

**SHREE H. N. SHUKLA INSTITUTE OF  
PHARMACEUTICAL EDUCATION AND  
RESEARCH**



**B.PHARM**

**(SEMESTER -I)**

**SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I**

**SUBJECT CODE: BP102TP**

**UNIT 5(b): POTENTIOMETRY**

## Content

**Potentiometry** - Electrochemical cell, construction and working of reference (Standard hydrogen, silver chloride electrode and calomel electrode) and indicator electrodes (metal electrodes and glass electrode), methods to determine end point of potentiometric titration and applications.

## INTRODUCTION

- In 1889, Nernst proposed an equation which states that the electrochemical cell potential is directly proportional to the concentration of the sample solution.
- In 1906, Cremer explained that the potential difference exists between the reference electrode and the indicator electrode.
- In 1909, pH electrode is developed for the measurement of the potential.
- Potentiometry is mainly used to determine the potential or the electromotive force of a sample solution.
- The potential is directly proportional to the concentration of the ions. The potential difference is determined by the electrochemical cell which is composed of pair of electrodes namely the indicator electrode and the reference electrode.

## 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.

This can be seen below:

- Reference electrode/salt bridge/analyte solution/indicator electrode Potentiometer
- The reference electrode is the electrode which consists of its own potential value and it is stable when dipped into the sample solution.
- The salt bridge is used to prevent the interference of the analyte solution with the reference solution.
- Analyte solution is the sample solution whose potential is to be measured.
- The indicator electrode is the electrode which responds to the changes in the potential of the analyte solution.
- The electromotive force of the complete cell is given by the following equation:

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

Where,

$E_{\text{reference}}$  is the electromotive force of the reference electrode;

$E_{\text{indicator}}$  is the electromotive force of the indicator electrode

$E_{\text{junction}}$  is the electromotive force at the junction of the liquid.

- The units for the potential are mille volts denoted by mV.

## THEORY

The main theory involved in the potentiometry is when the known potential electrode immersed in the sample solution then the potential is given by the Nernst equation:

$$E = E^{\circ} + (0.0592/N) \log c$$

Where,

E is the potential of the solution;

$E^{\circ}$  is the standard electrode potential;

n is the valency of the ions;

c is the concentration of the sample solution;

0.0592 is the value obtained from the  $RT/F$ , where R is the gas constant, T is the temperature in Kelvin, F is the Faraday's constant.

This can be achieved by the charge transfer process by the following steps:

- Electrons move from the reference electrode to the indicator electrode.
- The positive ions move to the cathode and negative ions move to the anode
- On the surface of the electrodes, electrons are transferred to ions.

## Factors Affecting Nernst Equation:

1. Temperature dependent.
2. Presence of additional potentials.

## ELECTRODES

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

1. Reference electrodes.
2. Indicator electrodes.

### Reference electrodes:

These are mainly used for the determination of the analyte by maintaining the fixed potential.

Examples: Standard hydrogen electrode.  
Silver–silver chloride electrode.  
Saturated calomel electrode.

Among these silver–silver chloride electrode is frequently used.

• **The reference electrodes are classified into two main classes. They are as follows:**

**1. Primary standard electrodes**

Example: Standard hydrogen electrode

**2. Secondary standard electrodes**

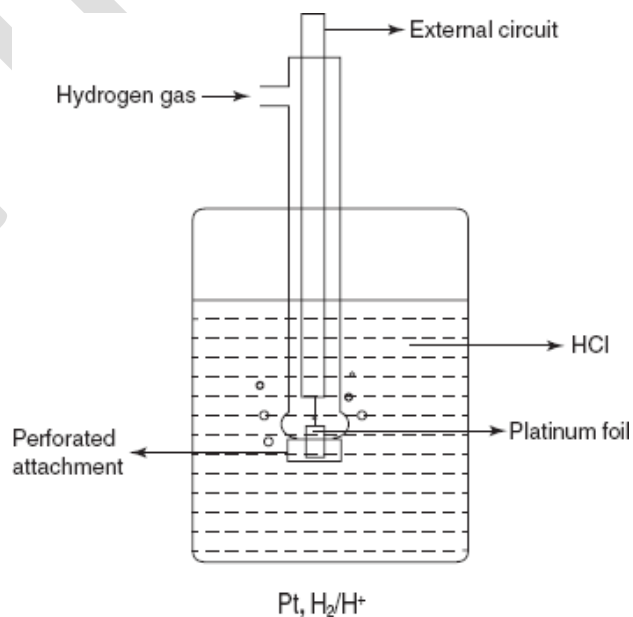
Examples: Silver–silver chloride electrode  
Saturated calomel electrode

❖ The ideal requirements of the reference electrodes are the following:

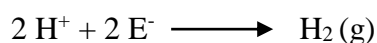
- It should be stable.
- It should be reversible.
- It should be responsible

#### **1. Standard Hydrogen Electrode:**

- This is used as the primary reference electrode. It consists of platinum foil which is coated with the platinum black and immersed in the HCl solution which contains the hydrogen ions.
- Hydrogen gas is passed over the platinum foil through the side tube. This is used for the entire pH range.

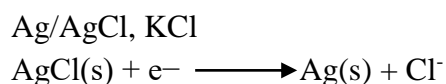


- The disadvantages of this electrode are the instability due to the presence of oxidizing or reducing agents and purity of the hydrogen.
- The reaction is as follows:



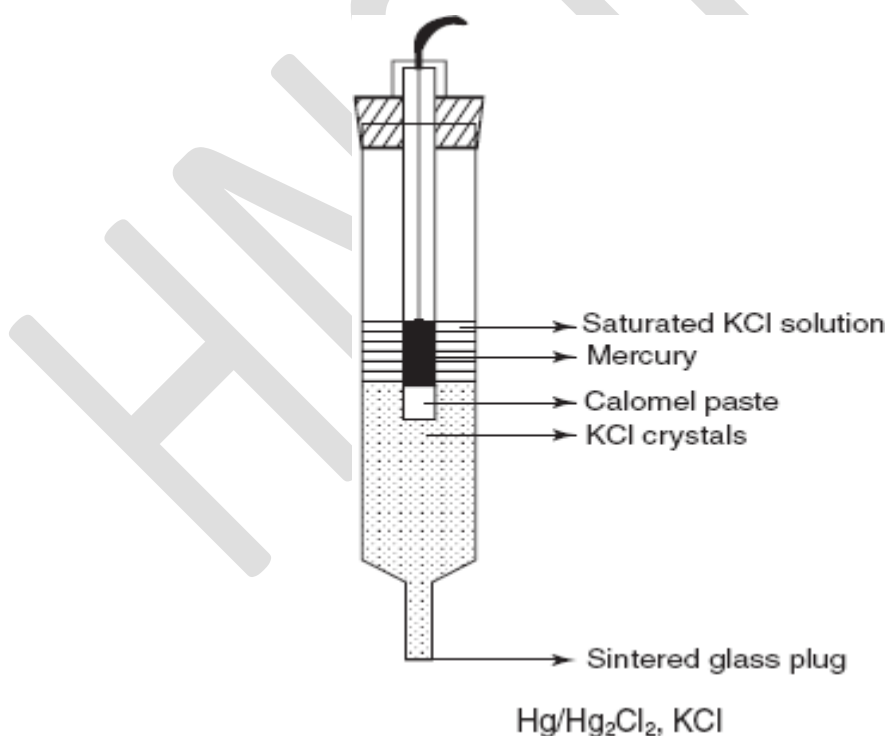
### 2. Silver-silver chloride electrode:

- Same as the saturated calomel electrode where the silver wire is coated with the silver chloride solution, here the wire is dipped in the saturated potassium chloride solution. The cell consists of the following:

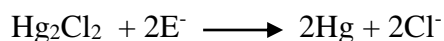


### 3. Saturated calomel electrode:

- It consists of porous disc at the base of the electrode which is clogged. Above it the glass tube is filled with the potassium chloride crystals. And above it is filled with the calomel paste which is prepared by grinding of mercury chloride with pure mercury and minute millilitre of the saturated potassium chloride solution.
- Then pure mercury is placed in the electrode vessel. The advantages are the easy to construct and highly stable.



The reaction is as follows:



### Indicator electrodes:

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

Examples: Hydrogen electrode.

Glass electrode.

Antimony–antimony oxide electrode.

- **There are two classes of indicator electrodes:**

1. Metal indicator electrodes
2. Ion-selective electrodes

1) **Metal-indicator electrodes:** These develop electric potential in response to a redox reaction on the metal surface. Platinum or Au are used as metal indicator electrodes.

These are very simple indicator electrodes. The main disadvantage is that they are not very selective. There are mainly three types of the 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.

➤ **Examples:**

Silver electrode dipped in the silver nitrate solution:



Copper electrode dipped in the copper sulphate solution:



#### Second kind electrodes:

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.

➤ **Examples:**



#### 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.

➤ **Examples:**

Pt-H<sub>2</sub> electrode

2) **Ion-selective electrodes:** These are composed of ion-selective membrane by which the ion crosses and it creates the imbalance. Then this opposes the further movement of the ion.

➤ **Examples:**

Glass membrane electrode

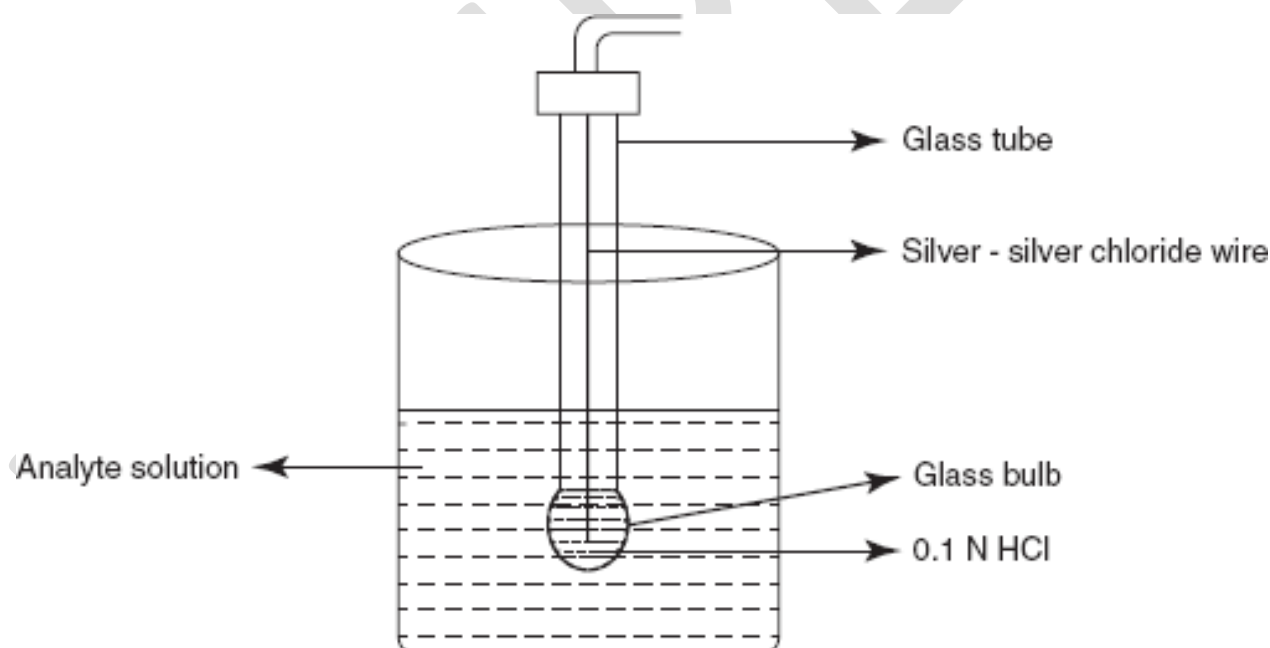
Antimony-antimony oxide electrode

**1. Glass membrane electrode:**

This is most commonly used ion-selective electrode. This responds to the change in the concentration of the hydrogen ions.

This is composed of glass tube with a thin glass bulb. In which the silver-silver chloride wire is immersed in it.

Lower part of the bulb consists of 0.1N of HCl. This overall setup is immersed in the solution whose potential is to be measured.



**2. Antimony-antimony oxide electrode:**

It is composed of the antimony rod dipped in the sample solution. When it is exposed to air it forms the antimony oxide. The main advantage is the stability. The main disadvantage is that it cannot be used in the presence of dissolved oxygen or oxidizing agents.

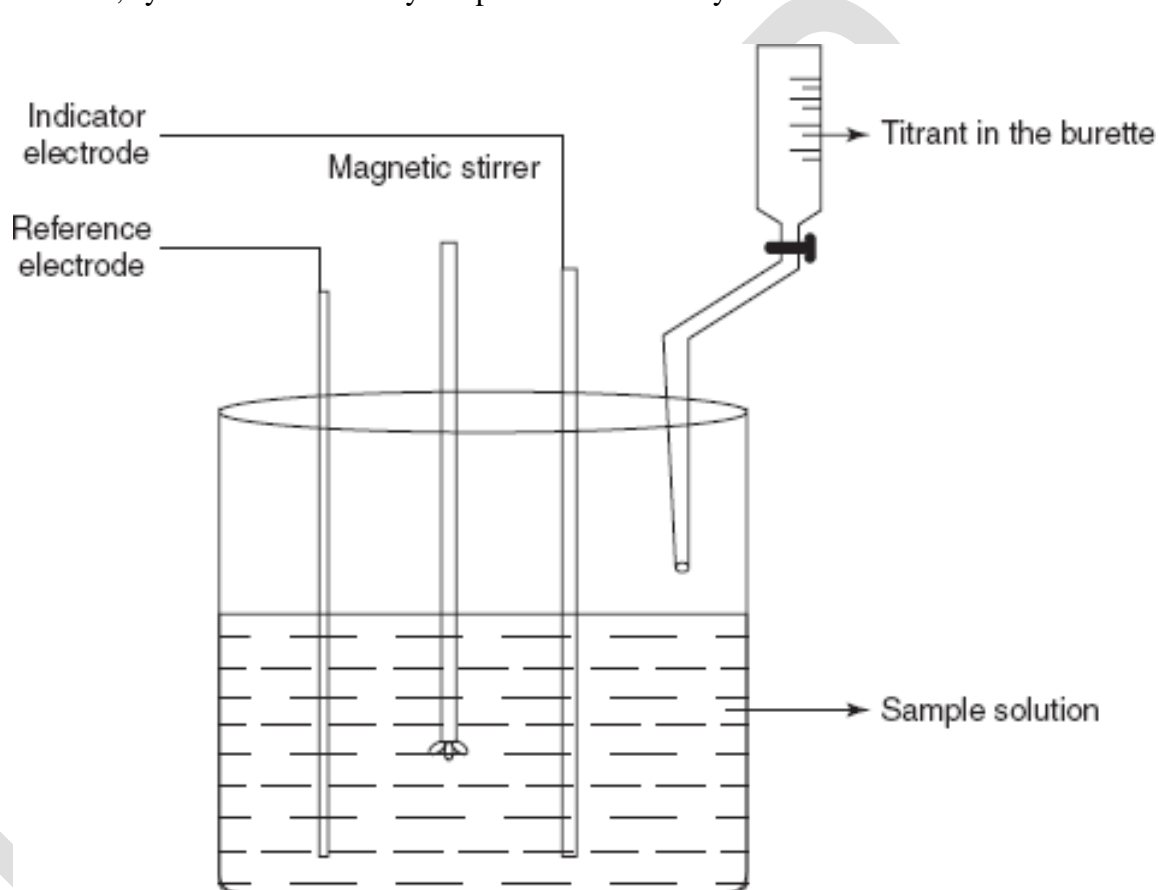


### POTENTIOMETRIC TITRATIONS

In potentiometric titrations, the end point is determined by the sudden change in the potential by the addition of the titrant to the sample solution. This is mainly due to the change in the concentration or ions activity in the sample solution.

A simple apparatus is required for simple potentiometric titration which is composed of the reference electrode, indicator electrode and a mechanical stirrer.

The end point is indicated by the rapid change in the potential. To measure the electromotive force of the electrode, system is measured by the potentiometer or by the electronic voltmeter.



**Potentiometric titration apparatus**

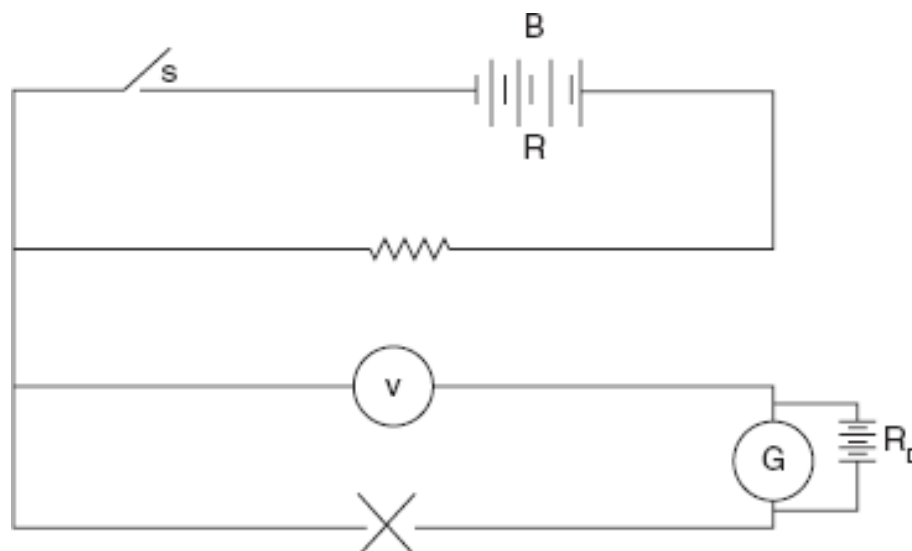
### INSTRUMENTS

- There are mainly three types of the instruments employed for potentiometric measurements. They are as follows:

#### 1. Non-electronic instrument:

It is composed of the battery which supplies the current and is attached to the set of dry cells. This setup is connected to the resistor R, voltmeter V and the galvanometer G. Then it is dipped in the sample solution and the potential is recorded.





### Non-electric potentiometer

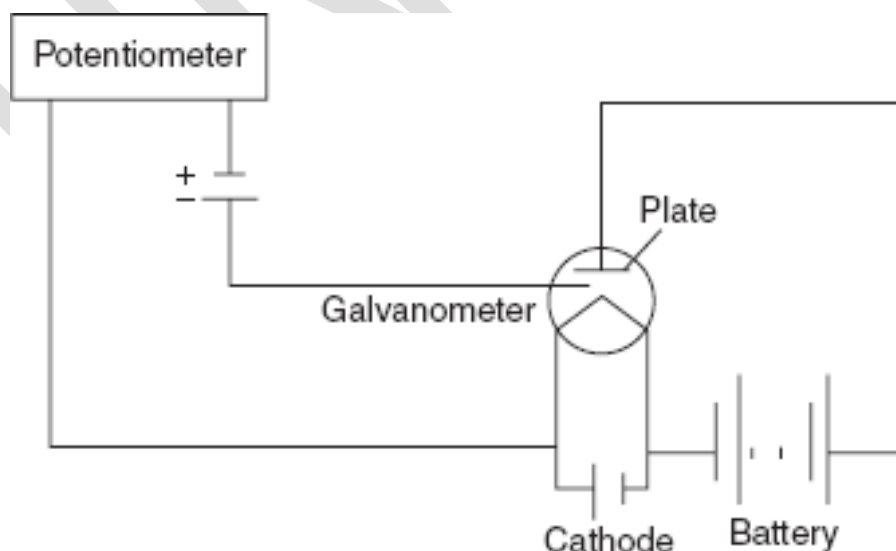
#### 2. Electronic instrument:

It is composed of electronic amplifier combined with the glass electrode which is commonly known as the pH meter.

The tube consists of the cathode C, a plate B and a grid C.

The cathode C is initially heated by the source which releases electrons captured by the plate B. Then small current is passed through the plate and the electrons are repelled by the cathode to the plate B.

Finally the setup is attached to the potentiometer which reads the potential of the sample solution.

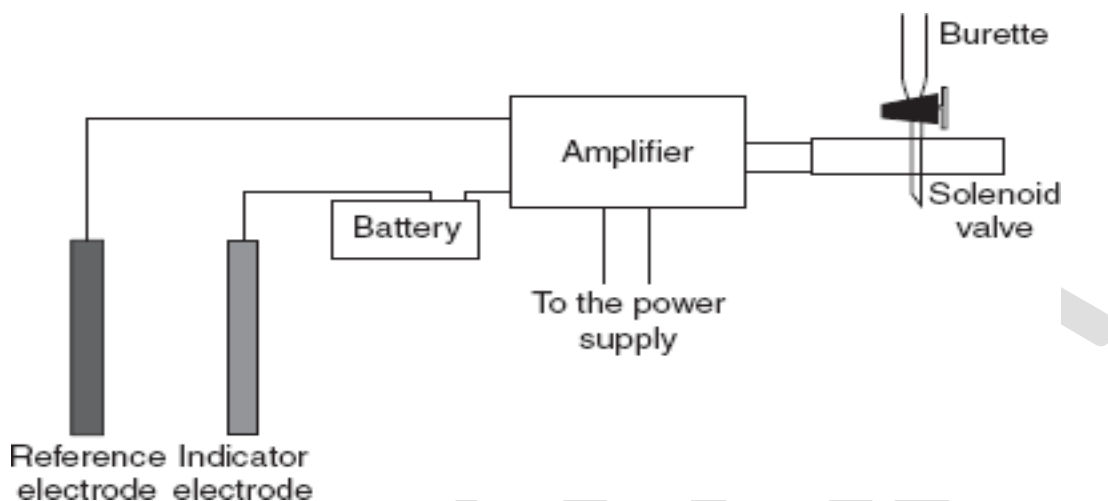


### Electric potentiometer

### 1. Automatic instrument:

This is the commonly used potentiometer for the potentiometric measurements. It consumes less time to complete the titration and produces the accurate results.

This is composed of a potentiometer and an amplifier which are immersed in the sample solution to detect the end point.



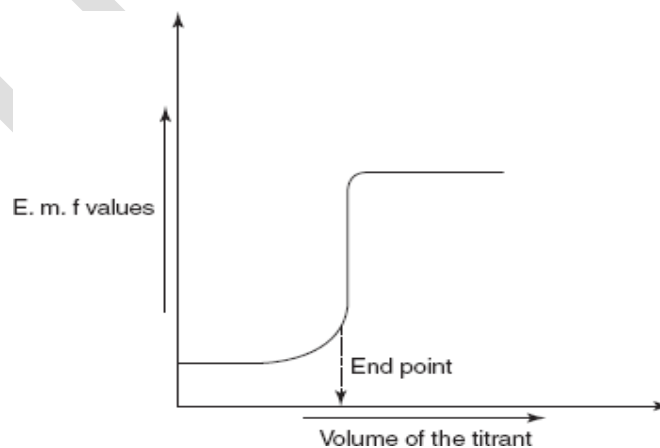
## Automatic potentiometer

### Types of Potentiometric Titrations

They are following types of potentiometric titration:

- 1) **Acid–base titrations:** This is mainly based on the changes in the concentration of the hydrogen and the hydroxyl ions which is caused by the neutralization.

A known amount of the sample which may be acid or base is taken in the beaker and is titrated with its subsequent acid or base.



### Acid-base titration curve:

Then immerse the indicator electrode, for example, glass electrode, and the reference electrode, for example, saturated calomel electrode. Then the potential difference is calculated from the following equation:

$$E = K - 0.0592 \text{ pH}$$

where K is the asymmetry potential.

Then the electromotive force values are plotted against the volume of the titrant.

**Example:** Acetic acid is titrated with the ammonium hydroxide.

- 2) **Redox Titrations:** These titrations are carried out by using the inert electrode. The sample is titrated with the oxidizing or the reducing agent. This oxidizes or reduces the sample solution which causes the potential difference. Then the potential is calculated from the following equation:

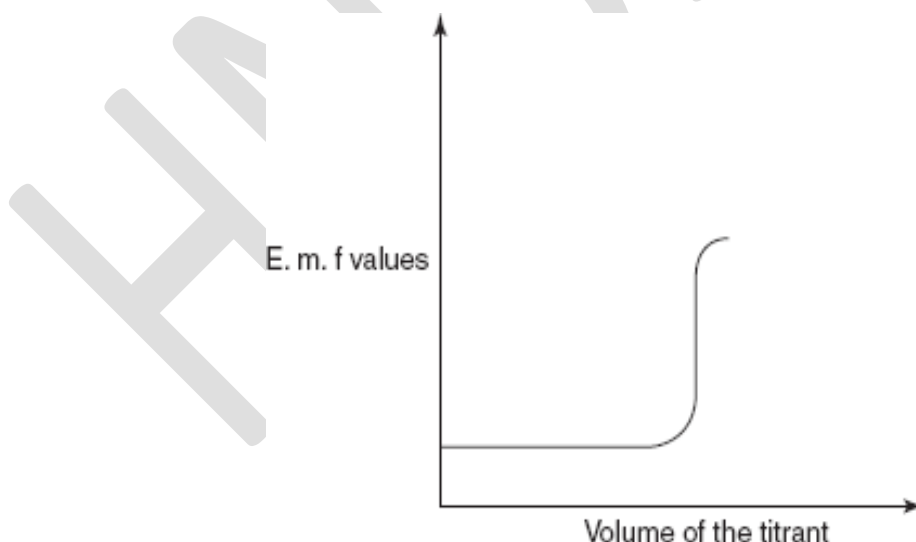
$$E = E^0 + 0.0592/n \log_{10} K$$

Where K is the equilibrium constant. Which is given by the following equation:

$$E = E^0 + 0.0592/n \log_{10} [\text{OX}]/[\text{Red}]$$

Where [OX] is the concentration of the oxidant; [Red] is the concentration of the reductant.

In this method, the reference electrode used is the saturated calomel electrode or the silver–silver chloride electrode. The indicator electrode used here is the platinum foil or wire. The plot between the e.m.f values and the volume of the titrant shows the following:



### Redox titration curve

- 3) **Precipitation titrations:** This method is mainly used in the quantitative determination of the metal ions by the precipitating agents. The end point is determined by the following equation:

$$E = E^0 + 0.0592/n \log_{10} [M^{n+}]$$

where  $[M^{n+}]$  is the concentration of the metal ions.

In this method, the reference electrode used is the saturated calomel electrode or hydrogen electrode and the indicator electrode used is the silver wire electrode.

**4) Complexometric titrations:** The complexometric is mainly used to determine the metal ions which are complexated by the complexing agents. For example, ethylene diamine tetra edetate solution which is a popular complexing agent. The reference electrode used in this method is the saturated calomel electrode and the indicator electrode used is the silver electrode.

**Example:** Silver ions are complexed with the cyanide ions as the titrant solution.

#### ADVANTAGES OF POTENTIOMETRY

- Inexpensive.
- Interpretation of the values is easy.
- Applicable for the coloured solutions also.
- Applicable to the dilute solutions.
- Broad specificity.

#### DISADVANTAGES OF POTENTIOMETRY

- Calibration of the instrument consumes more time.
- Interferences of the impurities are more.

#### APPLICATIONS OF POTENTIOMETRY

- Used in the determination of the % of acetyl salicylic acid in aspirin tablets.
- Used in the determination of the % acetic acid in the vinegar.
- Used in the determination of the carbonate.
- Used in the acid base titrations.
- Used in the precipitation titrations.
- Used in the complexometric titrations.
- Used in the biamperometry.
- Used for the estimation of the saccharin in the food components.