

POTENTIOMETRY

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Potentiometry

Principle: The principle involved in the Potentiometry is when the pair of electrodes is placed in the sample solution it shows the potential difference by the addition of the titrant or by the change in the concentration of the ions.



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:

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

where $E_{\text{reference}}$ is the electromotive force of the reference electrode, $E_{\text{indicator}}$ 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/ Hg₂Cl₂/ KCl

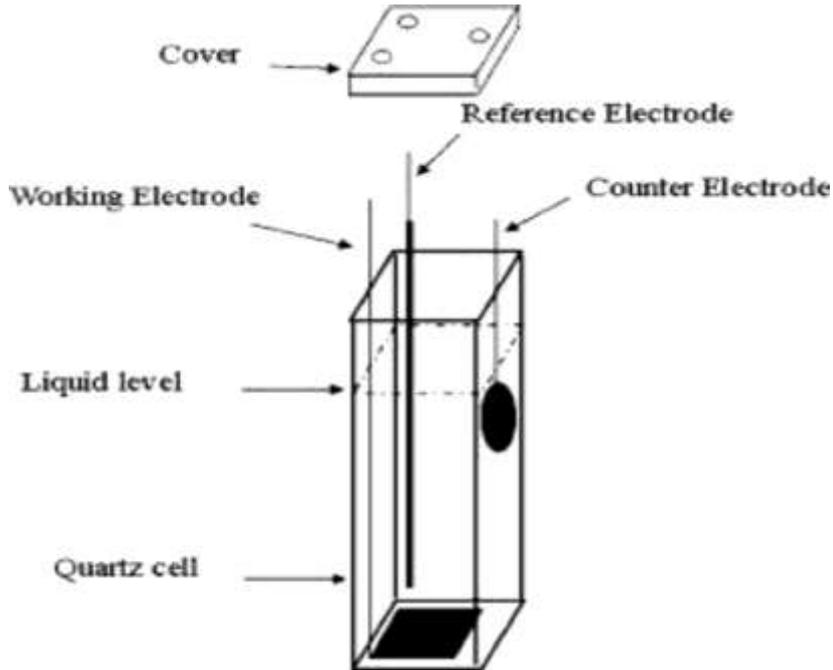
▪ **Third kind electrodes:** These electrodes are also known as inert electrodes and redox electrodes. They are composed of inert metal electrode immersed in the redox solution.

Ex: Pt-H₂ electrode

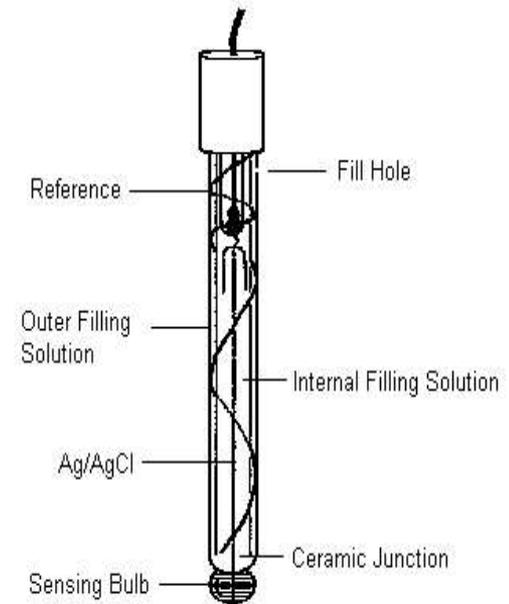
Ion selective indicators: These are composed of ion-selective membrane by which the ion crosses and it creates the imbalance.

Ex: Glass membrane electrode

Antimony –antimony oxide electrode.



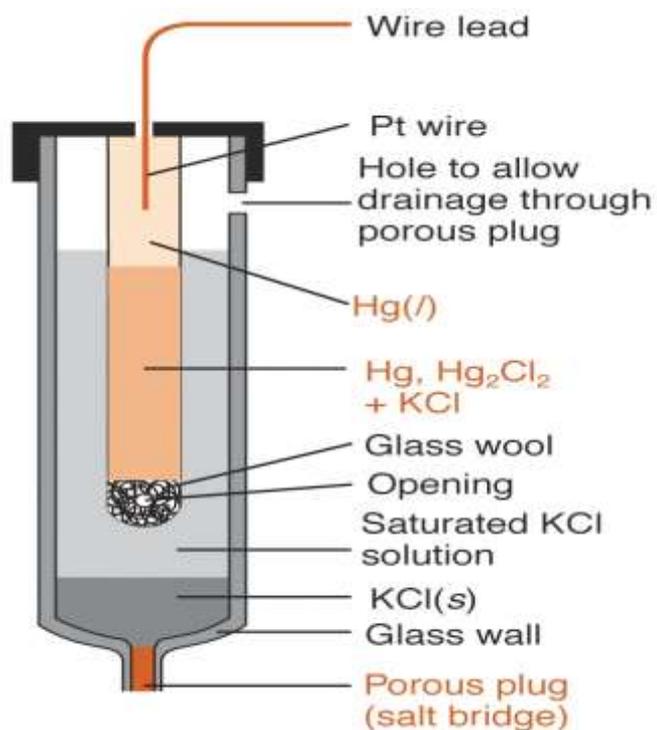
Antimony-antimony oxide electrode



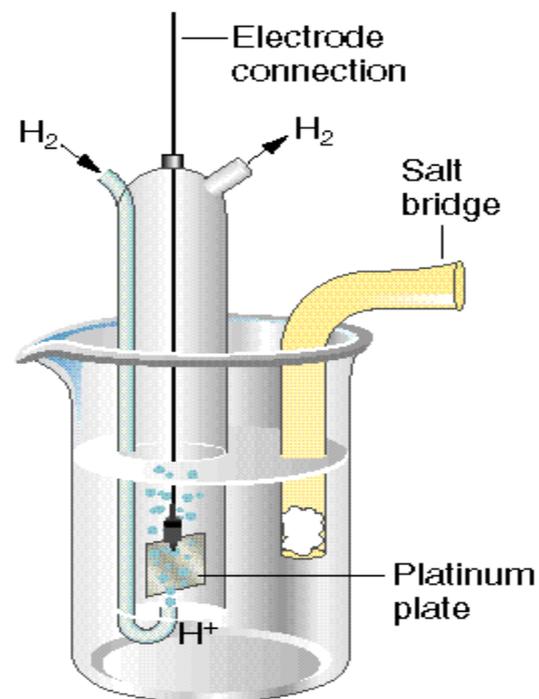
Glass electrode

Types of Potentiometric titrations:

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



Saturated calomel electrode

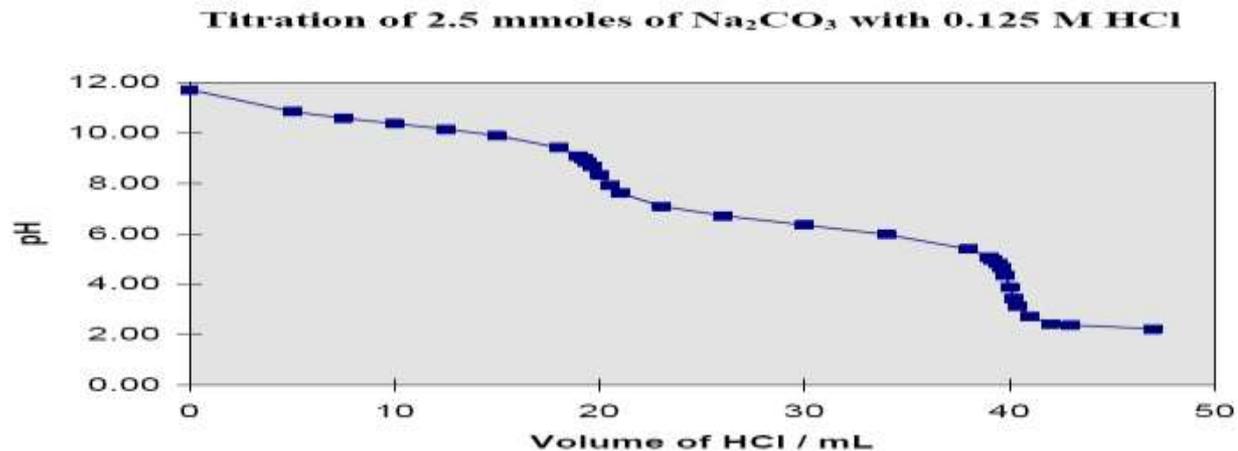


Standard hydrogen electrode

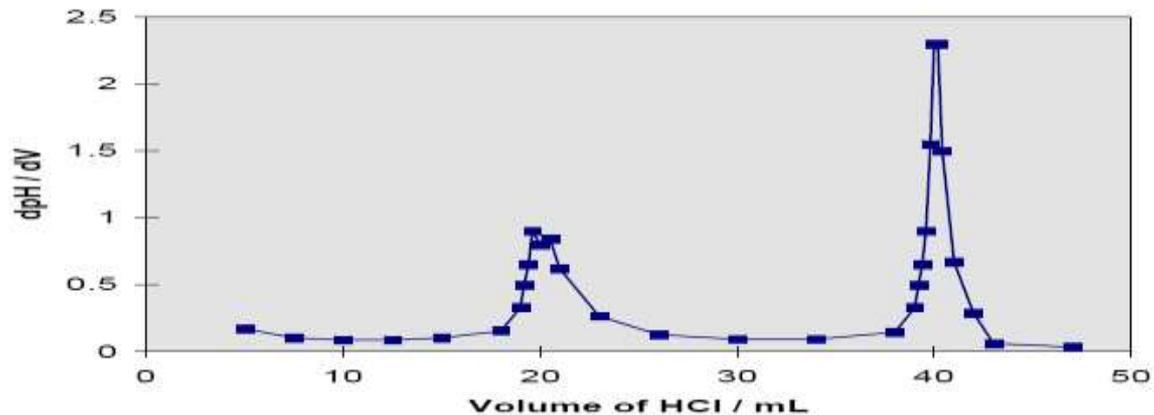
Acid-base reactions: Glass / calomel electrode for determination of pH.

ex: Titration of HCl with NaOH

Titration of CH_3COOH with NaOH

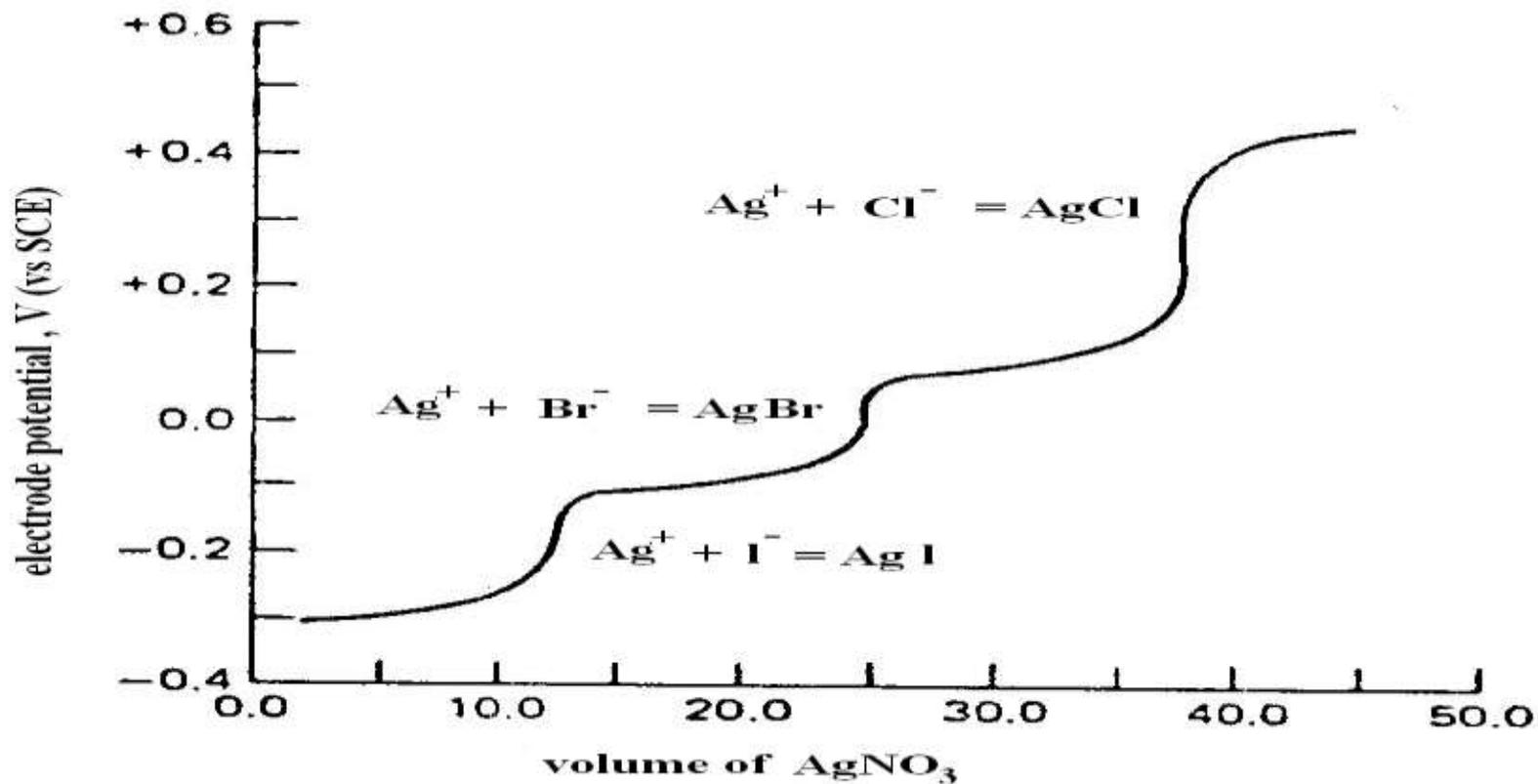


First Derivative



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

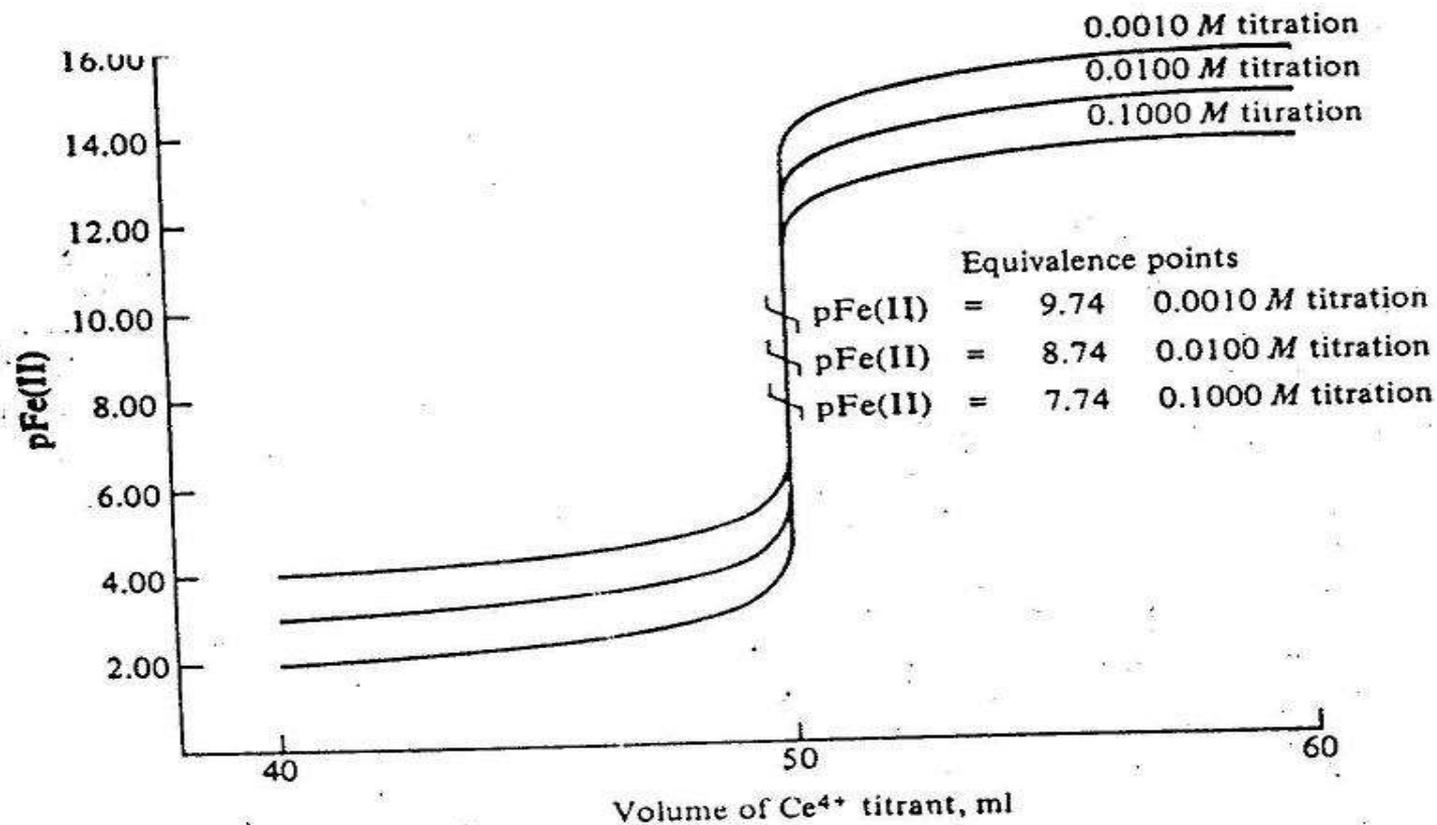
Ex: Titration of mixture of Cl^- & Br^- & I^- with AgNO_3



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

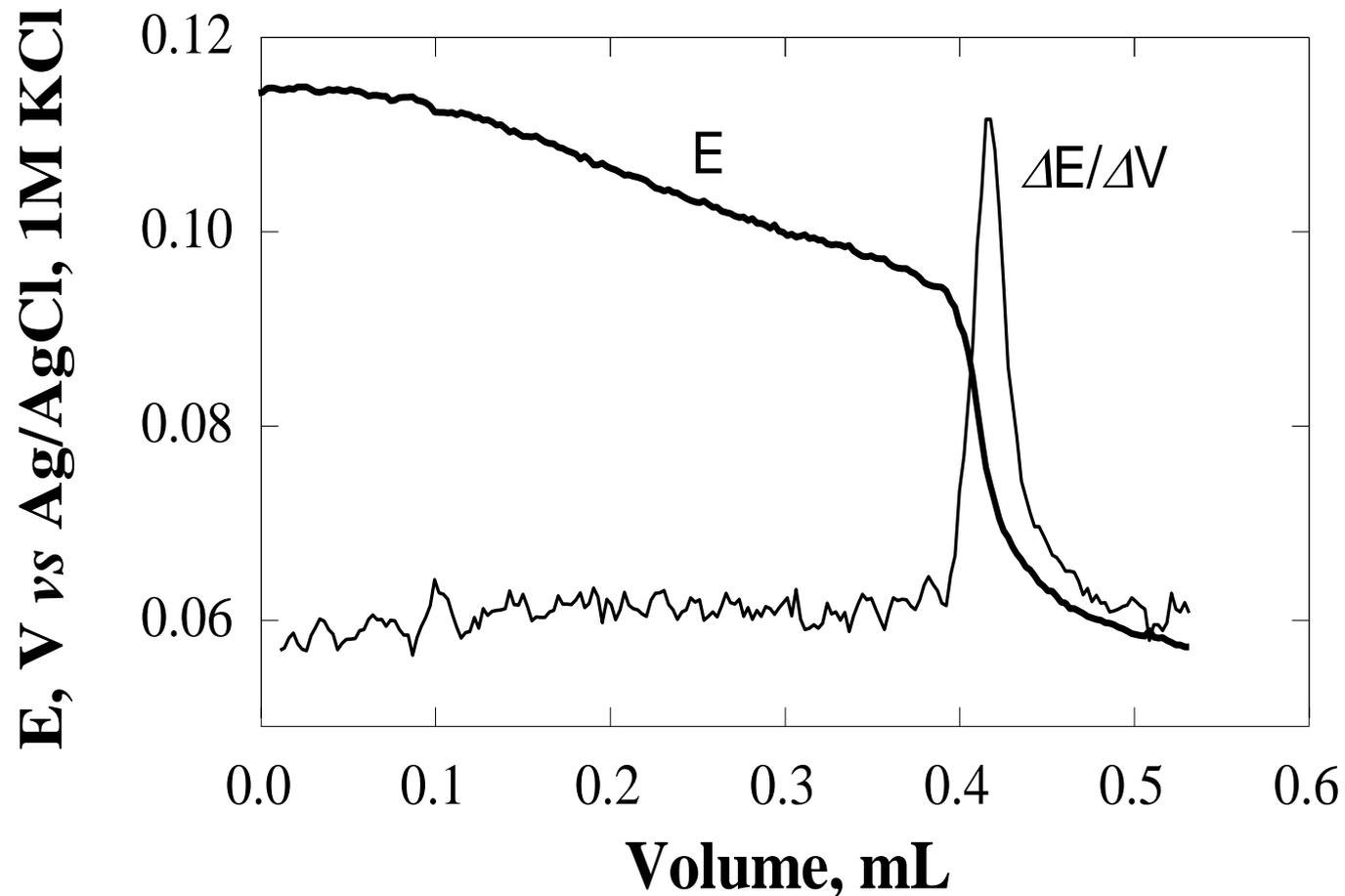
Redox titration: platinum electrode.

For example : reaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with $\text{Ce}^{4+}/\text{Ce}^{3+}$



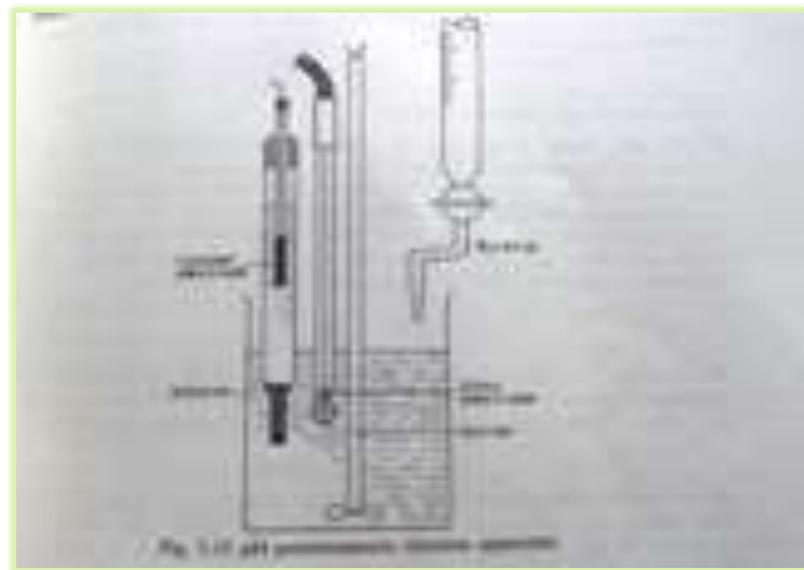
Titration of 50.00 ml Fe^{2+} vs. Ce^{4+} in 0.5 M H_2SO_4 .

Complex formation titration: metal and membrane electrodes for determination of many cations (mixture of Bi^{3+} , Cd^{2+} and Ca^{2+} using EDTA)



General method for potentiometry:

- Switch on the instrument
- Connect the saturated calomel electrode to the positive terminal or socket and the glass electrode to the negative. Arrange the calomel electrode and the paddle of the stirrer in such a way that it must be at the lower level of the glass electrode which is placed between them.
- Adjust the meter to zero and standardize the electrode system as above. as subsequent readings are to be taken with the stirrer motor running.



- Rinse the beaker and electrodes thoroughly with water, then with the solution to be titrated and place a measured volume in the beaker .add sufficient water to cover the bulb of the glass electrode adequately
- Switch on the stirrer and measure the pH of the solution.
- Add about 2ml of titrant ,allow sufficient time to mix and measure the pH of the solution.
- Add further quantities of titrant and as the end point is approached reduce to 0.1ml increments and measure the corresponding values of the pH.
- Obtain further readings of pH for about 5ml beyond the equivalence point. Switch the meter to standby and turn off the stirrer. wash the beaker and electrodes thoroughly with the distilled water.
- Plot a graph of pH (vs) titrant added. Read off the equivalence point from the graph and calculate any required data from this value. if the titration is of a weak acid against a base, calculate the pK_a value of the acid from the Henderson equation, which is valid over the range of PH4 to pH10

APPLICATIONS

- **Clinical chemistry:** Ion selective electrodes are present sensors for clinical samples because of their selectivity for analyte in complex matrices. The most common analytes are electrolytes such as Na, K, Ca, H, and Cl and dissolved gases such as CO₂
- **Environmental chemistry:** For analysis of CN⁻, NH₃, NO₃, F₃ in water and waste water.
- **Potentiometric titrations:** For determining the equivalence point of an acid base titration.
 - possible for redox, precipitation, acid-base, complexation as well as for all titrations in aqueous and non aqueous solvents.
- **Agriculture:** NO₃, NH₄, I, Ca, K, CN, Cl in soils, plant materials, feed stuffs, fertilizers.
- **Detergent manufacturing:** Ca, Ba, F for studying effects in water quality.

➤ Food processing:

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

➤ Assay of bisacodyl suppositories and assay of sulpha drugs can be estimated potentiometrically.



Automatic potentiometer

