

## AMPEROMETRIC TITRATIONS

Amperometry refers to the measurement of current under a constant applied voltage and under these conditions it is the concentration of analyte which determine the magnitude of current.

In Amperometric titration the potential applied between the indicator electrode (dropping mercury electrode) and the appropriate depolarizing reference electrode (saturated calomel electrode) is kept constant and current through the electrolytic cell is then measured on the addition of each increment of titrating solution.

In these titrations the current passing through the cell between the indicator electrode and reference electrode at a suitable constant voltage is measured as a function of the volume of the titrating reagent.

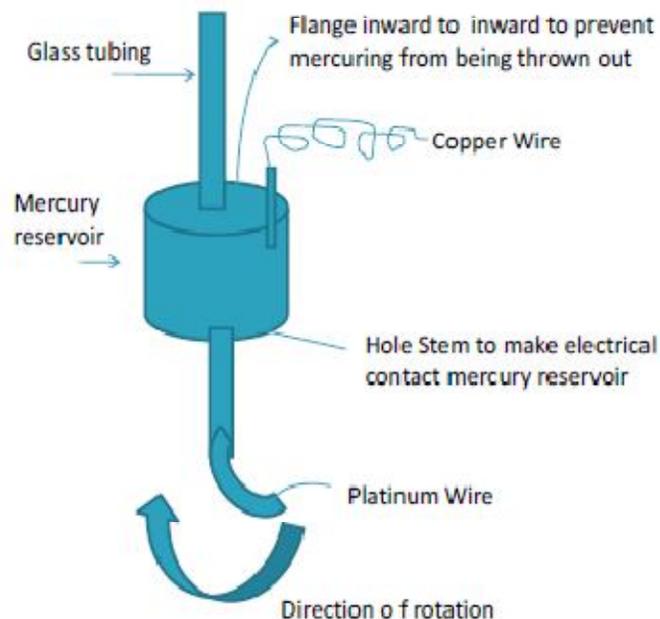
### **Principle:**

According to Ilkovic equation ( $I_d = 607 \times n \times D^{1/2} \times m^{2/3} \times t^{1/6} \times C$ ), the diffusion current (= limiting current - residual current) is directly proportional to the concentration of the electro-active material in the solution. If some of the electro-active material is removed by interaction with reagent, the diffusion current will decrease. This is the fundamental principle of amperometric titrations. The observed diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution: the end point is the point of intersection of two lines giving the change of current before and after the equivalence point.

### **Instrumentation:**

Amperometric titration can be carried out with a rotating platinum electrode (See Fig.). It consist of a glass tube of length 15 – 20 cm in length and 6 mm in diameter. The platinum wire extends 5-10 mm from the wall of glass tubing. The electrode is mounted on shaft of the motor and rotated at constant speed of 600 RPM . Electrical connection is made to the electrode by copper wire passing through the tubing to the mercury covering the platinum wire seal.

### Rotating Platinum electrode



#### Advantages:

- 1) Diffusion current is 20 times larger than DME which allows measuring the small concentration of ion.
- 2) The rotating platinum electrode can be used at positive potential up to + 0.9 Volt where as DME can be used only +0.4 volt to -2.0 Volt.
- 3) The electrode is simple to construct.
- 4) Steady diffusion state is reached quickly.
- 5) microconcentration of material can be determined because of the larger currents attend at rotating electrodes.

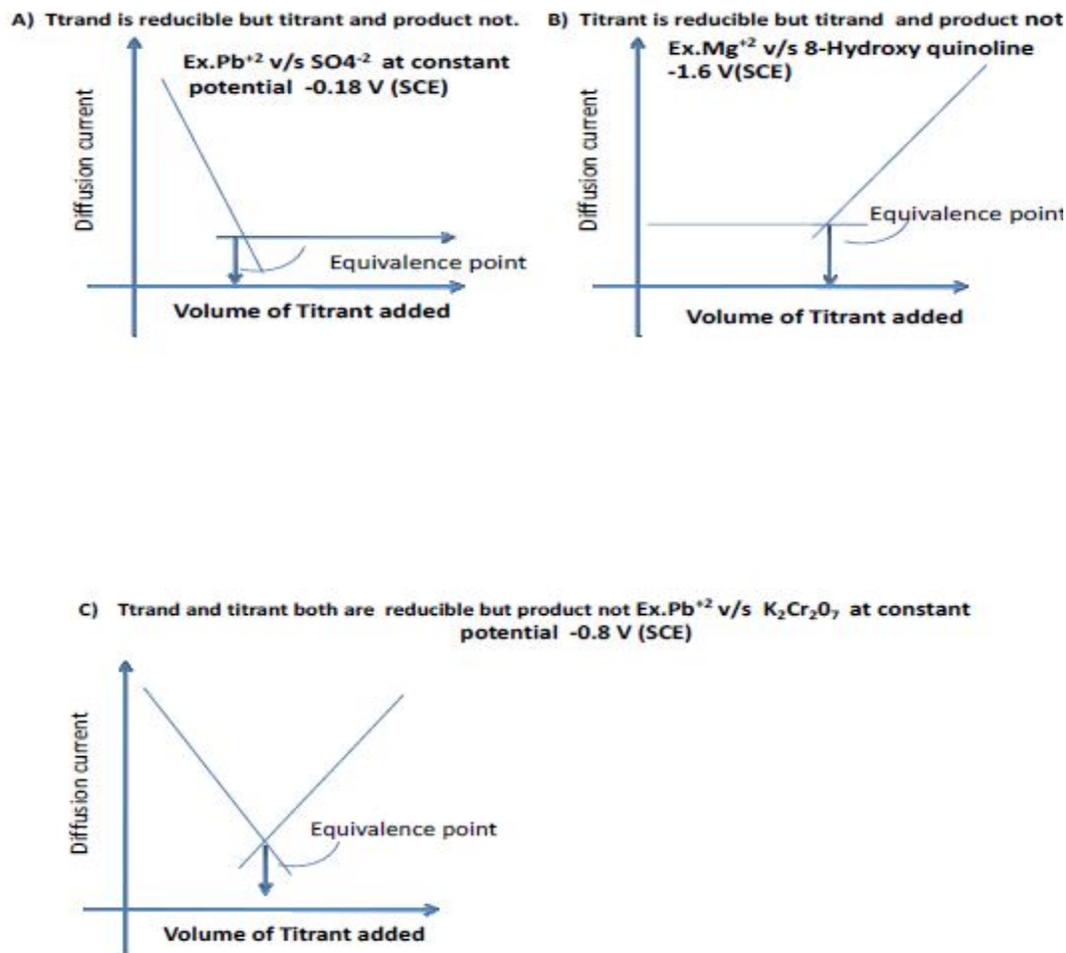
#### Titration Curves in Amperometry:

**Titrand + Titrant ----- □ Product.**

**A) Titrand is reducible but titrant and product not:** When solution containing  $Pb^{+2}$  ion is titrated against  $SO_4^{2-}$  ion. A precipitate of  $PbSO_4$  is formed. The titration can be performed at fixed potential  $-0.8$  Volt v/s saturated calomel electrode. As titration proceeds concentration of  $Pb^{+2}$  ion decreases and diffusion current also decreases till it becomes minimum at equivalence point. The diffusion current remains constant beyond end point. The values of diffusion current is plotted against the volume of titrant added. The resulting titration curves is straight line leveling off at end point. The intersection of two extra plotted portions of the curves gives the end point.

**B) Titrant is reducible but titrand and product not :** When solution containing  $Mg^{+2}$  ion is titrated against with the reducible species such as 8- hydroxy quinoline because  $Mg^{+2}$  ion does not undergoes reduction. Beyond the end point the 8- hydroxyl 4quinoline undergoes reduction. As its concentration increases diffusion current also increases.

**C) Titrand and titrant both are reducible but product not :** When solution containing  $Pb^{+2}$  ion is titrated against  $K_2Cr_2O_7$ . The titration is performed at potential of  $-0.8$  Volt v/s SCE. Diffusion current is decreases due to removal of  $Pb^{+2}$  ion. The current is minimum at the end point. On further addition of the titrant the current once again increases. V shaped curve is obtained.



### Advantages of amperometric titrations:

1. The titration can usually be carried out rapidly, since the end point is found graphically; a few current measurements at constant applied voltage before and after the end point suffice.
2. Titrations can be carried out in cases in which the solubility relations are such that potentiometric or visual indicator methods are unsatisfactory; for example, when the reaction product is markedly soluble (precipitation titration) or appreciably hydrolysed (acid-base titration). This is because the readings near the equivalence point have no special significance in amperometric titrations. Readings are recorded in regions where there is excess of titrant, or of reagent, at which points the solubility or hydrolysis is suppressed by the Mass Action effect; the point of intersection of these lines gives the equivalence point.

3. A number of amperometric titrations can be carried out at dilutions (ca  $10^{-4}M$ ) at which many visual or potentiometric titrations no longer yield accurate results.

4. 'Foreign' salts may frequently be present without interference and are, indeed, usually added as the supporting electrolyte in order to eliminate the migration current. If the current-voltage curves of the reagent and of the substance being titrated are not known, the polarograms must first be determined in the supporting .

**Applications:**

1. Widely applicable than Potentiometry and Polarography. This method is widely used for the determination of sulphate which could not be determined accurately by Potentiometric method due to lack of suitable indicator.
2. Successive determination of chloride, bromine, Iodide by using rotating microelectrode.
3. They are used as micro detectors in liquid chromatography.
4. In bioamperometric titration this technique is widely used in karl-fisher moisture titration.
5. Other applications are:
  - a) Phosphate with uranyl acetate
  - b) Lead with dichromate ions
  - c) Sulphate with lead nitrate
  - d) Cu, CO, Pt with
  - e) Iodine with mercuric nitrate