POTENTIOMETRY AND DETERMINATION OF pH

Presented By:

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OUTLINE

- Introduction
- Theory
- Types of Electrodes
- Determination of pH
- Potentiometric Titrations
- Advantages and disadvantages
- Applications of Potentiometry

INTRODUCTION AND PRINCIPLE

- Potentiometry is one type of electrochemical analysis methods. Electrochemistry is a part of chemistry, which determines electrochemical properties of substances. An electrical circuit is required for measuring current (unit: ampere, A) and potential (also voltage, unit: volt (V)) created by movement of charged particles. Galvanic cell (electrochemical cell, Fig. 1) serves as an example of such system.

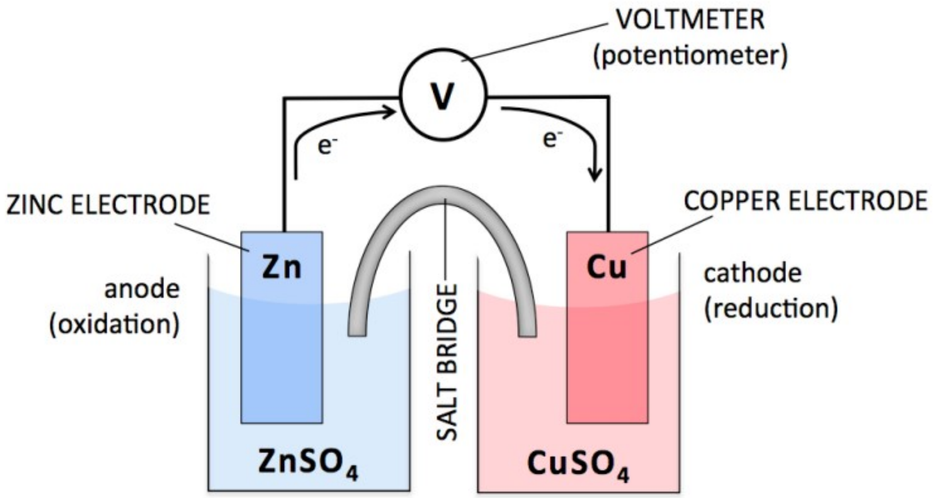


Figure 1. A galvanic electrochemical cell.

- Electrochemical cell consists of two solutions connected by a salt bridge and electrodes to form electrical circuit.
- Sample cell on figure 1 consists of solutions of $ZnSO4$ and $CuSO4$. Metallic Zn and Cu electrodes are immersed in respective solutions.
- Electrodes have contacts firstly through wires connected to the voltmeter and secondly through solutions and a salt bridge, forming an electric circuit.
- Salt bridge consists of a tube filled with saturated salt solution (e.g. KCl solution). The ends of the tube are capped with porous frits that prevent solutions from mixing, but permit movement of ions.

Three distinct charge transfer processes are described for the system in Fig 1:

- 1. Electrons move in electrodes and wires from zinc electrode to copper electrode.
- 2. Ions move in solutions:
  - a. In solution on the left, zinc ions move away from the electrode and sulfate ions move towards it.
  - b. In solution on the right, copper ions move towards the electrode and negatively charged ions (sulfate) away from it.
  - c. In salt bridge positive ions move right and negative ions left.
- 3. On the surfaces of electrodes electrons are transferred to ions or vice versa:
  - a. Zinc electrode dissolves: $Zn \rightarrow Zn^{2+} + 2e^-$
  - b. Metallic copper is deposited on the electrode surface: $Cu^{2+} + 2e^- \rightarrow Cu\downarrow$

Three processes mentioned above are important parts of a closed electrical circuit making the flow of electrical current possible.

THEORY

When a metal M is immersed in a solution containing its own ions e.g. Ag in AgCl solution, an electrode potential is established. The value of this electrode potential is given by the Nernst equation:

$$E = E_0 - \frac{RT}{nF} \ln a$$

E – electrode potential,

E0 – standard potential of the electrode,

R – universal gas constant (8.314 J/(K•mol)),

F – Faraday constant (96485 C/mol),

T – temperature in kelvins,

n – charge of the ion or number of electrons participating in the reaction,

a – activity of the ions. Activity of the ions is a function of concentration.

For solutions with concentrations lower than about 0.1 mol/l, activity can be approximated to concentration. Thus a logarithmic dependence exists between potential and the activity (concentration) of ions in solution.

POTENTIOMETRY: DEFINITION

- Potentiometry is based on the measurement of the potential of an electrode system (e.g. electrochemical cell).
- Potentiometric measurement system consists of two electrodes called **reference** and **indicator** electrode, potentiometer and a solution of analyte .
- Reference electrode is an electrode with potential which is:
  - a) independent of concentration of analyte (or other) ions in solution;
  - b) independent of temperature.
- Potential of an indicator electrode depends mainly on the concentration of the analyte ions (in this case hydrogen ions).
- Potentiometric measurements enable selective detection of ions in presence of multitude of other substances.

The reference electrode is the electrode which contains of its own potential value and it is stable when dipped into sample solution. The salt bridge is used to prevent the interference of the analyte solution with that of reference solution.

Here analyte solution is the solution whose potential is to be measured.

The indicator electrode is the electrode which responds to change in the potential of analyte solution

The electromotive force of the complete cell is given by the following equation:

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

where $E_{reference}$ is the electromotive force of the reference electrode ,$E_{indicator}$ is electromotive force of indicator electrode, $E_{junction}$ is the electromotive force at the junction of the liquid.

Theory:

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

$$E= E^0 +(0.592/n) \log c$$

Where E is the potential of the solution; E^0 is the standard electrode potential; n is the valency of the ions; c is the concentration of the sample solution; 0.592 is the value obtained from the RT/F; where R is the gas constant, T is the temperature in Kelvin, F is the faradays constant.

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

- Reference electrode
- Indicator electrode

❑ **Reference electrode**: These are mainly used for the determination of the analyte by maintaining the fixed potential.

Ex: Standard hydrogen electrode

- Silver silver chloride electrode
- Saturated calomel electrode

The reference electrodes are classified into two main classes they are as follows:

✓**Primary standard electrodes**
    ex: Standard hydrogen electrode
✓**Secondary standard electrodes**
    ex: silver-silver chloride electrode
        saturated calomel electrode

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

Ex: Hydrogen electrode.
    Glass electrode.
    Antimony –antimony oxide electrode.

There are two classes of indicator electrodes:

✓**Metal indicator electrodes**
✓**Ion-selective electrodes**

➢**Metal indicator electrodes:** These develop electric potential in response to redox reaction on the metal surface. Platinum or Au are 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.

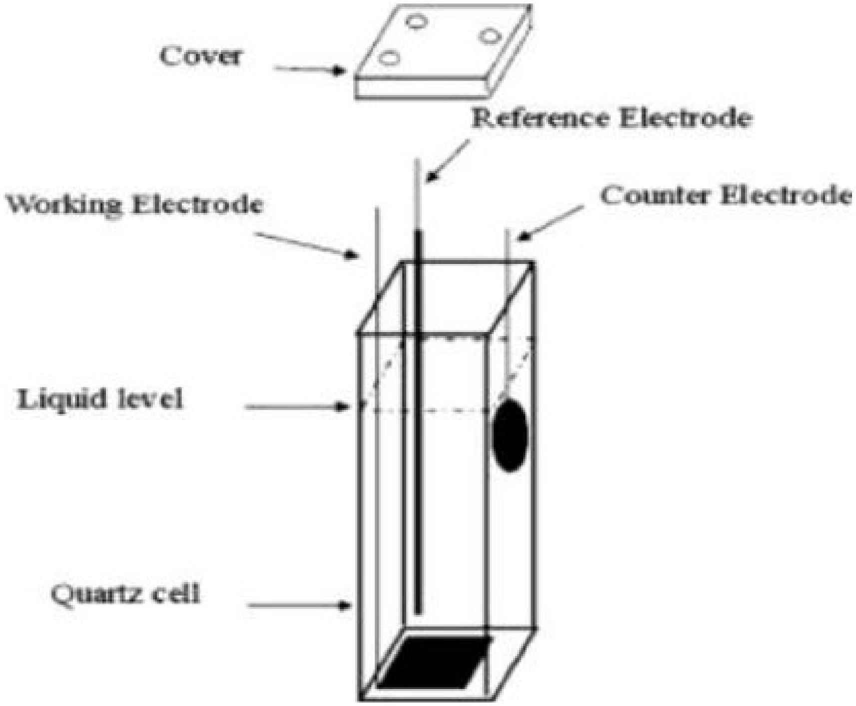
Ex: Ag/ AgCl/ KCl
$Hg/ Hg_2Cl_2/ KCl$

▪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.

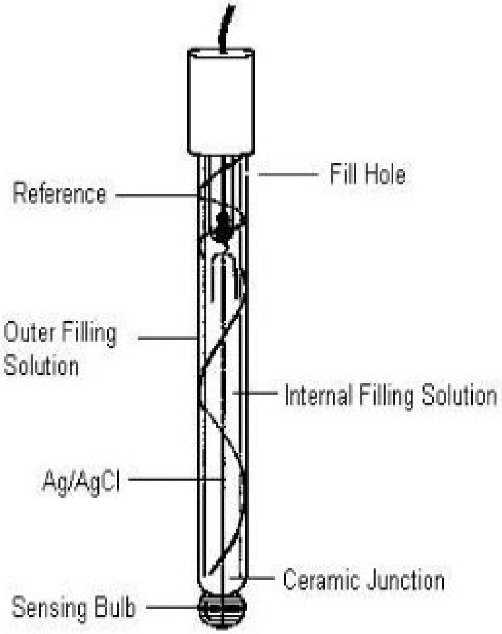
Ex: Pt-H_2 electrode

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

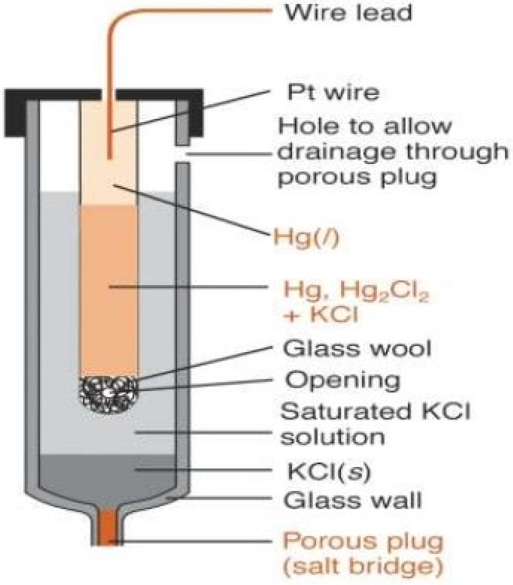
Ex: Glass membrane electrode
Antimony –antimony oxide electrode.



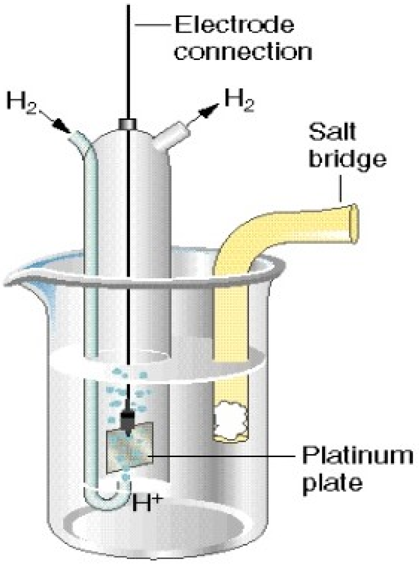
Antimony-antimony oxide electrode



Glass electrode



Saturated calomel electrode



Standard hydrogen electrode

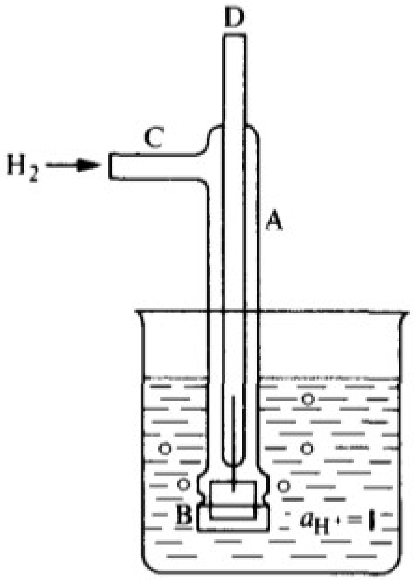


Figure 2: Standard Hydrogen Electrode

THE STANDARD HYDROGEN ELECTRODE

- The primary reference electrode is the normal or **standard hydrogen electrode**.
- As given in figure 2, this consists of a piece of platinum foil, coated electrolytically with platinum black, and immersed in a solution of hydrochloric acid containing hydrogen ions at unit activity. (This corresponds to 1.18 M hydrochloric acid at 25^{O}C.)
- Hydrogen gas at a pressure of one atmosphere is passed over the platinum foil through the side tube C and escapes through the small holes B in the surrounding glass tube A.
- Because of the periodic formation of bubbles, the level of the liquid inside the tube fluctuates, and a part of the foil is alternately exposed to the solution and to hydrogen.
- The lower end of the foil is continuously immersed in the solution to avoid interruption of the electric current.

The Standard Hydrogen Electrode

- Connection between the platinum foil and an external circuit is made with mercury in D. The platinum black has the property of adsorbing large quantities of atomic hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode.
- Under fixed conditions, viz. hydrogen gas at atmospheric pressure and unit activity of hydrogen ions in the solution in contact with the electrode, the hydrogen electrode possesses a definite potential.
- By convention, the potential of the standard hydrogen electrode is equal to zero at all temperatures.
- Upon connecting the standard hydrogen electrode with a metal electrode consisting of a metal in contact with a solution of its ions of unit activity and measuring the cell e.m.f. the standard electrode potential of the metal may be determined. The ce11 is usually written as :

$$\mathrm{Pt, H_2 | H^+}(a = 1) \vdots\vdots\, \mathrm{M}^{n+}(a = 1) | \mathrm{M}$$

THE CALOMEL ELECTRODE

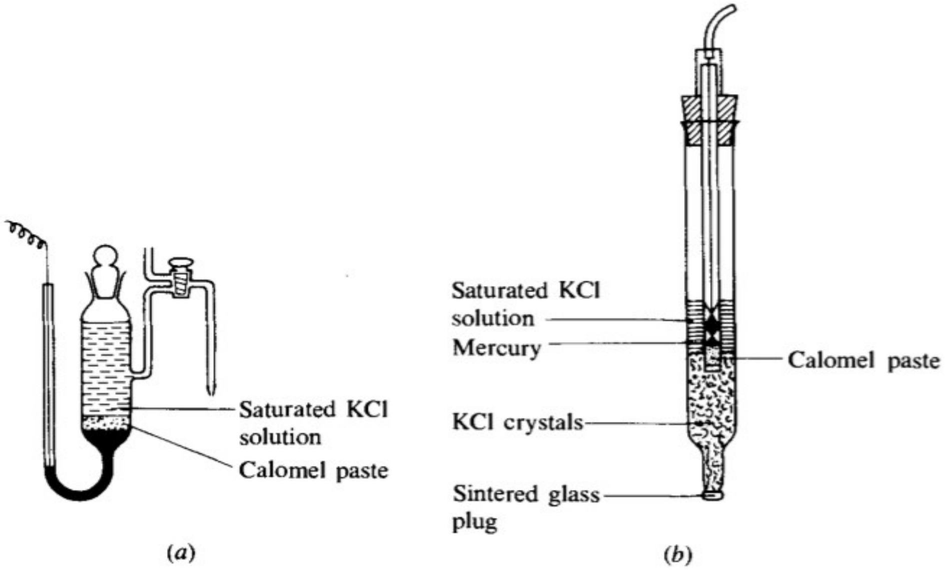


Figure 3: The calomel Electrode

- The most widely used reference electrode, due to its ease of preparation and constancy of potential, is the **calomel electrode**.
- A calomel half-cell is one in which mercury and calomel [mercury(I) chloride] are covered with potassium chloride solution of definite concentration; this may be 0.1 M, 1 M, or saturated.

THE CALOMEL ELECTRODE

- These electrodes are referred to as the decimolar, the molar and the saturated calomel electrode (S.C.E.) and have the potentials, relative to the standard hydrogen electrode at $25^{O}C$, of 0.3358,0.2824 and 0.2444 volt.
- Of these electrodes the S.C.E. is most commonly used, largely because of the suppressive effect of saturated potassium chloride solution on liquid junction potentials.
- However, this electrode suffers from the drawback that its potential varies rapidly with alteration in temperature owing to changes in the solubility of potassium chloride, and restoration of a stable potential may be slow owing to the disturbance of the calomel-potassium chloride equilibrium.
- The potentials of the decimolar and molar electrodes are less affected by change in temperature and are to be preferred in cases where accurate values of electrode potentials are required.
- The electrode reaction is:

$$Hg_2C1_2(s) + 2e \leftrightarrow 2Hg\ (liq) + 2C1^-$$

and the electrode potential is governed by the chloride-ion concentration of the solution.

THE CALOMEL ELECTRODE

- One form of calomel electrode is shown in Fig. 3 (a). It consists of a stoppered glass vessel provided with a bent side tube fitted with a three-way tap which carries a short upper and a long lower tube; the latter is drawn out to a constriction at the bottom end.
- A short platinum wire is fused into the bottom of the vessel so that it protrudes into the interior, and a narrow glass tube sealed to the bottom of the vessel is bent round parallel to the vessel.
- A little mercury placed in the bottom of this tube provides electrical connection with the interior of the vessel through the sealed-in platinum wire.
- Compact, ready-prepared calomel electrodes as shown in Fig.3 (b) are available commercially and find wide application especially in conjunction with pH meters and ion-selective meters.

THE SILVER-SILVER CHLORIDE ELECTRODE

- This electrode is next in importance to the calomel electrode as a reference electrode.
- It consists of a silver wire or a silver-plated platinum wire, coated electrolytically with a thin layer of silver chloride, dipping into a potassium chloride solution of known concentration which is saturated with silver chloride: this is achieved by the addition of two or three drops of 0.1 M silver nitrate solution.
- Saturated potassium chloride solution is most commonly employed in the electrode, but 1 M or 0.1 M solutions can equally well be used: the potential of the electrode is governed by the activity of the chloride ions in the potassium chloride solution.
- Commercial forms of the electrode are available and in general are similar to the calomel electrode depicted in Fig.(b) with the replacement of the mercury by a silver electrode, and calomel by silver chloride.
- The remarks concerning clogging of the sintered disc, and the use of ion exchange membranes and double junctions to reduce this are equally applicable to the silver-silver chloride electrode.

INDICATOR ELECTRODES

- The indicator electrode of a cell is one whose potential is dependent upon the activity (and therefore the concentration) of a particular ionic species whose concentration is to be determined. E.g. Glass electrode

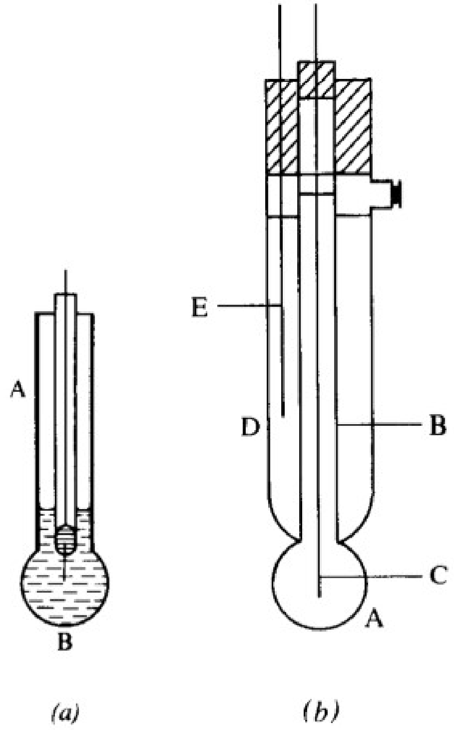


Fig. 4 (a) Glass Electrode
(b) Combination glass Electrode

GLASS ELECTRODE

- The glass electrode is the most widely used hydrogen ion responsive electrode hence used for pH determinations.
- Its use is dependent upon the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the hydrogen ion concentration of the solution.
- The basic arrangement of a glass electrode is shown in Fig. 4 (a); the bulb B is immersed in the solution of which it is required to measure the hydrogen ion concentration, and the electrical circuit is completed by filling the bulb with a solution of hydrochloric acid (usually 0.1 M), and inserting a silver-silver chloride electrode.

GLASS ELECTRODE

- Provided that the internal hydrochloric acid solution is maintained at constant concentration, the potential of the silver-silver chloride electrode inserted into it will be constant, and so too will the potential between the hydrochloric acid solution and the inner surface of the glass bulb.
- Hence the only potential which can Vary is that existing between the outer surface of the glass bulb and the test solution in which it is immersed, and so the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution.

COMBINATION GLASS ELECTRODES

- Glass electrodes are now available as combination electrodes which contain the indicator electrode (a thin glass bulb) and a reference electrode (silver-silver chloride) combined in a single unit as depicted in Fig. 4 (b).
- The thin glass bulb A and the narrow tube B to which it is attached are filled with hydrochloric acid and carry a silver-silver chloride electrode C.
- The wide tube D is fused to the lower end of tube B and contains saturated potassium chloride solution which is also saturated with silver chloride; it carries a silver-silver chloride electrode E. The assembly is sealed with an insulating cap.

COMBINATION GLASS ELECTRODES

- To measure the hydrogen ion concentration of a solution the glass electrode must be combined with a reference electrode, for which purpose the saturated calomel electrode is most commonly used, thus giving the cell:

Ag,AgCl(s)| HCl(O.l M)| Glass |Test solution ||
KCl(sat'd),Hg,Cl,(s) | Hg

- the operation of a glass electrode is related to the situations existing at the inner and outer surfaces of the glass membrane.
- Glass electrodes require soaking in water for some hours before use and it is concluded that a hydrated layer is formed on the glass surface, where an ion exchange process can take place.

COMBINATION GLASS ELECTRODES

- If the glass contains sodium, the exchange process can be represented by the equilibrium

$$\mathrm{H}^+_{\mathrm{soln}} + \mathrm{Na}^+_{\mathrm{glass}} \rightleftharpoons \mathrm{H}^+_{\mathrm{glass}} + \mathrm{Na}^+_{\mathrm{soln}}$$

- The concentration of the solution within the glass bulb is fixed, and hence on the inner side of the bulb an equilibrium condition leading to a constant potential is established.
- On the outside of the bulb, the potential developed will be dependent upon the hydrogen ion concentration of the solution in which the bulb is immersed.
- Within the layer of 'dry' glass which exists between the inner and outer hydrated layers, the conductivity is due to the interstitial migration of sodium ions within the silicate lattice.
- Under such condition, the measured e.m.f of the cell is equal to the pH of the solution.

MEASUREMENT OF PH

- **pH** is a measure of the acidity or alkalinity of a solution. The **pH** value states the relative quantity of hydrogen ions (H^+) contained in a solution. The greater the concentration of H^+ the more acidic the solution and the lower the **pH**. In this relationship, **pH** is defined as the negative logarithm of hydrogen activity.
- A pH meter is an electronic instrument used for measuring the pH (acidity or alkalinity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). A typical pH meter consists of special measuring probes (a glass electrode and a reference electrode) connected to an electronic meter that measures and displays the pH reading.

pH Meter

Types of pH meter

- Manual pH meter
- Digital pH meter

  - A manual pH meter

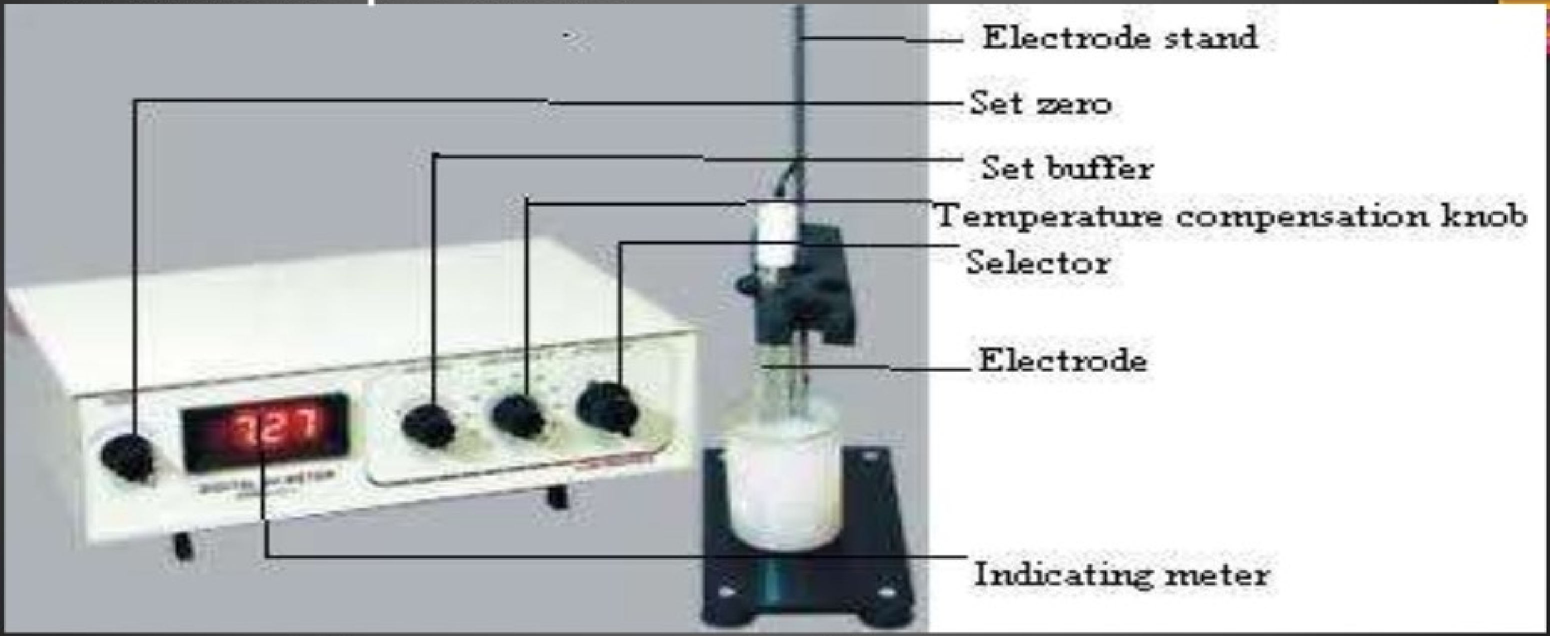
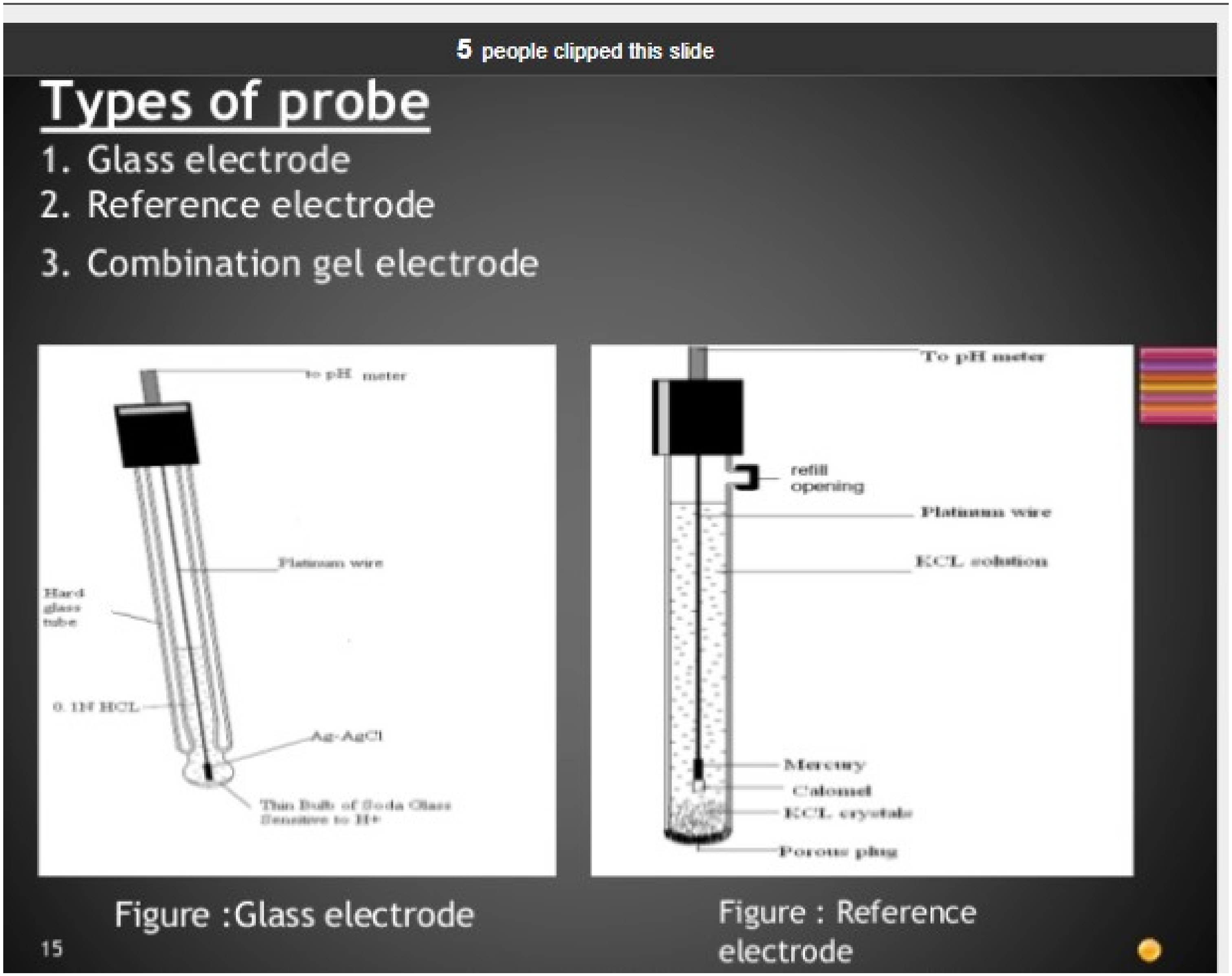


Figure : manual pH meter

- A digital pH meter

Figure : Digital pH meter



Types of probe

1. Glass electrode
2. Reference electrode
3. Combination gel electrode

Figure :Glass electrode

Figure : Reference electrode

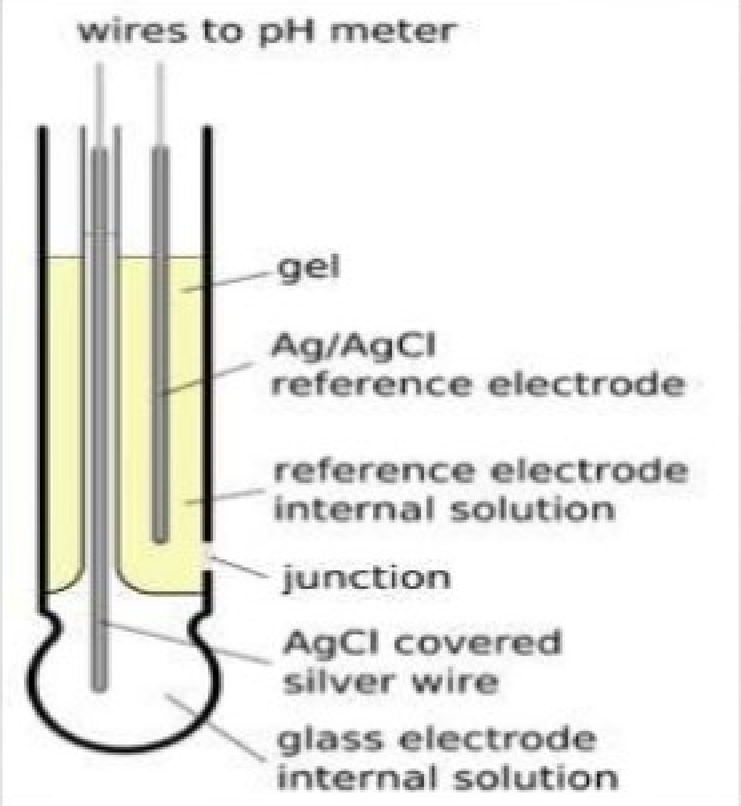


Figure : Combination gel electrode

Description: Under combination Glass Electrode

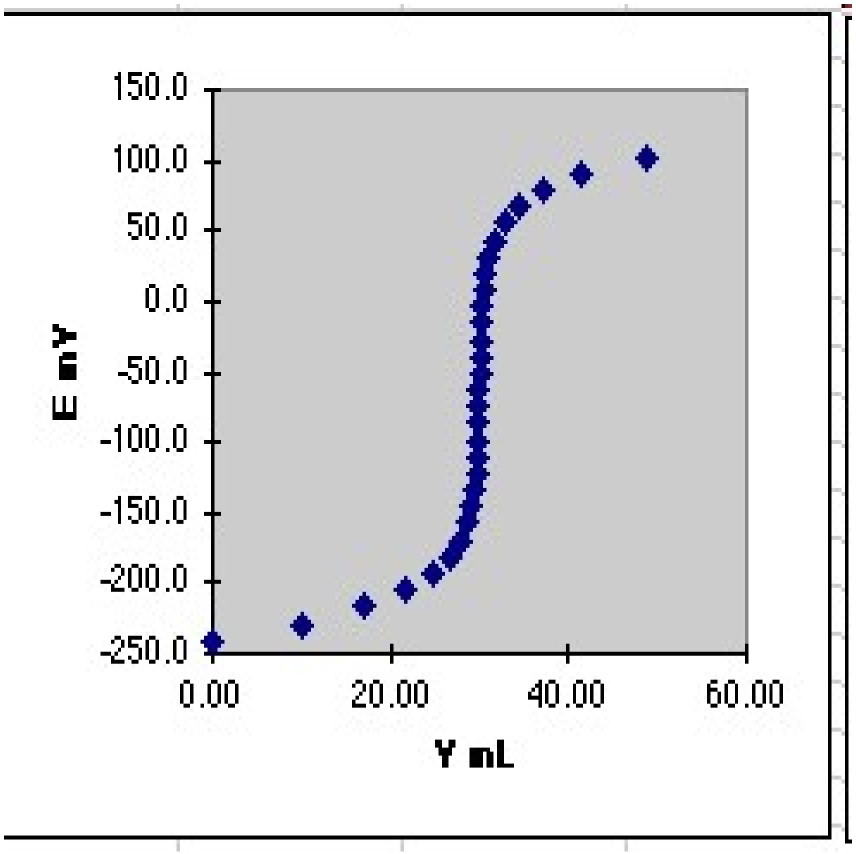
POTENTIOMETRIC TITRATION

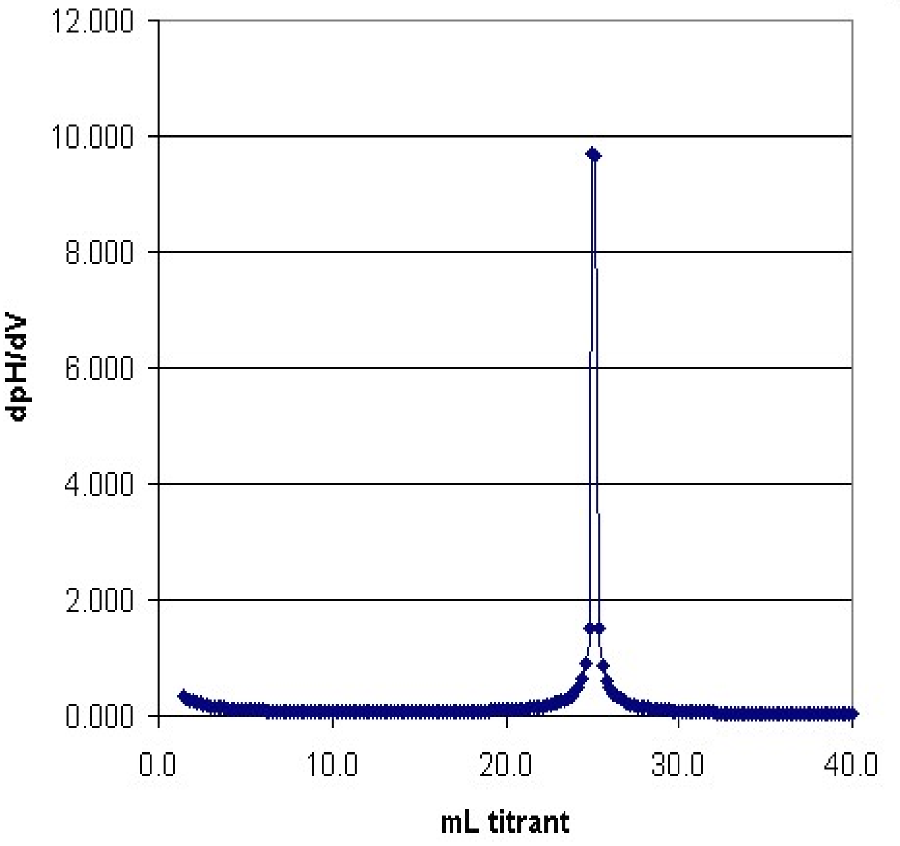
- Involves measurement of the potential of a suitable indicator electrode as a function of titrant volume
- Provides MORE RELIABLE data than the usual titration method
- Useful with colored/turbid solutions
- May be automated
- More time consuming

Types of Potentiometric titrations:

- Acid-base titration
- Redox titration
- Complexometric titration
- Precipitation titration

POTENTIOMETRIC TITRATION CURVES

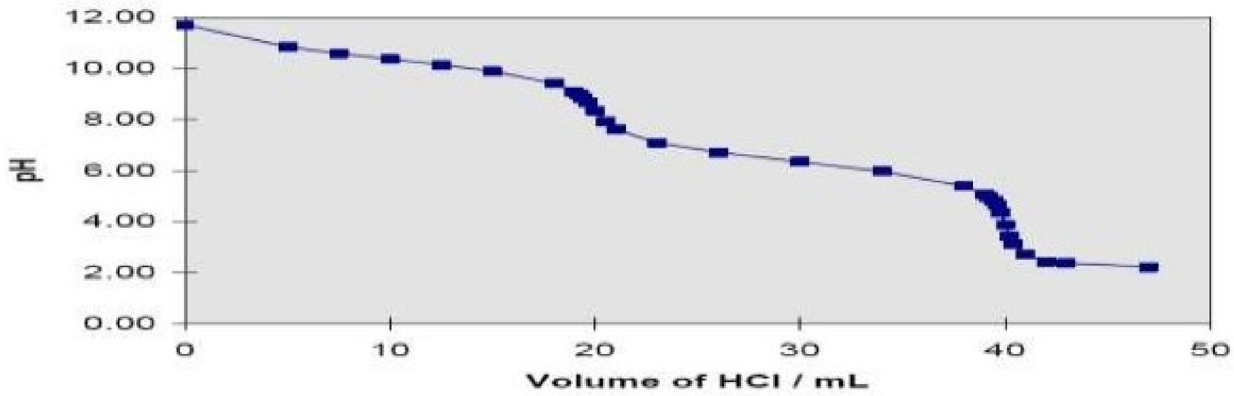




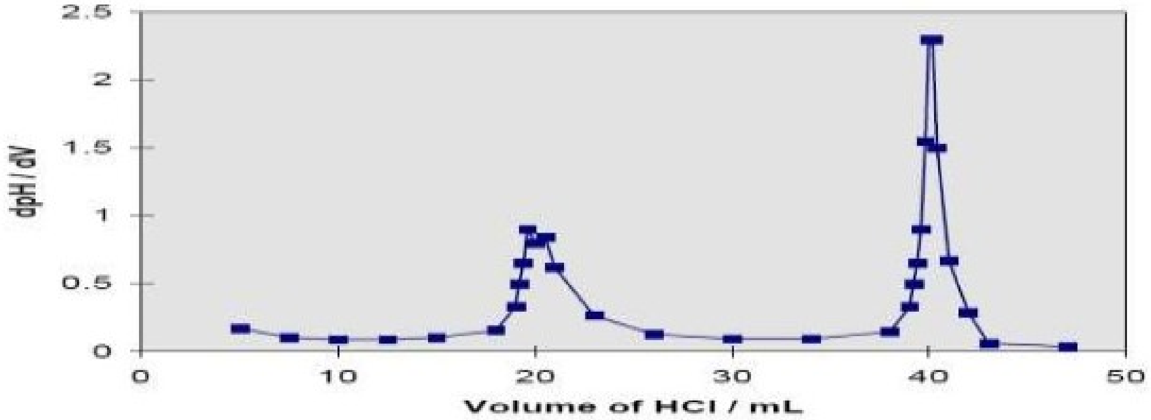
Acid-base reactions: Glass / calomel electrode for determination of pH.

ex: Titration of HCl with NaOH

Titration of CH_3COOH with NaOH



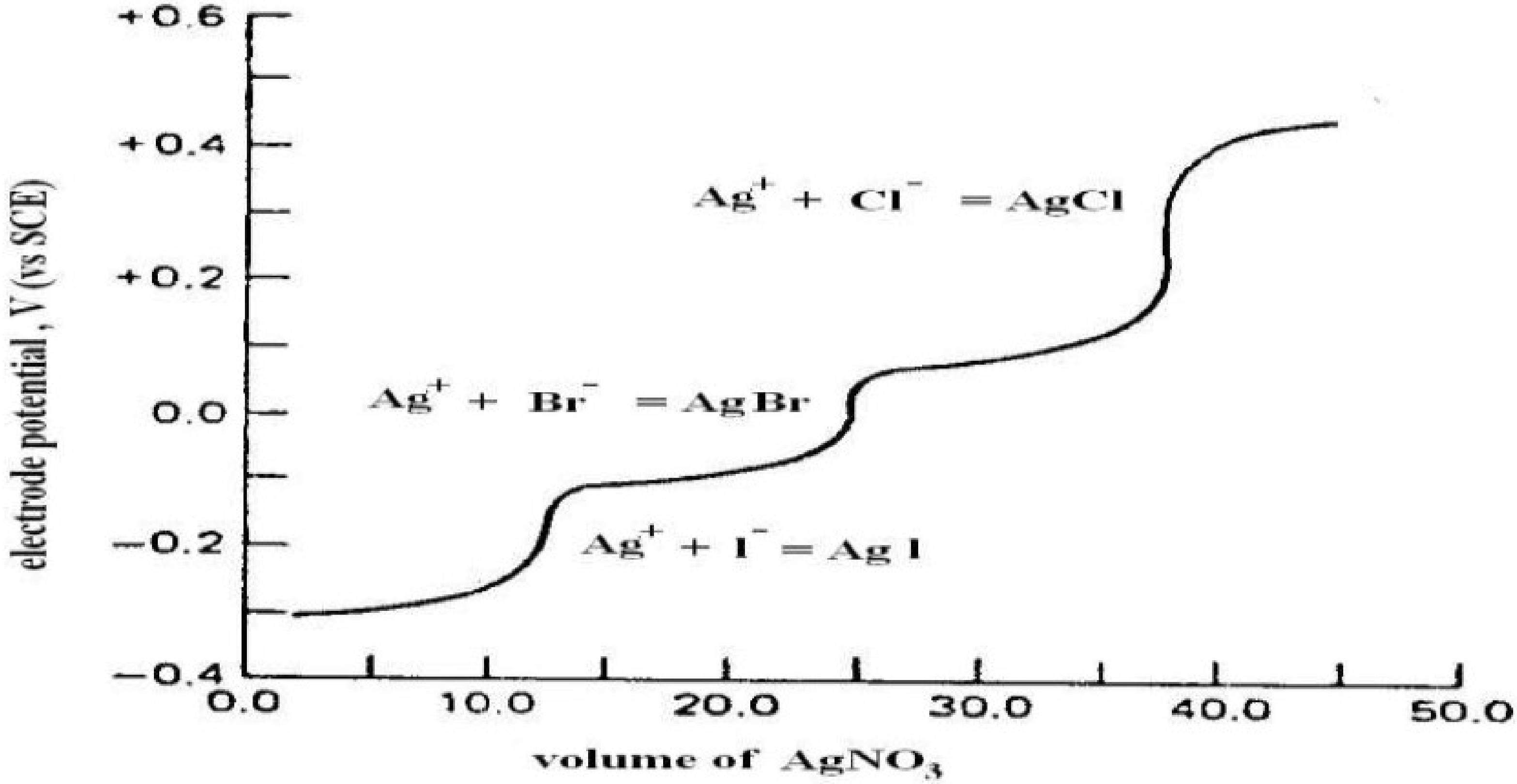
Titration of 2.5 mmoles of Na_2CO_3 with 0.125 M HCl



First Derivative

Precipitation reactions: Membrane electrodes for the determination of the halogens using silver nitrate reagent.

Ex:Titration of mixture of Cl^- & Br^- & I^- with $AgNO_3$



Potentiometric titration of I^-, Br^-, and Cl^- with $AgNO_3$

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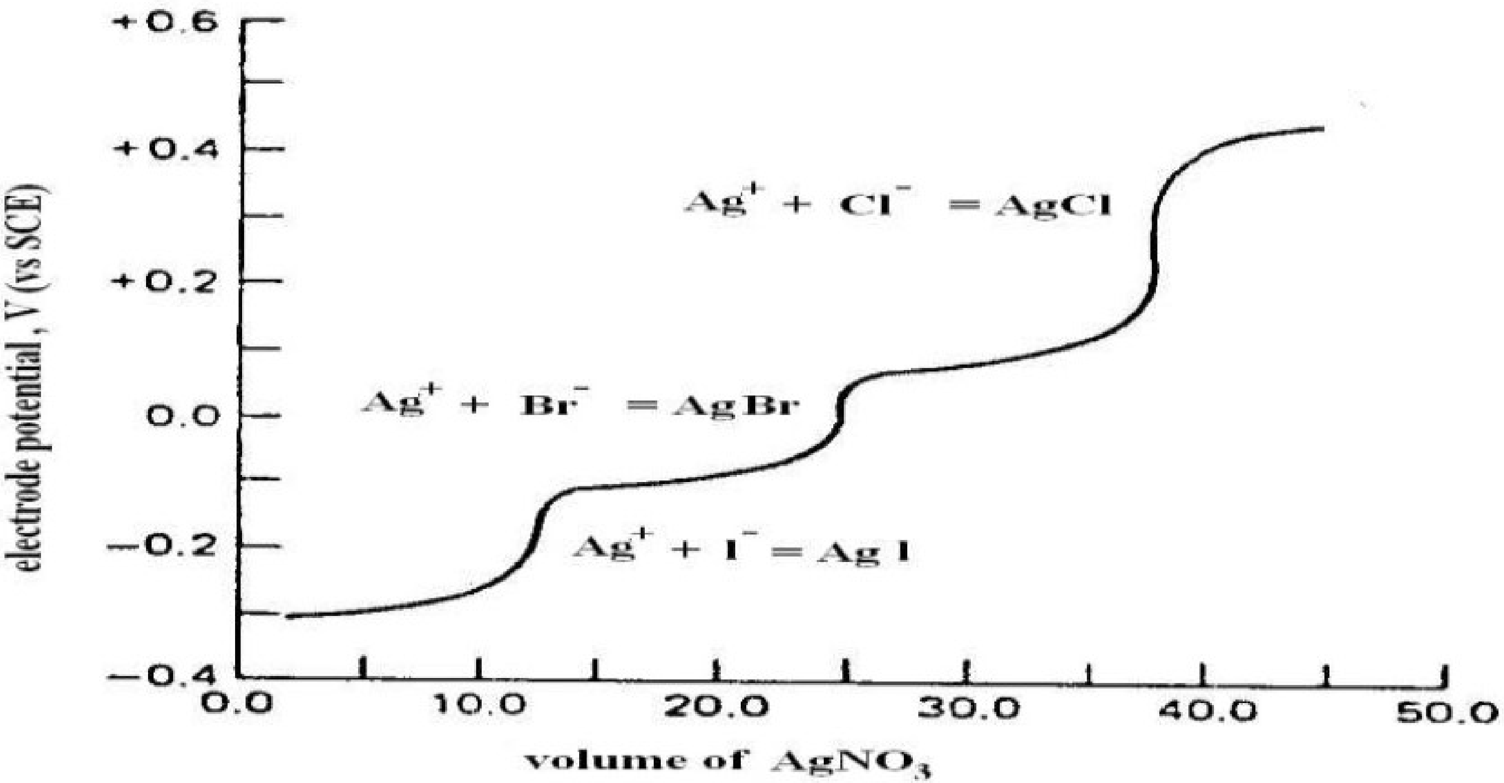
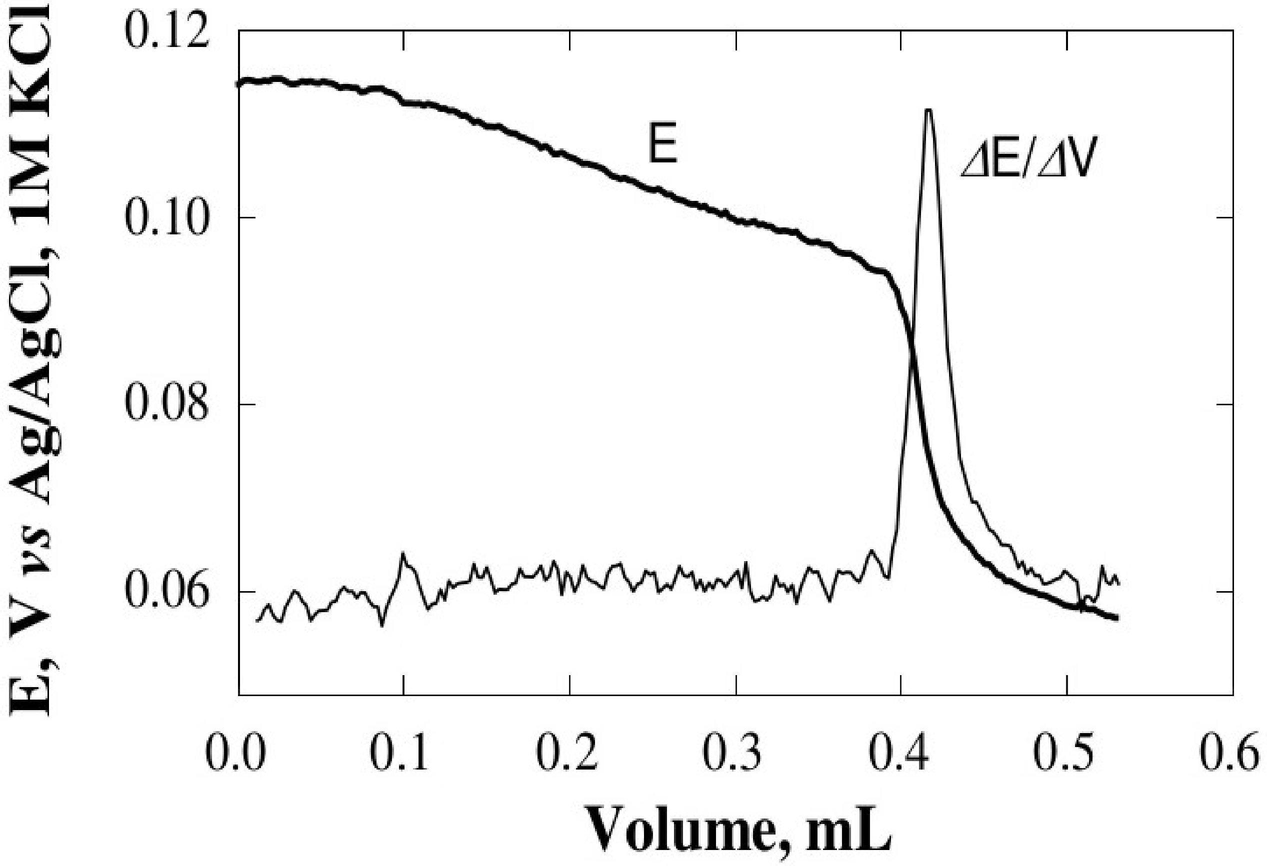


Potentiometric titration of I^-, Br^-, and Cl^- with $AgNO_3$

Complex formation titration: metal and membrane electrodes for determination of many cations (mixture of Bi3+, Cd2+ and Ca2+ using EDTA)



Application of Potentiometric Measurement

- Clinical Chemistry
  - Ion-selective electrodes are important sensors for clinical samples because of their selectivity for analytes in complex matricies.
  - The most common analytes are electrolytes, such as Na^+, K^+, Ca^{2+},H^+, and Cl^-, and dissolved gases such as CO_2.

- Environmental Chemistry
  - For the analysis of of CN^-, F^-, NH_3, and NO_3^- 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 nonaqueous solvents.

- Agriculture
  - NO_3, NH_4, 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
  - NO_3, NO_2 in meat preservatives
  - Salt content of meat, fish, dairy products, fruit juices, brewing solutions.
  - F in drinking water and other drinks.
  - Ca in dairy products and beer.
  - K in fruit juices and wine making.
  - Corrosive effect of NO_3 in canned foods

Thank You