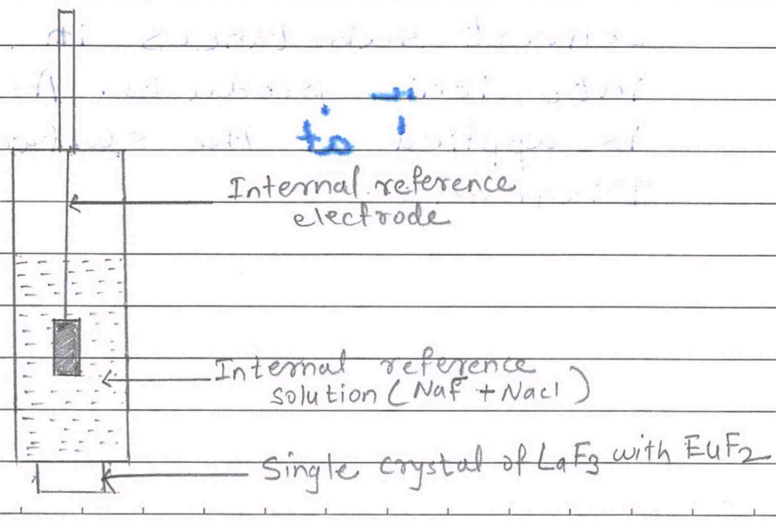
Merits :-

i) Portable
ii) Easy to handle
iii) Simple equipment.

ii) Solid state membrane electrode :-
This contains homogeneous mixture of a polycrystalline ionic compounds.

Two types - (a) Fluoride ion determination.
(b) Chloride —"— "—

(a) Fluoride ion determination :-
Construction / Composition :- The membrane is made from lanthanum tri-fluoride ($LaF_3$) crystal doped with europium floride ($EuF_2$).
The crystal is sealed at bottom of polymeric container containing internal ref. solⁿ ($NaF + NaCl$ or $KF + KCl$) with a ~~ref. ele~~ reference electrode.
Working :- $EuF_2$ produces holes in the crystal lattice of $LaF_3$ through which $F^-$ ions can pass. When electrode is in contact with the sample solⁿ, a potential develops across the membrane.
Diagram :-

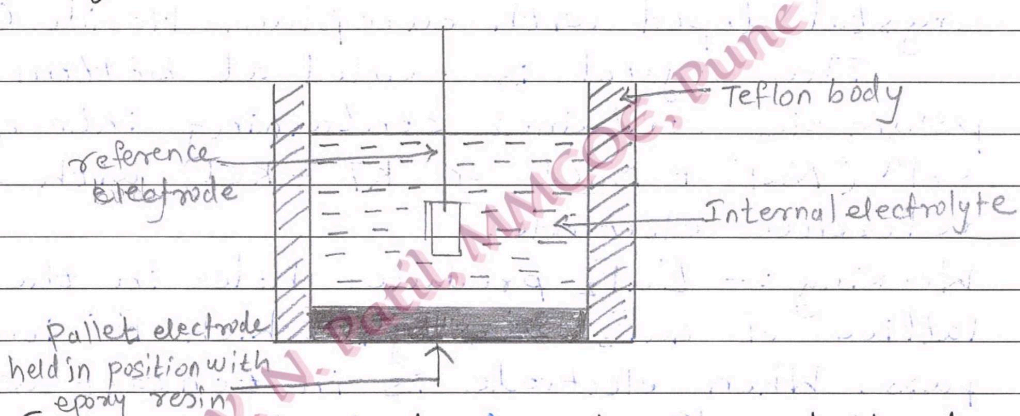


(b) Chloride ion determination :-

Composition / Construction :- Pallet of $Ag_2S$ & AgCl is used in this electrode using epoxy resin, electrode is made up of teflon.

Working :- When the electrode membrane is in contact with a solution containing chloride ions, an electrode potential develops. This potential is measured against a const. ref. potential.

Diagram :-

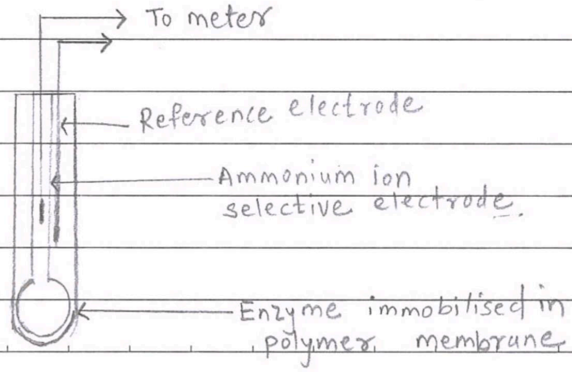



iii) Enzyme based membrane electrode :-

~~Construction / Composition~~ -

These electrodes use enzymes to convert substances in the solution into ionic products. A mobilized enzyme is applied at the surface of electrode.

Diagram :-



Construction / Composition :-

The enzyme urease is incorporated into a polyacrylamide gel which is allowed to set on the bulb of a glass electrode & filled by a nylon gauze.

Working :-

When the enzyme based membrane elect. is immersed into a solution containing urea $NH_4^+$ ions are produced which diffuse through the gel, thereby developing a boundary potential.

$$CO(NH_2)_2 + H_2O + H^{\oplus} \xrightarrow{Urease} 2NH_4^{\oplus} + CO_2$$

iv) Gas Sensing Membrane Electrodes :-

These electrodes are specific towards the ions into which gas is converted after it passes through the outer membrane.

e.g. $NH_3$, $NO_2$, $SO_2$, $CO_2$ & $H_2S$.

Construction / Composition -

The gas in the test solution diffuses through the membrane & reacts with the internal filling solution to form the ions. These ions are detected using a gas sensing electrode.

Membrane used - hydrophobic gas-permeable porous polymer membrane (Silicon rubber / teflon)

Working :- ~~e.g.~~

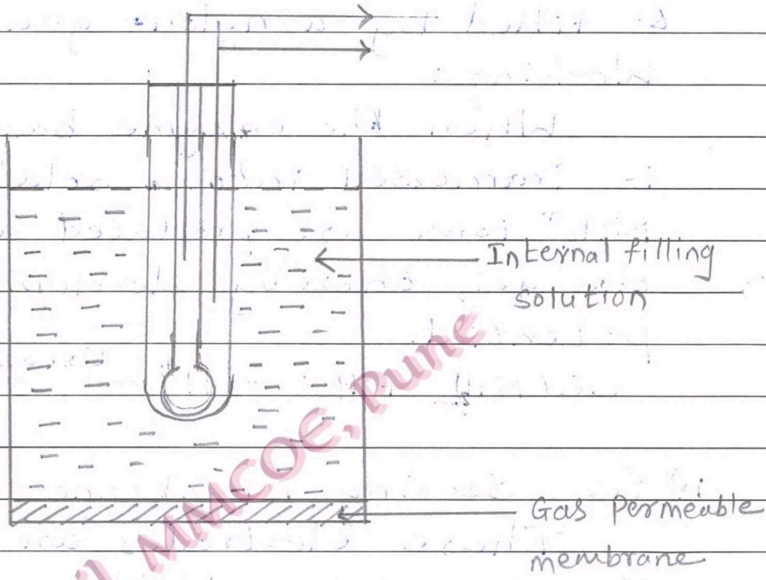
e.g. For $NH_3$ gas determination -

When electrode is dipped in dissolved $NH_3$ sample $sol^n$, it ($NH_3$) diffuses through memb. thereby forming boundary potential.

The boundary potential is developed bet$^n$ ammonium ions formed inside & outside ion selective electrode.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Diagram :-




Gas sensing membrane electrode

* Conductometriq :-

• Important terms involved in conductometry -

1) Resistance :→ $I \propto E \therefore E = RI$

(where I = current, E = Potential diff., R = Resistan

Def$^n$ - Current 'I' is directly proportional to E i.e. potential difference bet$^n$ 2 conductors through which current 'I' is flowing.

Unit :- ohm. $\Omega$

2) Conductance :→ $C = \frac{1}{R}$ Unit → $ohm^{-1}$ or mh

Def$^n$ - It is the reciprocal of resistance. (which allows the current to pass through conductors).

3) Specific Resistance or Resistivity :→

$\rho = R \times \frac{A}{l}$ (where $\rho$ = Resistivity, $l$ = length bet$^n$ conductors, A = area of cross section)

Def$^n$ - It is the resistance offered by unit length 'l' to the passage of electricity throug it.

Unit :→ ohm . cm

4) Specific Conductance or Conductivity :→

$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = C \times \frac{l}{A}$ [where k = specific conductance, $l$ = lengt bet$^n$ conductors, A = area of cross sec., C = conductan

Def$^n$ - It is the reciprocal of resistivity i.e. the conductance of sol$^n$ bet$^n$ 2 parallel electrodes kept 1 cm apart having area of cross sec. $1 cm^2$

Unit :- $ohm^{-1} . cm^{-1}$ or $mho . cm^{-1}$

5) Cell constant :→ Unit = $cm^{-1}$

$$= \frac{l}{A} \text{ or } = \frac{\text{specific conductance}}{\text{Measured conductance}}$$

Def$^n$ – It is the ratio of specific conductance to the measured conductance.

6). Equivalent Conductance ($\lambda v$) :-

$$= \frac{k \times 1000}{C}$$ [where k = sp. conductance, C = conc. of sol$^n$]

Unit :- $ohm^{-1} \cdot cm^{2} \cdot gm\text{-}equiv.^{-1}$

Def$^n$ – It is the conductance of a sol$^n$ containing 1 gm equivalent of an electrolyte at any particular concentration when placed bet$^n$ two electrodes 1 cm apart.

7) Molar Conductance ($\mu$) :→

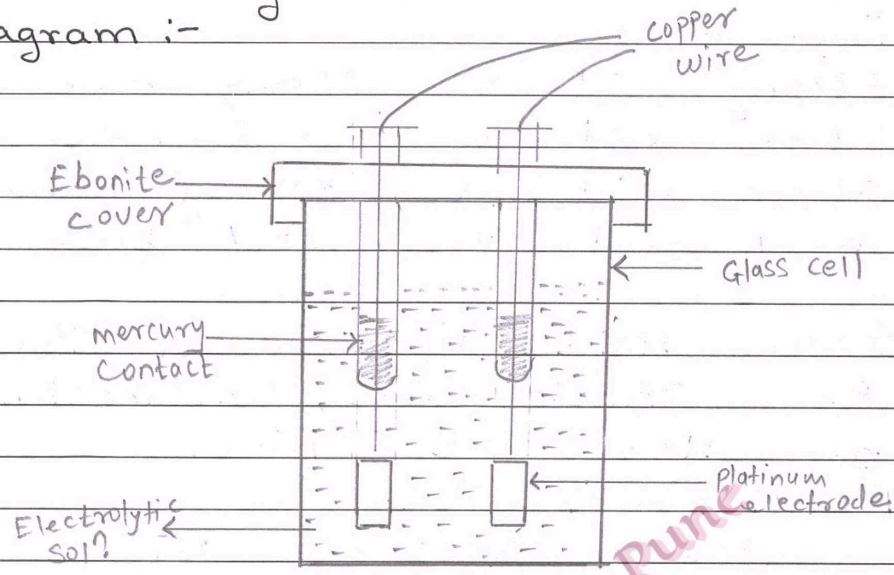
$$= \frac{k \times 1000}{M}$$ [where k = sp. conductance, M = molarity of sol$^n$].

Unit :- $ohm^{-1} \cdot cm^{2} \cdot gmol^{-1}$.

Def$^n$ – It is the conductivity of the sol$^n$ containing 1 mol of electrolyte when placed bet$^n$ two large electrodes 1 cm apart.

## * Conductivity Cell :→

Diagram :-




Construction :-

i) Measurement of conductance of a solution is done by using conductivity cell with alternating current.

ii) The most widely used conductivity cell has a pair of Pt electrodes kept 1 cm apart from each other.

iii) These Pt electrodes/Plates are coated with Pt black which are welded to Pt wires in two respective glass tubes.

iv) These are connected to Cu wires of circuit dipped in Hg (mercury) filled in glass tubes.

v) The whole conductivity cells is connected to wheatstone's bridge.

* Conductometric: Acid-Base titrations :→

Types -

1) Strong acid vs strong base
2) Strong acid vs weak base
3) Weak acid vs strong base
4) Weak acid vs weak base

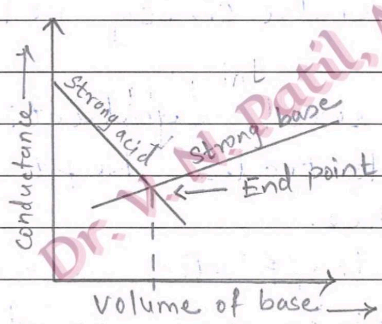
1) Strong Acid Vs Strong Base :→
(Re$^n$, Titration curve, Explanation)

e.g. HCl vs NaOH

Reaction -

$$\underset{\text{Flask}}{HCl} + \underset{\text{Burette}}{NaOH} \longrightarrow NaCl + H_2O$$

Titration curve -




Mobility order

$H^+ > Na^+$

$H^+ > Cl^-$

$OH^- > Na^+$

Explanation :- i) Initially conductance was observed high because of strong acid (~~dissociation~~ complete dissociation).

ii) During titration, as add$^n$ of NaOH takes place, conductance decreases rapidly due t replacement of highly mobile $H^{\oplus}$ by less mobile $Na^{\oplus}$ ions.

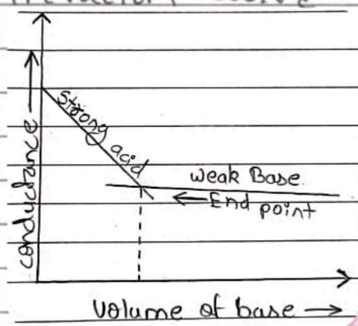
iii) At the end point, conductance is observed due to strong electrolyte NaCl.

iv) After equivalence / end point, conductance rises due to add$^n$ of excess of NaOH (strongly dissociating base).

2) Strong Acid Vs Weak Base →
(Re$^n$, Titration curve, Explana$^n$)
eg. HCl vs $NH_4OH$
Reaction –

$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$
Flask Burette Ammo. chloride

Titration curve –




Mobility order
$H^{\oplus} > NH_4^+$
$H^+ > Cl^-$
$OH^- > NH_4^+$



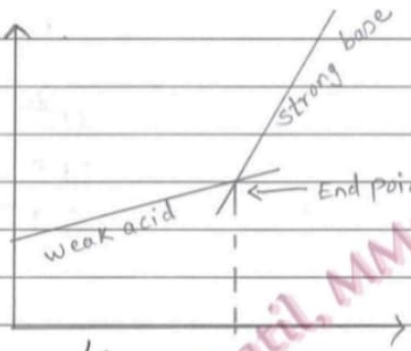
Explanation –
i) Initially conductance was observed high because of strongly dissociating HCl.
ii) On addition of $NH_4OH$, conductance decreases rapidly due to replacement of highly mobile $H^{\oplus}$ by slow moving $NH_4^+$ ions.
iii) At the end pt / equivalence point, conductance is observed due to $NH_4Cl$, electrolyte formation.
iv) After eq. / end point, conductance remains constant or slightly decreases due to add$^n$ of excess of weakly dissociating $NH_4OH$.

3) Weak Acid vs Strong Base :→
(Re$^n$, Titration curve, Explanation).
e.g. $CH_3COOH$ vs $NaOH$

Reaction :-

$$\underset{\text{Flask}}{CH_3COOH} + \underset{\text{Burette}}{NaOH} \longrightarrow \underset{\text{sodium acetate}}{CH_3COO^{\ominus}Na^{\oplus}} + H_2O$$

Titration Curve -




Mobility order
$Na^{\oplus} > CH_3COO^{\ominus}$
$H^{\oplus} > CH_3COO^{\ominus}$
$OH^{\ominus} > Na$

Explanation -
i) Initially conductance was observed low because of weakly dissociating $CH_3COOH$.
ii) On the addition of NaOH, conductance increases gradually due to formation of sodium acetate ($CH_3CO\bar{O}\overset{+}{Na}$) at an equivalence or end point.
iii) After equivalence / end point, on excess add$^n$ of NaOH conductance rises rapidly due to fast moving $OH^{\ominus}$ & $Na^{\oplus}$ ions.

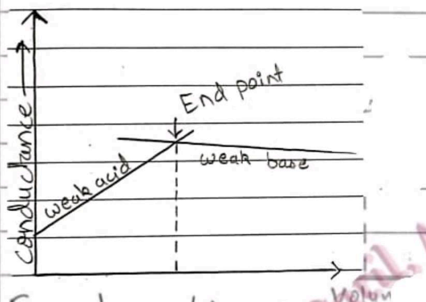
4) Weak Acid Vs Weak Base :→
(Reⁿ, Titration Curve, Explanation)
e.g. $CH_3COOH$ Vs $NH_4OH$

Reaction :-

$$CH_3COOH + NH_4OH \longrightarrow CH_3COO^-NH_4^+ + H_2O$$

Flask — Burette — Ammo. Acetate

Titration Curve :-






Explanation :-

i) Initially conductance was observed low due to weakly dissociating $CH_3COOH$.

ii) On addition of $NH_4OH$ from burette, conduct increases slowly due to formation of strong electrolyte ammonium acetate i.e. $CH_3COO^{\ominus}NH_4^{\oplus}$ at eq./end point.

iii) After eq./end point, conductance remains almost constant or slightly decreases due to addition of excess of weakly dissociating $NH_4OH$ solⁿ.

* pH metry :- $\boxed{pH = -\log[H^+]}$ pH = p = potential of Hydrogen

* Buffer solution -

Def$^n$ - The solution which is used to ~~ma~~ maintain pH of given solution even if small quantity of acid or base is added in it.

Types of Buffer sol$^n$ - ① Acidic & Basic

| | Acidic Buffer | Basic Buffer |
|---|---|---|
| Def$^n$ | It is a mixture of weak acid & salt of weak acid with strong base. | It is a mixture of weak base & salt of weak base with strong acid. |
| e.g. | $CH_3COOH + CH_3COO^{\ominus}Na^{\oplus}$ | $NH_4OH + NH_4^{\oplus}Cl^{\ominus}$ |
| Formula | pH of acidic buffer $= pKa + \log \frac{[salt]}{[weak\ acid]}$ | pH of basic buffer $= pkb + \log \frac{[salt]}{[weak\ base]}$ |

* Standardization or Caliberation of pH meter:-

i) pH meter is standardized / caliberated using pH 4, 7, 9 sol$^n$ using calomel as a reference & glass as an indicator electrode.

ii) Each time electrodes are washed with distilled water. Thus, pH meter is caliberated / standardized for acidic, neutral & basic solutions.

## * Measurement of pH of Strong Acid Vs Strong Base :→

e.g. HCl Vs NaOH

Reaction :-

$$\underset{\text{Flask}}{HCl} + \underset{\text{Burette}}{NaOH} \longrightarrow NaCl + H_2O$$

Explanation :-

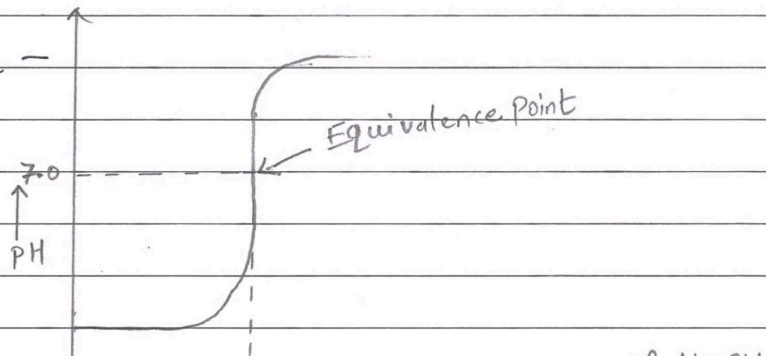
i) Initial stage - Initially burette is filled with std. NaOH solⁿ & pH is noted for given acidic solⁿ.

ii) Before eq. point - Before addition of NaOH from burette, pH of acidic solution (HCl) is observed as 1 to 2.

iii) At eq. point - During the addition of NaOH, pH goes on increasing, pH = 7

iv) After eq. point - After reaction completion, i.e. after equivalence point, pH goes on increasing towards basic value & becomes constant at pH 10.

Titration Curve -




Calculation - ① Normality of HCl ⇒

$$N_1V_1\ (HCl) = N_2V_2\ (NaOH$$

② Strength of HCl ⇒ Normality of HCl × Eq. wt. of HCl

$$\boxed{1\ ml\ 1N\ NaOH \equiv 36.5\ mg\ HCl}$$