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ELECTROMETRIC METHODS

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Abstract :

Electrometric techniques used in the analysis of atomic energy materials. This abstract examines its underlying principles - Potentiometric Titration, Conductometric Titration, Polarography, Amperometry. In any electrometric method, two electrodes are required; however, in many methods only the electrochemical phenomena associated with one electrode are useful. This electrode is referred to as the "sensitive," or "working," electrode of the pair; the other electrode is the reference or counter electrode.

Introduction :

The electrometric methods of analysis are divided into two main groups in this chapter. The first group comprises the methods in which measurement of an electrical quantity, such as potential, serves as the primary measurement of the substance being determined. The second group comprises the methods in which the measurement of an electrical quantity serves as a guide to the use of another measurement, such as titration with a standard solution. The second group also includes those methods in which electricity is used as a reagent in the analysis, but the quantity of electricity used does not serve as the measure of the substance being determined.

The electrometric method of pH determination is based on the measurement of potential of a pH cell, whereby the potential of a hydrogen sensitive electrode is directly proportional to pH, and pH is defined in an operational manner on a potentiometric scale.

Material on the theoretical background of the electrochemical phenomena associated with an electrometric method of analysis has been included to show the unifying principles involved, but this chapter is not intended to be a complete guide to the complexities of modern electrochemistry. The emphasis lies on the practical problems involved in applying electrochemical principles.

Similarly, material on the operating principles of the electrical equipment used in the methods of analysis has been included. Since improvements in the electronic and mechanical components used in the equipment are being made constantly, it would be expected that any equipment used today would become obsolete relatively quickly. Hence the emphasis is on principles rather than on details of operation.

Electrometric method Principle: The magnitude in the potential difference between glass and a solution containing hydrogen ion varies with concentration of H^+ concentration. Hence the pH of the solutions are determined by means of the electrodes. Hydrogen electrode and glass electrodes are used for this purpose.

Apparatus and General Principles :

Electrometric methods for routine analysis are not new, but their use was limited until the past 10 years or so because the apparatus for many of the potentially useful methods were inconvenient to use, time-consuming in operation, and unreliable in the hands of the routine analyst. The great promise of electrometric techniques has been partially fulfilled by the development of laboratory apparatus which, if not simple in design, is simple to use and is as reliable as conventional analytical apparatus and which eliminates many of the tedious and time-consuming features through automatic control systems and recording components. The great increase in reliability of the apparatus and the ready adaptation of electrometric techniques to automatic recording have led to the use of these techniques in automatic process analyzers.

1. POTENTIOMETRIC TITRATION :

Introduction :

Potentiometric method involves two types of measurements i.e change in the electrode potential or change in pH by the addition of titrant. The potential of an indicator electrode dipped into a solution of an electrolyte depends upon the concentration of ions in the solution. This titration is done in solution which shows change in potential or pH by addition of titrant. It involves two electrodes, indicator and reference electrode. Change in potential at indicator electrode is measured while potential at the reference electrode is kept constant. In this method, EMF of an electrolyte cell is calculated as -

$$E_{\text{cell}} = E_{\text{ref}} + E_{\text{ind}} + E_j$$

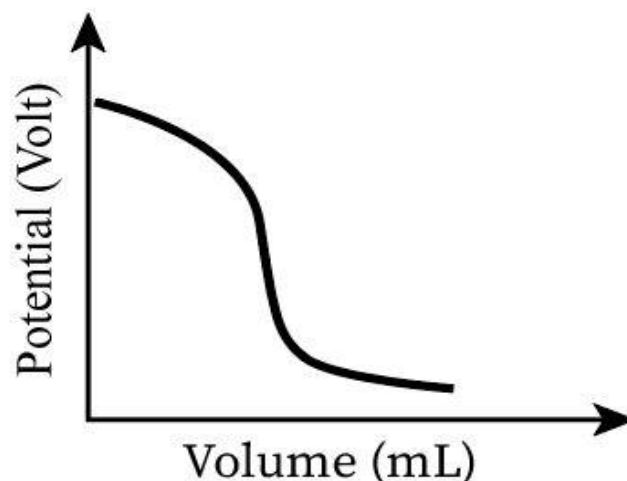
E_j junction remains constant.

$E_{\text{reference}}$ assumed to be independent of composition of the solution.

So, EMF of a cell becomes equal to EMF at the indicator electrode.

Principle :

Potentiometric titration is based on the principle that when the potential of the particular indicator electrode is measured in relation to some reference electrode, it is related to the concentration in the solution. At the end point there is sharp change in the potential of the indicator electrode. In this method, the change in electrode potential is measured. A graph plotted b/w indicator electrode potential and the volume of titrant. At the end point there is maximum change in potential.



Solution whose concentration is to be calculated is taken and titrant is added to it. After addition of each ml of titrant, electrode potential is measured. Then a graph is plotted b/w electrode potential and volume of titrant added. Sometimes, change of pH instead of change in potential is measured. A linear relation exist b/w pH of solution at a given temperature with potential E i.e.

$$E = K - 0.0591\text{pH}$$

Or

$$\Delta E/\Delta\text{pH} = -0.0591$$

K= constant potential (assymmetric potential)

For measuring, change in pH, potentiometric pH meters are used. For standardization of pH meter, buffer solutions of known pH are used.

Electrodes :

For determination of potential of a given solution, two electrodes are used. The two electrodes are combined to form a voltaic cell. One electrode is reference electrode whose potential is known and is a constant. Second electrode is indicator electrode which determines the potential of the solution under examination. There are two types of electrodes -

A) Reference electrode

B) Indicator electrode

A) Reference electrode :

It is also known as primary reference electrodes. Its potential is known to us and is a constant value. Various types of electrodes can be used as reference electrodes. These are of two types -

1) 1° electrode like NHE.

2) 2° electrode like Calomel, Silver-silver chloride, Mercury-mercury sulphate, etc.

1) 1° electrode Normal Hydrogen electrode (NHE) :

This is the most commonly used reference electrode.

Apparatus :

It consists of a glass tube having holes at its bottom. This tube consists of one more tube having platinum or copper wire with a platinum foil. Platinum foil is coated with platinum black. The hydrogen gas is passed through this tube which can come out from hole at the bottom of the tube. The whole tube is dipped into solution of 1.8M of HCL at 25°C. Some Hydrogen gas gets absorbed by the platinum black which allows the exchange of hydrogen from gaseous to ionic form. By this way, it acts as hydrogen electrode.

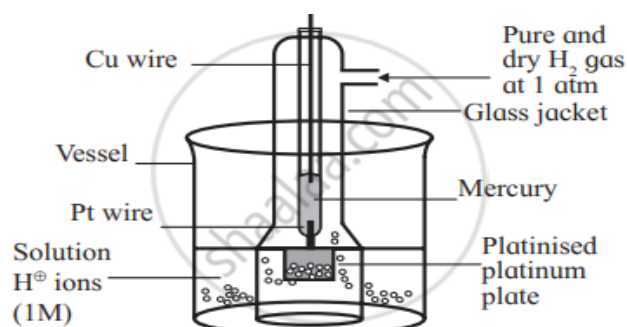
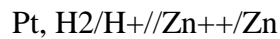


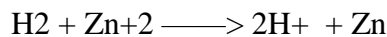
Fig. Normal hydrogen electrode (NHE)

Working :

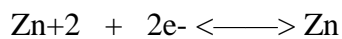
The potential of this electrode is taken as zero at all temperatures. When NHE is connected to other electrode (indicator) through the salt bridge, the potential of indicator electrode can be measured easily. For e.g. Zn electrode is connected to NHE through KCL salt bridge.



The cell reaction is



Half cell reaction is

**Advantages :**

- 1) It gives reproducible result.
- 2) It has no salt error.
- 3) It can be used over wide pH range.
- 4) It is a fundamental electrode.

Disadvantages :

- 1) The platinum black coating gets poisoned easily by substances like alkaloids, proteins, etc.
- 2) It is not useful in solutions containing strong oxidizing or reducing agents.
- 3) It is not useful in solution having metal ions that are below Hydrogen in potential series.
- 4) It is cumbersome to prepare and use daily.

2) 2° reference electrode :

Use of NHE as a standard standard electrode produces various practical difficulties. Some problems like poisoning of platinum black, interference due to presence of oxidizing agents or reducible ions in the solution etc are common. To overcome all these problems secondary reference electrodes are used.

a) Calomel electrode :

It is also known as Mercury-Mercurous chloride electrode.

Apparatus :

Various types of vessels are used for making calomel electrode. Generally, it consists of glass tube having a slide arm tube. Pure mercury is placed at the bottom of glass tube and is covered with a paste of calomel(mercury chloride) and KCL. The tube is filled with KCL solution through the side arm tube. A platinum wire is also placed at the centre of the glass tube which makes electrical connection with mercury. The potential of this calomel electrode depends upon the concentration of KCL solution used. Most commonly 0.1N KCL, 1N KCL or standard KCL solutions are used.

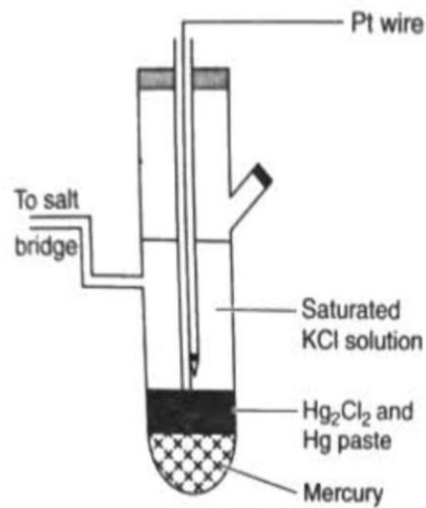


Fig. Calomel Electrode

Working :

When calomel electrode is connected with another electrode (indicator), EMF of the indicator electrode can be calculated. Half cell of calomel can be written as -



Calomel electrode can be connected to NHE for measuring pH of a solution i.e



$$\text{pH} = \frac{E_{\text{observed}} - E_{\text{calomel}}}{0.0591}$$

Advantages :

- 1) It can be used over wide pH range.
- 2) It can be used in various solvents.
- 3) It is sturdy.

Disadvantages :

- 1) It is unstable at temperature above 80°C.
- 2) It is not suitable when chloride ions show incompatibility.

b) Silver-silver chloride electrode :

It is used as a reference electrode. It is difficult to prepare.

Apparatus :

It consists of silver wire, coated with silver or platinum or copper wire. This wire is coated with a thin layer of silver chloride and is dipped in a solution of KCl of known concentration. Generally 0.1M KCl or saturated KCl solution is used.

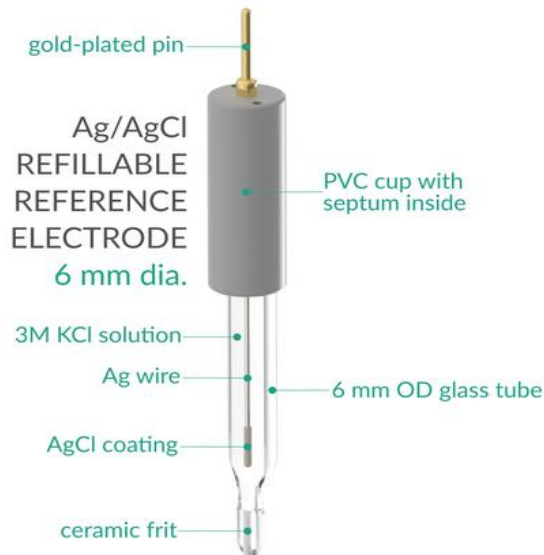
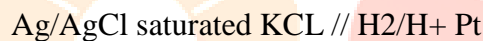


Fig. Silver-silver chloride electrode

Working :

The standard potential of this electrode is obtained by combining it with NHE. The EMF of the cell can be calculated i.e.



This electrode is used similarly as calomel electrode. It can't be used where chloride ions interfere.

c) Mercury-Mercurous sulphate electrode :

This electrode is useful where chloride ions have been found to interfere. This electrode is useful in solution containing sulphate ions. It consists of mercury in a solution containing sulphate ions and has been saturated with mercurous sulphate. The standard potential of indicator electrode can be determined by combining it with this electrode. Standard potential of this electrode when measured against NHE is 0.680 volts. The half cell can be written as -

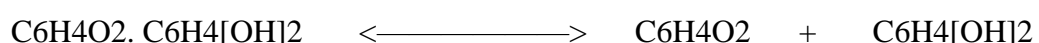


B) Indicator electrode :

In order to determine the EMF of a given solution proper indicator electrode is required. This electrode measures potential when it is connected to suitable reference electrode. So an electrode which is useful for measuring potential of pH of a solution is called as Indicator electrode. Various types of indicator electrodes are -

1) Quinhydrone electrode :

This electrode is mainly useful in measuring pH of a given solution. This electrode was introduced by E. Billman in 1921. Quinhydrone is a compound of quinine and hydroquinone and in solution form it gives equal molecules of these two substances. Quinhydrone electrode consists of a platinum wire dipped into a saturated solution of quinhydrone. In solution form quinhydrone gets dissociated into equal quantities of quinone and hydroquinones.



The electrode consists of a platinum wire into solution containing excess of quinhydrone. Platinum wire is generally cleaned with chromic acid and water. For preparing the quinhydrone, dissolve 60gm of ferric alum in 100ml of water and pour this solution into a warm solution of 5gm of hydroquinone in 60ml of water.

Advantages :

- 1) It is free from salt errors.
- 2) It is highly simple and gives rapid response.
- 3) It attains equilibrium very quickly.
- 4) It is not affected by presence of dissolved oxygen.
- 5) It is less sensitive than the hydrogen electrode to the presence of oxidizing agents.

Disadvantages :

- 1) It can not be used in the solution whose pH above 8.
- 2) It is not suitable for a long time.
- 3) The solution must be free from oxidizing and reducing agents.
- 4) The solution under examination gets contaminated.
- 5) It readily gets oxidized by air in alkaline medium.

2) Glass electrode :

This electrode is useful in determination pH of a solution. It involves no electron exchange but there occurs transfer of hydrogen ions. It consists of very thin walled glass bulb made from glass membrane of high electrical conductivity. The bulb contains HCl of a particular concentration and Ag/AgCl wire or platinum wire to make electrical contact. The glass membrane is made from soft soda lime glass containing lithium silicate and barium ions added to it. The measurement of pH of solution is based on the fact that when a glass surface is placed in a solution then a potential is established b/w the glass and the solution. The value of this potential depends upon hydrogen ions concentration of the solution.

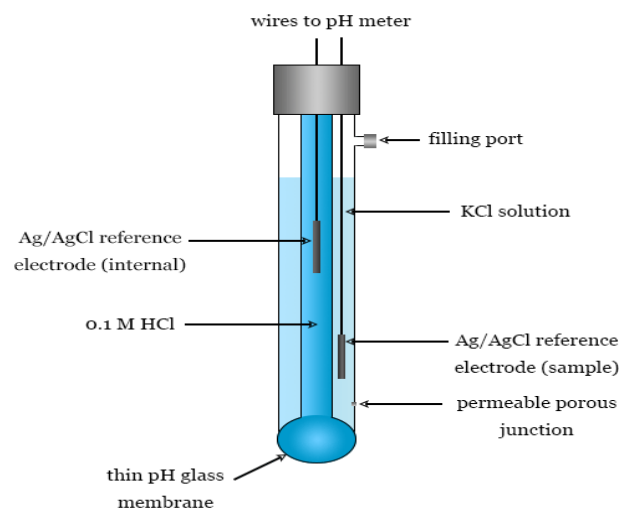


Fig. Glass electrode

Advantages :

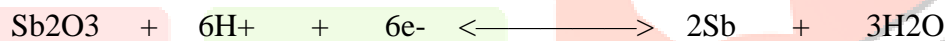
- 1) It is not affected by oxidizing and reducing agents in the solution.
- 2) It can be used over wide pH range i.e. from 0-9.
- 3) It is simple to operate.
- 4) It can be used in viscous, colored solution and suspensions.
- 5) It has no salt error.
- 6) Modern glass electrodes are very strong to withstand high pressure.

Disadvantages :

- 1) It is fragile, so should be handled carefully.
- 2) Minute scratches make glass electrodes useless.
- 3) It is not useful in highly alkaline solution as there occurs partial exchange of other cations than H⁺ ions.
- 4) It must be hydrated all the time.

3) Antimony Electrode :

This electrode is useful in determining pH of a solution. It consists of antimony rod coated with antimony trioxide i.e. antimony rod is covered with its oxide. The electrode reaction is -



The antimony electrode can be prepared by casting a stick of antimony in air. A wire is attached at one end of the antimony rod and other is placed into the solution whose pH is to be determined. EMF can be calculated by combining it with a suitable reference electrode.

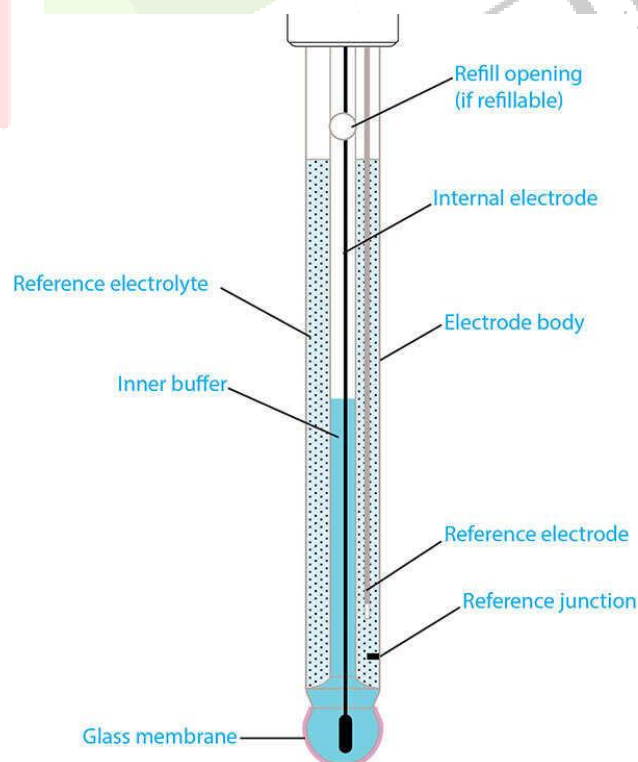


Fig. Antimony electrode

Advantages :

- 1) It is useful in viscous and turbid solutions.
- 2) It has wide pH range 2-8.
- 3) It is not affected by the presence of oxidizing agents.
- 4) It is sturdy and not easily broken.
- 5) It attains equilibrium rapidly and has low electrical resistance.

Disadvantages :

- 1) It suffers from a salt error.
- 2) Complexing agents if present in the solution causes interference.
- 3) It is not useful below pH 3 as the oxide gets dissolved.
- 4) It cannot be used in the presence of strong oxidizing agents.
- 5) Every time calibration is required.

Instrumentation of Potentiometric Titration :

An apparatus involved in Potentiometric Titration consists of a large glass vessel with a lid having opening for passing the nitrogen inlet tube, tip of burette and pair of electrodes. The glass vessel is placed on a magnetic stirrer with speed control knob. Two suitable electrodes are placed in a beaker and their ends are connected to Potentiometric unit. A solution whose potential is to be measured is placed in the beaker and titrant is added from the burette drop by drop.

Potentiometric unit consists of a high resistance galvanometer with lamp or magic eye. A measured volume of titrant is added with stirring and values of EMF or pH are recorded. Equivalence point can be found out graphically by plotting volume of titrant corresponding to maximum change of EMF/unit change of volume.

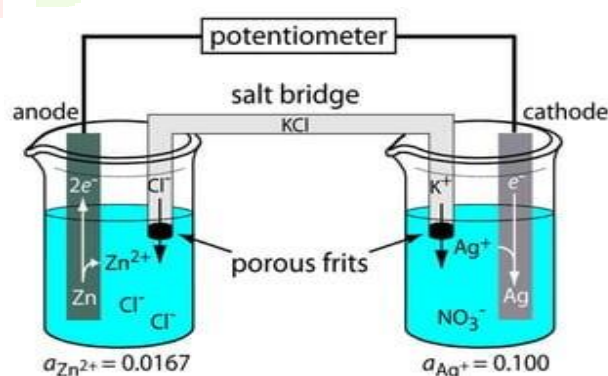


Fig. Method for determining End Point

Types of Potentiometric Titration :

1) Acid-Base Titration :

This type of Titration involves H^+ and OH^- ions. The indicator electrode used may be hydrogen, glass or antimony while calomel is used as a reference electrode. Dibasic, tribasic and polybasic acids can be titrated with alkali to full end point. The potential of any hydrogen electrode can be given by

$$E = E_0 - 0.0591pH$$

So, with the help of Potentiometric Titration end point of titration b/w acid and base can be determined easily.

2) Redox Titration :

Many redox titrations are possible by using Potentiometer. In this an inert indicator electrode generally platinum is used. This titration involves the transfer of electron from oxidized substances to reduce substances. So potential of indicator electrode is given by

$$E = E_0 + \frac{0.0591}{n} \log [Ag^+]$$

The equivalence point is shown by sudden inflection curve. From the standard values of reduction potential and the observed values of potential the ratio of concentration can be determined.

3) Precipitation Titration :

Potentiometric titration is possible only for limited types of reaction involving precipitation. The indicator electrode may be made of metal involved in the reaction for e.g. silver electrode is used in titration of halides against silver nitrate. The potential of this electrode is given by

$$E = \log [Ag^+]$$

Ag^+ is the ionic concentration of silver ions during the titration.

4) Complexation and EDTA Titration :

When a metal ion forms a complex with a ligand its potential can be determined by using proper indicator electrode. Generally an electrode of the metal whose ion is involved in complex formation is used.

Advantages of Potentiometric Titration :

- 1) The apparatus used is inexpensive and readily available.
- 2) It is useful for analysis of dilute solution.
- 3) This method is also applicable for colored solution.
- 4) It is easy to determine the end point by interoperating the titration curves.
- 5) Various components can be titrated in the same solution without possibility of different indicator interfering with each other.

2.CONDUCTOMETRIC TITRATION :

Introduction :

Conductometric titration are based on measurement of conductance of ions in a solution. The conductance is due to migration of ions. Conduction involves migration of positively charged ions towards cathode and negatively charged ions towards anode. The movement of ions occurs in such a way that the solution remains neutral throughout. So in Conductometric titration end point of a particular titration is detected by measuring through the conductance of solution. Conductance which is due to mobility of an ion depends upon many factors like charge, size, mass and degree of solvation of an ion. Conductometric titration are used in direct and indirect method of physiochemical analysis. It is mainly used in complexometric, acid-base and precipitation titration. It is also useful in calculating rate constant. The colored solution where an indicator has been found to be useful, end point can be detected easily by this method.

Advantages :

- 1) It is used for titration of mixture of weak and strong acids.
- 2) It can be used for titration of very dilute solution.
- 3) End point determined graphically so accurate results are obtained
- 4) It is useful for titration of weak acid with weak base (which do not give sharp colour change with indicator) as end point is detected by this method.
- 5) where no indicator gives satisfactory end point, solution can be titrated conductometrically

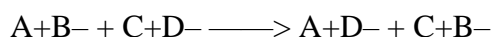
Limitations :

This method becomes less accurate as total electrolyte concentration increase. Also, the change in conductance gets masked by high salt concentration in the solution.

Principle :

Each cation and anion has different degree of ionic mobility (conductance). So when a solution of one electrolyte is added (titrant) to a solution of another electrolyte the overall conductance will depend upon whether a reaction occur b/w them or not. If no chemical reaction occurs then overall conductance of a solution will increase and each ion contribute to conductance of solution.

When a chemical reaction occurs replacement or substitution of ions takes place which decides that conductance will either increase or decrease. Conductometric titration is based on the principle of substitution of one ions of particular conductance by the ions different conductance.



Change in conductance depend upon mobility of C^+ ion. In Conductometric titration, titrant is added in small amount and after each addition of titration conductivity of the solution is measured. The graph is plotted b/w amount of titrant added and conductance of solution. The graph consists of two straight lines intersecting at a point known as equivalent points (end point). For e.g. when a solution of NaOH is added to solution of HCL, the highly mobile H^+ ions gets replaced with that of sodium ions with low mobility and the overall conductance of solution gets decreased.

Types of Conductometric titration :

(A) Acid base titration :

It can be classified into following types -

1) Titration of strong acid with strong base :-

For e.g. titration of HCL with NaOH. Initially there is replacement of highly mobile hydrogen ions with low mobility sodium ions so there is fall in conductance. After end point conductance gets increased due to excess of OH⁻ ions being by NaOH.

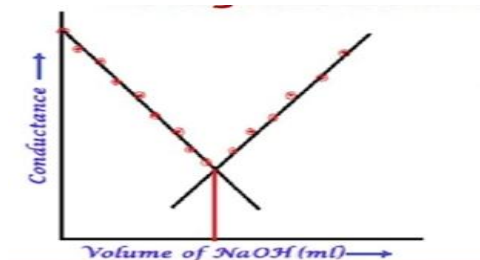


Fig. Titration of strong acid with strong base

2) Titration of strong acid with weak base :-

For e.g. titration of HCL with dil. NH₃ solution. Initially there is fall in conductance due to neutralization of H⁺ ions while at the end point graph became horizontal straight lines because ionization of NH₃ does not occur in presence of ammonium chloride which is formed during titration.

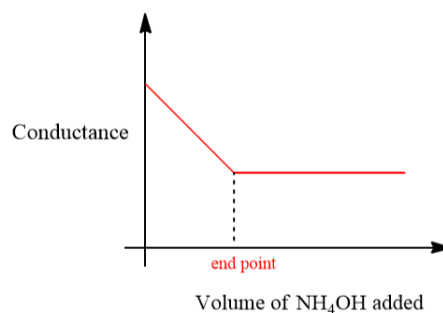


Fig. Titration of strong acid with weak base

3) Titration of weak acid with strong base :-

For e.g. titration of weak acetic acid with strong base like NaOH, initially the conductivity decreases and then there is increases in conductance with further additional of NaOH. After neutralization further additional of NaOH produces excess of OH⁻ as a result of this the conductance of the solution starts rising rapidly.

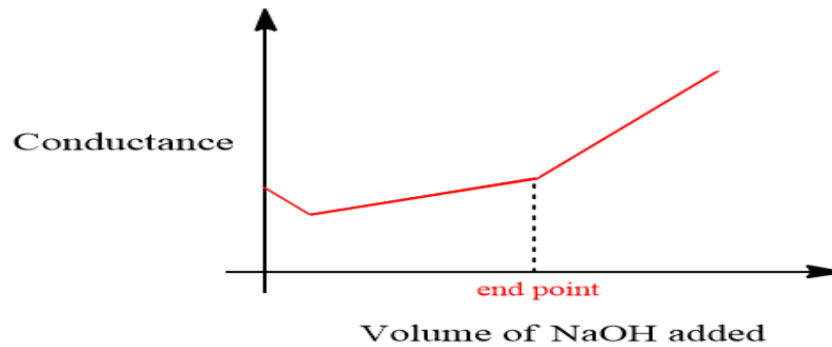


Fig. Titration of weak acid with strong base

4) Weak acid with weak base :-

For e.g. titration of acetic acid with weak base (aq.NH₃). The conductivity depends upon degree of ionization and concentration before end point. Conductance decrease as the anion formed suppresses the ionization. It reaches minimum value and then increase upto the end point. Conductance increase due to formation of salt of weak acid. After end point extra amount of ammonia solution has no effect on the conductance. This is due to suppression of ionization of ammonia by the Salt from during titration.

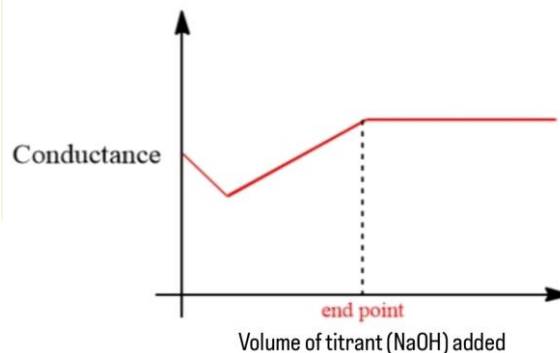


Fig. Titration weak acid with weak base

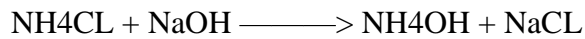
B) Replacement titration :

Titration of strong acid with sodium or potassium salt of acid causes replacement of weaker acid e.g Titration of acetic acid with HCL.



There is initial increase in conductance due to slightly greater ionic mobility of Cl⁻ ions than that of acetic ions. After end point conductance increase more rapidly due to addition of excess of HCL. The end

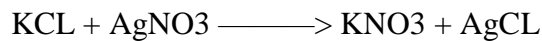
point can be determined by the information of two lines. Another example of titration is salt of weak base ammonium chloride with strong base NaOH.



The replacement titration are mainly useful in determining of alkaloids as alkaloids are weak base and insoluble in water.

C) precipitation titration :

The precipitation titration dose not involve H^+ and OH^- ions. So cannot be carried out much effectively as the acid base titration. In precipitation titration one pair of ions gets substituted for another. If a cation is to be precipitated, a titrant whose cation has less mobility is selected for e.g. titration of silver nitrate with KCl.



Initially with additional of AgNO_3 there is no change in conductance because Cl^- ions are replaced by nitrate ions and both have same ionic conductance but after and point excess of AgNO_3 causes a sudden increase in conductance.

D) Redox titration :

This is the only type of titration whose end point cannot be detected by the help of Conductometric titration. As Conductometric titration involves change in conductance but in redox titration large amount of acid or base are required for completion of a reaction hence does not cause much change in conductance. For this reason titration cannot be performed by using Conductometric titration.

Instrumentation :

There are two main components for measurement of conductance of an electrolytic solution.

1) Conductivity cell :

The solution whose conductance is to be measured is taken in a cell known as conductivity cell. These are generally made up of high quality glass (Pyrex), Quartz and sometime fitted with platinum electrodes. The electrodes usually consist of platinum sealed into glass tubes. Electrodes of the conductivity cell are connected to circuit by means of mercury placed in the tubes. There are different forms of conductivity cells. Some common types are—

- a) It consists of wide mouth bottle with cork having holes for passing two platinum wires. It is generally useful for low conductance measurements.
- b) It is helpful for measuring the conductance of precipitation type of reaction. It consists of electrodes which are fixed in the lid which is having opening for the stirrer and the burette. Electrodes are firmly fixed and the faces of electrodes plates are vertical and parallel.
- c) It consists of a wide bore glass tube, the tip of which has two platinum plates. Glass tube contains two fixed copper wire, the terminals of which are taken out for connection. Platinum plates are coated with platinum black to reduce polarization effect. For determining the cell constant, cell is placed in a standard solution of specific conductance at 25°C and resistance is measured. KCl solution (1M, 0.1M or 0.001M) is used as standard solution for determination of cell constant.

Electrodes :

These are generally up of two parallel sheets of platinum foil. These positions are fixed by sealing the connected tubes into the side of Conductivity cell. The electrodes are coated with platinum black to reduce polarization effect. Platinisation is done by using 3% solution of chloroplastic acid and 0.03% of lead acetate solution

Conductivity water:

It is generally used for preparing the whose conductance is to be measured. Ordinary distilled water is not used because it contains dissolved CO₂ and traces of other gases. So pure water used is known as conductance water. Pure conductance is prepared by distilled water containing and water is collected in a receiver fitted with soda lime tube.

2) Conductometer :

The apparatus used for conductance measurement is a form of wheat stone bridge also known as conductivity bridge. It is made by using wheat stone bridge circuit having four arms. Cell is placed in one arm and resistance constitutes the second arm. The other two arms are in the form of calibrated slide wire resistor. The detector used may be a galvanometer or ear phone or magic eye calibrated digital display. An alternating current of frequency 50-60 Hz is used in the circuit. A calibrate switch is there to calibrate the desired value of conductance. In order to determine the conductance, the conductivity cell is dipped into the solution and the terminals are connected to the conductivity bright. The selector switch is set to the proper conductance range and reading is recorded from galvanometer.

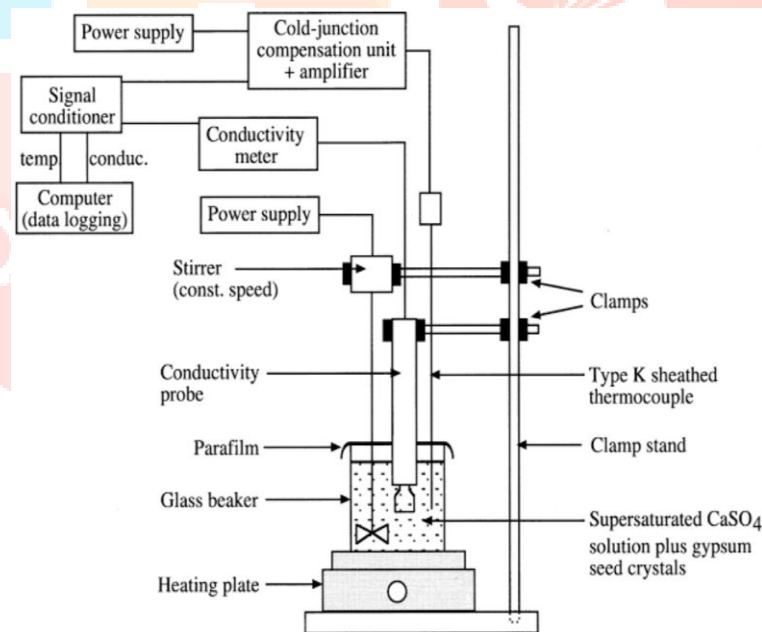


Fig. Conductometer

Application :**1) Determination of ionic product of water :-**

The product of ionic concentration of H^+ and OH^+ in gm moles per litre is constant at a constant temp. Is known as ionic product of water. The ionic product of water can be calculated by knowing the specific and equivalent conductance at infinite dilution i.e.

$$\lambda_a = K_a/C \times 100$$

Here K_a = specific conductance at infinite dilution

C = concentration (gm eq./ liter)

2) Determination of solubility of sparingly soluble salt :

Substance like $AgCl$, $BaSO_4$ etc. are regarded as sparingly soluble in water and their solubility cannot be determined easily by other chemical methods. Conductometric titration helps in determining the solubility of these sparingly soluble salt.

The saturated solution of these salt may be regarded as completely ionized. As small amount of salt of present in the solution gets completely dissociated so value of amount of salt present in the solution gets completely dissociated so value of

$$\lambda_v = \lambda_\infty \text{ (equivalent conductance at infinite dilution)}$$

$$\text{so, } \lambda_v = \lambda_\infty = kV \times V$$

V = volume containing one gm equivalent of solute.

According to Kohlrausch's law

$$\lambda_\infty = \lambda_\infty(\text{cation}) + \lambda_\infty(\text{anion})$$

By knowing the value of λ_∞ and K_v (specific conductance) the volume can be determined and from this solubility (S) can be calculated.

$$S = 1000 / V \times E$$

$$S = 100 \times E \times kV / \lambda_\infty$$

$$\text{Because } V = \lambda_\infty / K_v$$

3) Determination of basicity of an organic acid :-

According to Ostwald, basicity of an acid can be by-

$$\beta = \lambda_{1024} = \lambda_{32} / 10.8$$

Where λ_{1024} and λ_{32} = equivalent conductivities of sod. Salt of acid at dilution of 1024 ltrs and 32 ltrs/ gm. equivalent respectively.

4) kinetic studies :-

Rate of a reaction can be calculated with help of Conductometric titration. It is based on measurement of Conductivity before, during and at end of chemical reaction.

5) Determination of degree of dissociation of weak electrolytes :-

Determination of degree of dissociation of weak electrolytes can be calculated from equivalent conductance at infinite dilution i.e.

$$\alpha = \Lambda_v / \Lambda_\alpha$$

Λ_v = Equivalent conductance at dilution V.

Λ_α = Equivalent conductance at infinite dilution.

6) Determination of concentration :-

A series of dilution with known concentration of electrolyte is prepared and their conductivities are then electrolyte. Then the plotted b/w unknown solution is determined and its concentration is calculated by using calibration curve.

3. POLAROGRAPHY :

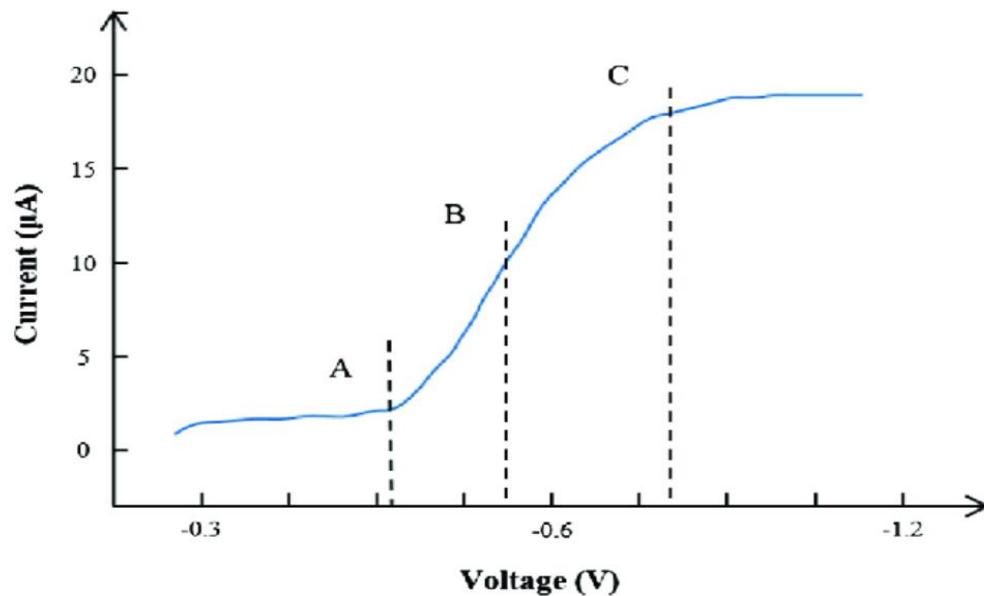
Introduction :

INTRODUCTION :- polarography is a branch of voltammetry in which relationship between current and voltage is obtained by using an electrolytic cell. Polarographic method was developed by Azech curves in which one of the electrode is dropping mercury electrode (DME). Current voltage curve are useful for determining the identity or concentration of a species reacting at DME. Basic idea of polarography is to pass the current between two electrodes, one large in area while other is very small.

Polar graphy is define as an instrumental technique which consist of measurement potential difference as current flows through the solution and the instrument used is known as polarography.

Principle :

This method is based upon the study of current voltage relationship. It consist of two electrode both are made up of Mercury. One electrode is larger in area then other. The larger elected is pole of Mercury and act as a reference electrode. The small electrode is a dropping Mercury electron (DME) that is drop of Mercury coming out of a fine capillary tube. This electrodes act as an indicator electrode. So DME is use as an indicator electrode. The reaction occur at it surface and also known as cathode while pole of Mercury act as anode. DME consider to be polarized electrode and once a chemical reaction has occurred on it surface, it become depolarization. Large pole of Mercury act as reference electrode and is incapable of polarization. It is also known as nonpolarible electrode. When a steady increasing voltage is applied across the cell, it is possible to obtain current voltage graph. The nature of graph helps in determining the nature and amount of material present in the solution.



For example, when to a solution containing leads ions in 1M KCL (supporting electrolyte) voltage is applied the positivity charged lead ions will we attracted to DME by an electrical force and a diffusion force due to concentration gradient formed at the surface of the electrode current start flowing through the cell. The applied voltage is increased with the time and the current produce is recorded. A graph is plotted between applied voltage and current produce. The concentration of sample solution can be calculated from Ilkovic equation -- $I_d = 607 n D^{1/2} c m^{2/3} t^{1/6}$.

Where ,

I_d =diffusion current in microampere .

n = no. of electron transferred .

c = concentration in mmol/litre .

D = diffusion coefficient in $\text{cm}^2\text{sec}^{-1}$

m = mass of Mercury drop flowing per sec. In mg.

t = drop time in second

Apparatus :

Polarographic apparatus consists of two main parts -

1. Polarographic cell
2. Electrical instrument

1) Polarographic Cell :-

It is of various type. The simple form consist of a beaker of glass with a lid.

A large pole of Mercury is placed at the bottom of beaker and connected electrically. This pool of Mercury at as a reference electrode or an anode terminal. This elected has large area so it does not polarized. The lead of the beaker has opening tube for passing nitrogen gas and tip of the dropping Mercury electro (DME).

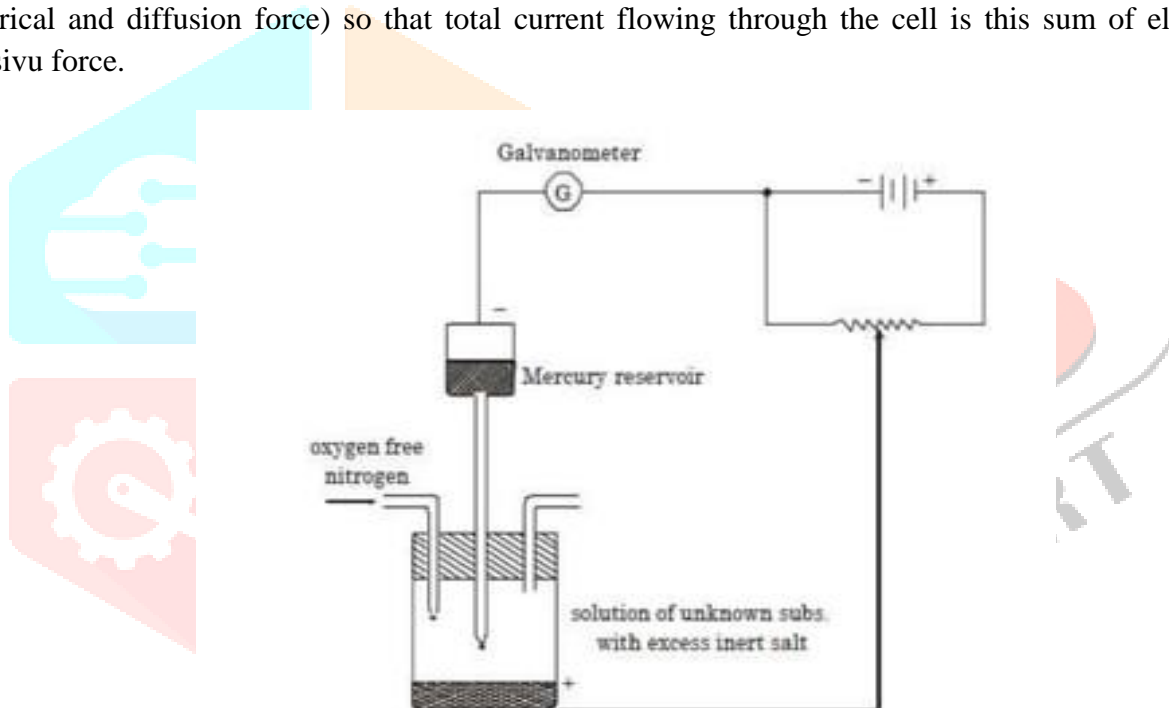
The DME consist of dropping funnel containing Mercury reservoir through which Mercury came out as a small dropped capillary. The length of capillary tube is about 5 to 10 cm and it is made up of glass. The tip of capillary is cut fine and horizontal. DME is adjust in such a way that it produce Mercury drop of weight about 6 – 10 mg in a time of 3-6 seconds. The DME is fitted on a heavy platform which is free from any vibration. DME act as a cathode and is known as indicator or microelectrod.

2) Electrical Instrument :-

This part consist of a battery which provide standard power supply , a variable potentiometer, EMF indicating voltmeter and a galvanometer which measure current. Both cathode and anode are connected across the end of battery. The applied voltage can be changed time to time. Potentiometer slide wire helps in charging applied potential. The current flowing through the cell is measured by the glavenometer. Air present in the cell must be removed by passing and inert gas like nitrogen before determination.

Working :

Let us consider a polarographic cell containing a solution cadmium chloride to which an external EMF is applied. The positively charge ions will migrated towards the indicator or microelectrod by two (electrical and diffusion force) so that total current flowing through the cell is this sum of electrical and diffusivu force.



And applied voltage is increased, the current is recorded and graph will be obtained. The graph obtained is known as polarographic wave.

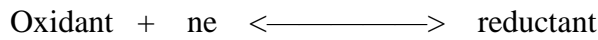
Initially there is very small rise in current from A to B and is known as residual current and it is due to supporting electrolytes and impurities present in the sample. Residuel current is the sum of faradic current (i) and condenser current (i) . The faradic current is due to reducible impurities present in the sample while condenser current is due to charge of each drop of Mercury.

At point B elected potential become equal to the decomposition potential of cadmium ions. So at this point the current increase very fast up to point C and at this point it is known as limiting current. Beyond this there is no increase in current. At point D all the current is electroreducible current.

At point E the voltage is known as half wave potential ($E_{1/2}$). At the point the concentration of oxidised and the reduced forms at electrode surface became equal. Half wave potential ($E_{1/2}$).

This potential is the one half of the distance between the residual and limiting current. It is found on steeply rising portion of the current voltage curve. Half wave potential is at a point on a polarographic wave where

the current is one half of diffusion current for a given substance. For example, the reversible reduction of an oxidant at DME is given as below,



APPLICATIONS :

- The two major applications of polarography qualitative analysis and quantitative analysis.

1] QUALITATIVE ANALYSIS :

- Auantitative identification of a given sample can be done from half wave potential of the current vs voltage graph. The value of half wave potential is directly related to standard potential for redox reaction under study. This method is useful for environmental analysis and the Marine study. Qualitative analysis also help in characterization of organic matter and various metal interactions

2] QUANTITATIVE ANALYSIS :

- Olarography is useful in determining the concentration of drugs, metal ions etc. In the given sample. Concentration of particular substance can be calculated from Ilkovic equation as

$$I_d = 607 n D^{1/2} c m^{2/3} t^{1/6}$$

There are various method by which quantitative estimation can be done.

a) Direct comparison method :-

— In this the diffusion current of standard solution of an ion is compared with that of unknown sample and then by using Ilkovic equation the diffusion current quotient i.e I_d/C is calculated.

b) standard curve method :-

— In this various concentration of the standard solution are prepared and their diffusion currents are calculated. Then a plot of diffusion current vs concentration is plotted. Unknown sample solution is prepared, its diffusion current is measured and with the help of plot concentration of unknown solution can be calculated easily.

c) internal standard method :-

— This method is best on the fact that relative diffusion current does not depend upon the capillary properties. In this method for standard substance i.e . Internal standard is added to each solution (sample and standard solution) and the ratio of i_{dl} / i_{dl} is calculated. This ratio is known as pilot ion ratio. The pilot ion ratio of the standard ions and the test ions are calculated and from this the concentration of unknown test solution can be determined.

d) standard addition method :-

—In this method polarogram of unknown solution of known volume is recorded and to this known quantity of standard substance is added and the second polarogram is recorded. The concentration of unknown solution can be determine from the increase in diffusion current.

3] OTHER APPLICATIONS :-

a) determination of inorganic compounds :-

Polarograph is useful in determination of cation and anion in the presence of other interfering ions. For example determination of bromates, iodate, nitrate etc . Polarogram of this substance gets affected by pH of the solution so buffers are used.

b) determination of organic compound :-

Polarography is helpful in determination of structure, quantitative identification of compound and for the quantitative analysis of mixture of organic compounds. Estimation of sugars can also be carried out with the help of polarography. The composition of the given metal complex can be easily studied.

c) Estimation of dissolved oxygen :-

Amount of oxygen dissolved in aqueous solution or organic solvent can be calculated with the help of polarography. In this method oxygen wave are measured and the amount of dissolved oxygen can be calculated. Dissolved oxygen produce reaction waves.

d) pharmaceutical applications :-

Drugs like acetazolamide, chlormphenicol, epinephrine etc can be analyzed by this method. Sulphonamides can we determined in the solution of tetraalkylammonium salts. Tetracycline can also we determined polarographically. Analgesics and antipyretics can be calculated in nitrate solution after diluting with a buffer solution with the help of polarography.

4 . AMPEROMETRY :

INTRODUCTION :-

Amperometry is useful in determination of ions and drugs upto 10^{-4} M concentration. Principle of polarography and amperometric titrations are same. This method is comparable with other method like potentiometry , conductometry etc . This method is more accurate than polarography because result obtained because not depend upon the characteristic of the capillary and this supporting electrolytes.

In amperometric titration, the voltage applied across the two electrodes kept constant and the current passing through the cell is measured and plotted against the volume of titration added.

PRINCIPLE :-

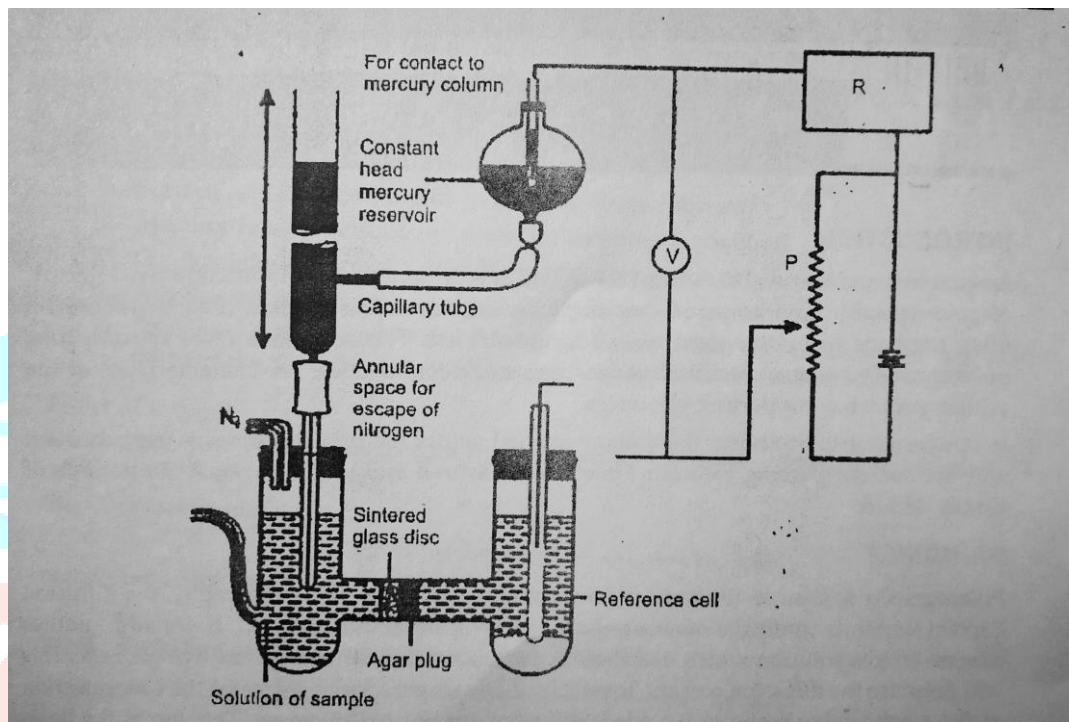
Polarography is used as the basis of amperometric titration. Polarography, the diffusion current depend upon the concentration of the electroactive material. If we added another reagent to the solution which decrease the concentration of the electroactive materials, this will decrease the diffusion current. Inversely , any agent which increase the concentration of electro active material is added ,diffusion current will increase. This form the basis of amperometric titration.

The measurement of diffusion current as a function of volume of titration added at applied voltage is the principle of amperometric titration full stop a graph is plotted between diffusion current and ml of titration added. It consist of two line. The point where the two lines intersect given equivalence point.

INSTRUMENTATION :-

The basic assembly is almost same as that polarographic cell. Some suitable modification are also made, if required.

It consists of glass beaker with a glass lid with opening for a tip of beuret , dropping Mercury electrodes (DME) and gas vent to pass through. A pool of mercury is also placed at the bottom of the beaker. This act as a reference electrode while DME act as indicator electrodes. Terminals of the to electrodes are connected to -ve and +ve ends on a battery. Slide wire potentiometer and glovanometer is also placed into the circuit. Calomel electrodes can also be used as reference electrodes. The voltage applied across the indicators electrodes and reference electrodes kept constant. Galvanometer measured the diffusion current after each addition of the titration.



Sometimes, instead of DME, rotating platinum microelectrodes can be used. It has following advantages—

- 1) it can be used at +ve potential where DME cannot be used.
- 2) it is easy to construct and handle.
- 3) it gives better result as rotation of platinum electrodes increase with increase in diffusion current.

Removal of oxygen is necessary in amperometric titrations. Oxygen is removed by passing pure nitrogen before the titration for about 2 minute.

PROCESS OF AMPEROMETRIC TITRATION :

Amperometric titrations are done by using DME or rotating platinum electrodes. The solution to be titrated is placed in the titration vessel. The capillary of DME is immersed in the solution. The indicator electrodes and reference electrodes are connected by a galvanometer. Beurette containing titrate is also introduced into the solution. Magnetic stirrer is also used. If rotating electrode is used there is no need of stirrer as electrode itself acts as a stirrer. Nitrogen is passed through the solution to remove any oxygen present in it.

A suitable potential is applied to the electrodes by means of battery. After each addition of the titration, diffusion current is measured by the galvanometer. The current intensity is then plotted against the volume of titration added. The end point is obtained from the intersection of two lines on the graph.

ADVANTAGES OF AMPEROMETRIC TITRATION :

Various type of amperometric titration curve are as follows —

- 1) It has higher accuracy than polarography.
- 2) It does not depend upon the capillary characteristics of the DME.
- 3) It is easy to handle and carry out.
- 4) Amperometry is not affected by the presence of other electrolytes and foreign salts.
- 5) Dilute solution can be titrated easily with great accuracy.
- 6) Depolarizing substance can be easily determined by the method.
- 7) It is not necessary to maintain constant current during the titration.

DISADVANTAGE OF AMPEROMETRIC TITRATION :

- 1) Due to co precipitation result of are not accurate.
- 2) Constant applied potential is required all the time.

PHARMACEUTICAL APPLICATION OF AMPEROMETRIC TITRATION :-

- a) Many metal ions reducible at a particular applied voltage can be titrated by this method by using non-reducible titration.
- b) Mixture of ions like iodine, bromide, chloride can be titrated with silver nitrate by using amperometry.
- c) Various anions can be titrated easily by using metal ions solution as the titrant. For example, determination of lead against the dichromate, zinc against EDTA etc.
- d) Collage number of inorganic chemicals as well as organic pharmaceutical drugs can be analysed by amperometry. Some of the examples are -
 - i) Thiourea in 1M sulphuric acid by using silver nitrate as titrant.
 - ii) Vitamin C dissolved in water and then titrated with ferric nitrate.
 - iii) Phenobarbitone first dissolved in ethanol-water mixture and then titrated with mercuric acetate in acetic acid.
 - iv) Strychnine and cocaine can be titrated with silicotungstic acid using 0.3N hydrochloric acid as a medium.

Acknowledgement :

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