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Review Article

POTENTIOMETRY- ARTICLE REVIEW**E.Nagadeepthi* , B.Venkataramana, K. Sai Sangeetha, U.Manjula , P. Bhargavi**
Dr.K.V.subbareddy Institute of Pharmacy. Kurnool**Abstract:**

Potentiometry is a method used to determine the potential differences between a reference electrode (Sakshi electrode pvt. Ltd) and an indicator electrode (Schutz carbon electrodes pvt. Ltd) which form the electro chemical cell that are dipped in solution to be analysed. The potentiometer (Spectralab instruments pvt. Ltd) Potentiometric probes were used in direct potentiometry as attractive sensing tools. Potentiometric titrations are the methods used for the determination of the end points via first derivative, second derivative and third derivative methods. These methods are precise and robust. Measured potential can be used to determine the quantity of analyte in terms of concentration. Theoretical simulations and experimental results support the validity of this approach.

Keywords: Electrolyte solution, electrode potential, glass electrode, derivative curves.

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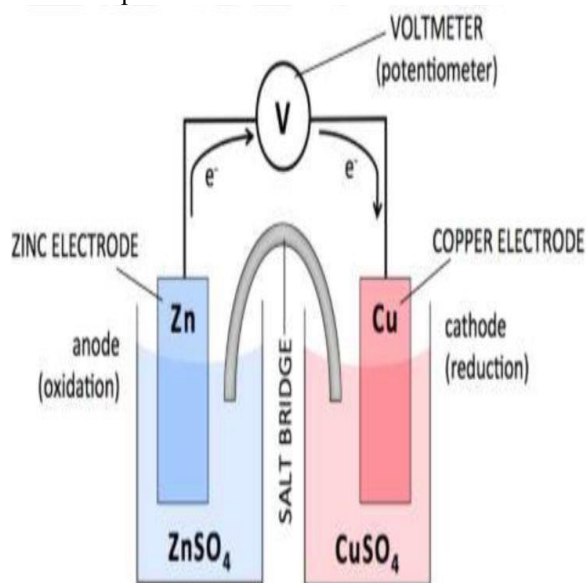
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INTRODUCTION:

Potentiometry is a classical analytical technique with roots before the 20th century. It is based on the measurement of potential of an electrode system. In the presence of multitude of other substances, it enables the selective detection of ions. It is one of the electrochemical analytical methods. An electric circuit is used to measure the current and potential created by the flow of charged particles. For complete electrochemical cell from which the negligible current is drawn the EMF is given by:

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

where, E_{ind} , E_{ref} and E_j are the potentials of the indicator electrode, reference electrode and liquid junction potential respectively. The potentiometric methods include two major types of an analysis. One is direct measurement which involves the direct measurement of an electrode potential from which the activity of an active ion may be derived. Other kind is indirect potentiometric method which measures the variation in EMF brought by the addition of a titration of the sample.



Description of charge transfer process is as follows:

1. Movement of electrons from zinc electrode to copper electrode.
2. In the solution zinc ions move away from the electrode and sulphate ions move towards the electrode.
3. Positive ions move towards right and negative towards left in salt bridge.
4. On the surface of electrodes electrons are transferred to ions.

5. Zinc dissolves and metallic copper deposits is seen.

FUNDAMENTALS OF POTENTIOMETRY:

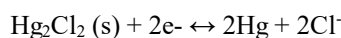
The electrode potential is developed and given by Nernst equation. Whenever metal ion immersed in a solution containing its own ions M^{n+} .

$$E = E^\circ + \frac{RT}{nF} \ln a_{M^{n+}}$$

The value of an electrode potential E can be established by linking the calomel electrode and measuring the EMF of the resultant cell. It can be deduced from the reference electrode. It is also possible to measure the potential directly via direct potentiometer. This involves the use of an electrode of second kind. For example, Ag-AgCl electrode formed by coating a silver wire with AgCl. This measures the concentration of chloride ion in the solution. The basic functions of potentiometer are as follows:

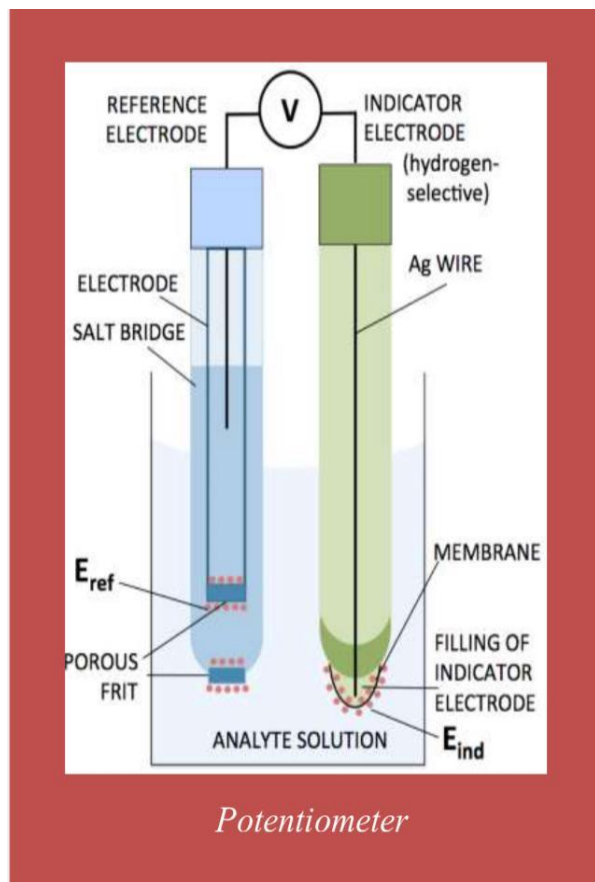
- To measure the electric potential or voltage.
- By rotating the potentiometer wheel, we are changing the voltage applied to the resistor, which results in light coming out from the LED.
- To control electrical devices such as volume controls on audio equipment.
- It works as a rheostat and provides varying resistance depending on the flow.

Furthermore, the requirements and methodologies used to accomplish the analysis are modified day by day by the researchers working in this field to improve the routine analytical methods. The equipment required for direct potentiometric measurements includes an ion-selective electrode, a reference electrode, and a potential-measuring device. The ion-selective electrode is an indicator electrode capable of selectively measuring the activity of a particular ionic species. Ion-selective electrodes are mainly membrane-based devices, consisting of selective ion-conducting materials, which separate the sample from the inside of the electrode. It is necessary to select an appropriate electrode both indicator and reference depending on chemically reacting components in various titrations. Reference electrode is the electrode with a potential which is independent of concentration and temperature. It must be reversible and obeys the Nernst equation. It gives the stable potential with time and always returns to its original position after the passage. The common reference electrode used in potentiometer is calomel electrode $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (satd), KCl (xM) and the half-cell reaction is as follows:



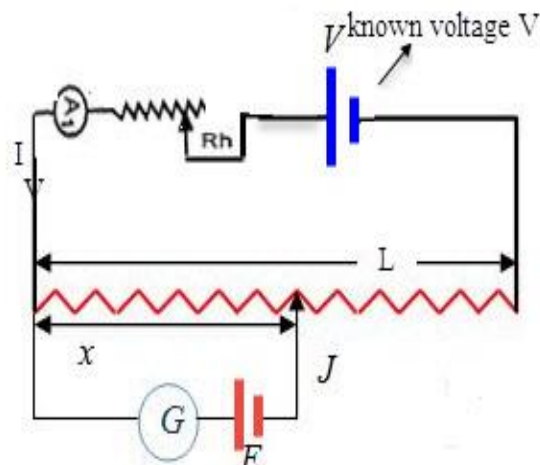
A reference electrode, E_{ref} , is a half-cell having a known potential that remains constant at constant

temperature and independent of the composition of the analyte solution. Another is an indicator electrode having a potential that varies with variations in the concentration of an analyte. Metallic indicator electrode and membrane electrodes are types of indicator electrodes.



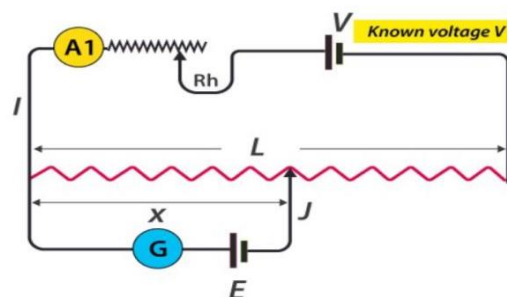
CONSTRUCTION OF POTENTIOMETRY:

A potentiometer consists of a resistive element and a sliding contact. The sliding contact is known as the wiper and is used to vary the resistance offered by the potentiometer. The internal circuitry of a potentiometer comprises of a constantan (a copper-nickel alloy) or manganin (an alloy of copper, manganese, and nickel) wire and a metre rod. One end of the wire is connected to a switch called a tapping key, which is further connected to a rheostat. A driving voltage source is connected between the rheostat and an ammeter. The voltage source is responsible to maintain a constant flow of current in the circuit, while the ammeter functions to monitor this value of the current. The second terminal of the ammeter is connected to the other end of the constantan or manganin wire, thereby completing the circuit of a potentiometer.



WORKING PRINCIPLE OF POTENTIOMETRY:

A potentiometer basically works on the principle of varying the resistance of a fixed resistor by moving the sliding/rotary contact or the wiper. By displacing the position of the wiper, the length of the resistive constantan or manganin wire is altered. This change in the length of the wire is proportional to the change in the resistance offered to the circuit. Also, the resistance is inversely proportional to the cross-sectional area of the wire; however, it is difficult to vary the cross-section of a wire. Hence, the cross-sectional area of the wire and the current flowing in the circuit is maintained constant and the length of the resistive wire is made variable. In a potentiometer, input is applied across the fixed terminals, whereas the output is noted between the movable and a fixed terminal. The potentiometer consists of L which is a long resistive wire and a battery of known EMF V whose voltage is known as driver cell voltage. Assume a primary circuit arrangement by connecting the two ends of L to the battery terminals. One end of the primary circuit is connected to the cell whose EMF E is to be measured and the other end is connected to galvanometer G . This circuit is assumed to be a secondary circuit.



The working principle depends on the potential across any portion of the wire which is directly proportional

to the length of the wire that has a uniform cross-sectional area and current flow is constant. Following is the derivation of used to explain the potentiometer working principle:

$$V=IR \text{ (Ohm's law)}$$

Where as,

I: current

R: total resistance

V: voltage

POTENTIOMETER:

It is an instrument for "Measuring the potential or Emf of a solution by using the set of Indicator electrode and reference electrode".

ELECTRODES:

The electrode is defined as an electrical conductor that carries electric current to the non-metallic circuit parts of a circuit, such as an electrolyte, semiconductor, or vacuum. The word electrode is derived from two Greek words: electron, which means "amber"; and hodos, which means "a way". So, the word electrode refers to a path for electricity to travel. Since metals are excellent conductors of electricity, they are used in the manufacturing of electrodes.

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

➤ REFERENCE ELECTRODE:

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

Ex: Standard hydrogen electrode,
Saturated calomel electrode, and
Silver - silver chloride electrode.

The REFERENCE ELECTRODE is classified into two main classes they are as follows.

Primary standard electrode.

Ex: Standard hydrogen electrode.

secondary standard electrodes.

Ex: Standard calomel electrode, and
Silver- silver chloride electrode.

➤ INDICATOR ELECTRODE:

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

Ex: Hydrogen electrode,

Glass electrode, and

Antimony- antimony oxide electrode.

These are two classes of indicator electrode.

- Metal indicator electrode,
- Ion – selective electrode.

Metal indicator electrode:

These develop electric potential in response to redox reaction on the metal surface. Platinum or Au is used as metal indicator electrodes. These are mainly classified into three types of 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.

Ex: silver electrode dipped in the silver nitrate solution.

copper electrode dipped in the copper sulphate solution.

• Second kind electrode:

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.

Ex: Ag/ AgCl/ KCl
Hg/ Hg₂Cl₂/ KCl

• 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.

Ex: Pt-H² electrode.

Ion selective indicator:

These are composed of ion-selective membrane by which the ion crosses and it creates the imbalance.

Ex: glass membrane electrode,
Antimony -antimony oxide electrode.

S.NO	DRUGS	TITRANT	INDICATOR ELECTRODE	REFERENCE ELECTRODE
1	Amoxicillin sodium	Mercuric nitrate	Pt/Hg	Hg-mercurous sulphate
2	Acebutalol HCl	NaOH	Glass	SCE/Ag-AgCl
3	Dextromorphan HCl	NaOH	Glass	SCE/Ag-AgCl
4	DiphenoxylateHCl	Ethanolic NaOH	Glass	SCE/Ag-AgCl
5	Disulfiram	Ag ₂ NO ₃	Silver	SCE
6	Hydralazine HCl	Potassium iodate	platinum	SCE
7	Lomustine	silvernitate	silver	Calomel
8	Metoclopramide HCl	NaOH	Glass	SCE
9	Naldixic acid	Ethanolic sodium of hydroxide	Glass	Ag-AgCl
10	Phenobarbitone sodium	NaOH	Glass	SCE
11	Promithazine HCl	NaOH	Glass	SCE
12	propranalololHCl	NaOH	Glass	SCE
13	Sodium stibogluconate injection	Ferric ammonium sulphate	pt	Ag-AgCl

INSTRUMENTATION

The measurements of potential are generally employed from the non-electronic, electronic, and automatic instruments. Every kind of potentiometric measurement requires a suitable galvanic cell consisting of an indicator electrode and a stable reference electrode. The reference electrode may be immersed directly in the sample solution or brought in contact with it through a salt bridge. The type of an indicator electrodes is either noble metal ions or ion selective electrodes. The commonly used electrodes systems in potentiometry are described as follows:

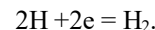
REFERENCE ELECTRODE:

- Standard Hydrogen Electrode,
- Saturated Calomel Electrode, and
- Silver-Silver Chloride Electrode.

STANDARD HYDROGEN ELECTRODE (SHE):

The standard hydrogen electrode (SHE) is the universally accepted reference electrode. The metal electrode has a small piece of platinum foil with finely divided platinum, usually termed as platinum black because of its dark look. The coated foil is immersed in an acidic medium having concentration of 0.1N, and through which H₂ gas is bubbled. The Pt-black-foil possesses a relatively large-surface-area thereby allowing it to absorb an appreciable amount of H₂ gas, ultimately bringing it into direct contact with the surrounding H⁺ ions at the electrode surface.

The half-cell reaction may occur in either direction depending upon the type of electrode which is coupled with it.



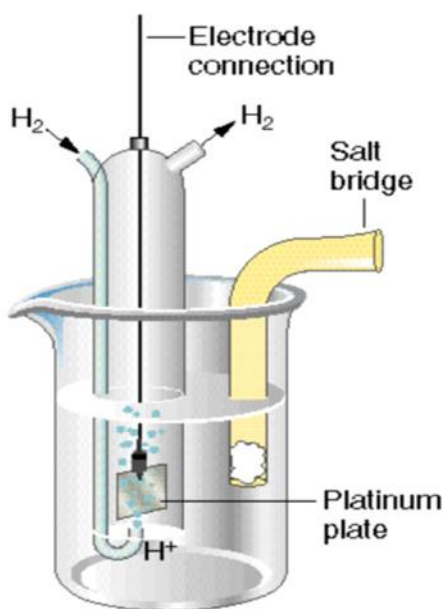


Fig. Standard Hydrogen Electrode

CONSTRUCTION:

The Standard Hydrogen Electrode is made of the following parts:

- 1) Platinized platinum electrode: it's made of a mesh which is attached to a platinum rod and the mesh is itself platinized nothing but coated with platinum black, hence giving a platinized platinum electrode.
- 2) Hydrogen blow: A small provision is made into the electrode system through which a hydrogen gas is allowed to enter in it which reacts with platinized platinum electrode during the working of electrode system, to improve the reaction kinetics.
- 3) Solution of the acid with activity of $H^+ = 1 \text{ mol dm}^{-3}$: An acidic solution is filled inside a glass cylindrical system of acidity/ H^+ ion concentration is one mole per decimetre cube. nothing but 1 M HCl.
- 4) Hydro seal for prevention of the oxygen interference
- 5) Reservoir through which the second half-element of the galvanic cell should be attached. The connection can be direct, through a narrow tube to reduce mixing, or through a salt bridge, depending on the other electrode and solution. This creates an ionically conductive path to the working electrode of interest.

WORKING:

This is a gas electrode. It consists of a thin rectangular platinum foil which is coated with fresh platinum black to increase the adsorption capacity of the metal. This is welded and the end of it is fused into the inner tube through the base. In the inner tube, little mercury is taken, and a Cu wire is introduced to make the external electrical contact. The inner tube is enclosed in an outer jacket having an inlet tube for sending in H_2 gas and has a perforated wider base for the escape of excess of H_2 . This unit is dipped in HCl taken in a beaker such that the metal foil remains in the solution. When pure and dry H_2 gas is passed through the inlet tube, a part of the gas gets adsorbed and the excess bubbles out through the perforations. Between the H_2 gas absorbed on the surface of the metal and H^+ of the solution, an equilibrium is established, and electrical double layer of opposite charges is formed. The potential developed is called H_2 electrode potential.

In the above system, when the H_2 gas at a pressure of 1 atm (1 bar) is bubbled through 1M HCl, the electrode (constructed) or formed is called STANDARD HYDROGEN

ELECTRODE (SHE) or Normal H_2 electrode (NHE).

This is represented as $Pt, H_2 / H^+(760 \text{ mm of Hg})$

The standard H_2 electrode potential is defined as the potential that is developed between the H_2 gas adsorbed on the pt metal and H^+ of the solution when the H_2 gas at a pressure of 760 mm of Hg is in equilibrium with H^+ of unit concentration.

The magnitude of SHE potential is zero. It is used-

- 1) For the determination of electrode potential of metal electrode system.
- 2) For the determination of pH of the solution.

ADVANTAGES:

- It can be used over the entire ph.
- It can be used as a reference electrode when dipped with standard acid solution and as an indicator electrode when dipped into a sample solution.
- It is the primary reference standard against which the potentials of other electrodes are measured.

DISADVANTAGES:

- It is affected by the presence of oxidizing agent and reducing agent.
- It is rather difficult to regulate the pressure of H_2 gas to be exactly 1 ATM throughout the experiment.
- Platinum foil gets easily poisoned by the impurities present in the H_2 gas and Hel solution.

STANDARD CALOMEN ELECTRODE:

It essentially consists of a platinum wire immersed in a slurry made up of pure mercury, solid mercurous chloride Hg_2Cl_2 , and aqueous saturated solution of Kcl, packed in the inner-tube having a small hole. The outer-tube contains a saturated solution of Kcl having a porous ceramic fibre at its lower end. It serves as a salt-bridge which allows the entire set-up immersed directly into the solution to be measured.

The porous ceramic fibre permits electrical contact between one side of the salt-bridge and the solution under the examination and serves as a barrier between the said two solutions. The small opening at the top end of the salt-bridge tube serves as a fill-hole through which either Kcl solution may be filled or replaced as and when required.

It consists of an outer glass tube with a crack in the end of the tube. A crack is made by an asbestos filament or fitted porcelain plug or quartz fibre. A mercury and mercurous chloride paste is filled in the inner tube, which is connected to the saturated potassium chloride solution in the outer tube through a small opening. The saturated potassium chloride solution in the outer tube can be easily renewed through a lateral hole. Calomel, i.e., mercurous chloride is a sparingly soluble salt.

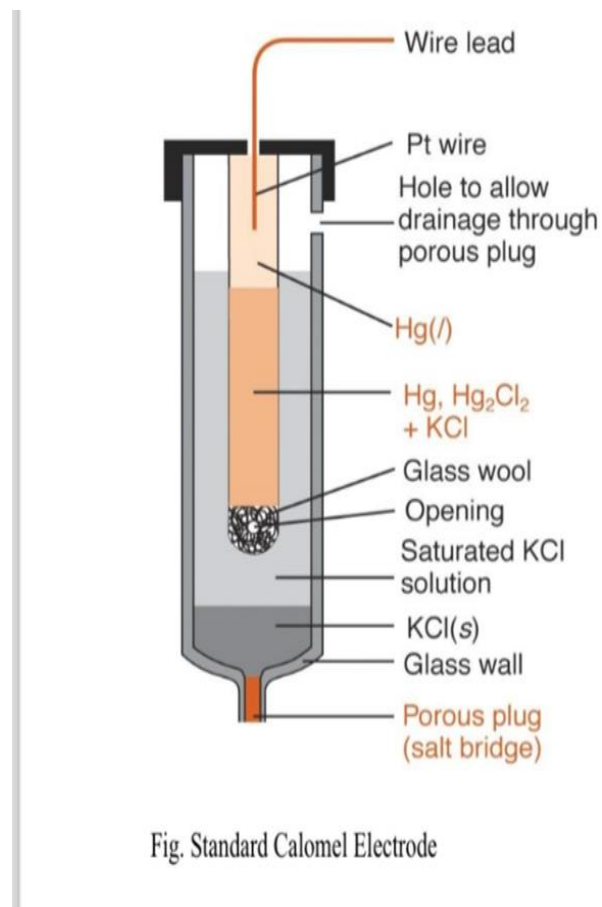


Fig. Standard Calomel Electrode

CONSTRUCTION:

- It consists of a glass tube in the bottom of which is a layer of Hg.
- Over the Hg layer, there is a layer of solid mercurous chloride. (Hg_2Cl_2).
- The remaining portion is filled with normal, decinormal or saturated KCl.
- A Pt wire is dipped into the Hg layer is used for making electrical contact.
- The side tube is used for contacting a salt bridge.

It consists of inner tube packed with mercury at the bottom and mercurous chloride and mercuric chloride is placed above the mercury. The outer tube is filled with a Kcl solution of known concentration (or) saturated Kcl solution. A Pt wire is kept immersed into the mercury to obtain electrical contact. A porous disc act as salt bridge. The stopper in the outer tube may be removed when additional sat'd Kcl is needed.

The calomel electrode act as anode (or) cathode depending on the nature of the other electrode of the cell.

WORKING:

- 1) It can act as an anode or cathode depending on the electrode potential of the coupled electrode.
- 2) If it can act as anode,
 - a. $2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$
- 3) Here the electrode potential of the coupled electrode is greater than calomel electrode.
- 4) If it can act as cathode, $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$
- 5) Here the electrode potential of the coupled electrode is less than that of calomel electrode.
- 6) Depending up on the concentration of the KCl solution used, various values of electrode potential are reported.

Saturated - 0.2422V (SCE)

1 N - 0.2810V (NCE)

0.1 N - 0.3335(DCE)

The Saturated calomel electrode (SCE) is a reference electrode based on the reaction between elemental mercury and mercury chloride. It has been widely replaced by the silver chloride electrode; however, the calomel electrode has a reputation of being more robust. The aqueous phase in contact with the mercury and the mercury chloride (Hg_2Cl_2 , "calomel") is a saturated solution of potassium chloride in water. The electrode is normally linked via a porous frit to the solution in which the other electrode is immersed. This porous frit is a salt bridge.

ADVANTAGES:

- Entire pH range.
- Mercury ion reacts with fewer samples as compared to silver- silver electrode.
- Sturdy electrode.

DISADVANTAGES:

- Temperature coefficient is large.
- Take longer time to established.
- Chloride ion solution show incompatibility.

SILVER-SILVER CHLORIDE ELECTRODE:

Silver-Silver chloride electrode which comprises of a silver wire coated with silver chloride and is duly placed in a 1 M K^+Cl^- solution saturated with AgCl . The silver-silver chloride electrode is another frequently used reference electrode. It is prepared by plating a layer of silver chloride onto a metallic silver wire and immersing in a solution containing chloride ions (usually KCl) of known concentration which is also saturated with silver chloride.

When a large excess of chloride ion (potassium chloride) is present, the contribution of chloride ions

obtained from dissolution of silver chloride can be (in the half cell) controlled by the concentration of potassium chloride (which remains constant). The experimental value of potential for an electrode prepared by saturated solution of potassium chloride is 0.199 V.

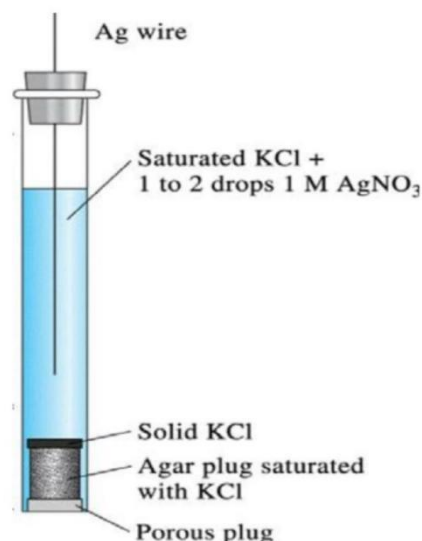


Fig. Silver-Silver Chloride Electrode

CONSTRUCTION:

The body of the electrode is made from 4 mm glass tube. Ceramic Porous glass is available in 4 mm diameter rod and serves as the ionic conducting electrical pathway between the inside of the reference electrode and the bulk of your cell. It has low electrical resistance (under 10 kohm for the common filling solutions) and a modest leak rate. The electrical resistance of the reference electrode 'frit' is an important factor in determining the stability and speed of your potentiometer in actual use. The leak rate may be important because of possible contamination of your solution by the reference electrode filling solution and vice versa.

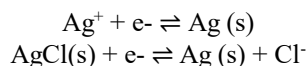
The Ceramic frit (about 1/8" long) is attached to the glass tube by 'heat shrink' Teflon tubing. The heat-shrink tubing should be cut flush with the end of the Ceramic frit to prevent trapping any air bubbles. The cap is conveniently made from scrap Teflon or plastic cap, or protector made to fit 5/32" OD tubing. It should be snug, but easily removable for replenishing the filling solution.

A variety of filling solutions can be used to fill the above electrode skeleton. The most used are saturated KCl or 3.5M KCl. KCl has the uncanny ability to 'creep' and form a crusty layer of solid KCl where the solution is exposed to the air. And a silver wire is inserted which is coated with silver chloride on it, into the KCl solution.

WORKING:

A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements. For environmental reasons it has widely replaced the saturated calomel electrode. For example, it is usually the internal reference electrode in pH meters, and it is often used as reference in reduction potential measurements. As an example of the latter, the silver chloride electrode is the most used reference electrode for testing cathodic protection corrosion control systems in sea water environments. The electrode functions as a redox electrode and the equilibrium are between the silver metal (Ag) and its salt—silver chloride (AgCl, also called silver(I) chloride).

The corresponding half-reactions can be presented as follows:



ADVANTAGES:

- Easy to manufacture.
- Shows potential rapidly & it attains equilibrium between -30°C & 135° C & is reproducible.
- Stable & accurate even wide temperature fluctuation.

DISADVANTAGES:

- It reacts with samples.

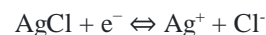
INDICATOR ELECTRODES:

- (a) Metal Electrode,
- (b) Glass Electrode, and
- (c) Hydrogen electrode.

GLASS MEMDRANE ELECTRODE:

The oldest and still most widespread ion-selective electrode that is used to measure pH, is the glass electrode. As a rule, it is constructed in one body directly with a suitable reference electrode. The ability of the glass electrode to indicate the concentration of H⁺ can be simply explained by the fact that the glass membrane (a well with very thin walls blown from special glass) is permeable to H⁺ and impermeable to other ions. A silver wire covered with a layer of AgCl is immersed in the internal electrolyte. Depending on the acidity of the measured solution, the concentration

of H⁺ inside the flask changes. Cl⁻ ions do not pass through the membrane, so to maintain the electro neutrality of the solution, the reaction takes place at the electrode.



If we immerse the electrode in an acidic solution, the excess of H⁺ ions will cause more Cl⁻ ions to be released from the AgCl paste. This consumes more electrons from the silver wire and the electrode gets a more positive voltage compared to the reference. Conversely, in an alkaline environment, excess Cl⁻ will donate its electrons and the electrode will have a more negative voltage. A silver wire coated with AgCl paste is most often used as a reference electrode in pH-meter, but this time it is immersed in a KCl solution with a precise concentration. The potential of the reference electrode is not affected by the concentration of H⁺ ions. The electrolyte of the reference electrode is conductively connected to the measured solution by means of a bridge with a ceramic partition (frit).

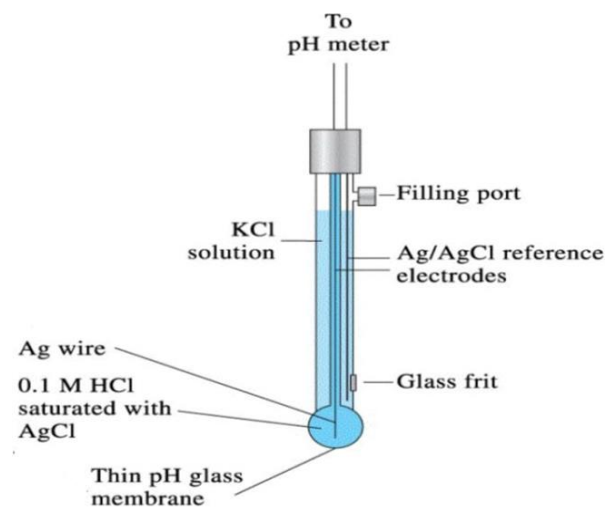


Fig. Glass Electrode

CONSTRUCTION:

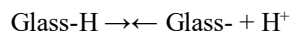
A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The combination electrode consists of the following parts (see the drawing):

1. A sensing part of electrode, a bulb made from a specific glass.
2. Internal electrode, usually silver chloride electrode or calomel electrode.

3. Internal solution, usually a pH=7 buffered solution of 0.1 mol/L KCl for pH electrodes or 0.1 mol/L MCl for pH electrodes.
4. When using the silver chloride electrode, a small amount of AgCl can precipitate inside the glass electrode.
5. Reference electrode, usually the same type as 2.
6. Reference internal solution, usually 0.1 mol/L KCl.
7. Junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fibre.
8. Body of electrode, made from non-conductive glass or plastics. The bottom of a pH electrode balloons out into a round thin glass bulb. The pH electrode is best thought of as a tube within a tube. The inner tube contains an unchanging 1×10^{-7} mol/L HCl solution. Also inside the inner tube is the cathode terminus of the reference probe. The anodic terminus wraps itself around the outside of the inner tube and ends with the same sort of reference probe as was on the inside of the inner tube. It is filled with a reference solution of KCl and has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge.

WORKING:

The simplest explanation for the working of the thin glass electrode is that the glass acts as a weak acid (Glass-H).



The hydrogen ion activity of the internal solution is held constant. When a solution of different pH from the inside meets the outside of the glass membrane, the glass is either deprotonated or protonated relative to the inside of the glass. The difference in pH between solutions inside and outside the thin glass membrane creates electromotive force in proportion to this difference in pH.

ADVANTAGES:

- Response slight change in the pH of the test solution is very fast.
- It is unaffected by oxidizable & reducible substances also coloured liquids, gases, or the presence of moderate salt except sodium salts.
- Lithium & silica glass membrane can be used wider range of pH.
- A combination of glass electrode & reference electrode in one single unit has increased the ease of handling the system.

DISADVANTAGES:

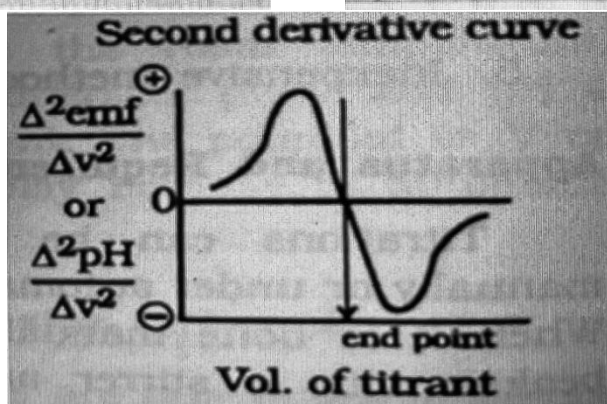
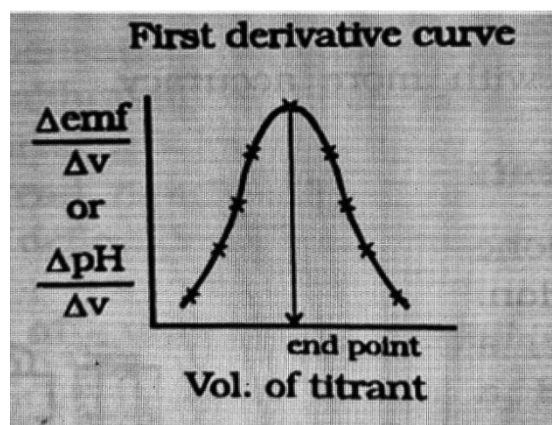
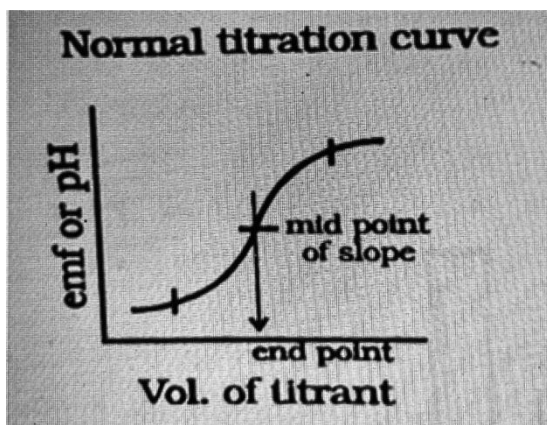
- Glass electrode is fragile & hence, needs careful handling.
- Scratches on the glass bulb alter the response from the glass electrode.
- It is not used for dehydrating agents & colloidal substances.
- Glass electrode provides a very high internal resistance & hence, is not useful in simple potentiometers.

Method of detecting end point:

When Indicator method is not suitable, we use potentiometric method of determining end point. It is done graphically by using.

- A normal titration curve i.e. a plot of emf (vs) volume of titrant or pH (vs) volume of titrant.
- First derivative curve i.e. a plot of $\Delta E/\Delta v$ or $\Delta \text{pH}/\Delta v$ (vs) volume of titrant.
- Second derivative curve i.e. a plot of $\Delta^2 E/\Delta v^2$ or $\Delta^2 \text{pH}/\Delta v^2$ (vs) volume of titrant.

In a potentiometric titration, at the end point, the rate of change of potential is maximum. The method of detecting the end point is explained in the following diagram.



METHOD TO DETERMINE END POINT OF POTENTIOMETRY TITRATION:

By measuring the addition of titrant until the entire test substance undergoes reactions, the amount of a given test substance can be determined. Through this process after the titration, the potential difference between the electrodes (namely the reference electrode and the indicator electrode) is determined under conditions in which the equilibrium of thermodynamics is maintained and no disturbance of thermodynamic equilibrium results from the current passing through the electrodes. Potentiometric titration is a method used in laboratories for measuring analytes' concentration. Analytes are characterized using this method. There are no chemical indicators involved with this method. The electrostatic potential is instead measured across the material. The volumetric method involves measuring the potential between two electrodes (reference and indicator) concerning the volume of reagent added.

POTENTIOMETRIC TITRATION:

It's a volumetric method in which potential between two electrodes (reference & indicator) is measured as

a function of added reagent volume. Types of Potentiometric titrations:

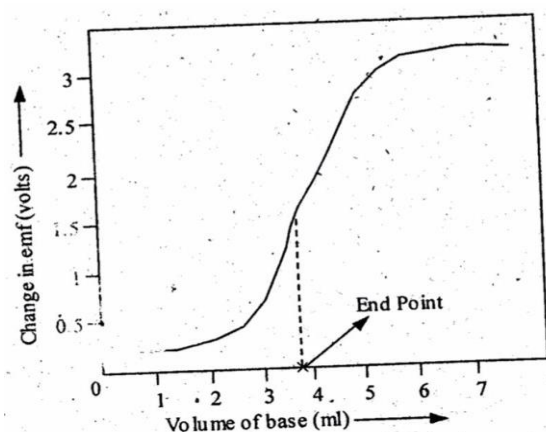
- Acid-base titration,
- Redox titration,
- Complexometric titration,
- Precipitation titration, (or) titrations of sparingly soluble salts.
- Diazotization titrations.
- Non-aqueous titrations.

ACID -BASE TITRATION:

- Neutralization titrations are performed with standard solutions of strong acids or bases. While a single solution (of either acid or base) is sufficient for the titration of a given type of analyte, it is convenient to have standard solutions of both acid and base available in case back titration is needed to locate the end point more exactly.
- Acid-base titrations are based on neutralization reaction.



- It involves reaction between the analyte and an acidic or basic titrant to give a salt along with neutral water.
E.g.: $\text{HCl} + \text{Na}^+\text{OH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- Water is formed by the interaction of H ions of the acid (i.e., HCl) and OH ions of the base (i.e., NaOH).
- In acid-base titration, standard solution of acid is used for the quantitative estimation of a base and standard solution of base is used for estimation of an acid.
- In case of strong acid vs. strong base titrations, the end point is reached when the pH of the solution is equal to 7.
- However, for weak acids and bases, the end point need not occur at pH 7.
- Changes in the e.m.f. of an acid is measured after each successive addition of the base. These values of e.m.f. are plotted against volume of base to give a titration curve as follows:

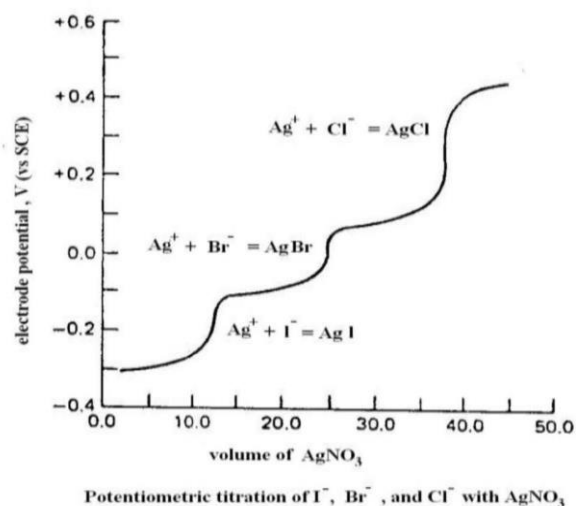


PRECIPITATION TITRATION:

- Volumetric methods based upon the formation of slightly soluble precipitate are called "precipitation titration".
- Precipitation titrations involve reaction between the titrant and the analyte to form sparingly soluble salts.
- Precipitation titrations can be performed under the following conditions:
 - (a) The precipitate should be formed rapidly.
 - (b) The precipitate formed should not interfere with the end point during the titrations.
 - (c) Precipitate should not have any adsorbing effects i.e.; it should not absorb the solute.

(d) Precipitate should be insoluble or sparingly soluble.

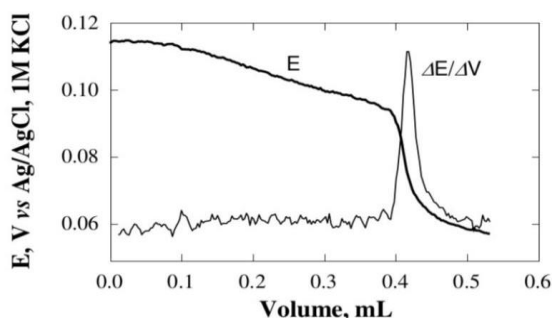
- Precipitation titrations are carried out for metallic ions like Ag, Cu, Hg, Pb etc. which form sparingly soluble salts with the titrants.
- End point is depending on solubility of the precipitate and on the concentration of analyte.
- In the titration of AgNO_3 with KCl, KCl is added in small volumes to the titrate. As the titration proceeds, Ag^+ ions get precipitation as AgCl.
$$\text{AgNO}_3 + \text{KCl} \rightarrow \text{AgCl} + \text{KNO}_3$$
- With each increment of KCl, concentration of Ag ions decreases, and potential of the electrode increases.
- Near the end point, the electrode shows a sharp change in the potential due to precipitation of all the Ag ions as AgCl. The values of electrodes potential are plotted against the volume of KCl added. End point is depicted as the point of maximum inflexion in the titration curve.



COMPLEXOMETRIC TITRATION:

- Complexometric titrations are based on the formation of a complex between the analyte and the titrant.
- Complexometric titrations can also be defined as the reactions in which simple metal ions are converted into metal complex by addition of a reagent known as ligand or complexing agent.

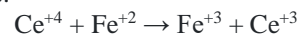
- EDTA is the most used titrant for the titration of metal ions. It forms the covalent bonds with the metal ion to give stable metal complex.
- The donor species (or called ligands) must have at least one pair of unshared electrons for bond formation.
- Metal and membrane electrodes for determination of many cations (mixture of Bi^{3+} , Cd^{2+} and Ca^{2+} using EDTA).
- In this, an indicator electrode made up of the same metal, the ion of which is involved in the complex formation.
- E.g., Titration of mercuric cyanide with silver chloride in the presence of silver electrode.
- Titration of cyanide ions with silver ions results in the formation of silver cyanide complex which is seen as follows:
- $\text{Ag}^+ + 2 \text{CN}^- \rightarrow [\text{Ag}(\text{CN})_2]^-$ (chemically stable).



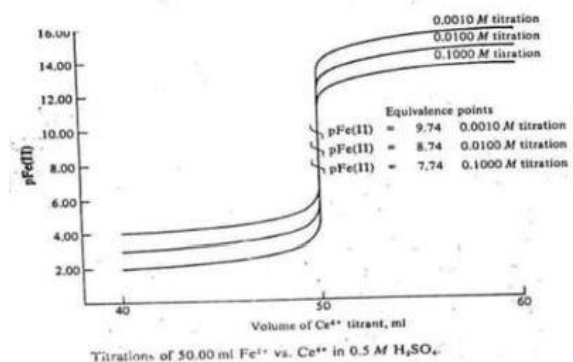
OXIDATION REDUCTION TITRATION:

- A redox titration is a type of titration based on a redox reaction between the analyte and titrant.
- Redox titration may involve the use of a redox indicator and/or a potentiometer.
- Common examples of a redox titration are treating a solution of iodine with a reducing agent and using starch as an indicator. Iodine forms an intensely blue complex with starch. Iodine (I_2) can be reduced to iodide (I^-) by e.g. thiosulphate. $\text{S}_2\text{O}_3^{2-}$ and when all iodine is spent the blue colour disappears. This is called an iodometric titration.
- Redox titrations are based on the oxidation-reduction reaction between the analyte and the titrant. Both the oxidation and reduction occur simultaneously. One substance becomes reduced in the process of oxidising another.

- It involves the transfer of electrons from the substance being oxidised to the substance being reduced.
- Example: $\text{Ce}^{+4} + \text{Fe}^{+2} \rightarrow \text{Ce}^{+3} + \text{Fe}^{+3}$
- Redox titrations involve two half reactions. Each half reaction involves a redox conjugate pair whose standard potentials are used to calculate the net standard potential of the reaction.
- The net standard potential of the reaction is given as:

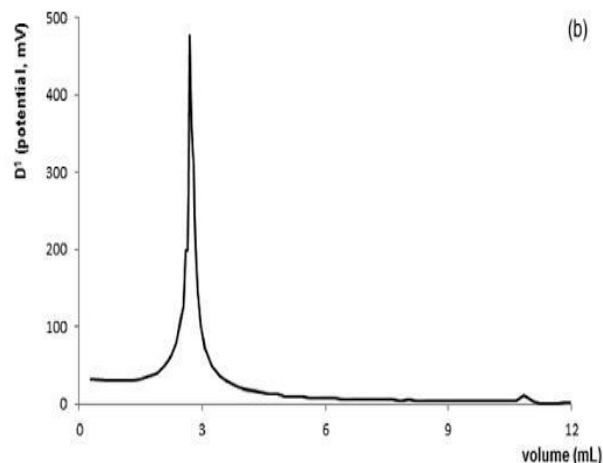
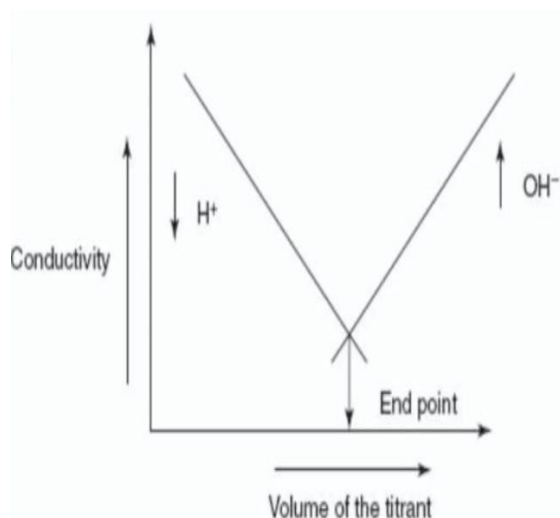


- At the beginning of the titration when Ce^{+4} ions are added to Fe^{+2} ions, Ce^{+4} ions are converted to Ce^{+3} ions (reduction), while Fe^{+2} ions are converted to Fe^{+3} ions (oxidation).
- The number of Fe^{+3} ions created during the reaction will remain equal to the number of Ce^{+3} (cerrous) ions because of each mole of Ce^{+3} is created. Therefore, throughout the titration, $[\text{Fe}^{+3}] = [\text{Ce}^{+3}]$.



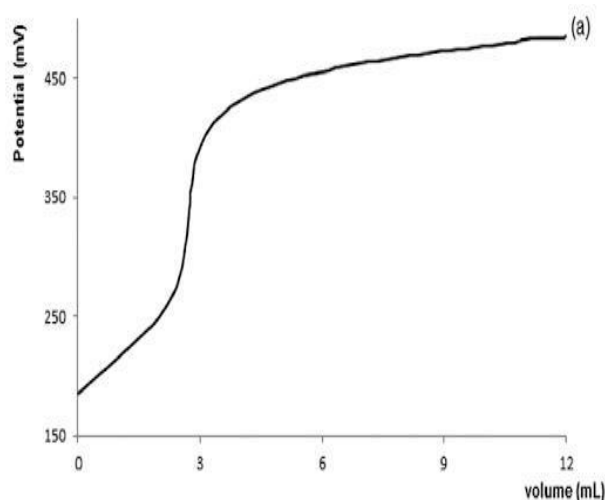
DIAZOTIZATION TITRATION:

- [Analytes (drugs or substances) containing primary aromatic amino groups are titrated against sodium nitrite in acidic medium to give diazonium salts. The end point of titration is determined by potentiometry.]
- Examples of drugs containing primary amino groups which are potentiometrically titrated are dapsone, sulphacetamide, procainamide, amino alkaloids etc.
- Primary aromatic amino group against sodium nitrate
- The indicator electrode is used for glass electrode and reference electrode used in saturated calomel electrode.



NON-AQUEOUS TITRATION:

- Titrations which are carried out in the absence of aqueous medium are called as non-aqueous titrations.
- These are used for the assay of certain weak acids and bases which gives poor end points in aqueous solutions. Substances, which are insoluble in water but soluble in non-aqueous solvents, can be titrated by non-aqueous titrations.
- Acidic Titrant: Perchloric acid, Fluor sulphonic acid, p-toluene sulphonic acid.
- Basic Titrants: Sodium methoxide, Potassium methoxide, Lithium methoxide, Tetra alkyl ammonium hydroxide.



APPLICATION:

branches of Chemistry, industries, engineering, and several other technologies. The possibility of the determination of low level of pollutants has prompted the use of these methods in environmental studies.

➤ Clinical Chemistry:

- Ion- selective electrodes are important sensors of clinical samples because of their selectivity for analytes in complex metricise.
- The most common analytes are electrodes, such as Na⁺, K⁺, Ca²⁺, H⁺, Cl⁻, and dissolved gases such as CO₂.

➤ Environmental Chemistry:

- For the analysis of CN⁻, F⁻, NH₃, and NO₃⁻, in water and wastewater.
- One potential advantage of an ion-selective electrode is the ability to incorporate it into a flow cell for the continuous monitoring of wastewater streams.

➤ Potentiometric Titrations:

- Use a pH electrode to monitor the change in pH during the titration.
- For determining the equivalence point of an acid-base titration.
- Possible for acid-base, complexation, redox, and precipitation titrations, as well as for titrations in aqueous and non-aqueous solvents.

➤ Agriculture:

- NO₃, NH₄, Cl, K, Ca, I, CN in soils, plant material, fertilizers, and feedstuffs.

➤ Detergent Manufacture:

- Ca, Ba, F for studying effects on water quality.

➤ Food Processing:

- NO₃, NO₂, in meat preservatives.

- Salt content of meat, fish, dairy products, fruit juices, brewing solutions.
- F in drinking water and other drink.
- Ca in dairy products and beer.
- K in fruit juices and wine making.
- Corrosive effect of NO, in canned foods.
- **Pharmaceutical industry:**
- Determination of equilibrium constants.
 - of ionic product of water.
 - of dissociation constant of acids.
 - of NO₃, NO₂ in meat preservatives.
- To study the solubility and solubility product of sparingly soluble electrolytes.
- Health - Measurement of pH of blood for diagnosis of acidosis or alkalosis.
- Pharmaceutical Industry - To determine the pH of given chemical agents and for the detection of end point in potentiometric titration of certain drugs.
- Pollution monitoring: Estimation of CN, F, S, Cl, NO₃, in industrial water and F in drinking water.

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