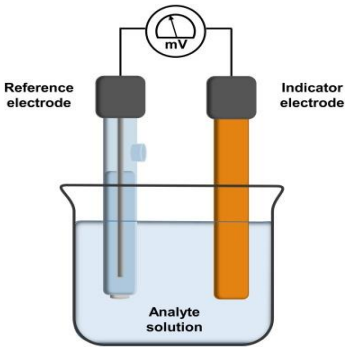
19CH103– ENGINEERING CHEMISTRY

Unit-5 INSTRUMENTAL METHODS OF ANALYSIS

POTENTIOMETRY

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.



- The reference electrode is the electrode which contains of its own potential value and it is stable when dipped into sample solution.
  Here analyte solution is the solution whose potential is to be measured.
- The indicator electrode is the electrode which responds to change in the potential of analyte solution
- The electromotive force of the complete cell is given by the following equation:

$$E_{cell} = E_{reference} + E_{indicator} + E_{junction}$$

where $E_{reference}$ is the electromotive force of the reference electrode ,$E_{indicator}$ is electromotive force of indicator electrode, $E_{junction}$ is the electromotive force at the junction of the liquid.

- The main theory involved in the potentiometry is, when the known potential electrode immersed in the sample solution then the potential is given by **Nernst equation**:
  $$E = E^0 + (0.592/n) \log c$$

- Where E is the potential of the solution; E^0 is the standard electrode potential; n is the valency of the ions; c is the concentration of the sample solution; 0.592 is the value obtained from the RT/F; where R is the gas constant, T is the temperature in Kelvin, F is the faradays constant.

Electrodes: These are mainly used to measure the voltages. Mainly two electrodes are used in the potentiometry .They are as follows:

- Reference electrode
- Indicator electrode

- **Reference electrode**: These are mainly used for the determination of the analyte by maintaining the fixed potential.

Ex: Standard hydrogen electrode
Silver silver chloride electrode
Saturated calomel electrode

The reference electrodes are classified into two main classes they are as follows**:**

- ✓ **Primary standard electrodes**
  ex: Standard hydrogen electrode
- ✓ **Secondary standard electrodes**
  ex: silver-silver chloride electrode saturated calomel electrode

- **Indicator electrode:** It is used to measure the potential of the analyte solution comparing with that of reference electrode . Its potential is directly proportional to ion concentration.

Ex: Hydrogen electrode.
Glass electrode.
Antimony –antimony oxide electrode. There are two classes of indicator electrodes:

- ✓ **Metal indicator electrodes**
- ✓ **Ion-selective electrodes**

- **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.
- **Ion selective indicators:** These are composed of ion-selective membrane by which the ion crosses and it creates the imbalance.
  Ex: Glass membrane electrode

Types of Potentiometric titrations:

- Acid-base titration
- Redox titration
- Complexometric titration
- Precipitation titration

APPLICATIONS

- **Clinical chemistry**: Ion selective electrodes are present sensors for clinical samples because of their selectivity for analyte in complex matrices. The most common analytes are electrolytes such as Na, k ,Ca ,H, and Cl and dissolved gases such as CO_2

- **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.
- possible for redox, precipitation, acid-base, complexation as well as for all titrations in aqueous n non aqueous solvents.

- **Agriculture:** NO_3 ,NH_4 ,I ,Ca, K ,CN, Cl in soils, plant materials, feed stuffs, fertilizers.

- **Detergent manufacturing**: Ca, Ba, F for studying effects in water quality.

- **Food processing:**
  - ✓ Salt content of meat fish dairy products fruit juices brewing solutions
  - ✓ Ca in dairy products and beer
  - ✓ K in fruit juice and wine making
  - ✓ Corrosive effects of NO_3 in canned foods
  - ✓ F in drinking water and other drinks
  - ✓ NO_3 and NO_2 in meat preservatives