

CH 2252 Instrumental Methods of Analysis

Unit – II

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Electro Analytical Methods

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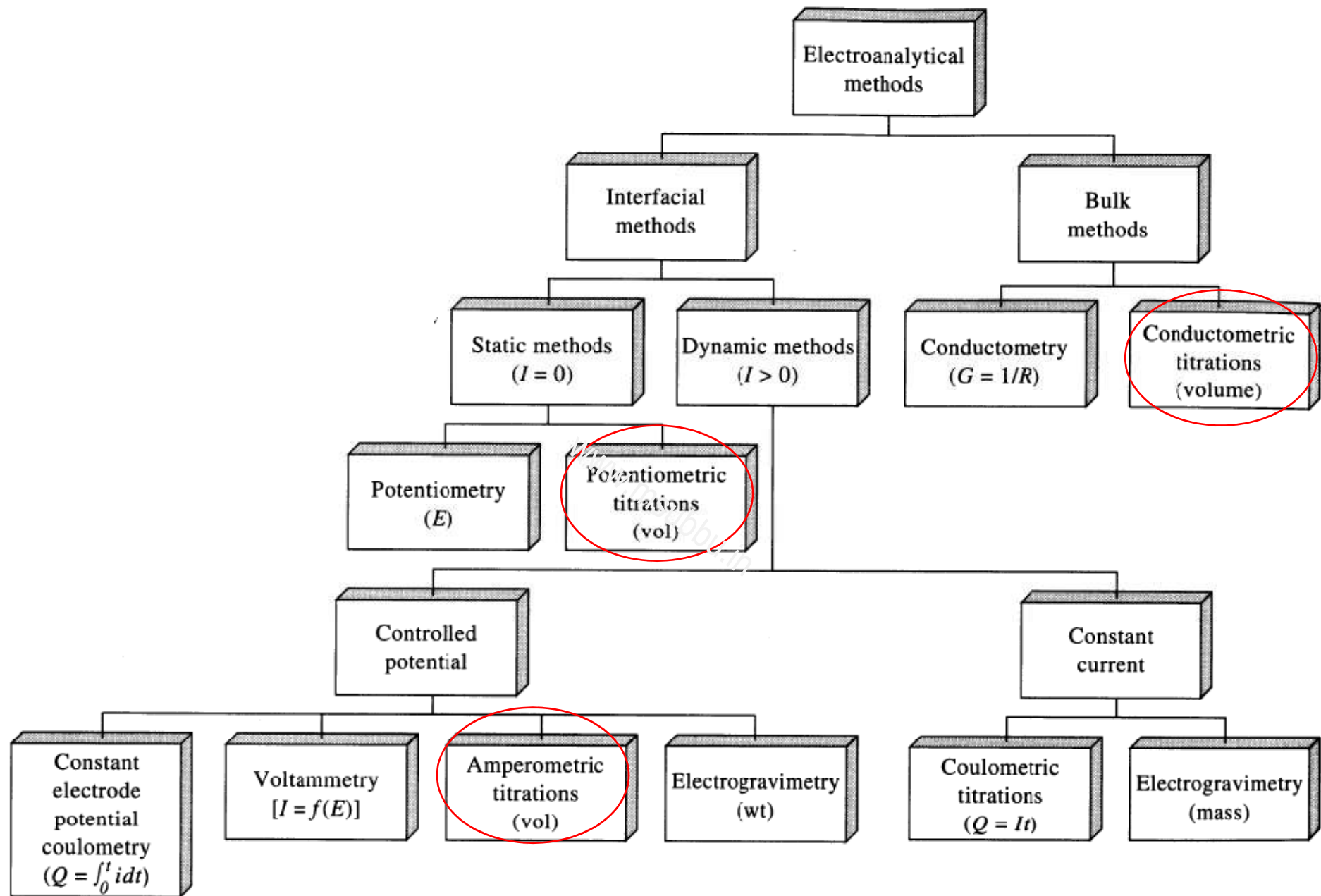
Contents

- Conductometric Titrations: Instrumentation-Types-Advantages-Application;
- Potentiometric Titrations: Instrumentation-Types-Advantages-Application;
- Measurement of pH: Instrumentation-Applications; Ion selective electrodes: Electrode setup-Applications.;
- Amperometric titrations: Principle-instrumentation- Application

Introduction

- Diverse analytical techniques, some highly sensitive, have been developed based on measurements of current, voltage, charge, and resistance in electrochemical systems.
- One variable is measured while the others are controlled.

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Conductometry

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Basics

- Ohm's law: Resistance of metal wire,
 $R = E/i$
where E is the voltage applied (V)
i is the current flow through the wire (A)
R is the resistance of the wire (Ω)
- Dependence of resistance on the dimensions of the cell:
 $R = \rho L/A$
where ρ is resistivity, L is the distance between electrodes, A –
cross sectional area of electrodes
- Electrolytic conductivity of solution:
 $\kappa = 1/\rho = (L/A)/R$

The units of electrolytic conductivity are: $\Omega^{-1} \cdot \text{m}^{-1}$

SI unit is S/m, but practical measurement units are usually in $\mu\text{S}/\text{cm}$. (S – Siemen)

Introduction

- In conductometry an alternating (AC) voltage is applied across two electrodes immersed in the same solution. The applied voltage causes a current to flow. The magnitude of the current depends on the electrolytic conductivity of the solution.
- This method makes it possible to detect changes of composition in a sample during chemical reactions (e.g., during a titration) although the measurement itself cannot identify the species carrying the current. All ions in solution contribute to the electrical conductivity, so this is not a specific method of analysis
- Conductivity or conductance measurements are used routinely to monitor water quality and process streams. Conductivity detectors are used for measuring ion concentrations in commercial ion chromatography instruments

Conductometric Titrations

- When one ion is replaced in solution by a different ion with a significantly different equivalent conductivity, a change in total conductivity occurs
- *Conductometric titrations*, in which conductance measurements are used for end-point detection, can be applied to the determination of numerous substances
- The principal advantage to the conductometric end point is its applicability to the titration of very dilute solutions
- Conductometric titrations become less accurate at high electrolyte concentrations

Instrumentation

- Conductance is usually measured with an alternating current between two identical, platinized platinum electrodes.
- Use of an alternating current prevents the buildup of reaction products around either electrode and consequently prevents polarization of the solution
- The electrodes must be rigidly held at a fixed distance apart during the titrations in order to prevent changes in conductance

Power Sources

- Use of an alternating current source eliminates the effect of Faradaic currents.
- There are, however, both upper and lower limits to the frequencies that can be employed; audio oscillators that produce signals of about 1000 Hz are the most satisfactory.
- For less refined work, an ordinary 60-cycle current, stepped down from 110 to perhaps 10 V, is also used.

Temperature Control

- The temperature coefficient for conductance measurements is about $2\%/^{\circ}\text{C}$; as a consequence, some temperature control is ordinarily required during a conductometric measurement.
- For many purposes, it is sufficient to immerse the cell in a reasonably large bath of water or oil, which is at room temperature.

Factors affecting the conductance

- The conductance of an ion in solution is related to the charge, size, and concentration of the ion.
- A comparison of ions about the same size and concentration reveals that the conductance is greater for ions of greater charge
- As the size of ion decreases, its conductivity increases
- As the concentration of a particular ion increases, the conductance owing to the ion increases

Molar conductivities at infinite dilution, at 25°C

Ion	S.cm ² /mol	Ion	S.cm ² /mol
H ⁺	349.8	OH ⁻	198.6
Na ⁺	50.1	Cl ⁻	76.4
NH ₄ ⁺	73.4	Formate	55
Ca ²⁺	119	Acetate	41
Fe ³⁺	204	Benzoate	32

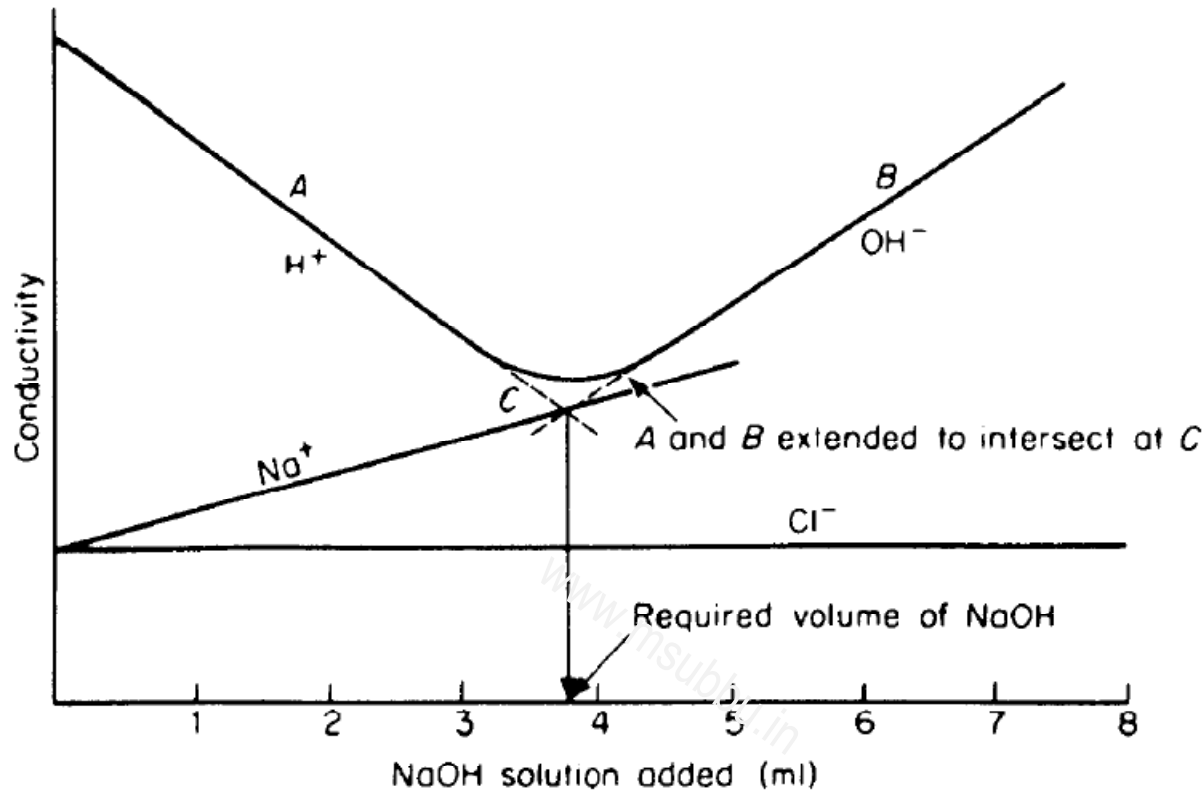
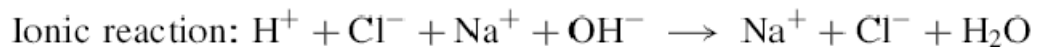
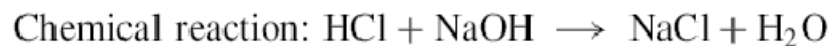
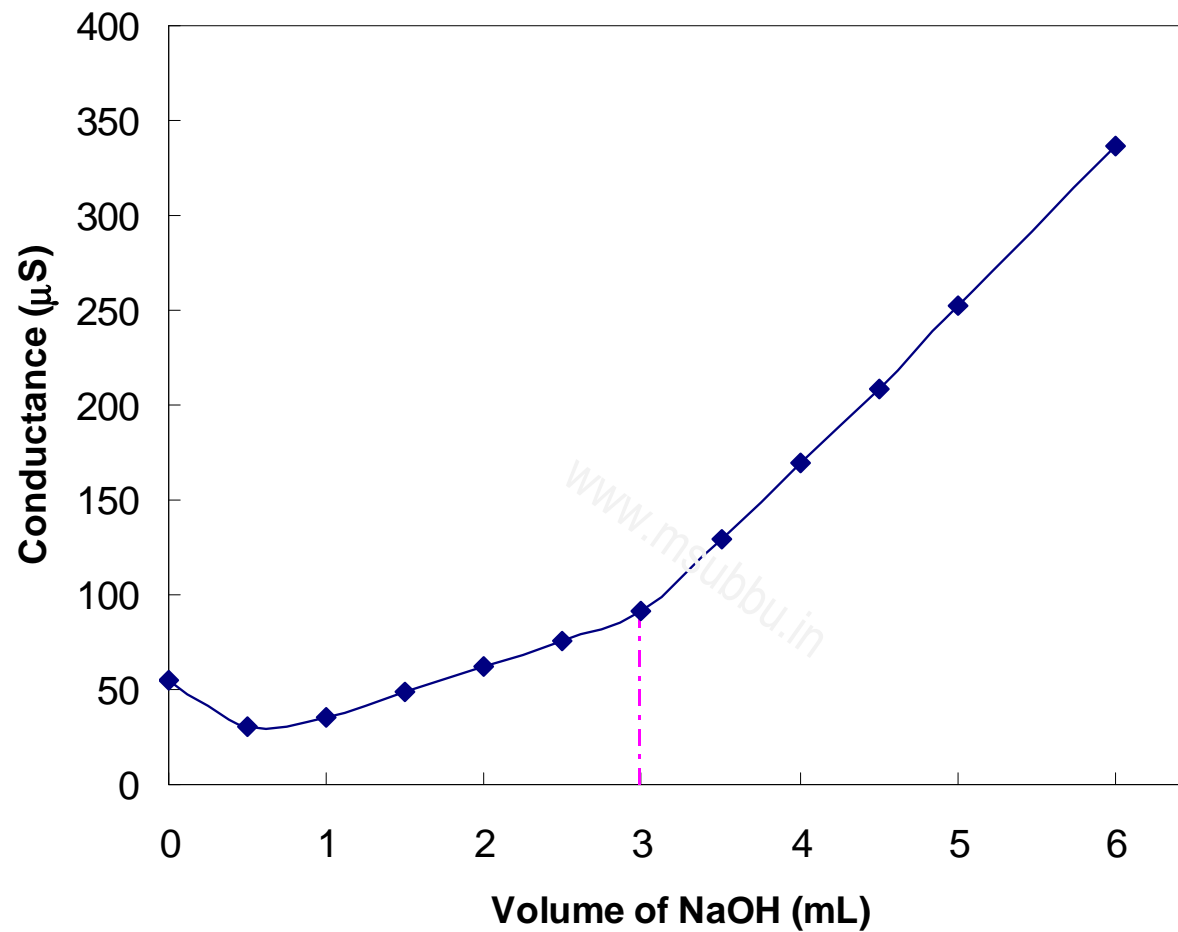


Figure 15.22 Solution conductivity during an HCl–NaOH titration. Point C is the neutralization point.



At the equivalence point, the concentrations of hydrogen and hydroxide ions are at a minimum and the solution exhibits its lowest conductance. A reversal of slope occurs past the end point



Conductometric Titration of Acetic acid with NaOH

Braun, Introduction to Instrumental Analysis, McGraw-Hill, 1987

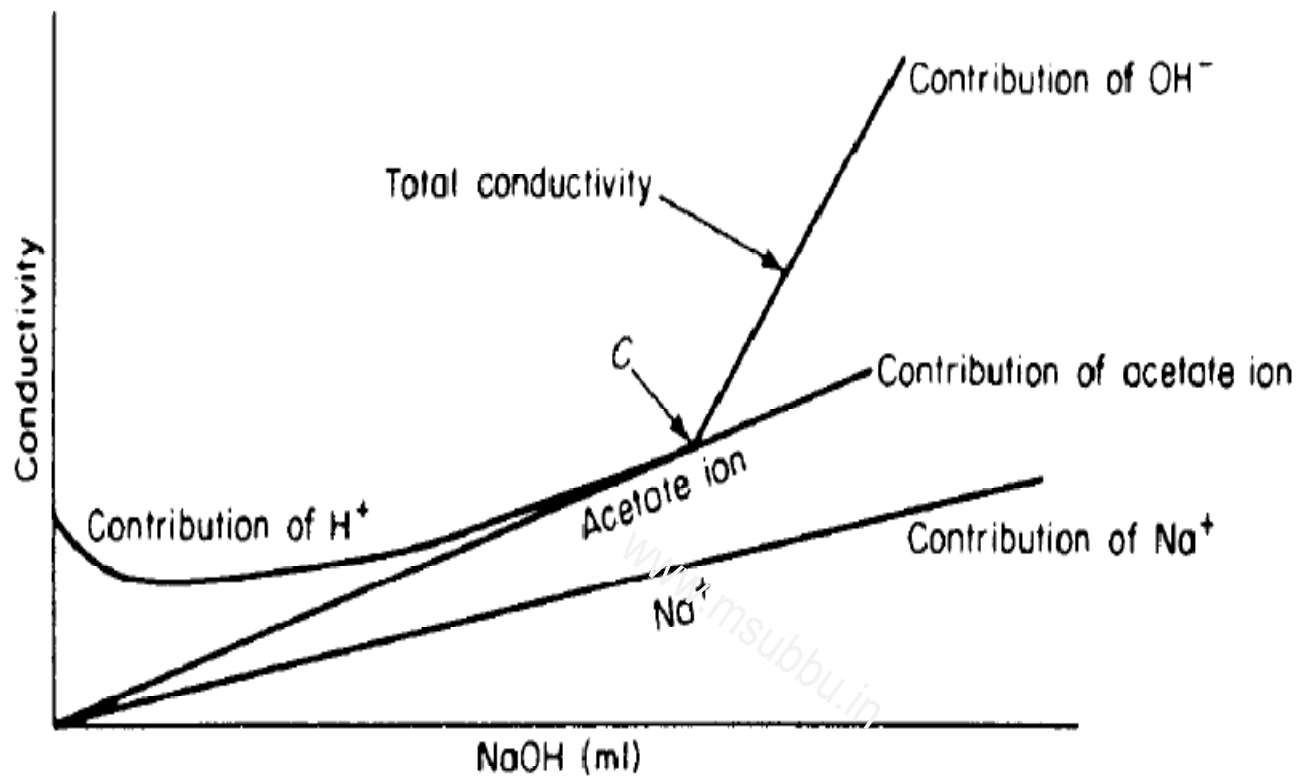
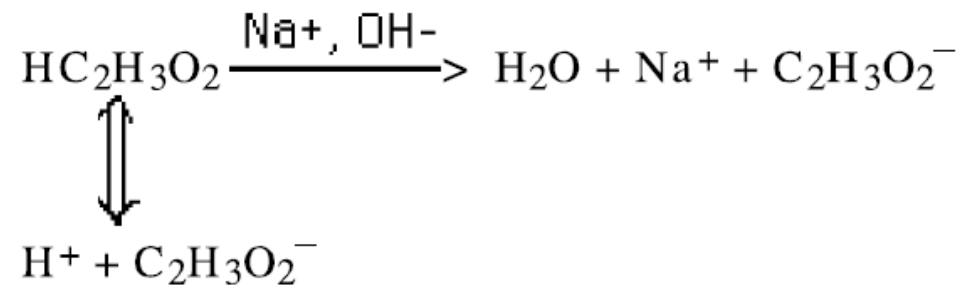
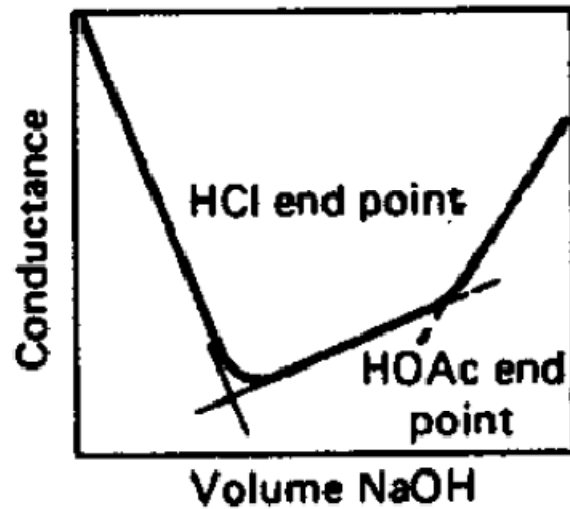


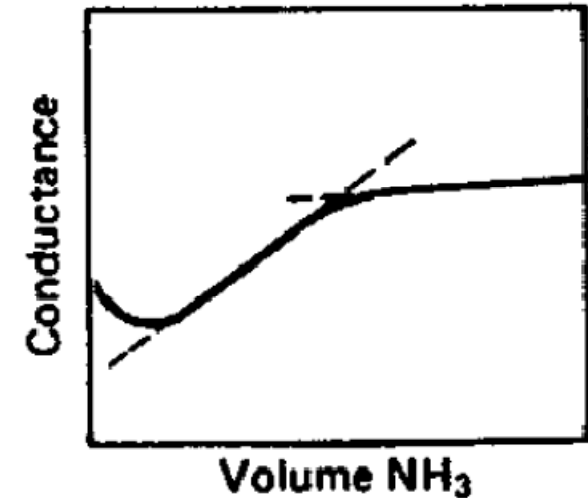
Figure 15.23 Solution conductivity during an acetic acid–NaOH titration. Point C is the neutralization point.



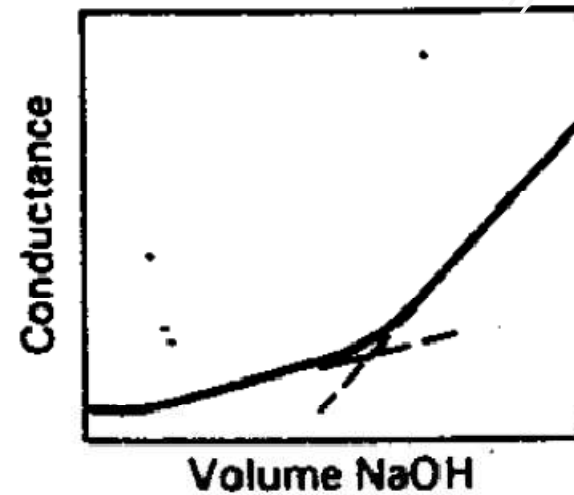
Conductometric Titrations



Mixture of HCl and Acetic acid with NaOH



Weak acid with aqueous NH₃



Weak acid with NaOH

Potentiometry

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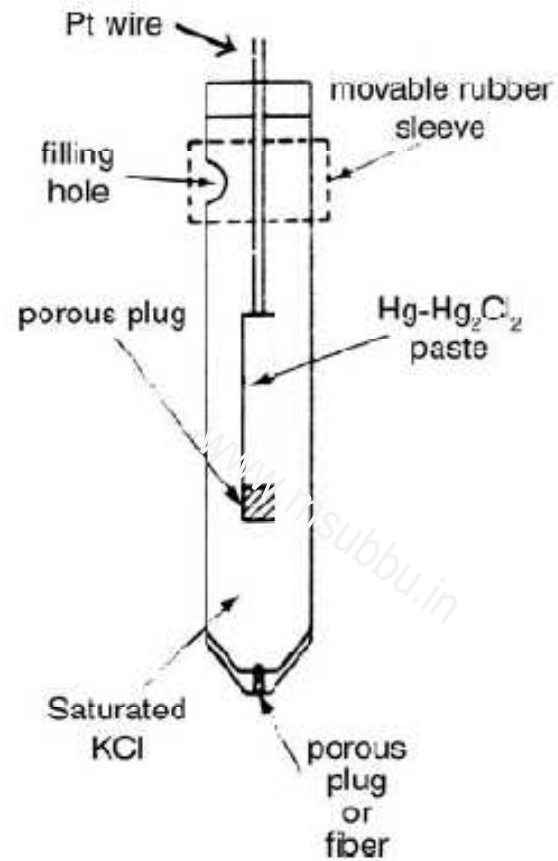


Introduction

- Potentiometry measures the potential developed by a cell consisting of an indicator electrode and a reference electrode
- In theory, the indicator electrode response is a measure of the activity of a single component of the solution, the analyte. In practice, the indicator electrode is calibrated to respond to concentration rather than activity and is usually not specific for a single analyte.
- The potential, E_{cell} , is measured under negligible current flow to avoid significant changes in the concentration of the component being measured. Modern potentiometers permit measurement of potential with currents $< 1 \text{ pA}$, so potentiometry can be considered to be a nondestructive technique
- Potentiometry is the basis for measurement of pH, ion-selective electrode measurements, and potentiometric titration

Reference Electrodes for Potentiometry

- The common reference electrodes used in potentiometry are the SCE and the silver/silver chloride electrode.
- The choice of reference electrode depends on the application. For example, the Ag/AgCl electrode cannot be used in solutions containing species such as halides or sulfides that will precipitate or otherwise react with silver.



The saturated calomel electrode (SCE).

$$E = +0.244 \text{ V for the SCE}$$

Indicator Electrodes

- The indicator electrode is the electrode that responds to the change in analyte activity.
- An ideal indicator electrode should be specific for the analyte of interest, respond rapidly to changes in activity, and follow the Nernst equation.
- There are no specific indicator electrodes, but there are some that show a high degree of selectivity for certain analytes.
- Indicator electrodes fall into two classes, metallic electrodes and membrane electrodes.

Metallic Electrodes

- A metal electrode of the **first kind** is just a metal wire, mesh, or solid strip that responds to its own cation in solution. Cu/Cu^{2+} , Ag/Ag^+ , Hg/Hg^+ , and Pb/Pb^{2+} are examples of this type of electrode. There are significant problems encountered with these electrodes. They have poor selectivity, responding not only to their own cation but also to any other more easily reduced cation.
- A metal electrode of the **second kind** consists of a metal coated with one of its sparingly soluble salts (or immersed in a saturated solution of its sparingly soluble salt). This electrode responds to the anion of the salt. For example, a silver wire coated with AgCl will respond to changes in chloride activity
- Electrodes of the **third kind** - respond to changes of different ion than metal electrode

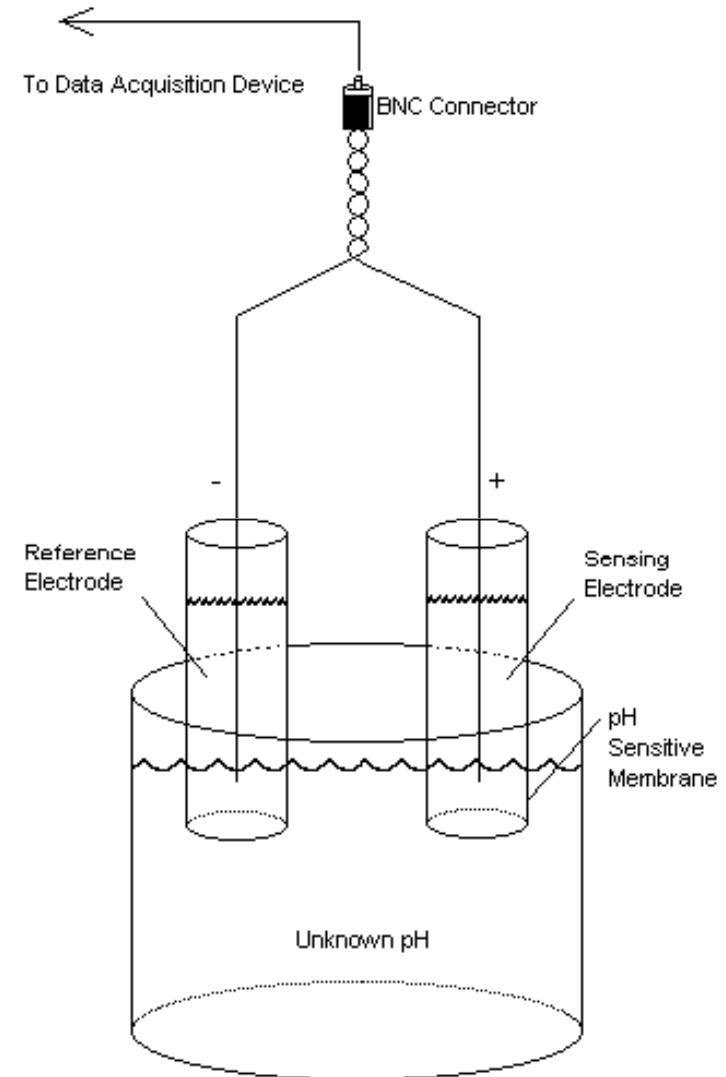
Membrane Electrodes

- Membrane electrodes are a class of electrodes that respond selectively to ions by the development of a potential difference (a type of junction potential) across a membrane that separates the analyte solution from a reference solution.
- The potential difference is related to the concentration difference in the specific ion measured on either side of the membrane
- Because these electrodes respond to ions, they are often referred to as **ion-selective electrodes** (ISEs)
- They are capable of detecting concentrations as low as 10^{-12} M for some electrodes
- To avoid writing small concentrations in exponential form, the term p_{Ion} has been defined

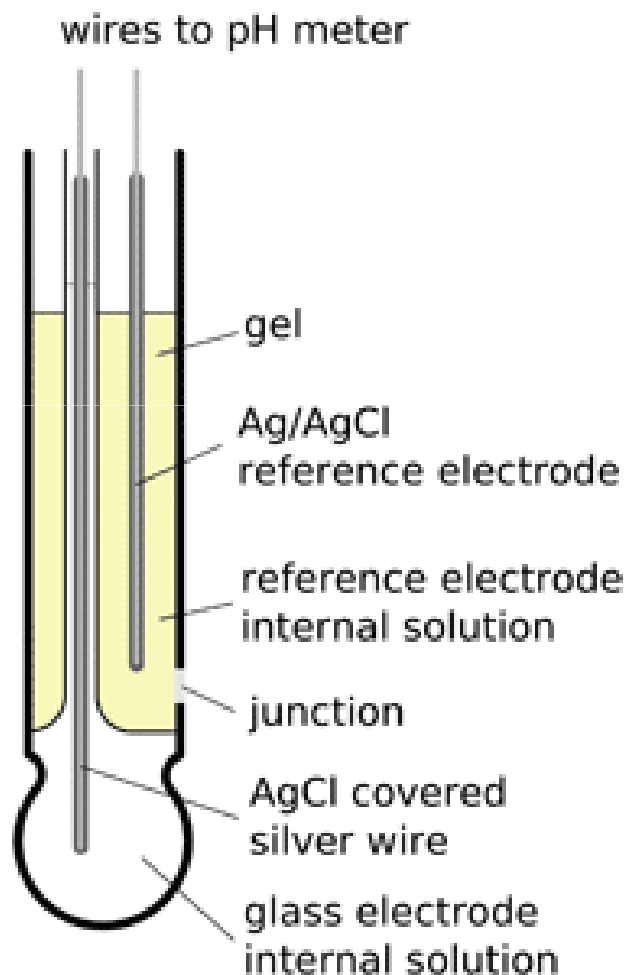
$$p_{\text{Ion}} = -\log[\text{Ion}]$$

pH measurement

- One of the most important applications of potentiometry is the determination of $[H^+]$ or the pH of a solution, where pH is defined as the negative logarithm to the base 10 of the hydrogen ion activity



pH electrode

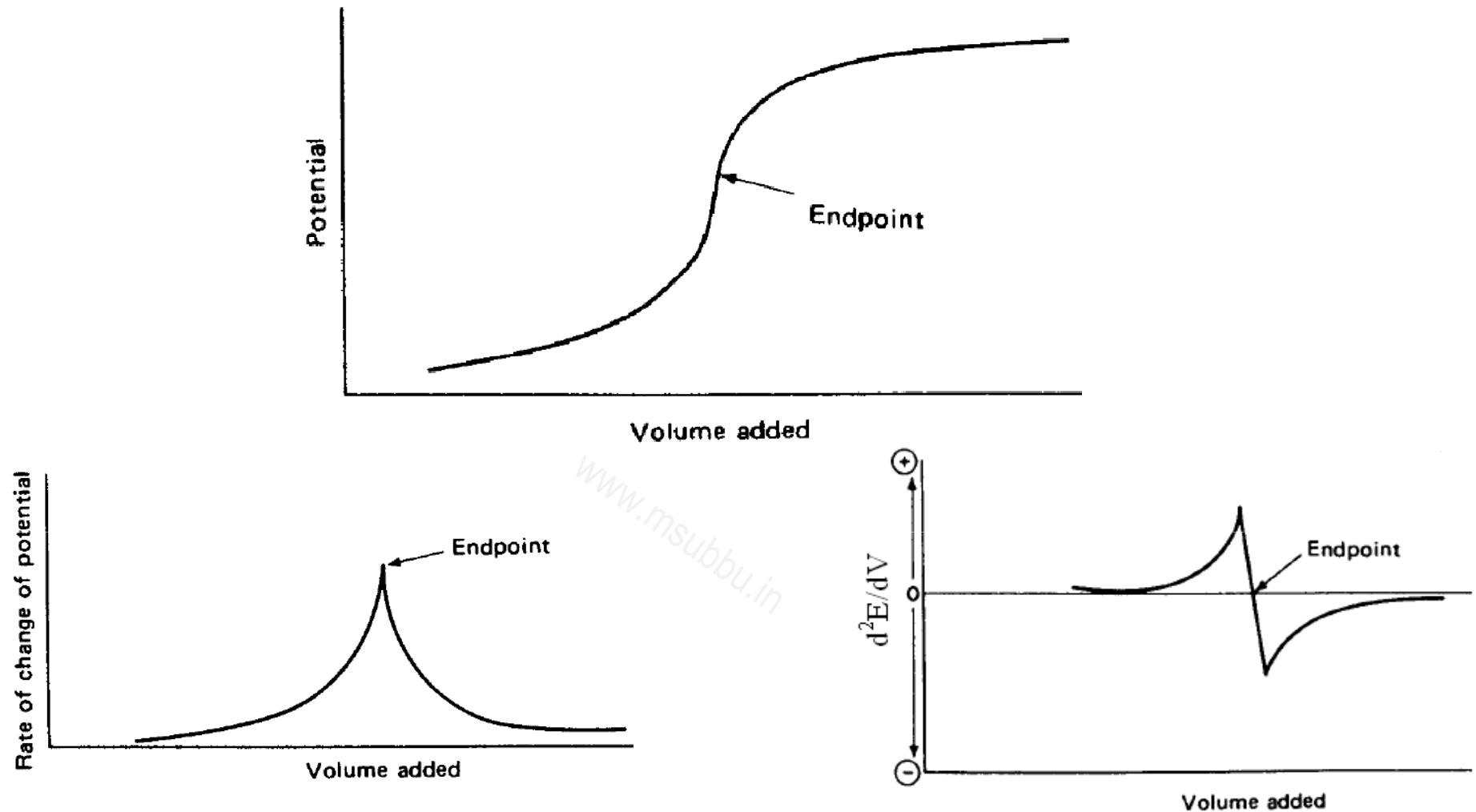


- The majority of pH electrodes available commercially are combination electrodes that have both glass H^+ ion sensitive electrode and additional reference electrode conveniently placed in one housing.
- For some specific applications separate pH electrodes and reference electrodes are still used - they allow higher precision needed sometimes for research purposes.
- In most cases combination electrodes are precise enough and much more convenient to use.

Potentiometric Titrations

- Potentiometry is a useful way to determine the endpoint in many titrations.
- For example, the concentration of Ag^+ ion in solution can be used to determine the equivalence point in the titration of Ag^+ with Cl^- .

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In dilute solutions, nonaqueous solvents and titrations involving slower reactions, the titration curve may be flatter (the inflection point hard to find) and difficult to interpret. The problem can be simplified by using equipment that records the first and/or second differential of the titration curve.

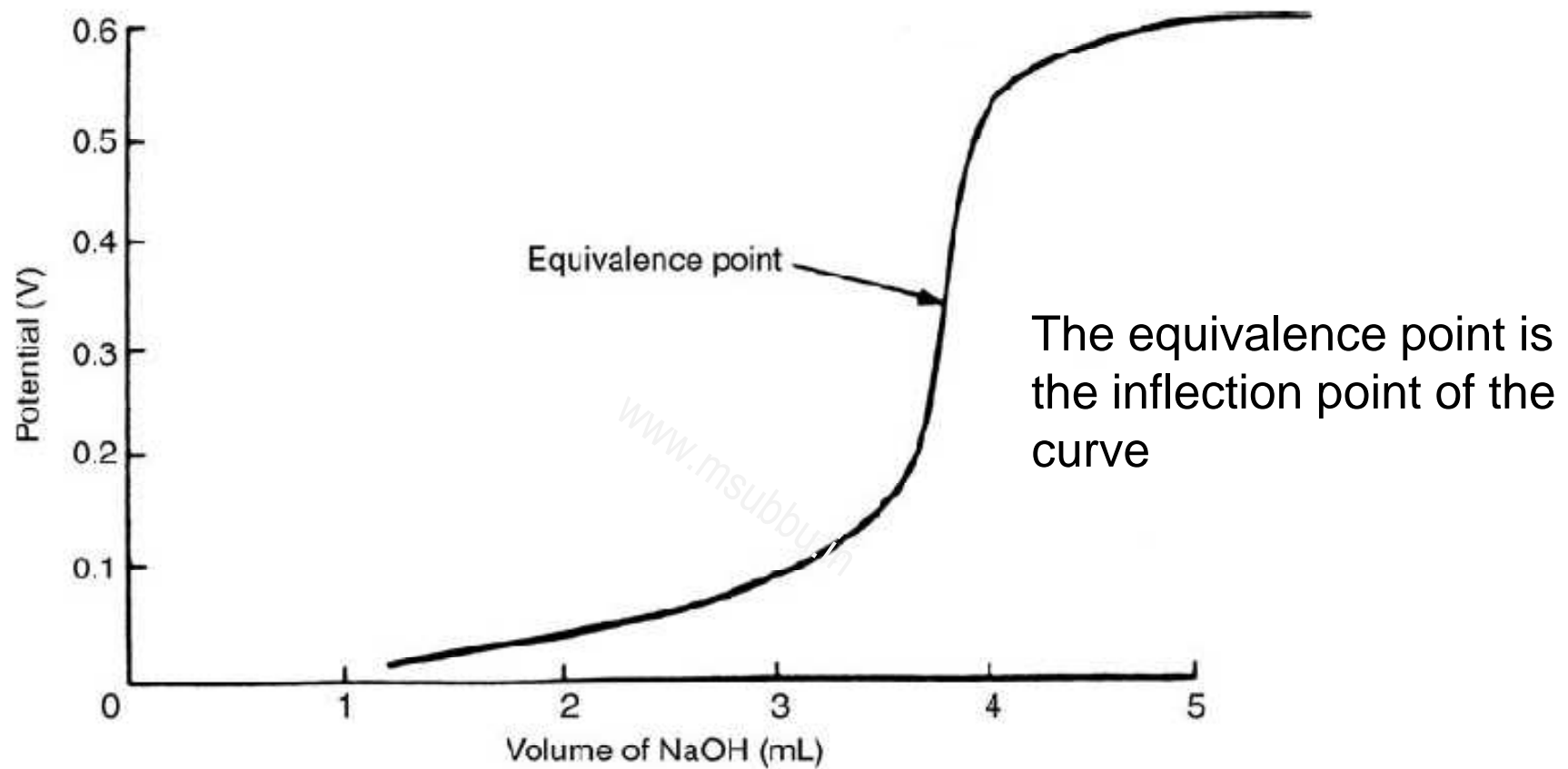


Figure 15.17 Schematic plot of the potentiometric titration of a strong acid with NaOH. A pH electrode can be used as the indicator electrode.

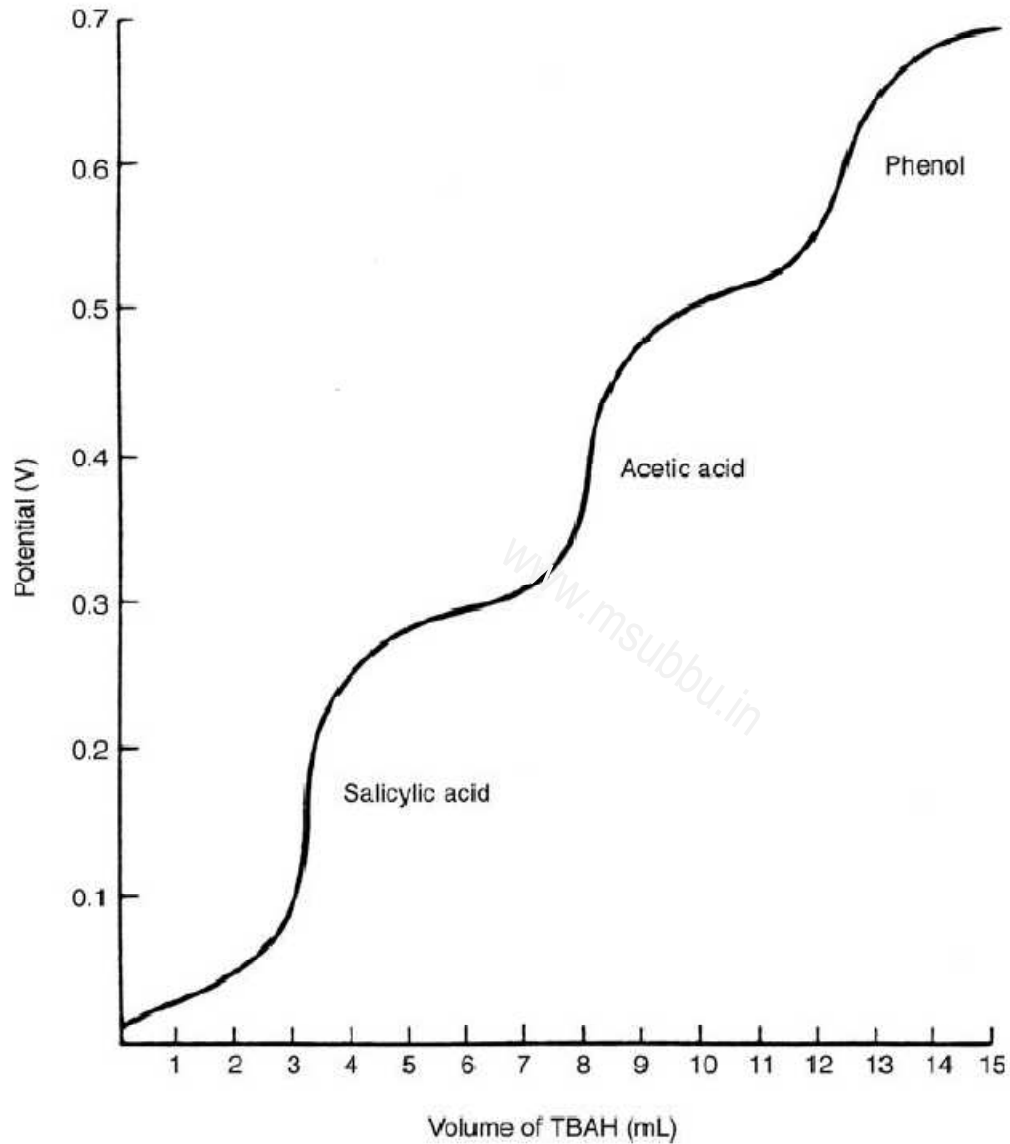


Figure 15.18 Schematic plot of the potentiometric titration of three weak acids with tetrabutylammonium hydroxide. Note the equivalence points after the addition of 3.5, 8.5, and 13.0 mL of titrant.

Amperometry

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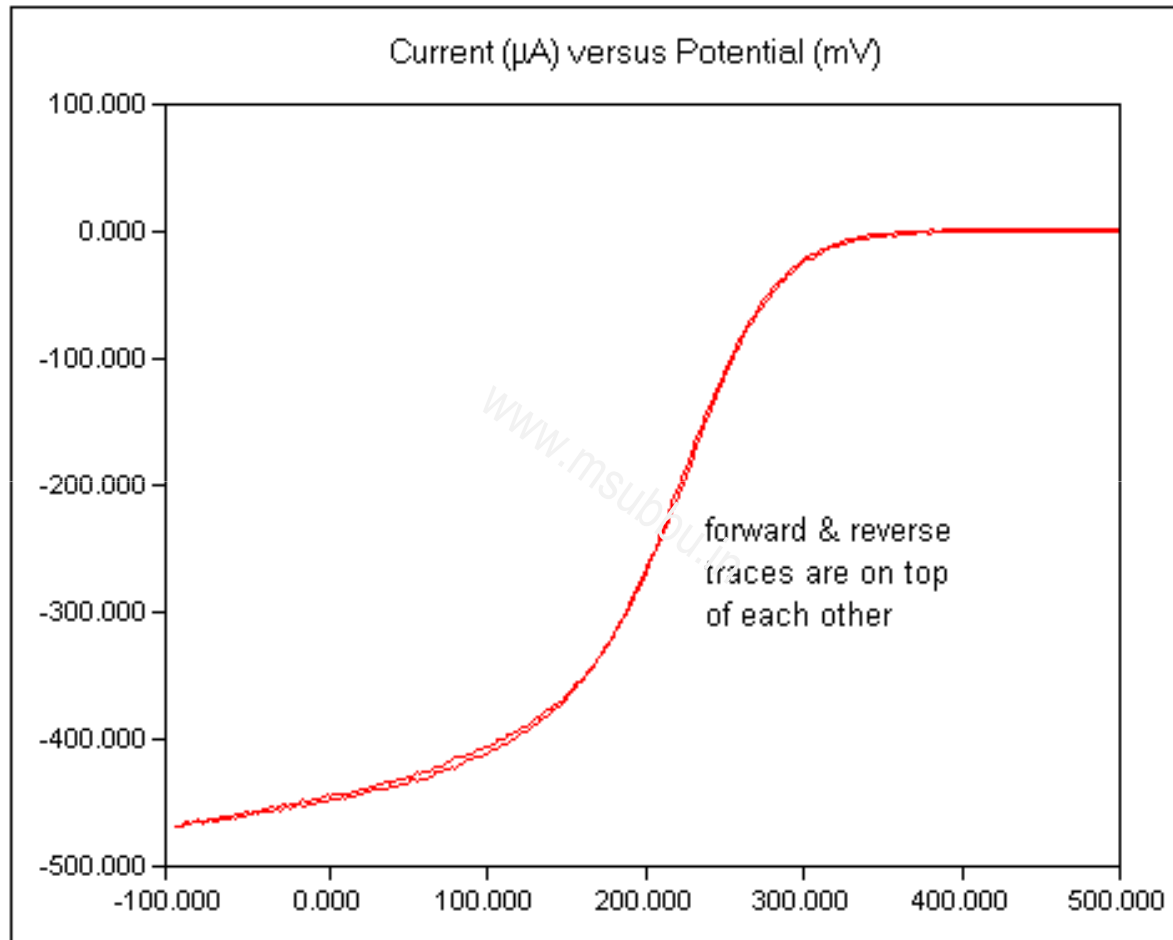
Introduction

- Amperometry is the measurement of current at a fixed potential. An analyte undergoes oxidation or reduction at an electrode with a known, applied potential. The amount of analyte is calculated from Faraday's law.
- Amperometry is used to detect titration endpoints, as a detector for liquid chromatography and forms the basis of many new sensors for biomonitoring and environmental monitoring applications.
- Amperometry is the electroanalytical technique in which the potential of the indicator electrode is adjusted to a fixed value on the plateau of the voltammetric wave of an electroactive species, and the current flowing through the electrode is measured as a function of concentration.

Voltammetry

- Voltammetry is a technique in which a varying potential is applied to an electrode in a sample solution. The electrode at which the potential is applied is the *indicator* or *working* electrode. The current flowing through the electrode is monitored as a function of the applied potential. The plot of current as a function of potential is a polarogram or voltammogram.
- Polarography is a type of voltammetry that uses an electrode whose surface is renewed as the potential is varied. A mercury electrode in which mercury is continuously flowing into the mercury drop is used for polarography.
- The potential at which current starts to flow corresponds to the energy that is required to initiate an oxidation or reduction of a chemical species at or near the indicator electrode surface. Because the energy varies with the chemical species, the potential can be used for qualitative analysis. The current flow is proportional to the concentration of redox species and is used for quantitative analysis.

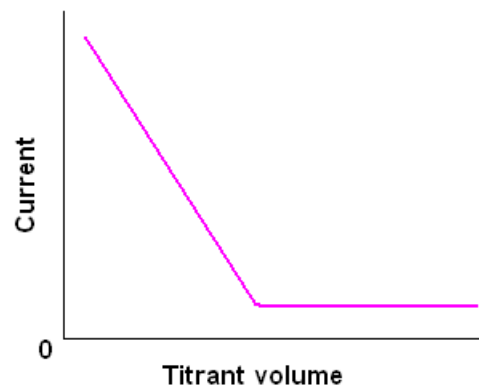
Voltammogram



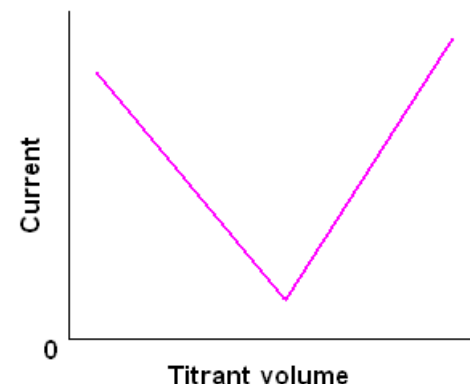
Amperometric Titration

- Amperometry has primarily been used as a method for locating the end points of titrations involving an electroactive species. The current is directly proportional to the concentration of electroactive species in the solution and it decreases or increases during the reaction as the concentration of the electroactive species changes.
- The endpoint of an amperometric titration is located by extrapolation of the straight line portions of the titration curve, before and after the endpoint.

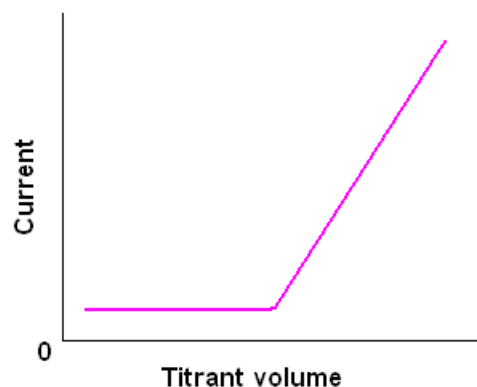
Amperometric Titration Curves



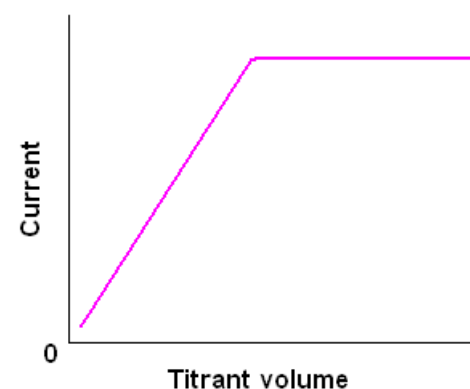
(a) Titration of an electroactive titrand with a non-electroactive titrant to yield a non-electroactive product



(b) Titration of an electroactive titrand with an electroactive titrant to yield a non-electroactive product



(c) Titration of a non-electroactive titrand with an electroactive titrant to yield a non-electroactive product

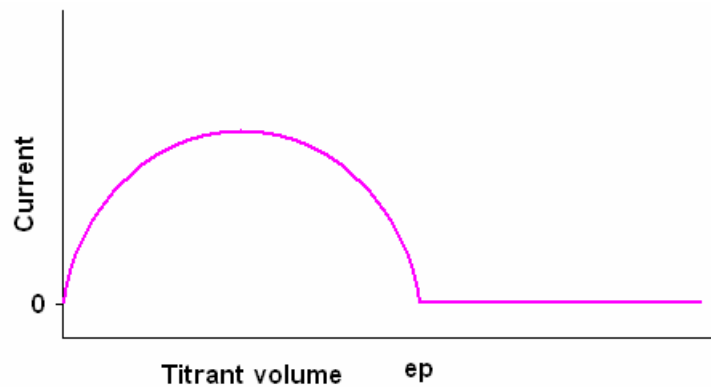


(d) Titration of a non-electroactive titrand with a non-electroactive titrant to yield an electroactive product

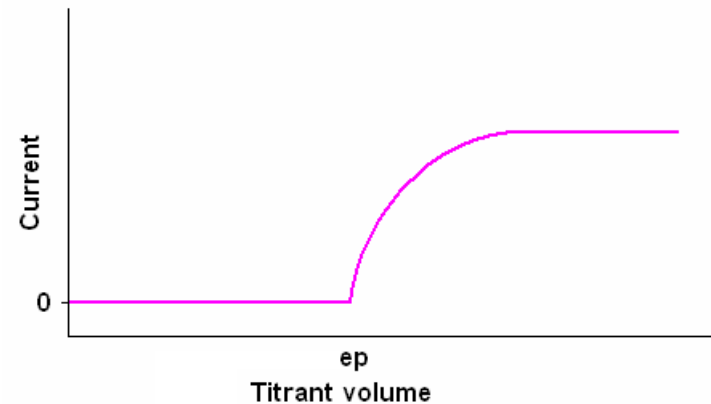
Amperometric Titration with Two Indicator Electrodes

- It is an electroanalytical technique in which the current is measured between two indicator electrodes.
- Usually the indicator electrodes are identical platinum electrodes which are rigidly held at a fixed distance from each other in the cell.
- The emf between the two electrodes is normally between 0.01 and 0.25 V (typically 50 mV).
- Sensitivity of the technique increases with increasing emf; however, if emf is too large, the accuracy of the titration can decrease.

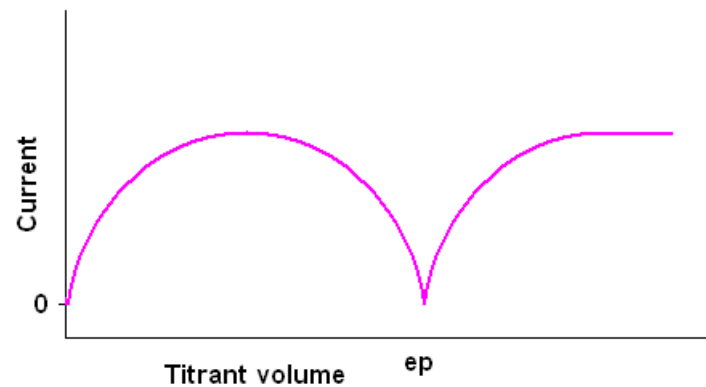
Amperometric Titration with Two Indicator Electrodes



(a) only titrand is reversibly electroactive



(b) only titrant is reversibly electroactive



(c) both titrand and titrant are reversibly electroactive

ep – end point