SRI AKILANDESWARI WOMEN’S COLLEGE, WANDIWASH

AMPEROMETRY

Class : II PG Chemistry

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- ☐ Appratus used for amperometric titration
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INTRODUCTION :

- Amperometry is one of the electrochemical method.
- It is concerned with the measurement of current under constant applied voltage.
- It is a form of quantitative analysis.
- When indicator method is not suitable we use amperometric method for determinaton of end point.
- Amperometric titration are otherwise called as polarographic titration because of similarity in principle.

PRINCIPLE:

- In amperometric titration, the potential applied between the indicator electrode and the appropriate depolarising reference electrode is kept constant & current pass through the cell , it is then measured during the titration.
  - Indicator electrode : Dropping mercury electrode. (DME)
  - Reference electrode : Saturated calomel electrode

- During the titration the concentration of electro-reducible ion changes & hence the dffusion current also changes.
- According to Ilkovic equation :

$I_d = 607\ n\ CD^{1/2}\ m^{2/3}\ t^{1/6}$

where,

I_d =Diffusion current due to electro-reducible ions.

n = No. of electrons involved in the reduction of one molecule .

C = Concentration expressed in mmol/ lit .

D = Diffusion coeff. of ions (cm2/sec).

m= Wt. of mercury flowing through capillary (mg/sec)

t = Drop time in second.

CONDITION FOR PERFORMING AMPEROMETRIC TITRATION:

- Both should be reducible .
- the potential applied should limiting current.

APPRATUS USED FOR AMPEROMETRIC TITRATION :

- Dropping mercury electrode :
  - Capillary tube about 10 - 15 cm.
  - Internal diameter of capillary 0.05mm.
  - A vertical distance being maintained between DME & the solution.
  - Drop time : 1-5 se
  - Drop diameter – 0.5 mm

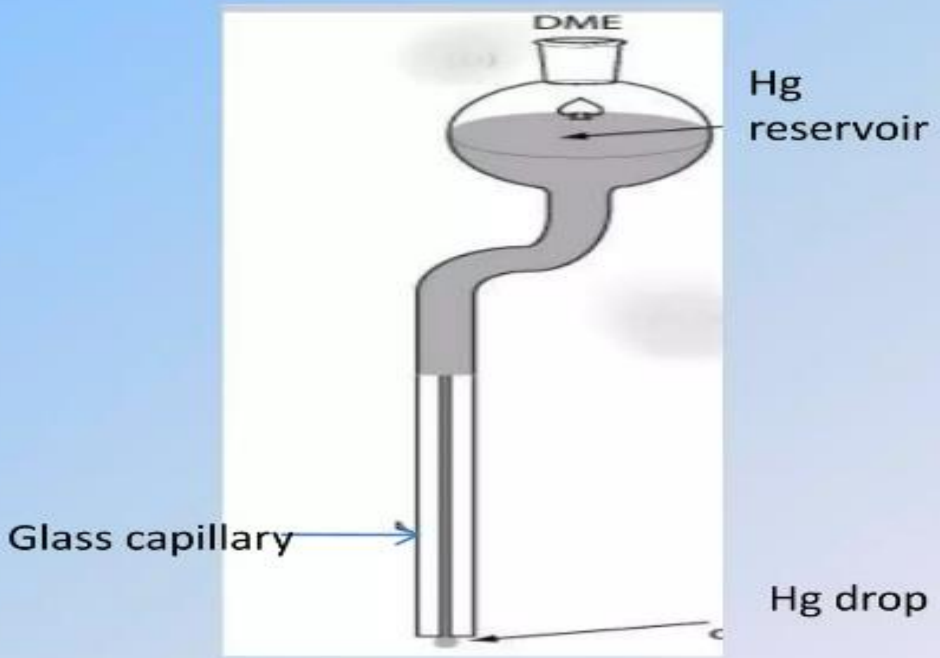

Fig. Dropping Mercury Electrode

• Rotating Platinum Micro-electrode :

- It consist of a glass rod with a bent platinum wire at about 600 rpm .
- Wire contacts are made through a mercury reservoir at the top so the potential can be applied & the current is produced

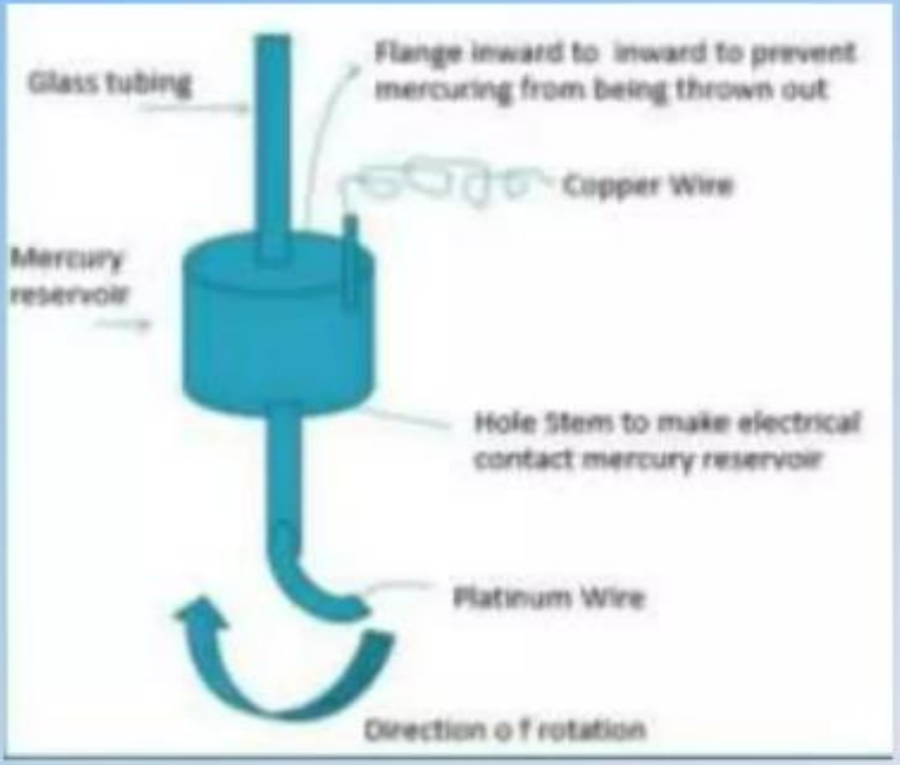

Fig. Rotating Platinum Micro-Electrode

Advantages of Using RPME over DME :

- Mercury cannot be used as electrode at positive potentials because of its oxidation, RPME is used.
- Diffusion current is 20 times larger than DME which allows to measure the small concentration of ion.
- 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.
- The electrode is simple to construct.

Types of amperometric titrations:

- Titration of reducible ions vs non reducible ions.
  eg . Lead (pb^{2+}) vs sulphate ions (SO$_4$)
- Titration of non reducible ions vs reducible ions.
  eg . Chloride (Cl$^-$) vs silver (Ag^{2+})
- Titration of reducible ion vs reducible ions.
  eg. Lead (pb^{2+}) vs Dichromate ion (Cr^2 O$_7$ $^{2-}$)
- Redox titration (oxidant and reductant).
  eg. Ferric (fe^{3+}) ions vs titanous ions (ti)
- End point techniques (karl fischer).
  (Determination of water using karl fischer reagent)

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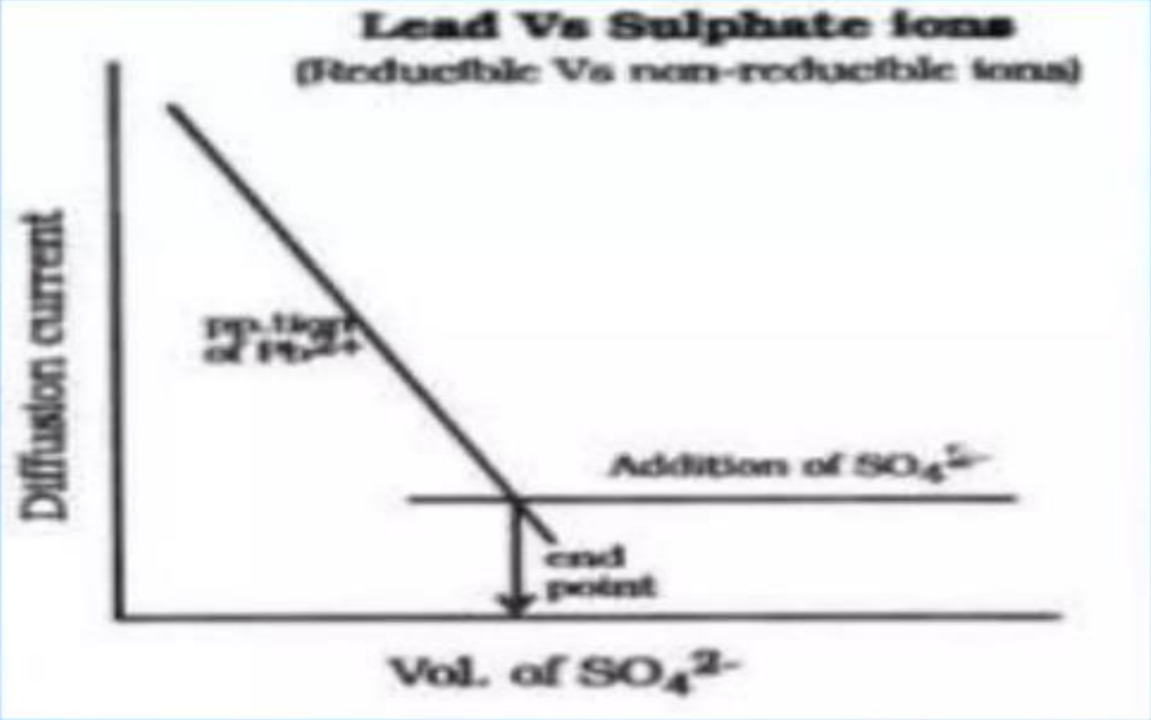
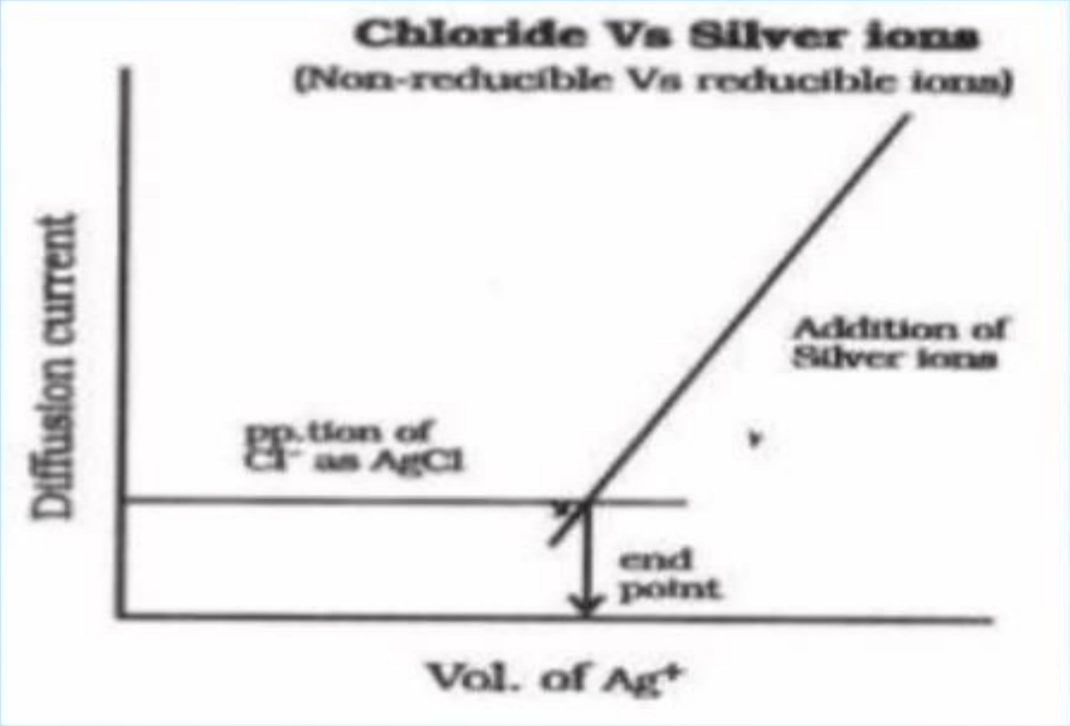


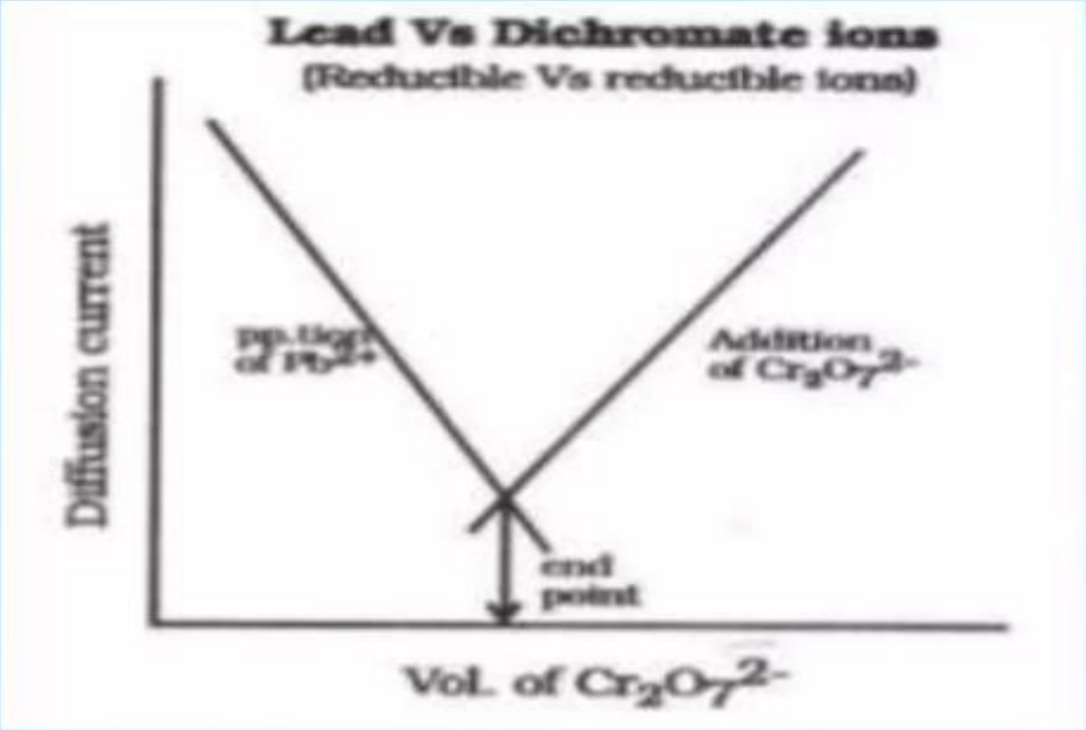
- Titration of non reducible ions vs reducible ions.

  eg . Chloride (Cl^-) vs silver (Ag^{2+})



- Titration of reducible ion vs reducible ions.

  eg. Lead (pb^{2+}) vs Dichromate ion (Cr^{2} O$_{7}$ $^{2-}$)



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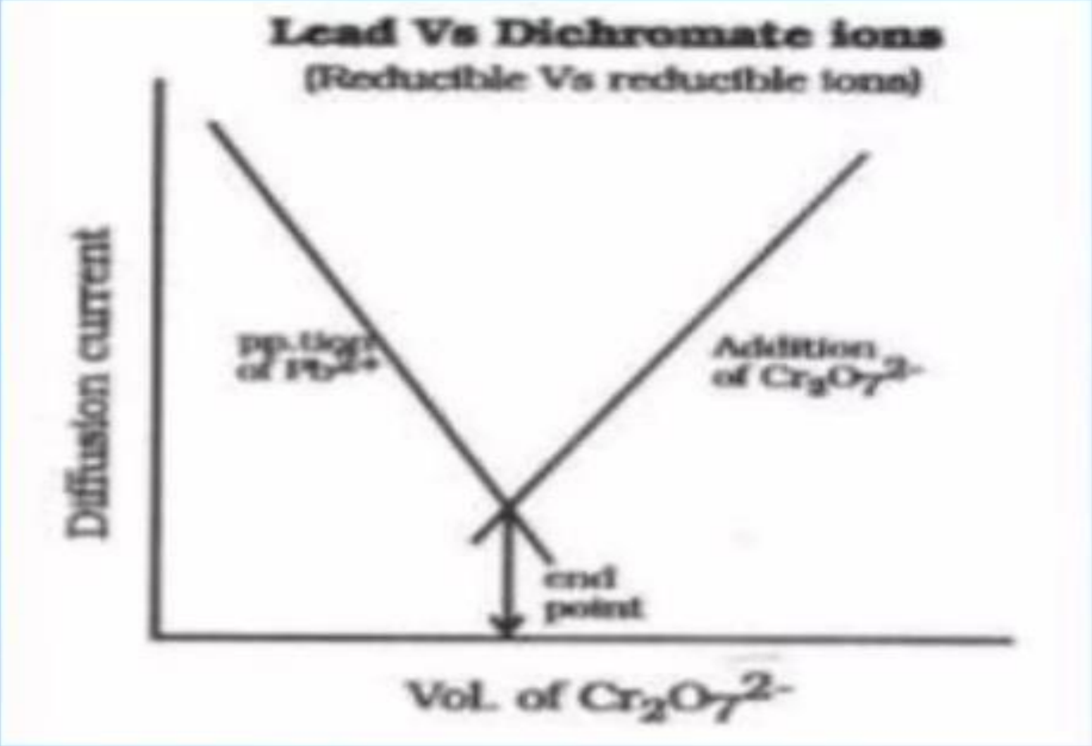
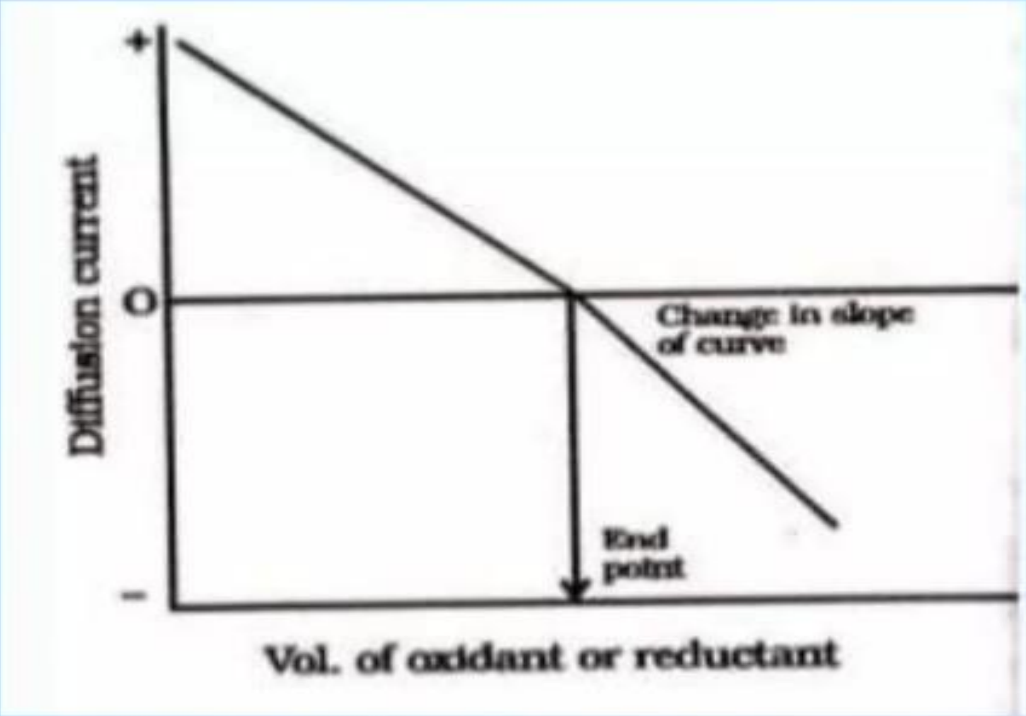


- Redox titration (oxidant and reductant).
  eg. Ferric (fe^{3+}) ions vs titanous ions (ti)

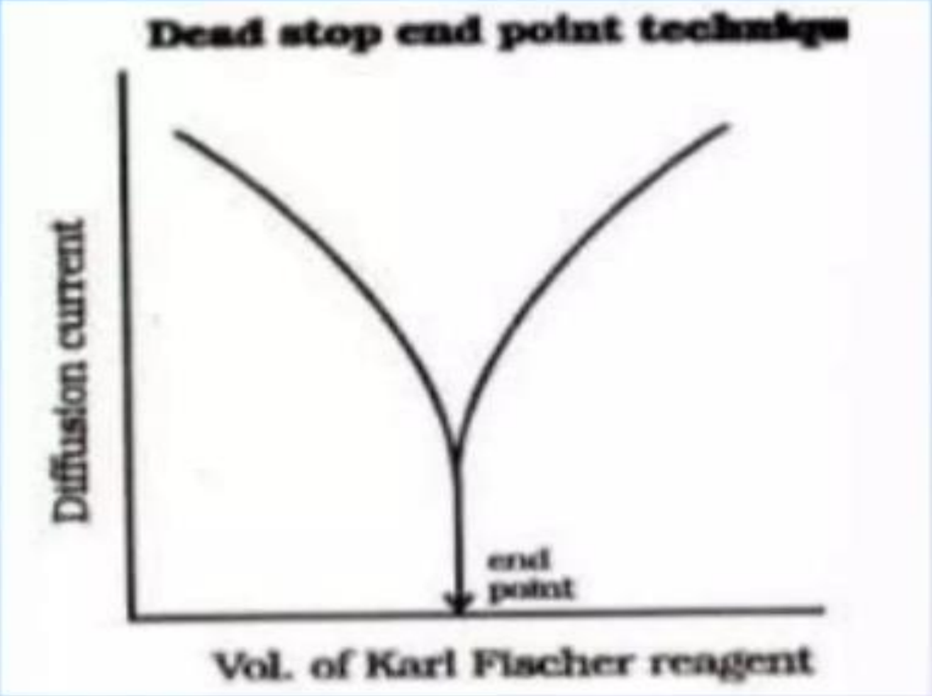


➢ End point techniques (karl fischer).

(Determination of water using karl fischer reagent) :

➢ A small potential is applied between the two similar platinum electrodes .

➢Addition of KF reagent (solution of iodine and SO_2 in pyridine and methanol) then till the end point. Where current is decrease at end point and only one electrode is depolarised and current is zero.



Advantages of Amperometric titration:

- Both reducible as well as non- reducible ions groups can be determine.
- Dilute solution can be analysed.
- The reaction carryout can be reducible or irreversible.
- The appratus is simple and temprerature need not be provided constants.

Application of Amperometric titration :

- Amperometric titration :
  - ➢ quantitative in nature.
  - ➢ used and determine the end point.
- Determination of water by using karl fischer reagent.
- Amperometric dectector - (HPLC)Amperometric dectector can detect very low conc. of reducible ions & they can easily determine.
- Quantification of ion or mixture of ions.

Disadvantages of amperometric titration

- Inaccurate result are sometime obtained.
- The foreign substance should not be present in a larger concentrations than the substance to be titrated.

THANK

YOU