Potentiometry

Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution. To do this, two electrodes are used, an indicator electrode (the glass electrode and metal ion indicator electrode) and a reference electrode. Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half cell with the interested ions in the test solution. The reference electrode forms the other half cell.

Principle: The principle involved in the Potentiometry is when the pair of electrodes is placed in the sample solution; it shows the potential difference by the addition of the titrant or by the change in the concentration of the ions.

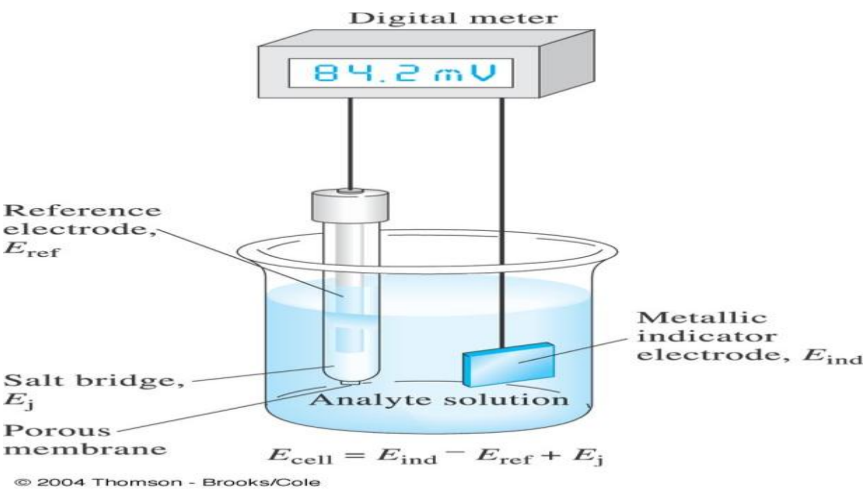

Fig. Electrochemical Cell/ Potentiometric Titration

The accurate, precise and effective potentiometric measurements can be made with the help of the following *two* types of electrodes namely:

REFERENCE ELECTRODES

(*a*) Standard Hydrogen Electrode,
(*b*) Saturated Calomel Electrode, and
(*c*) Silver-Silver Chloride Electrode.

INDICATOR ELECTRODES

(*a*) Metal Indicator Electrode, and
(*b*) Membrane Indicator Electrode

Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode (SHE), is considered to be the universally accepted reference electrode. The metal electrode has a small piece of platinum foil with finely divided platinum, usually termed as **platinum black** because of its dark look. The coated foil is immersed in an acidic medium having concentration of 0.1N, and through which H_2 gas is bubbled. The Pt-black-foil possesses a relatively large-surface-area thereby allowing it to absorb an appreciable amount of H_2 gas, ultimately bringing it into direct contact with the surrounding H+ ions at the electrode surface.

Silver-Silver Chloride Electrode

Silver-Silver chloride electrode which comprises of a Silver wire coated with Silver chloride and is duly placed in a 1 M KCl solution saturated with AgCl.

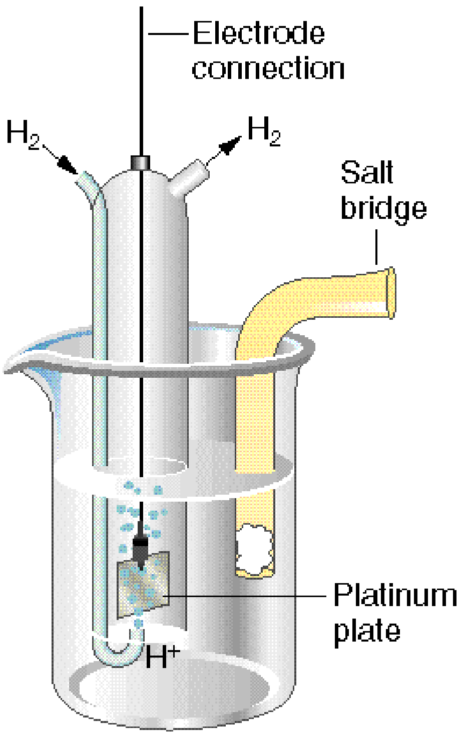

Fig. Standard Hydrogen Electrode

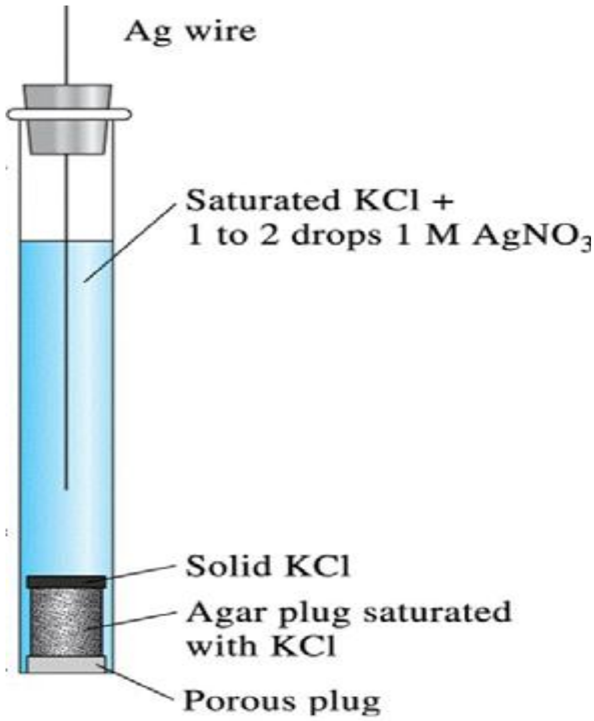

Fig. Silver-Silver Chloride Electrode

Saturated Calomel Electrode

It essentially consists of a platinum wire immersed in a slurry made up of pure mercury, solid mercurous chloride Hg_2Cl_2 (commonly known as **calomel**), and aqueous saturated solution of KCl, packed in the inner-tube having a small hole. The outer-tube contains a saturated solution of KCl having a porous ceramic fiber at its lower end. It serves as a salt-bridge which allows the entire set-up immersed directly into the solution to be measured. The porous ceramic fiber permits electrical contact between one side of the salt-bridge and the solution under the examination and serves as a barrier between the said two solutions. The small opening at the top end of the salt-bridge tube serves as a fill-hole through which either KCl solution may be filled or replaced as and when required.

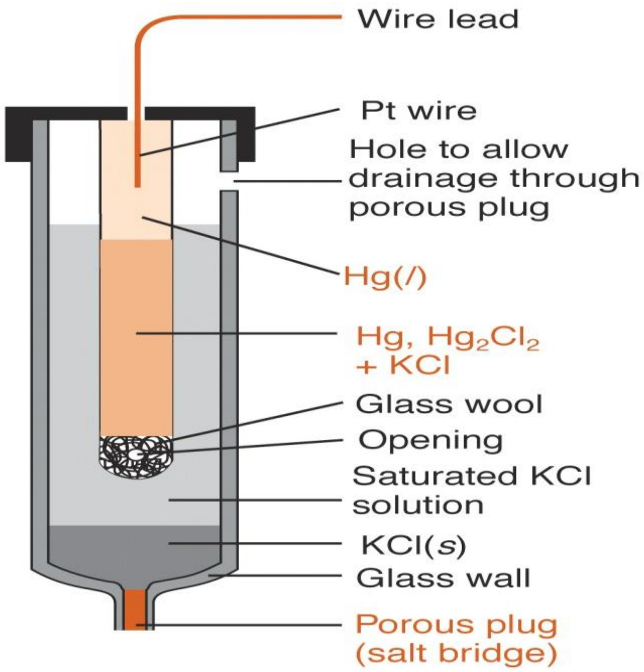

Fig. Standard Calomel Electrode

Metal indicator electrodes

These develop electric potential in response to redox reaction on the metal surface. Platinum or Au are used as metal indicator electrodes. These are mainly classified into three types of electrodes used in the potentiometry. They are as follows.

- First kind electrodes: They are composed of the metal rod immersed in its metal solution. These electrodes respond to the ionic activity of the electrode.
  Ex: silver electrode dipped in the silver nitrate solution.
  copper electrode dipped in the copper sulphate solution.
- Second kind electrode: These are composed of the metal wires coated with the salt precipitates. These electrodes respond to the changes in the ionic activity through the formation of the complex.
  Ex: Ag/ AgCl/ KCl
  Hg/ Hg_2Cl_2/ KCl
- Third kind electrodes: These electrodes are also known as inert electrodes and redox electrodes. They are composed of inert metal electrode immersed in the redox solution.
  Ex: Pt-H_2 electrode

Membrane Indicator Electrodes (or Ion-Selective Electrodes)

The underlying principle of this type of electrode is that the potential developed due to an unequal charge generated at the opposing surfaces of a 'special' membrane. The resulting charge at each surface of the membrane is controlled and monitored by the exact position of an equilibrium involving analyte ions, which in turn, depends upon the concentration of those ions present in the solution.
These are classified further into the following *four* kinds, namely :

(*i*) Glass membrane electrodes,
(*ii*) Polymer (liquid) membrane electrodes,
(*iii*) Crystalline membrane electrodes, and
(*iv*) Gas-sensing electrodes

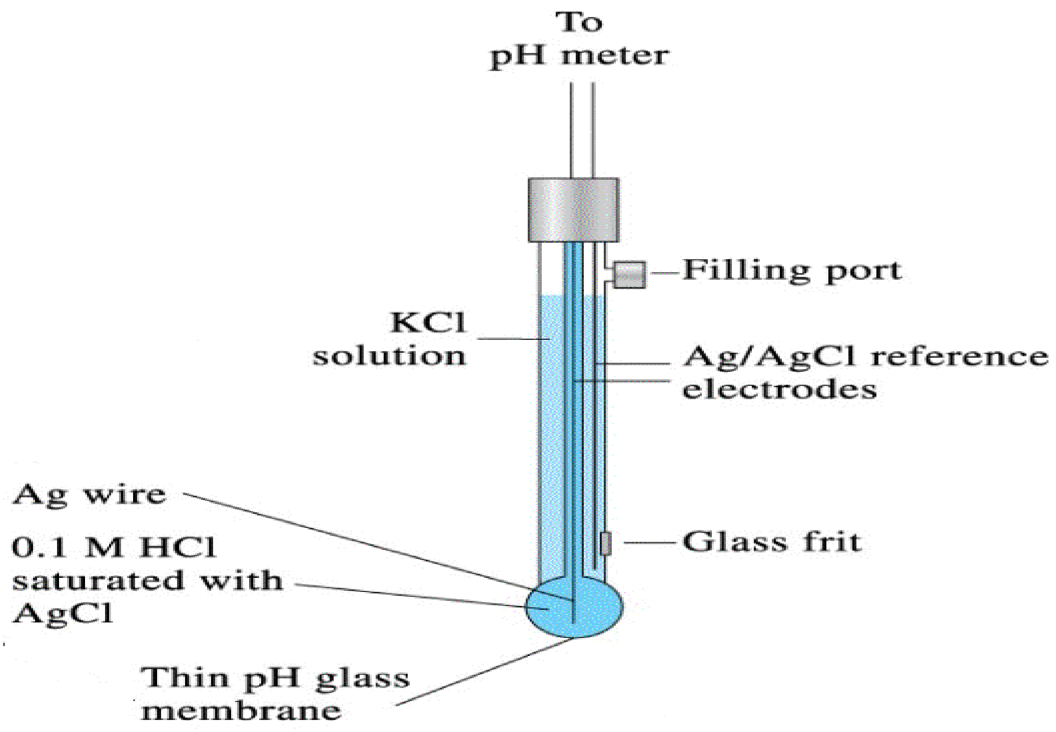

Fig. Glass Electrode

General method for potentiometry

- Switch on the instrument.
- Connect the saturated calomel electrode to the positive terminal or socket and the glass electrode to the negative.
- Adjust the meter to zero and subsequent readings are to be taken with the stirrer motor running.

- Rinse the beaker and electrodes thoroughly with water, then with the solution to be titrated and place a measured volume in the beaker. Add sufficient water to cover the bulb of the glass electrode adequately.
- Switch on the stirrer and measure the pH of the solution.
- Add about 2ml of titrant, allow sufficient time to mix and measure the pH of the solution.
- Add further quantities of titrant and as the end point is approached reduce to 0.1ml increments and measure the corresponding values of the pH.
- Obtain further readings of pH for about 5ml beyond the equivalence point.
- Switch the meter to standby and turn off the stirrer. Wash the beaker and electrodes thoroughly with the distilled water.
- Plot a graph of pH (vs) titrant added. Read off the equivalence point from the graph and calculate any required data from this value.

Applications

- **Environmental chemistry**: For analysis of CN^- ,NH_3, NO_3, F_3 in water and waste water.
- **Potentiometric titrations**: For determining the equivalence point of an acid base titration, for redox, precipitation, complexation as well as for all titrations in aqueous and non aqueous solvents.
- **Agriculture:** NO_3 ,NH_4 ,I ,Ca, K ,CN, Cl in soils, plant materials, feed stuffs, fertilizers.
- **Detergent manufacturing**:
    1. Ca, Ba, F for studying effects in water quality.
    2. Salt content of meat fish dairy products fruit juices brewing solutions
    3. Ca in dairy products and beer
    4. K in fruit juice and wine making
    5. Corrosive effects of NO_3 in canned foods
    6. F in drinking water and other drinks
    7. NO_3 and NO_2 in meat preservatives