UNIT-5

CONDUCTOMETRY

It is the measurement of conductivity of a solution due to mobility of cations & anions towards respective electrodes.

Conductivity (C) is inversely proportional to resistance (R) of a solution.

$$\boxed{C = 1/R}$$

The unit of conductivity is mhos

Accordingly

$$\boxed{R = E/I}$$

where E = Potential difference
I = current which flows through

The unit of Resistance (R) is ohms, Potential difference (E) is volts & that of current (I) is amperes.

The resistance (R) of a solution depends upon the length (l) & cross section (a) of the conductor through which conductivity takes place.
Therefore

$$\boxed{\rho = \frac{Rl}{a}}$$

where ρ = specific resistance

Hence

$$\rho = \frac{aR}{I}$$

Specific Resistance (ρ) - is the resistance offered by a substance of 1 cm length and 1 sq cm surface area.

unit of measurement - ohm cm

Specific Conductivity (K_v) - is the conductivity offered by a substance of 1 cm length and 1 sq cm surface area.

Unit of measurement - mhos cm^{-1}

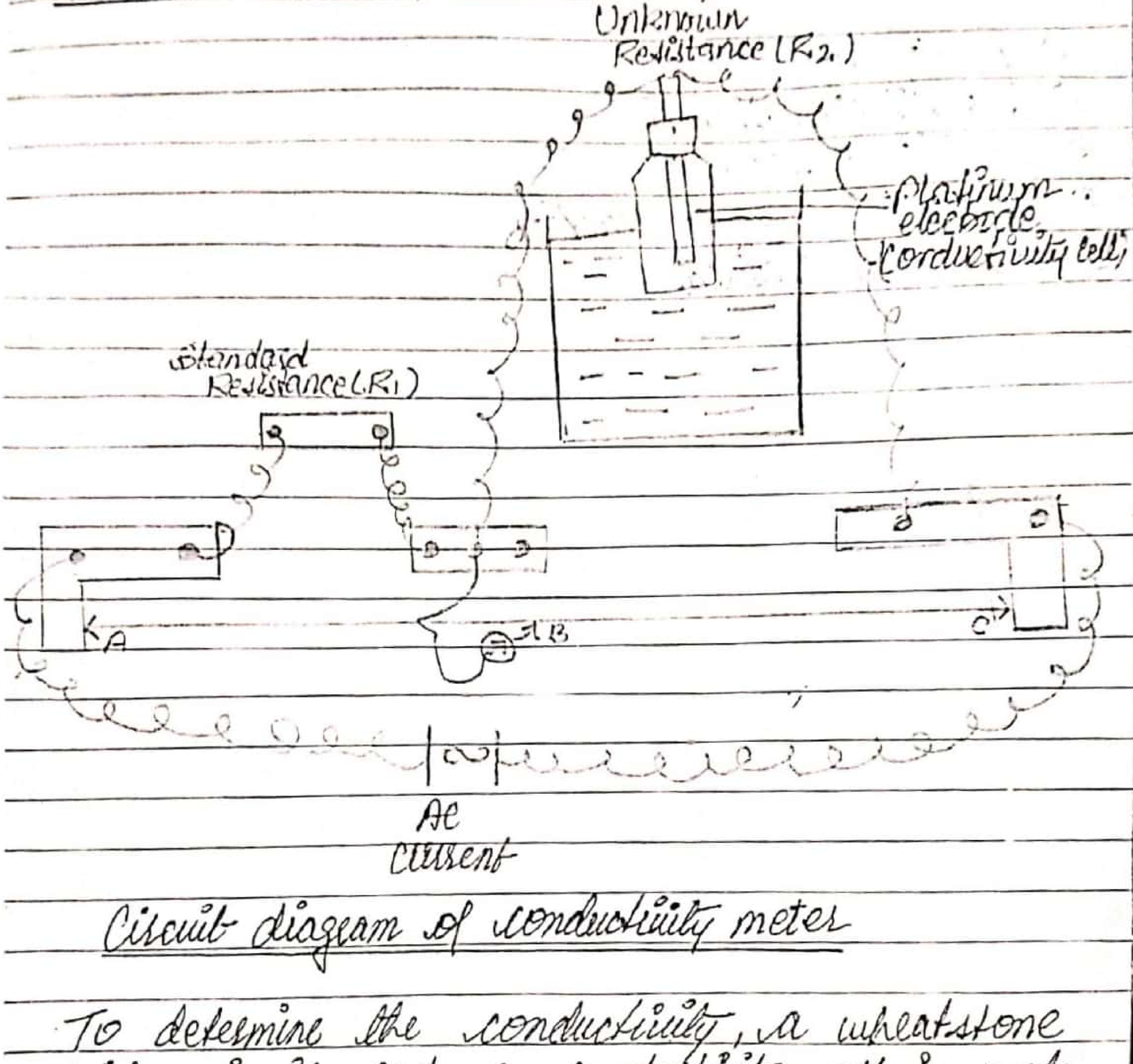
$$\therefore K_v = 1/\rho$$

Equivalent Conductivity (λ_v) - is the conductivity of a solution containing equivalent wt of the solute b/w electrodes 1 cm apart and 1 sq cm surface area.

unit of measurement - mhos cm^{-1}

Molar conductivity (μ_v) - is the conductivity of a solution containing molecular weight of the solute between electrodes 1 cm apart + 1 sq cm surface area.

Measurement of Conductivity



Circuit diagram of conductivity meter

To determine the conductivity, a wheatstone bridge circuit and a conductivity cell is used. There are different types of conductivity cells. They are madeup of Platinum + coated c̄ platinum black. The different electrodes used depends upon the conductivity of the solution.

Application -

① Purity of water -
② Quantitative Analysis
③ Salinity of sea water
④ Equilibrium in ionic reaction
⑤ No indicator required.

POTENTIOMETRY

It consists of measuring the potential or emf (electromotive force) of a solution using a set of indicator and reference electrode. The potential of a solution depends on the nature & concentration of the ions of the drug substance. The potential is measured in mv using a Potentiometer, which has an indicator electrode & reference electrode.

Indicator electrode responds to change in emf or PH of a solution.
eg - glass electrode

Reference electrode is the one which has a standard potential on its own & its potential does not change to whichever solution it is dipped into.
eg - Standard Hydrogen electrode

NERNST EQUATION

The potential (E) of a metal electrode at 25°C immersed into a solution of its own ions is given by -

$$E = E^0 + \frac{0.0592}{n} \log C$$

where -

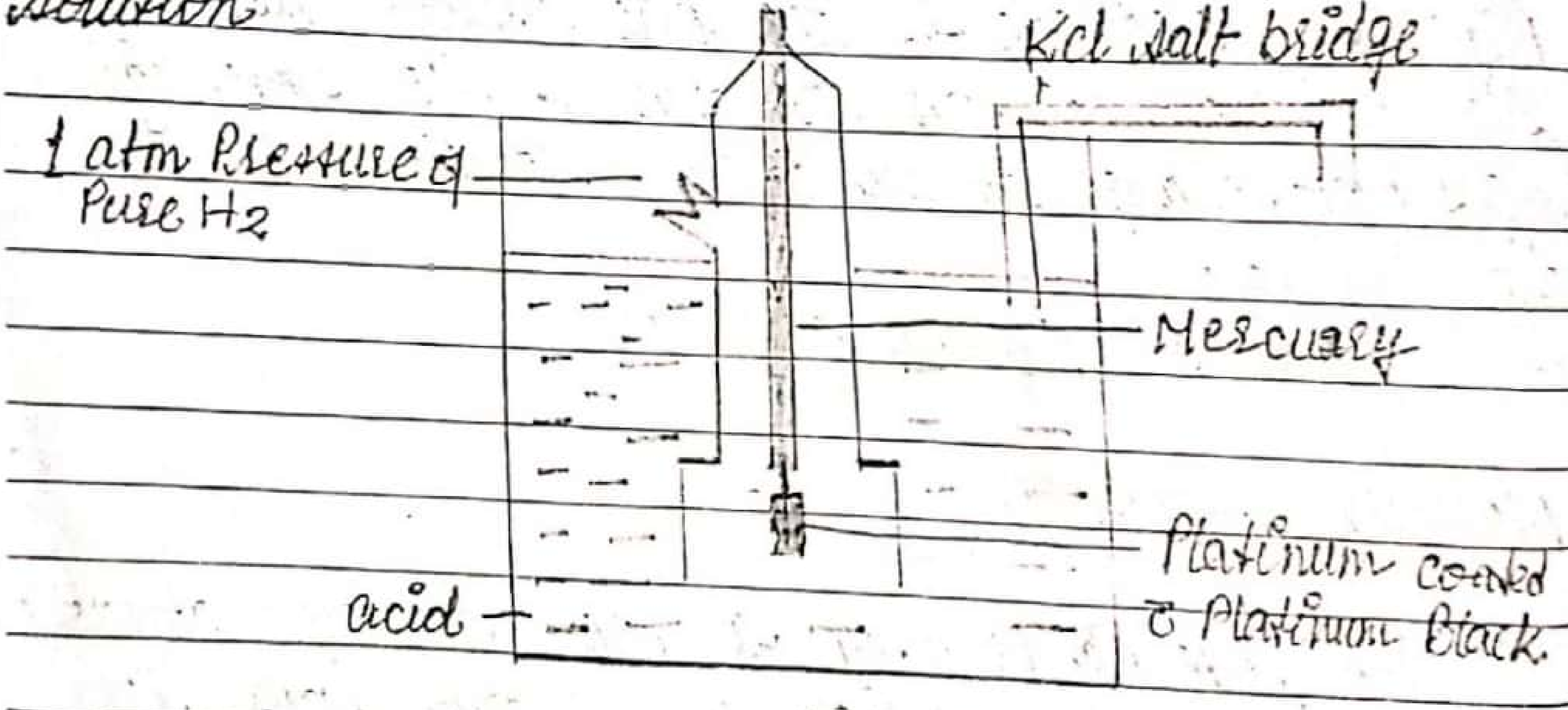
E^0 - Standard Potential of metal
n - valency of ions
C - concentration of ions

Reference electrode -

① **Hydrogen electrode** - is the primary standa against which potentials of other electrodes are measured. It can be used as Indicator as well as reference electro.

Construction

It consist of a platinum foil coated with platinum black and has wire contacts through mercury. This is enclosed in a glass covering through which hydrogen is passed at 1 atmospheric pressure continuously and dipped into the solution of standard acid or unknown solution.



Hydrogen Electrode

* It can be used as a reference electrode when dipped with standard acid solution and as an Indicator electrode when dipped into a sample solution.

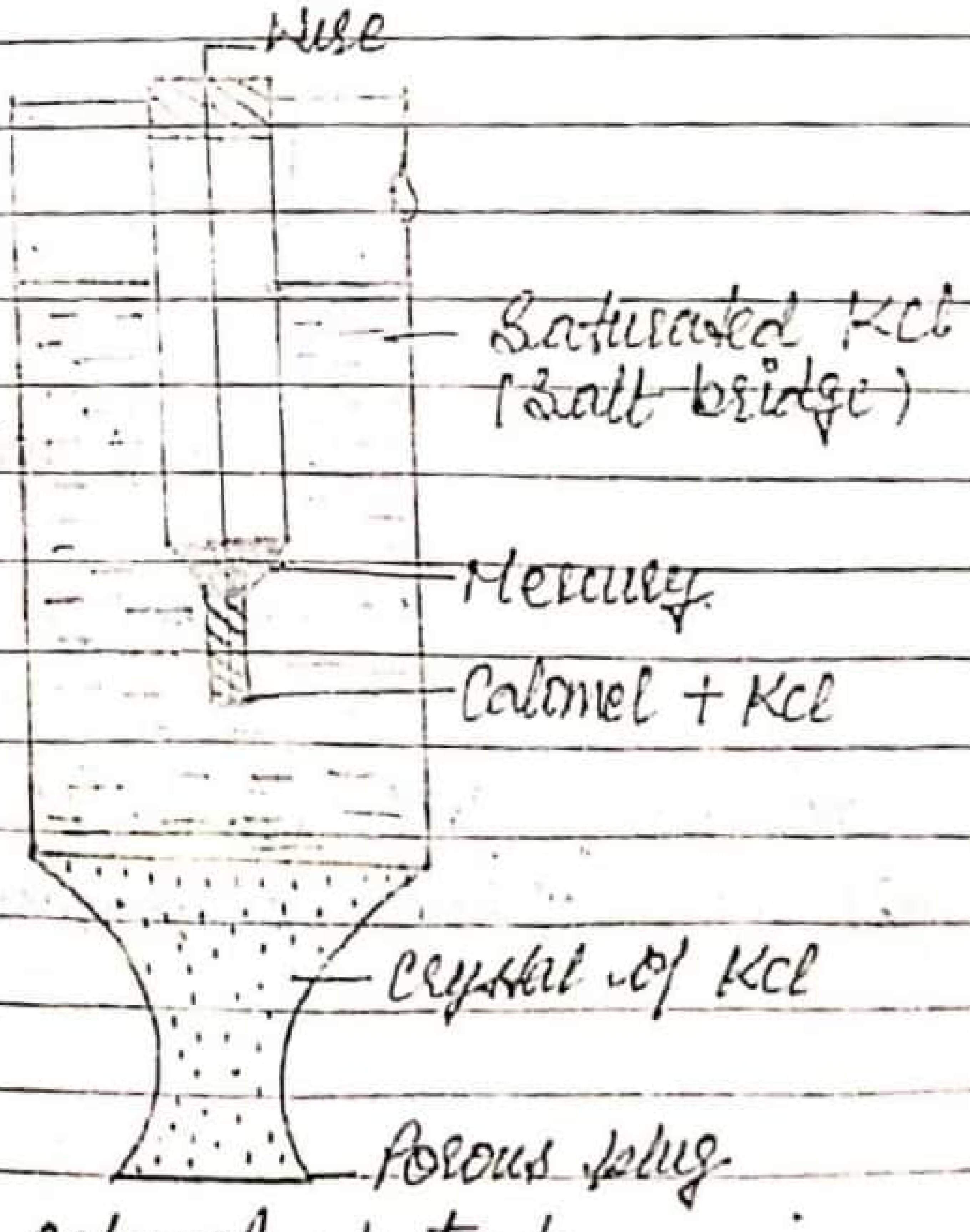
Saturated calomel electrode -

It is the other important Reference electrode.

Construction -

It consist of an inner Jacket & outer sleeve. The inner Jacket (Tube) has wire contact with mercury & plugged with a mixture of calomel (Hg_2Cl_2) + KCl. This is surrounded by an outer sleeve & the tip is filled with crystals of KCl and porous plug of asbestos. The space between the inner Jacket and outer sleeve is filled with either saturated KCl or 1 N KCl or 0.1N KCl on which potential of the electrode depends upon.

The potential of this half cell depends upon
① Concentration of Potassium chloride used
② Temperature



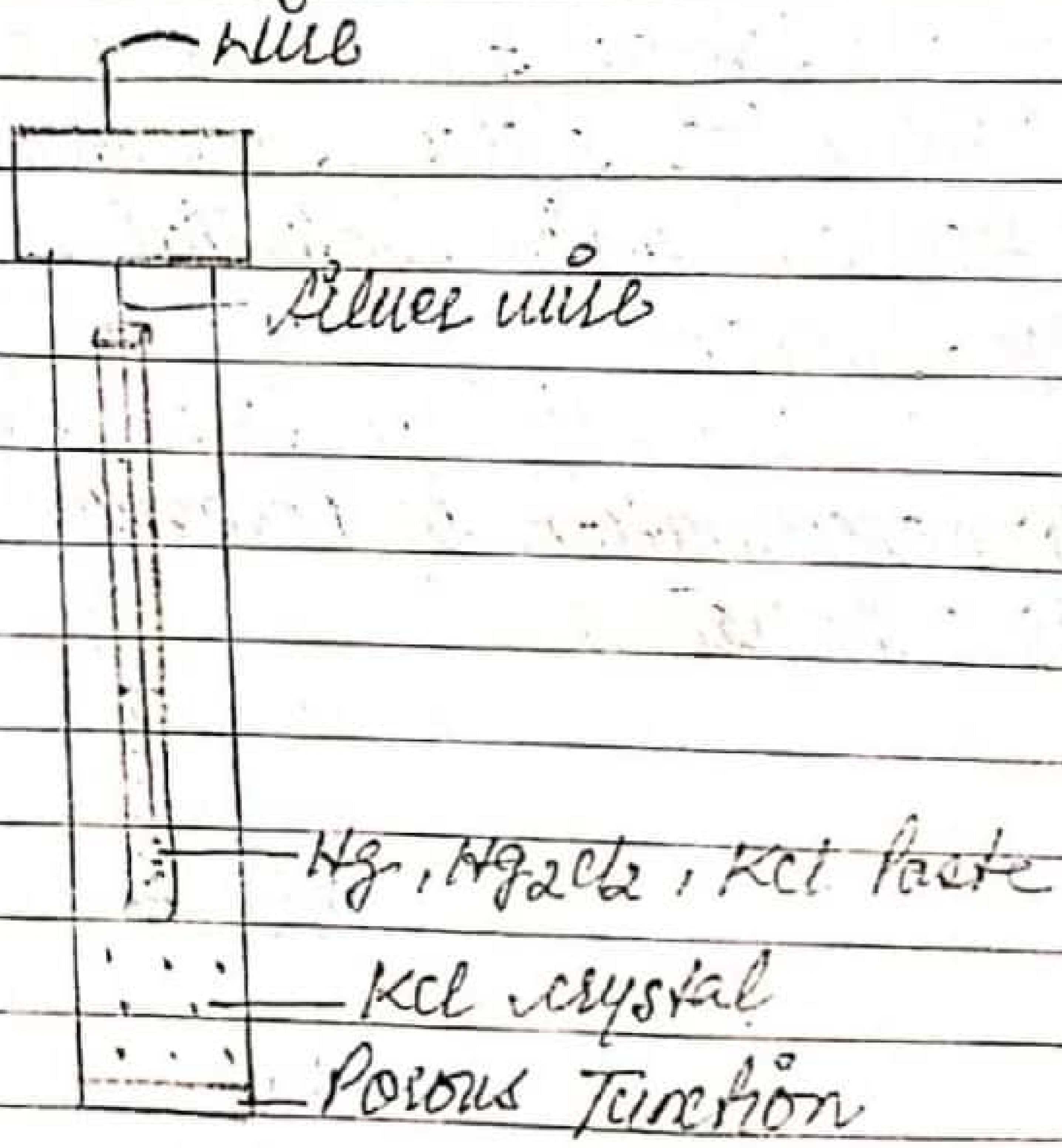
Saturated calomel electrode

3. <u>Silver - Silver chloride electrode</u>- It is also a type of Reference electrode

<u>Construction</u> -

It is simply a silver wire coated with electrolytically with silver chloride and dipped into potassium chloride.

The potential of this half-cell also depends upon temperature as well as concentration of potassium chloride used.



Silver - Silver chloride electrode

It is easy to use but it is difficult to prepare.

Indicator Electrodes -

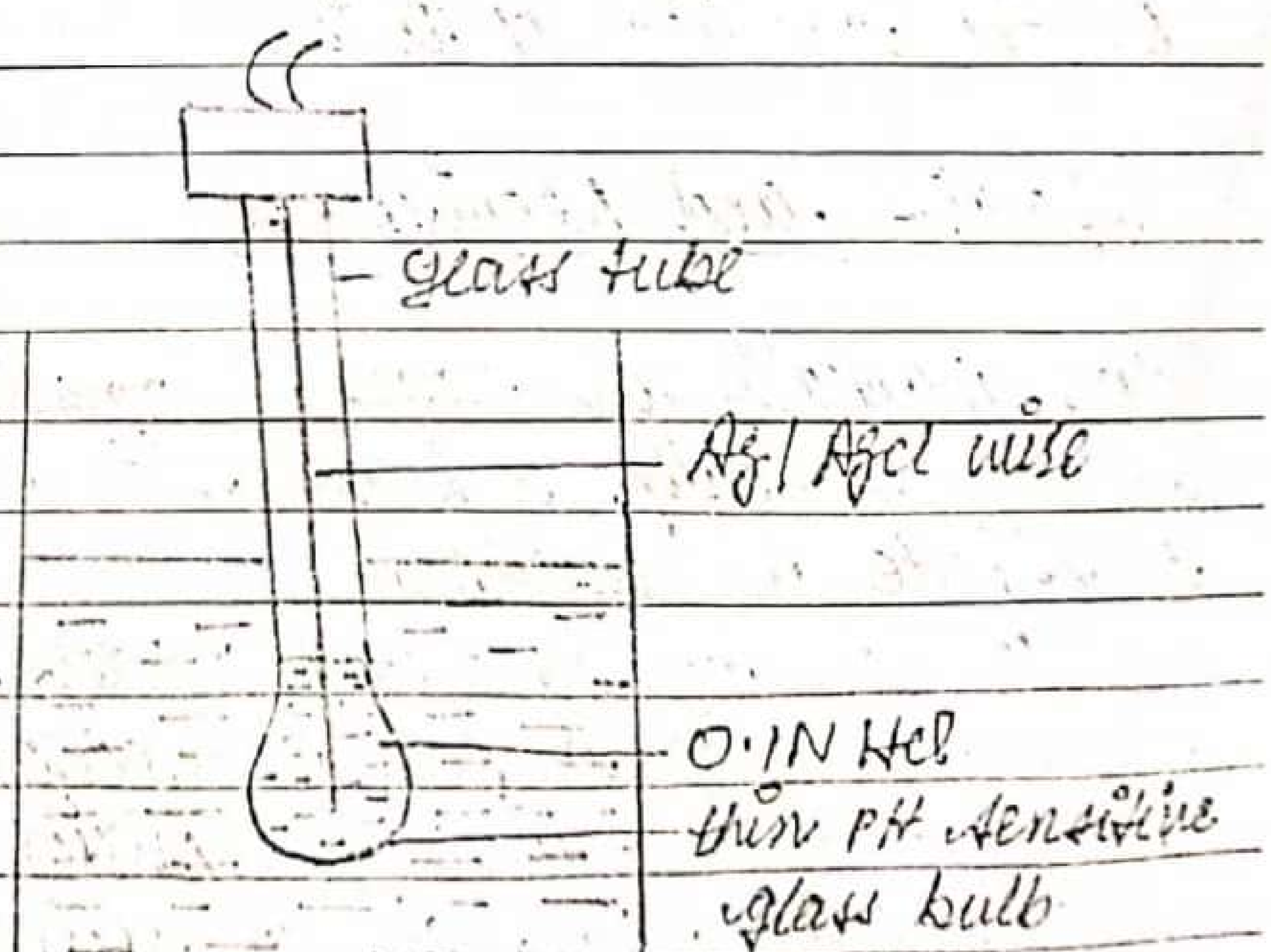
Indicator electrode indicates the potential of pH of a solution in comparison to a reference electrode of a known Potential.
eg - Hydrogen electrode, Glass electrode

Glass electrode -

It is a type of Indicator electrode

Construction -

It consist of a glass tube with a thin pH sensitive glass bulb at its tip. It has a silver - silver chloride wire at the centre of the tube and the lower tip of the wire immerses into the 0.1N HCl filled in the glass tube. This assembly acts as an indicator electrode & is dipped into a solution whose pH or potential is to be known.



Glass Electrode

Antimony-Antimony oxide electrode.

It consist of an Antimony rod dipped into a solution whose potential or pH has to be determined.

Antimony oxide (Sb_2O_3) is formed on exposure to air.

Reac^n - $Sb + H_2O \rightarrow SbO^+ + 2H^+ + 3e$

It can be used from pH 3 to pH 8

It is not easily poisoned or damaged

It can be used even with viscous fluids.

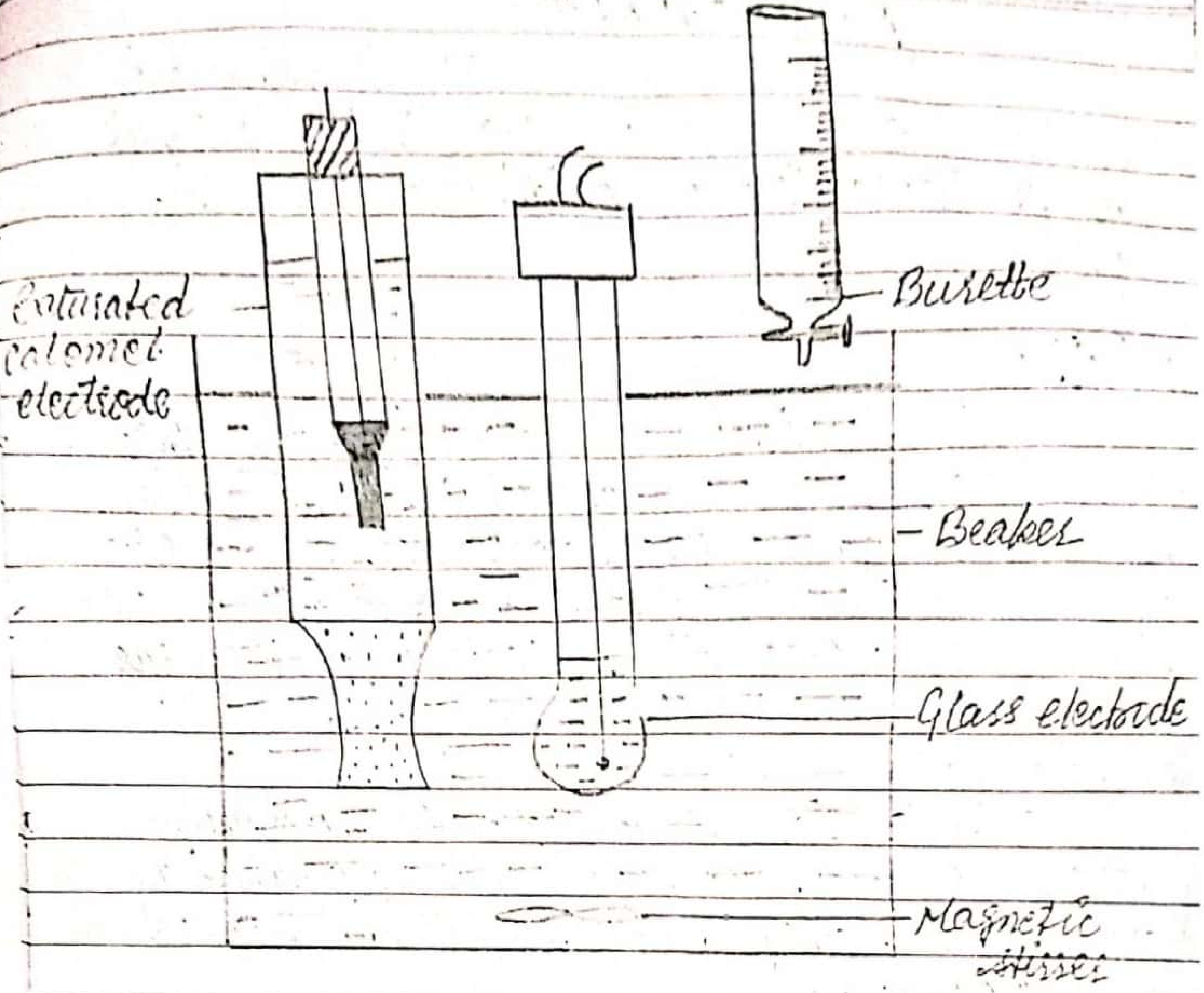
Potentiometric Titration

These are titration in which the end-point of titration can be determined by measuring the potential or changes in the potential of a solution caused by the addition of titrant

Apparatus and Requirements

Titration can be done manually or under automation. When it is done manually, a beaker with a stirrer and a pipette are sufficient.

In case of automated models, a sample cell which can hold a pair of electrode, inlet for titrant and a stirrer for mixing the solution are essential. The pair of reference & indicator electrodes depends on the type of titration i.e acid-base or redox titration



Apparatus for Potentiometric titration

Application -

① Acid - base titration
② Redox titration
③ Diazotisation titration
④ Precipitation titration
⑤ complexometric titration

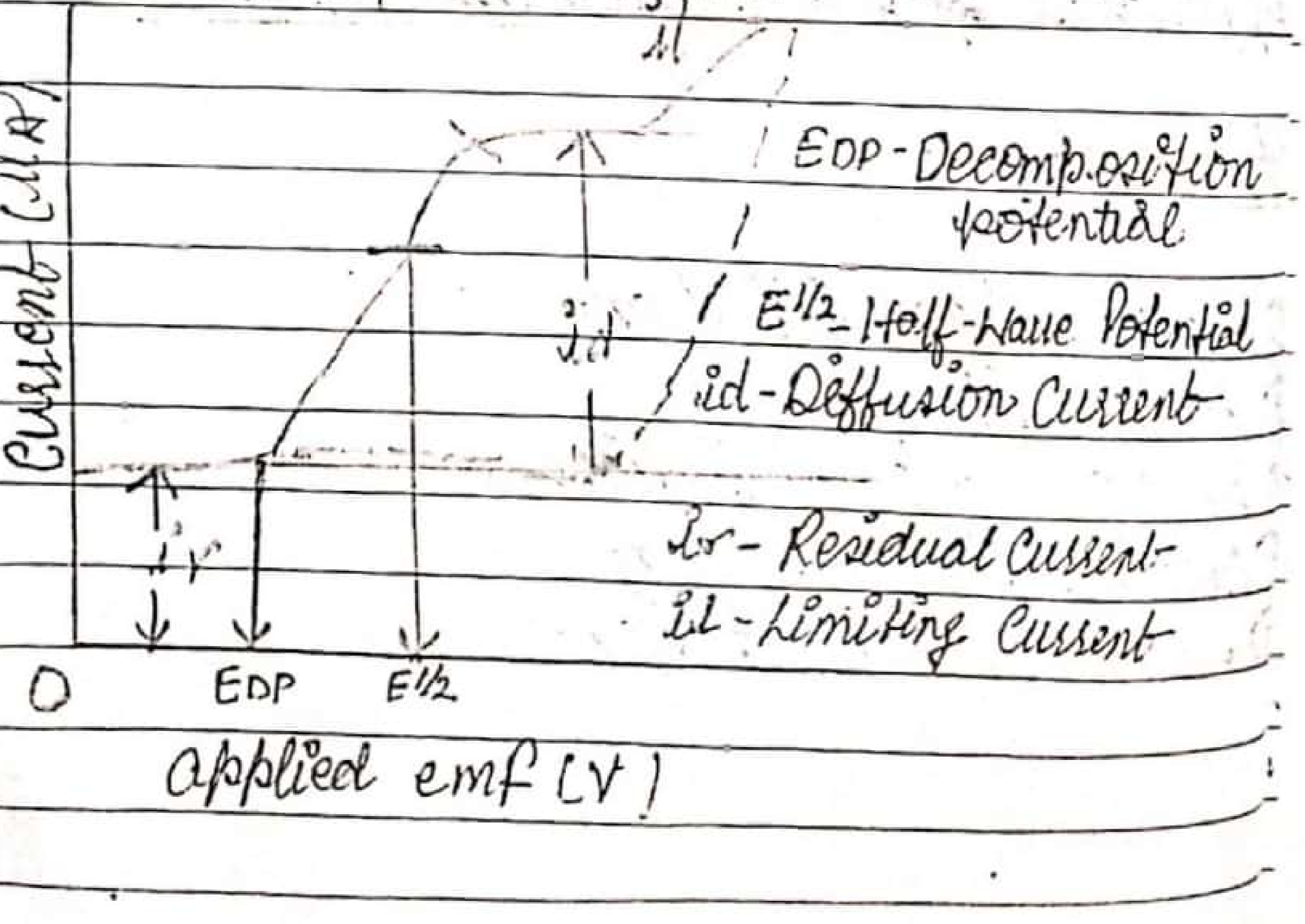
POLAROGRAPHY

It is applied for the qualitative or quantitative analysis of electroreducible or oxidisable elements or groups

Principle-

The principle in polarography is that a gradually increasing negative potential (voltage) is applied between a polarisable and non-polarisable electrode and the corresponding current is recorded. From the current-voltage curve qualitative + quantitative analysis can be performed.

This technique is called as Polarography the instrument used is called Polarograph and the current-voltage curve recorded is called as Polarogram.



Different Types of Current in Polarography

① Residual Current (i_r) - It is the sum of the relative larger charging current and a very small Faradic current.

② Migration Current (i_m). It is due to migration of cation from the bulk of the solution towards cathode due to diffusive force. this depend on the proportion of analyte of interest and the supporting electrolyte. To eliminate the migration current, a large proportion of supporting electrolyte eg- 50-100 times the amount of electroreducible ion is added

③ Diffusion Current (i_d) - It is due to the actual diffusion of electroreducible ion from the bulk of the sample to the surface of the mercury droplet due to concentration gradient.

④ Limiting Current (i_l) - Beyond a certain Potential the current reaches a steady value called as the limiting current.

At this point,

the rate of diffusion of ions is equal to the rate of reduction and the state of electrode is said to be concentration polarized.

Ilkovic Equation –

$$\boxed{i_d = 607\, n C D^{1/2} m^{2/3} t^{1/6}}$$

Where

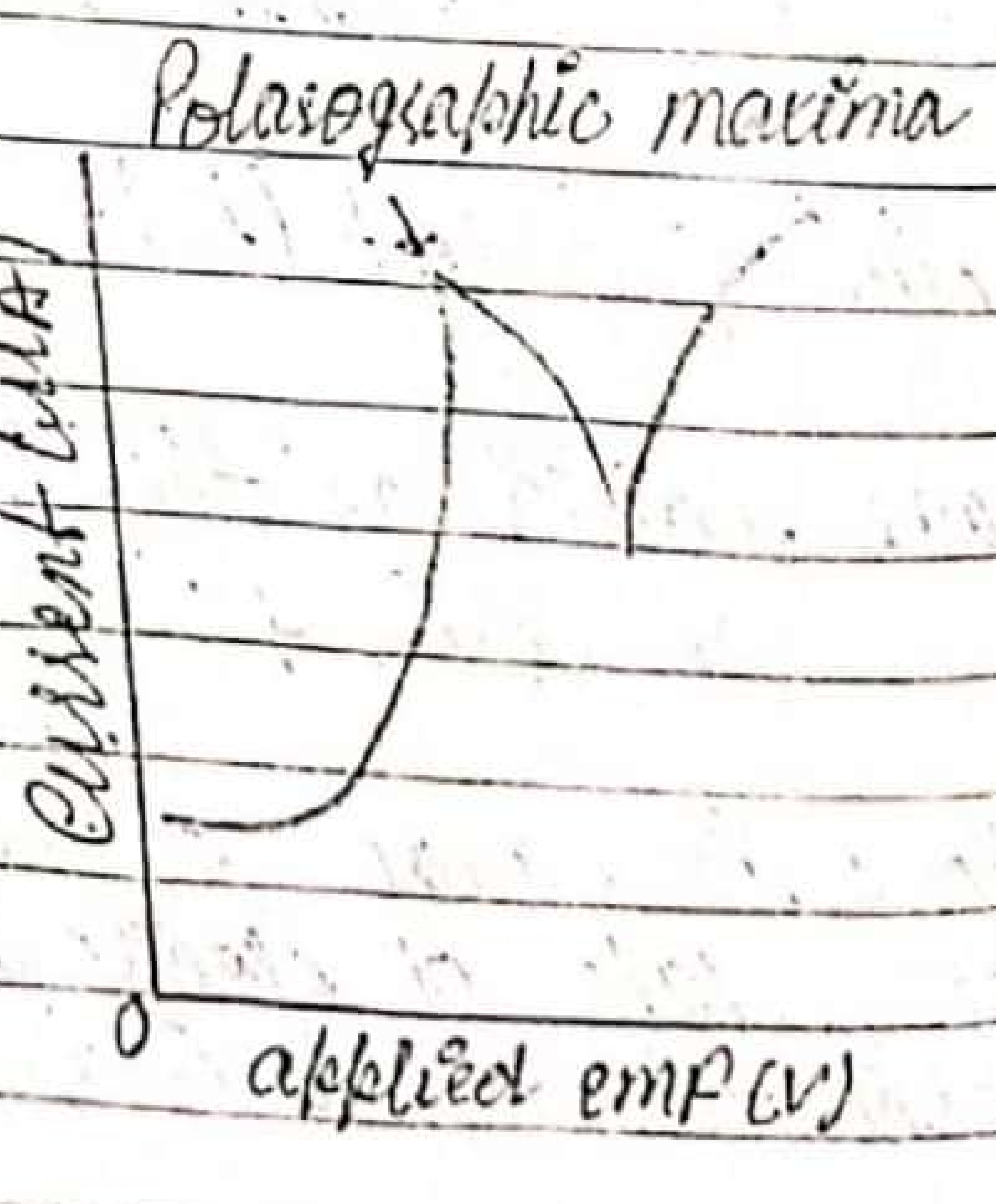
i_d = diffusion current due to Electro reducible ions.
n = no. of electrons involved in reduction of one molecule
C = conc. expressed in m mol/lit
m = wt. of mercury flowing through capillary (mg
t = droptime in seconds (2 to 7 seconds)

Dropping Mercury Electrode (DME)

It is a
Polarisable electrode and a gradually increasing negative potential can be applied easily.

Polarographic Maxima

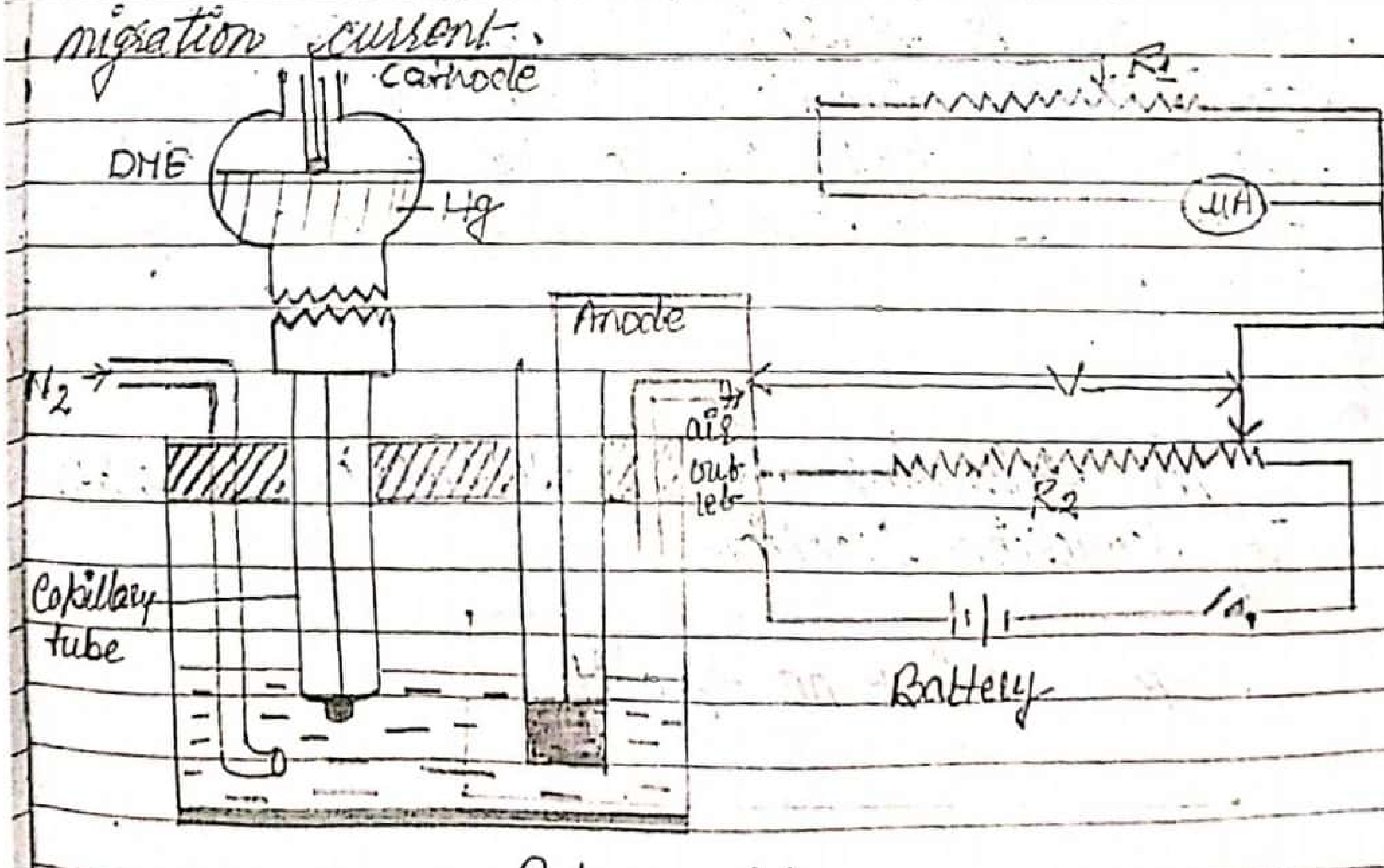
When a current voltage curve is recorded, a hump is normally seen in the absence of maxima suppressors c/a polarographic Maxima.



Method of Analysis

The polarographic apparatus consist of a polarisable electrode (DME) and a reference electrode (saturated calomel electrode) which is a non-polarisable electrode. Between these electrodes, the required Potential range (0 to -3v) can be applied. It consist of a sample cell, in which the sample solution to be analysed is kept. It is made of glass & has tapering edge at the bottom to hold the mercury after the droplets have been formed.

The capillary is dipped into the solution to be analysed & the height of reservoir is adjusted in such a way that droptime of 2-7 seconds is set. supporting electrolyte like Potassium chloride (50-100 times the sample conc^n) is added to the sample solution to eliminate migration current.



Polarograph