

**PES MODERN COLLEGE OF PHARMACY (FOR LADIES), MOSHI**

Lecture synopsis

Sub: Pharmaceutical ANALYSIS I

Sr. No.	Proposed Topic	Proposed Syllabus
1.	Pharmaceutical analysis	Definition and scope, Different techniques of analysis
2.	Pharmaceutical analysis	Methods of expressing concentration
3.	Pharmaceutical analysis	Primary and Secondary standards
4.	Pharmaceutical analysis	Errors : Sources of errors, types of errors
5.	Pharmaceutical analysis	Methods of minimizing errors, Accuracy, precision and significant figures
6.	Acid base titration	Theories of acid base indicators
7.	Acid base titration	Classification of acid base titrations
8.	Acid base titration	Theory involved in titrations of strong, weak, and very Weak acids and bases,
9.	Acid base titration	Neutralization curves
10.	Acid base titration	Preparation and standardization of sodium hydroxide
11.	Acid base titration	Hydrochloric acid, sulphuric acid
12.	Acid base titration	Estimation of ammonium chloride
13.	Non aqueous titration	Non aqueous titration: Solvents
14.	Non aqueous titration	Acidimetry and alkalimetry titrations,
15.	Non aqueous titration	Estimation of sodium benzoate
16.	Precipitation titrations	Theory, Mohr's method
17.	Precipitation titrations	Volhard's method ,Modified Volhard's method
18.	Precipitation titrations	Fajans method
19.	Precipitation titrations	Estimation of Sodium Chloride I.P.
20.	Complexometric titration	Theory
21.	Complexometric titration	Classification
22.	Complexometric titration	Metal ion indicators, masking and demasking reagents
23.	Complexometric titration	Estimation of Calcium gluconate I.P.
24.	Gravimetry	Principle and steps involved in gravimetric analysis
25.	Gravimetry	Purity of the precipitate
26.	Gravimetry	Co-precipitation and post precipitation
27.	Gravimetry	Estimation of Barium sulphate I. P.
28.	Redox titrations	Concepts of oxidation and reduction
29.	Redox titrations	Preparation and standardization of Potassium Permanganate I. P
30.	Redox titrations	Ceric Ammonium Sulphate I. P./B. P
31.	Redox titrations	Sodium Thiosulphate I. P./B. P.
32.	Redox titrations	Types of redox titrations (Principles and applications)
33.	Redox titrations	Permanganometry

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Sub: Pharmaceutical ANALYSIS I

34.	Redox titrations	Cerimetry, Iodimetry, Iodometry
35.	Redox titrations	Bromatometry, Dichrometry, Titrations with Potassium Iodate I. P.
36.	Conductometry	Introduction, Conductivity cell
37.	Conductometry	Conductometric titrations
38.	Conductometry	Applications.
39.	Potentiometry	Electrochemical cell, construction and working of reference (Standard Hydrogen Electrode
40.	Potentiometry	Silver Chloride Electrode and Calomel Electrode) and Indicator Electrodes (Metal electrodes and Glass Electrode),
41.	Potentiometry	Methods to determine end point of potentiometric titration and applications
42.	Polarography	Principle
43.	Polarography	Ilkovic Equation.
44.	Refractometry	Introduction, refractive index, specific and molar refraction
45.	Refractometry	Measurement of RI, Abbe's refractometer and applications.

Name of topic/lesson – Introduction to Pharmaceutical analysis

Subtopic: Definition and scope, Different techniques of analysis

Objective: To Study about Definition, scope and Different techniques of analysis

Topic Outcomes: At the end of topic you will

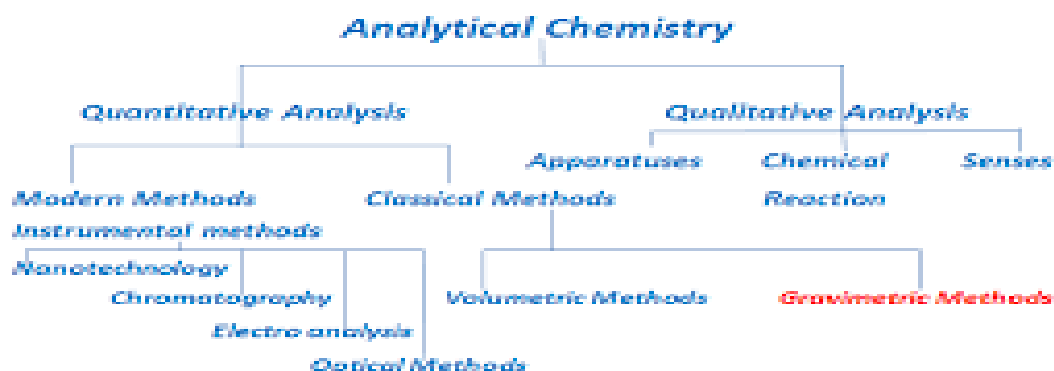
1. Know about definition of Pharmaceutical analysis
2. Learn different techniques of analysis

**Definition:** Pharmaceutical analysis is a branch of practical chemistry that involves a series of process for identification, determination, quantification and purification of a substance, separation of the components of a solution or mixture, or determination of structure of chemical compounds.

### Importance of Pharmaceutical Analysis

- identity of the drug in the formulated product.
- Determination of active ingredient or additional impurities.
- stability of the drug.
- rate of drug from its formulation.
- identity and purity of pure drug that meet specification.
- concentrations of specified impurities.
- concentrations of drug in plasma or biological fluids.
- determine  $pK_a$  values, partition coefficients, solubilities, and stability of drug under development.

### Classification of Analytical Chemistry



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4<sup>th</sup> edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Subtopic: Methods of expressing concentration**

**Objective: To Study about Methods of expressing concentration**

**Topic Outcomes:** At the end of topic you will

1. Know about Methods of expressing concentration
2. Different calculations of solution preparation

**Methods of expressing Concentration of a solution**

The concentration of solution is defined as the amount of solute present in the given quantity of the solution.

It can be expressed in the following ways:

1. Strength
2. Molarity
3. Molality
4. Mole fraction
5. Normality
6. Mass percentage
7. Volume percentage

**Molarity (M)**

**Molality-** A molal solution contains 1 mole of solute per one kilogram of solution ( 1 lit. of solvent) is called as **Molality**.

$M = \frac{\text{mol of solute}}{L \text{ of solution}}$  · Molality is indicated by **M**

$$N = \frac{\text{Number of mol. Wt. of substance}}{1000 \text{ gm of Solution (1Kg)}}$$

Weight Percent  $\left(\frac{W}{W}\right) = \frac{\text{Weight Solute}}{\text{Weight Solution}} \times 100\%$

Volume Percent  $\left(\frac{V}{V}\right) = \frac{\text{Volume Solute}}{\text{Volume Solution}} \times 100\%$

Weight /Volume Percent  $\left(\frac{W}{V}\right) = \frac{\text{Weight Solute, g}}{\text{Volume Soln, L}} \times 100\%$

Mole Fraction of Solute,  $X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$

Mole Fraction of Solute,  $X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$

Where,  $X_{\text{solute}} + X_{\text{solvent}} = 1$

The Normality of the solution can also be expressed in terms of mass and equivalent mass,

$$\text{Normality} = \frac{\text{mass of solute}}{\text{equivalent mass of the solute (E)} \times \text{volume of solution in liters (V)}}$$

In terms of weight, normality of the substance can be expressed as,

$$\text{Normality} = \frac{W_g}{\frac{E_g}{\text{equiv}} \times V (\text{liter})} = \frac{W \text{ equiv/L}}{W \times V}$$

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4<sup>th</sup> edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Lecture No: 3**

**Subtopic: Primary and Secondary standards**

**Objective: To Study about Primary and Secondary standards**

**Topic Outcomes:** At the end of topic you will

1. Understand primary and secondary standard
2. Ideal requirements and examples of primary and secondary standard

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**Properties of Primary Standards**

Primary standards are typically used in titration to determine an unknown concentration and in other analytical chemistry techniques. Titration is a process in which small amounts of a reagent are added to a solution until a chemical reaction occurs. The reaction provides confirmation that the solution is at a specific concentration. Primary standards are often used to make standard solutions (a solution with a precisely known concentration). NaCl, Zn, KHP

A good primary standard meets the following criteria:

- high level of purity
- low reactivity (high stability)
- high equivalent weight (to reduce error from mass measurements)
- not likely to absorb moisture from the air (hygroscopic) to reduce changes in mass in humid versus dry environments
- non-toxic
- inexpensive and readily available

**Secondary Standard Definition**

A related term is "secondary standard". A secondary standard is a chemical that has been standardized against a primary standard for use in a specific analysis. Secondary standards are commonly used to calibrate analytical methods. NaOH, once its concentration has been validated through the use of a primary standard, is often used as a secondary standard.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Lecture No: 4**

**Name of topic/lesson – Introduction to Pharmaceutical analysis**

**Subtopic: Errors: Sources of errors, types of errors**

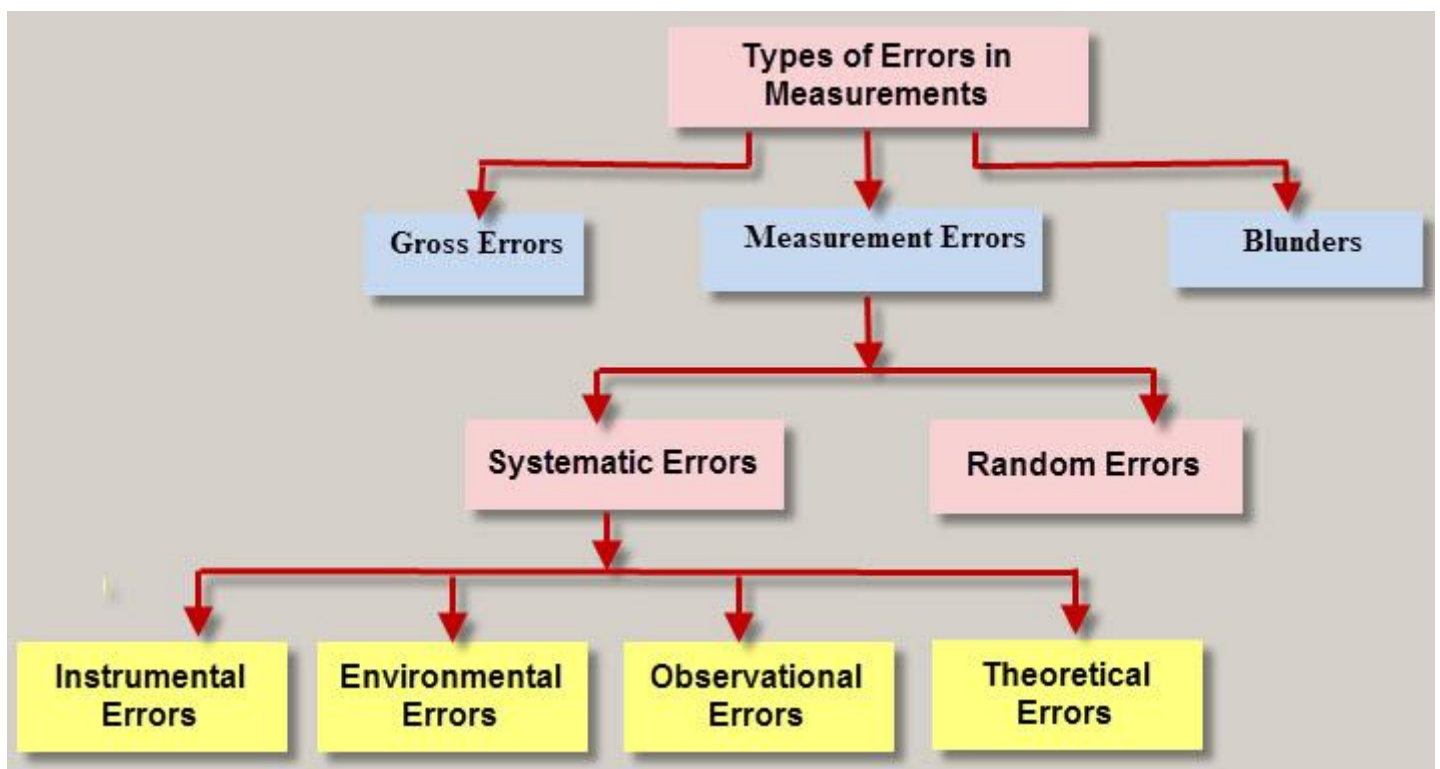
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**Objective: To Study about Errors: Sources of errors, types of errors**

**Topic Outcomes:** At the end of topic you will

1. Learn about meaning and sources of error
2. Understand types of error

The **error** of an experiment is the difference between the experimental and accepted values. **Error**=experimental value-accepted value. If the experimental value is less than the accepted value, the **error** is negative. If the experimental value is larger than the accepted value, the **error** is positive.



## References

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**Lecture No: 5**

**Name of topic/lesson – Introduction to Pharmaceutical analysis**

**Subtopic: Methods of minimizing errors, Accuracy, precision and significant figures**

**Objective: To Study about Methods of minimizing errors, Accuracy, precision and significant figures**

**Topic Outcomes:** At the end of topic you will

1. Learn about methods of minimizing error
  2. Understand concepts of accuracy, precision and significant figures
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## MINIMISATION OF ERRORS

Systematic errors can often be materially reduced by one of the following methods.

- \* Calibration of apparatus and application of corrections
- \* Running a blank determination
- \* Running a control determination
- \* Use of independent methods of analysis
- \* Running parallel determinations
- \* Standard addition
- \* Internal standards
- \* Amplification methods
- \* Isotopic dilution

**Accuracy** refers to the closeness of a measured value to a standard or known value.

**Precision** refers to the closeness of two or more measurements to each other

**Significant figures:** Each of the digits of a number that are used to express it to the required degree of accuracy, starting from the first non-zero digit.

**There are three rules on determining how many significant figures are in a number:**

- Non-zero digits are always **significant**.
- Any zeros between two **significant** digits are **significant**.
- A final zero or trailing zeros in the decimal portion **ONLY** are **significant**.

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
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**Lecture No: 6**

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Acid Base theories, indicators**

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**Objective: To Study about Acid Base theories, indicators**

**Topic Outcomes:** At the end of topic you will

1. Define acid, base
2. Understand theories of acid base

The Arrhenius Theory	The Brønsted-Lowry Theory	The Lewis Theory
<p>Acids are substances that contain hydrogen</p> <p>Bases are substances that contain hydroxyl, OH, group</p>	<p>An acid is a proton donor (H<sup>+</sup>).</p> <p>A base is a proton acceptor.</p>	<p>Acids are <u>electron pair acceptors</u>.</p> <p>Bases are <u>electron pair donors</u>.</p>
HCl and NaOH	NH <sub>3</sub> and H <sub>2</sub> O	BF <sub>3</sub> and NH <sub>3</sub>

### Ostwald's Theory-

According to this theory

Acid-base indicators are weak organic acid or base

They possess different colours in ionised & unionised state .

The colour of the indicator depends upon the relative proportions of the unionised indicator molecules & its ions.

Phenolphthalein is a weak acid whose unionised molecule is colourless while ion is red in colour.

### Modern Quinonoid theory-

According to this theory

An acid- base indicator is dynamic equilibrium mixture of two tautomeric forms, one form is benzenoid while other is quinonoid.

### **References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda,Nirali Prakashan

**Lecture No: 7**

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Classification of acid base titrations**

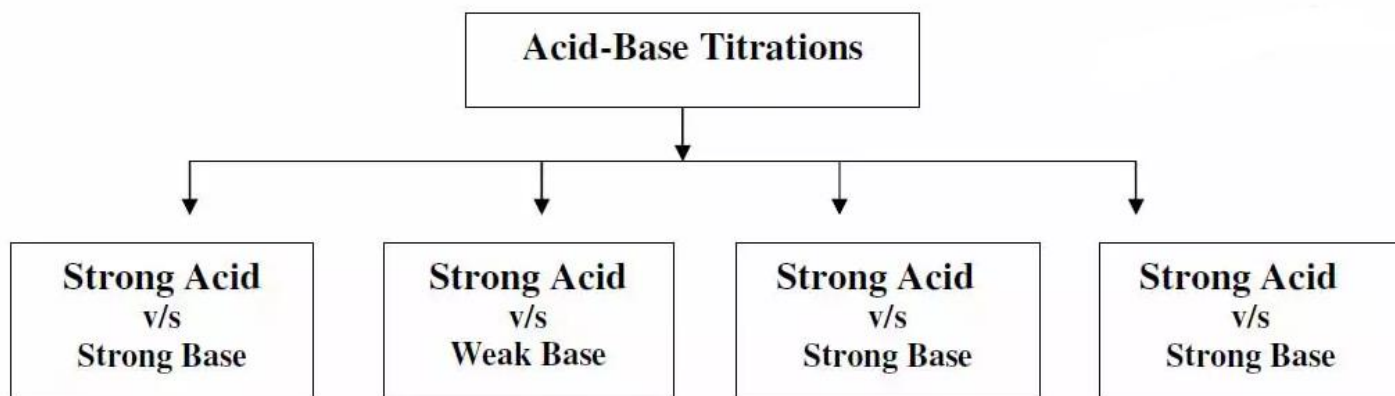


**Objective: To Study about Classification of acid base titrations**

**Topic Outcomes:** At the end of topic you will

1. Understand classification of acid base titration

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**Lecture No: 8**

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Theory involved in titrations of strong, weak, and very weak acids and bases**

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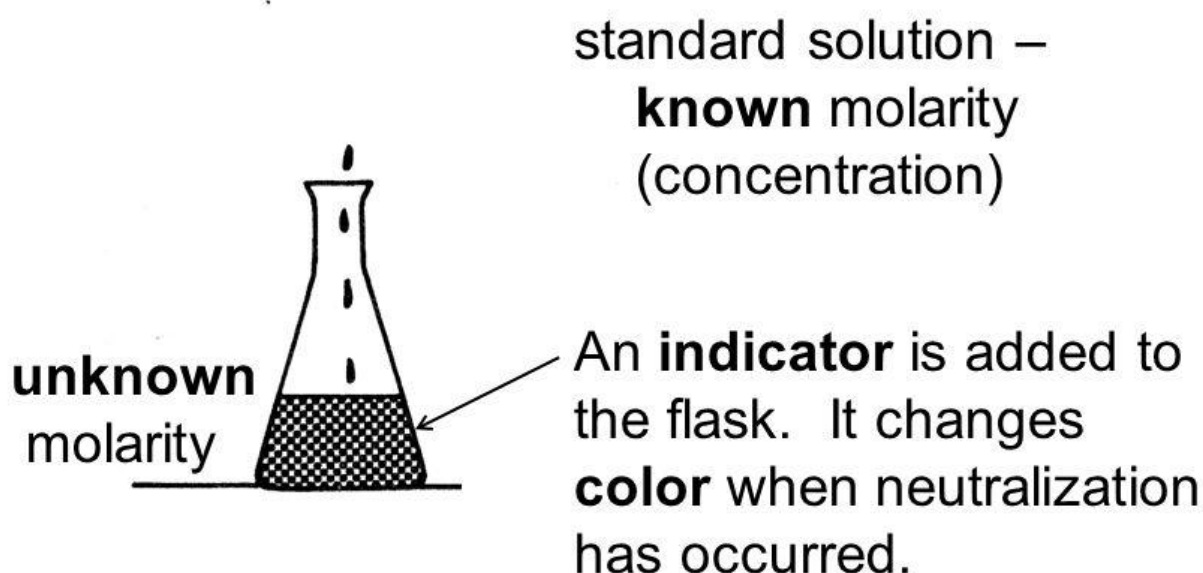
**Objective:** To Study about Theory involved in titrations of strong, weak, and very weak acids and bases

**Topic Outcomes:** At the end of topic you will

1. Learn theory of SA vs SB
- 

## V. Acid-Base Titration

Titration is the process of adding a measured volume of an acid or base of **known** molarity (the **standard** solution) to an acid or base of **unknown** molarity until **neutralization** occurs.



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**Lecture No: 9**

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Neutralization curves**

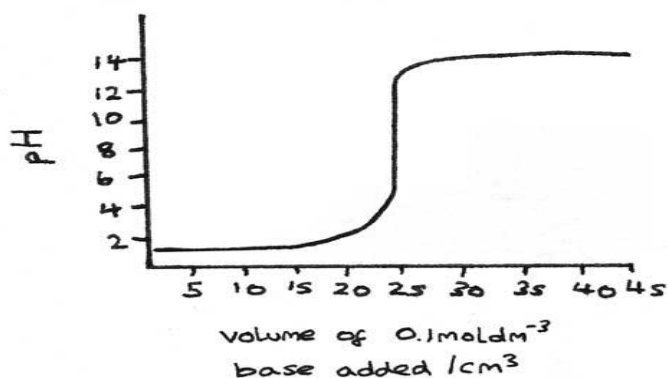
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**Objective:** To Study about Neutralization curves

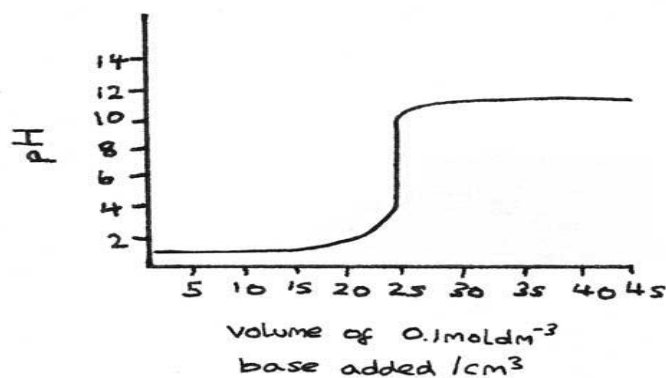
**Topic Outcomes:** At the end of topic you will

1. Understand neutralization curves
2. Neutralization curve of SA,SB,WA,WB

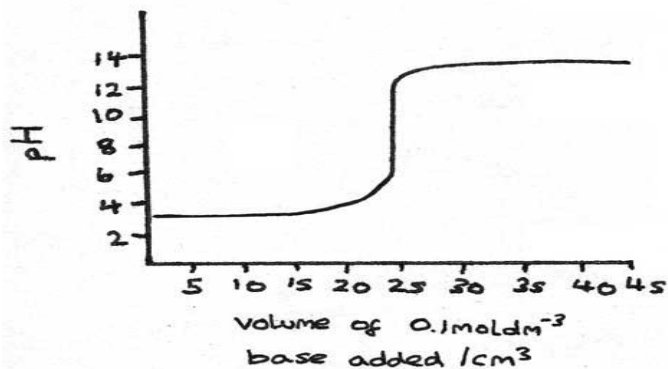
Strong acid-strong base



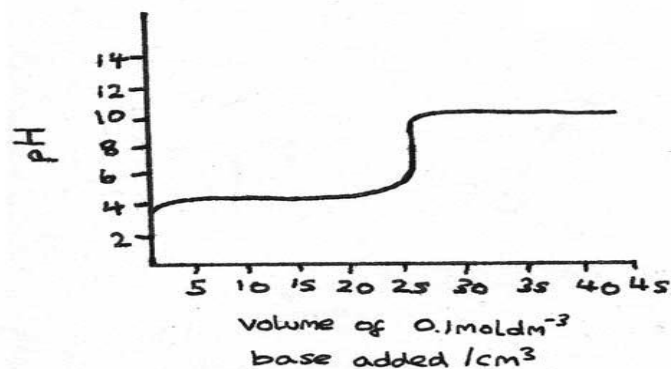
Strong acid-strong base



weak acid - strong base



weak acid - weak base



## References

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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Lecture No: 10**

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Preparation and standardization of sodium hydroxide**

**Objective: To Study about Preparation and standardization of sodium hydroxide**

**Topic Outcomes:** At the end of topic you will

1. Understand preparation of NaOH
2. Standardization of NaOH

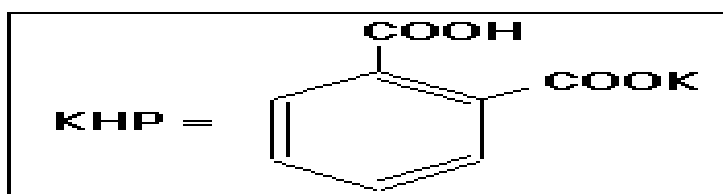
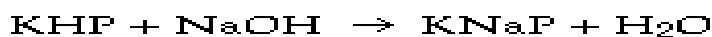
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**Standardization:** The process of using a known amount of one reagent to determine the concentration of another reagent is known as standardization.

**Preparation of approximately NaOH 0.1 M solution:** Weigh 4 g of NaOH pellets in a clean, preweighed 100-mL beaker on a balance. Put 250 mL of distilled water into a clean 1000 mL volumetric flask. Add the NaOH pellets completely. When the NaOH has dissolved completely, add distilled water up to the marking. Mix thoroughly.

### STANDARDIZATION OF THE NaOH SOLUTION

1. Weigh required quantity of KHP; add 50 ml of distilled water to KHP sample #1.
2. Add 2 drops of phenolphthalein indicator. Swirl to dissolve the KHP completely.
3. On the report sheet, record the initial reading of the NaOH.
4. Add NaOH dropwise till colorless solution turns pink. Take reading in thrice and calculate the molarity.



### References

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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

### Lecture No: 11

**Name of topic/lesson – Acid Base Titration**

**Subtopic: Preparation and standardization of Hydrochloric acid, sulphuric acid**

**Objective: To Study about Preparation and standardization of Hydrochloric acid, sulphuric acid**

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**Topic Outcomes:** At the end of topic you will

1. Understand preparation of Hydrochloric acid, sulphuric acid
  2. Standardization of Hydrochloric acid, sulphuric acid
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- **Sulphuric Acid Solution Preparation**

Take 2.74 ml of conc. Sulphuric acid and dilute it upto 1000 ml of distill water

- **Sulphuric Acid Solution Standardization**

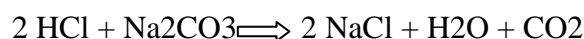
Weigh accurately about 0.2 g of anhydrous Sodium Carbonate, previously heated at about 270°C for 1 hour. Dissolve it in 100 ml of water and add 0.1 ml of methyl red solution. Add the **acid** slowly from a burette, with constant stirring, until the solution becomes faintly pink.

- **Hydrochloric Acid Solution Preparation**

Take 8.5 ml of conc. Sulphuric acid and dilute it upto 1000 ml of distill water

- **Hydrochloric Acid Solution Standardization**

Weigh accurately about 1.5 g of anhydrous Sodium Carbonate, previously heated at about 270°C for 1 hour. Dissolve it in 100 ml of water and add 0.1 ml of methyl red solution. Add the **acid** slowly from a burette, with constant stirring, until the solution becomes faintly pink.



## References

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## Lecture No: 12

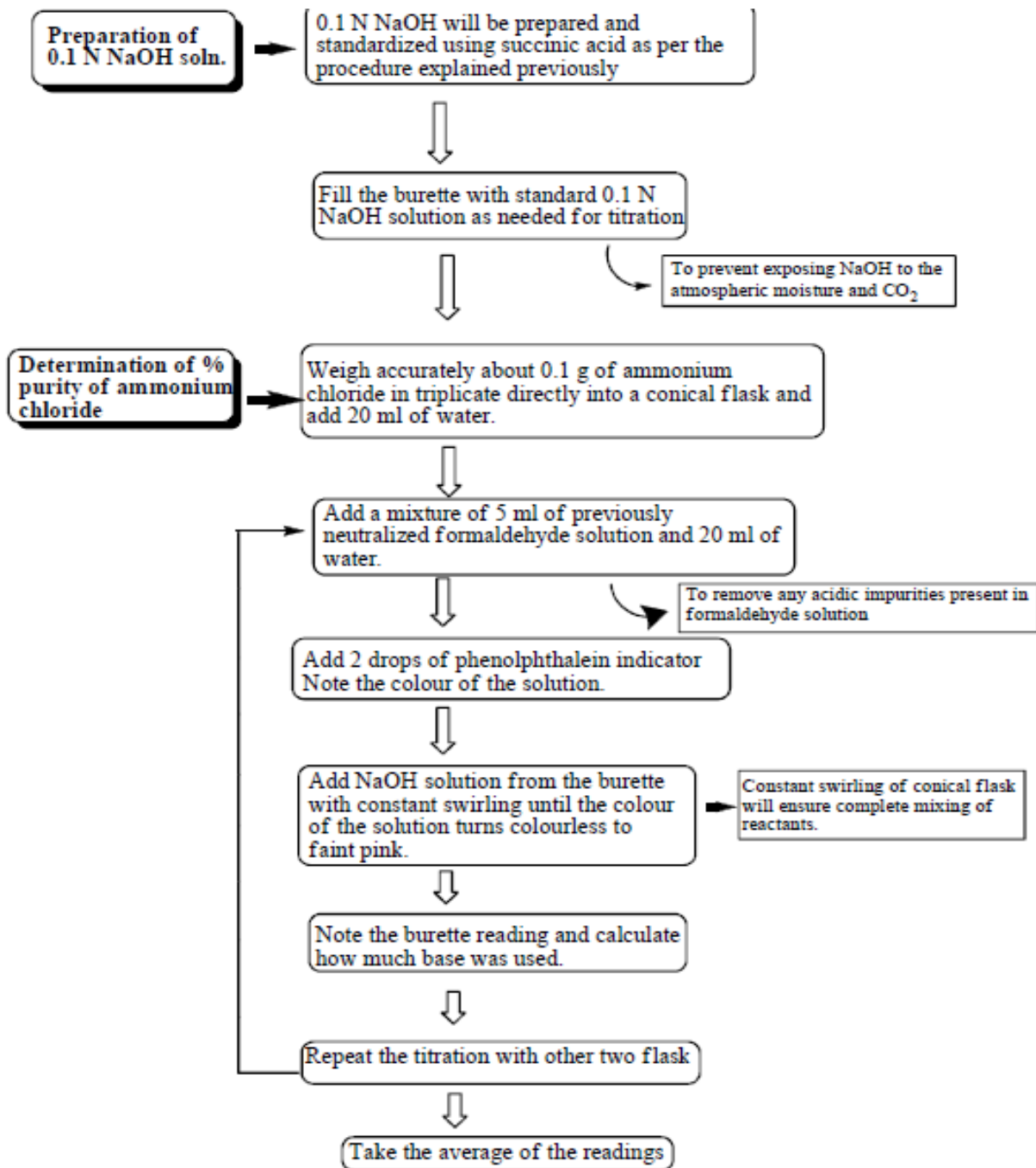
### Name of topic/lesson – Acid Base Titration

#### Subtopic: Estimation of ammonium chloride

**Objective:** To Study about Estimation of ammonium chloride

**Topic Outcomes:** At the end of topic you will

1. Know about ammonium **chloride** monograph
  2. Know about ammonium **chloride** estimation
-





**Calculation for percentage purity:**

<b>Descriptive method</b>
$1000 \text{ ml of } 1 \text{ N NaOH} = 53.5 \text{ g eq. of } \text{NH}_4\text{Cl}$ $17.6 \text{ ml of } 0.1 \text{ N NaOH} = \frac{53.5 \times 17.6 \times 0.1}{1000}$ $= 0.0942 \text{ g}$ $0.101 \text{ g of sample contains} = 0.0942 \text{ g of}$ $\text{NH}_4\text{Cl}$ $100 \text{ gm of sample contain} = \frac{0.0942 \times 100}{0.101}$ $= 93.28 \%$

**References**

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**Lecture No: 13****Name of topic/lesson – Non aqueous titration****Subtopic: Non aqueous titration: Solvents****Objective: to Study about Non aqueous titration: Solvents**

**Topic Outcomes:** At the end of topic you will

1. Understand basic concept of non aq acid base titration
  2. Know about solvents used in non aq titration
- 

**Non aqueous titration** refers to a type of **titration** in which the analyte substance is dissolved in a solvent which does not contain water. This procedure is a very important one in pharmacopoeial assays.

Types of Non Aqueous Solvents

Typically, there exist four types of solvents used in the non aqueous titration of a given analyte. These are:

- **Aprotic Solvents** – these solvents are neutral in charge and are chemically inert. They also generally have a low dielectric constant. Examples of these types of solvents include chloroform and benzene.
- **Protophilic Solvents** – these solvents have a basic character and tend to react with the acids they come in contact with, leading to the formation of solvated protons. Examples of protophilic solvents are ammonia and pyridine.
- **Protogenic Solvents** – these solvents have a more acidic character and tend to have a leveling effect on the bases they come in contact with. Examples of protogenic solvents used in non aqueous titration are sulfuric acid and acetic acid.
- **Amphiprotic Solvents** – these solvents have properties which are protophilic as well as protogenic. Examples of these types of solvents are acetic acid and alcohols.

## Non-aqueous Titrations

- **Theory**
- Non-aqueous titrations is the **most titrimetric** procedure used in pharmacopoeial assays and serves a double purpose, as it suitable for the titration of weak acids and bases and provides a solvent in which organic compounds are soluble.
- The most commonly used procedure is the titration of organic bases with **perchloric acid in acetic acid**
- Water behaves as both a weak acid and weak base; thus in aqueous environment, it can compete effectively with very weak acids and bases with regard to proton donation and acceptance.

## Solutions

es

es

## Nonaqueous

1. Elixirs
2. Spirits
3. Collodions
4. Glycerins
5. Liniments
6. Oleo Vitamin

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Non aqueous titration

Subtopic: Acidimetry and alkalimetry titrations

**Objective: To Study about Acidimetry and alkalimetry titrations**

**Topic Outcomes:** At the end of topic you will

1. Understand the concept of Acidimetry and alkalimetry titrations
  2. Know about difference between Acidimetry and alkalimetry titrations,
- 

## Assay by non aqueous titration

### Acidimetry in non aqueous titration—

It can be further divided in to two types,  
namely ;

1. Titration of primary , secondary, tertiary amines.
2. Titration of halogen acid salts of bases.

### Alkalimetry in non aqueous titration---

#### *Titration of acidic substances*

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda,Nirali Prakashan

**Objective: To Study about Estimation of sodium benzoate**

**Topic Outcomes:** At the end of topic you will

1. Understand the monograph of sodium benzoate
2. Know about estimation of sodium benzoate

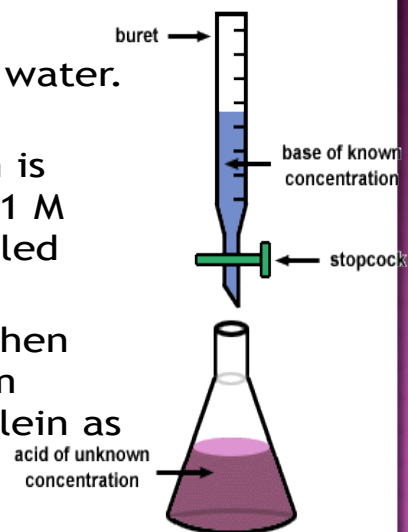
**TESTS Assay**

Each 20.42 mg of  $\text{KHC}_6\text{H}_4(\text{COO})_2$  is equivalent to 1 ml of 0.1 N perchloric acid.

Crystal Violet I'S Dissolve 100 mg of crystal violet in 10 ml of glacial acetic acid.

**ASSAY TEST:**

- ◉ Dissolve 1.0 g of ammonium chloride in 20 ml of distilled water.
- ◉ Add a mixture of 5 ml formaldehyde solution which is previously neutralized with 0.1 M NaOH (why?) and 20 ml distilled water.
- ◉ Leave it for 2 minutes, and then titrate slowly with 1M sodium hydroxide using Phenolphthalein as indicator.



**References**

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**Lecture No: 16**

**Name of topic/lesson** – Precipitation titrations

**Subtopic:** Theory, Mohr's method

**Objective: To Study about** Theory of precipitation titration , Mohr's method

**Topic Outcomes:** At the end of topic you will

1. Understand the Theory of precipitation titration
  2. Learn about Mohr's method
- 

### **Principle of Precipitation Titration**

The main **principle** of the **precipitation titrations** is that the quantity of the added precipitating reagent or precipitant is equivalent to the substance being precipitated.

#### **An example**

**Precipitation titration** reaction is the Mohr method, which is used to find the concentration of halide ions in solution (particularly Cl<sup>-</sup> and Br<sup>-</sup>). First, the **sample** to be analyzed is **titrated** with a AgNO<sub>3</sub> solution, which results in the **precipitation** of a white silver solid AgCl.

The **Mohr's method** involves the use of a silver nitrate solution as the titrant for the determination of chlorides and bromides in the presence of potassium chromate indicator. When a chloride containing solution reacts with a standard solution of silver nitrate, it results in the formation of silver chloride.

#### **References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda,Nirali Prakashan



Name of topic/lesson – Precipitation titrations

Subtopic: Volhard's method, Modified Volhard's method

Objective: To Study about Volhard's method, Modified Volhard's method

Topic Outcomes: At the end of topic you will

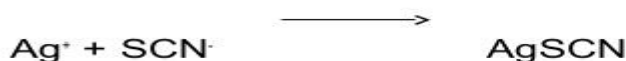
1. Learn Volhard's method
2. Learn Modified Volhard's method

## STEPS OF VOLHARD'S METHOD:

- Analyte is treated with the measured excess of Silver nitrate:



- The unreacted Silver ions are titrated with a standard solution of Thiocyanate ion, using Fe(III) as indicator:



- The first slight excess of Thiocyanate ion gives Red colour of  $FeSCN^{2+}$ :



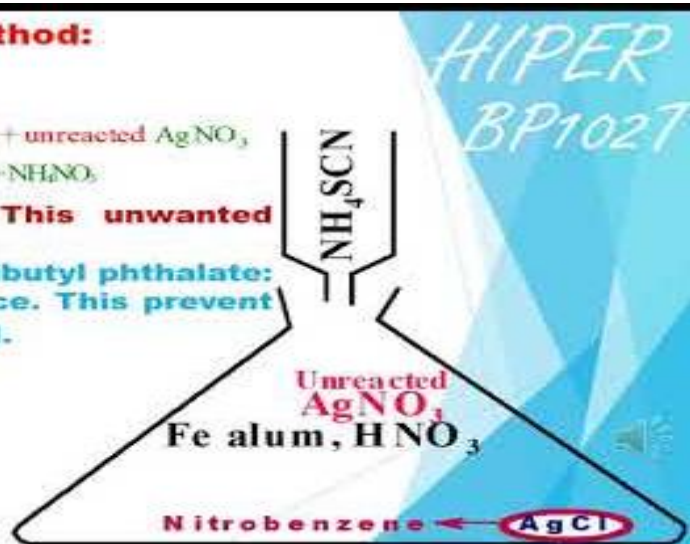
### Modified Volhard's method:



$NH_4SCN + AgCl \rightarrow AgSCN \downarrow$ . This unwanted reaction is prevented by

1. Addition of Nitrobenzene or dibutyl phthalate: It form film at precipitate surface. This prevent reaction between  $NaSCN$  &  $AgCl$ .

..... of precipitate.

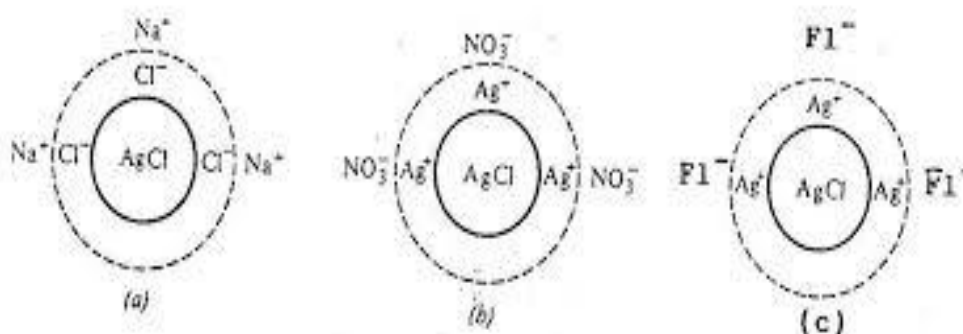


### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

## Fajan's method (indicator adsorption method)

- The precipitation titration in which silver ions is titrated with halide or thiocyanate ions in presence of adsorption indicator is called **fajan's method**
- Since the adsorption of indicator takes place at end point the method is also called indicator adsorption method
- The indicator, which is a dye, exists in solution as the ionized form, usually an anion



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Precipitation titrations

Subtopic: Estimation of Sodium Chloride I.P.

Objective: To Study about Estimation of Sodium Chloride I.P.

Topic Outcomes: At the end of topic you will

1. Know about monograph of NaCl

2. Learn estimation of NaCl

---

**Assay** Weigh accurately about 0.2 g of Sodium Chloride, previously dried, dissolve in 50 mL of water, and titrate with 0.1 mol/L silver nitrate VS while shaking vigorously (indicator: 3 drops of fluorescein sodium TS).

Each mL of 0.1 mol/L silver nitrate VS  
= 5.844 mg of NaCl

**Containers and storage** Containers—Tight containers.

#### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

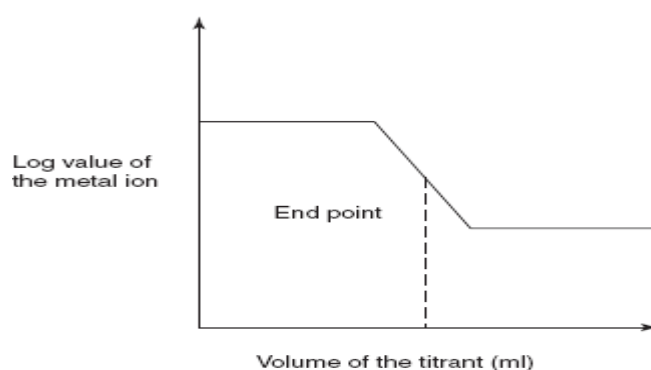
**Topic Outcomes:** At the end of topic you will

1. Understand the theory of complexometric titration
  2. Learn definition of complexometric titration
- 

**Complexometric** Titration is in the detection of mixtures of different metal ions present in the solution. When each drop of titrant is added, the **reaction** reaches an equilibrium state swiftly.

### Principle of Complexometric Titration:

Many principles of acid-base titrations are used in complexometric titration. In complexometric titration, the free metal ions disappear as they are changed into complex ions. In acid-base titrations, the end point is marked by sudden change in pH. Similarly, in EDTA titration, if we plot pM (negative log of metal ion concentration) v/s volume of titrant, we will find that at the end point, the pM rapidly increases. This sudden pM raise results from removal of traces of metal ions from solution by EDTA.



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Complexometric titration****Subtopic: Classification****Objective: To Study about Classification of Complexometric titration****Topic Outcomes:** At the end of topic you will

1. Understand the Classification of complexometric titration
2. Learn definition of each class of complexometric titration

**Direct Titration:**

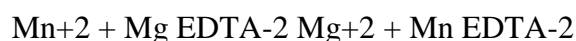
It is the simplest and the most convenient method used in chelometry. In this method, the standard chelon solution is added to the metal ion solution until the end point is detected. This method is analogous to simple acid-base titrations. E.g.-calcium gluconate injection, calcium lactate tablets and compound sodium lactate injection for the assay of calcium chloride.

**Back Titration:**

In this method, excess of a standard EDTA solution is added to the metal solution, which is to be analyzed, and the excess is back titrated with a standard solution of a second metal ion. E.g. - Determination of Mn. This metal cannot be directly titrated with EDTA because of precipitation of  $Mn(OH)_2$ . An excess of known volume of EDTA is added to an acidic solution of Mn salt and then ammonia buffer is used to adjust the pH to 10 and the excess EDTA remaining after chelation, is back titrated with a standard Zn solution kept in burette using Eriochrome blackT as indicator. This method is analogous to back titration method in acidimetry. e.g.- ZnO

**Replacement Titration:**

In this method the metal, which is to be analyzed, displaces quantitatively the metal from the complex. When direct or back titrations do not give sharp end points, the metal may be determined by the displacement of an equivalent amount of Mg or Zn from a less stable EDTA complex.



Mn displaces Mg from Mn EDTA solution. The freed Mg metal is then directly titrated with a standard EDTA solution. In this method, excess quantity of Mg EDTA chelate is added to Mn solution. Mn quantitatively displaces Mg from Mg EDTA chelate. This displacement takes place because Mn forms a more stable complex with EDTA. By this method Ca, Pb, Hg may be determined using Eriochrome blackT indicator.

**Indirect Titration:**

This is also known as Alkalimetric titration. It is used for the determination of ions such as anions, which do not react with EDTA chelate. Protons from disodium EDTA are displaced by a heavy metal and titrated with sodium alkali.



e.g. - Barbiturates do not react with EDTA but are quantitatively precipitated from alkaline solution by mercuric ions as 1:1 complex.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan



Name of topic/lesson – Complexometric titration

Subtopic: Metal ion indicators, masking and demasking reagents

Objective: To Study about Metal ion indicators, masking and demasking reagents

Topic Outcomes: At the end of topic you will

1. Know about metal ion indicators
2. Learn definition of masking and demasking reagents

S.No.	Name of the Indicator	Colour change	pH range	Metals detected
1.	Mordant black II	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
	Eriochrome blackT			
	Solochrome blackT			
2.	Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
3.	Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
4.	Methyl Blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
	Thymol Blue	Blue to Grey	10-12	
5.	Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
6.	Sodium Alizarin sulphonate	Blue to Red	4	Al, Thorium
7.	Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
			4-5	Pb, Zn
			5-6	Cd, Hg

Masking agents act either by precipitation or by formation of complexes more stable than the interfering ion-EDTA complex. Masking by Precipitation: Many heavy metals e.g.- Co, Cu and Pb, can be separated either in the form of insoluble sulphides using Sodium sulphide.

Masking by Complex formation: Masking agents form more stable complexes with the interfering metal ions.

The different masking agents used are enlisted below:

- Ammonium fluoride will mask aluminium, iron and titanium by complex formation.
- Ascorbic acid is a convenient reducing agent for iron(III) which is then masked by complexing as the very stable hexacyanoferrate(II) complex. This latter is more stable and less intensely coloured than the hexacyanoferrate(III) complex.
- Dimercaprol (2,3-Dimercaptopropanol); (CH<sub>2</sub>SH.CHSH.CH<sub>2</sub>OH).

**Demasking:** It is the process in which the masked substance regains its ability to enter into a particular reaction. This enables to determine a series of metal ions in one solution containing many cations.

Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd and Ca. the following method of analysis is followed:

1. Direct titration of the mixture with the EDTA gives the sum of the 3 metals.
2. Cu and Cd may be masked with the addition of cyanide to the solution, leaving only Ca ion.
3. When formaldehyde or chloral hydrate is added to the cyanide containing mixture, only Cd is demasked and the EDTA titrates the sum of Ca and Cd. In this manner, the concentration of three ions is determined by 3 individual titrations.

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Complexometric titration**

**Subtopic: Estimation of Calcium gluconate I.P.**

**Objective: To Study about Estimation of Calcium gluconate I.P.**

**Topic Outcomes:** At the end of topic you will

1. Know about calcium gluconate
  2. Learn Estimation of Calcium gluconate I.P.
- 

**Calcium Gluconate:** An accurately weighed quantity (0.8gm) is dissolved in water (150ml) containing dil HCl (5ml). to the acidified solution is added, solution of NaOH (15ml), murexide indicator (4mg), solution of naphthol green (3ml). The reaction mixture is titrated with M/20 disod. EDTA until the solution is deep blue in colour.

1ml of M/20 disod. EDTA  $\equiv$  0.02242gm of Ca gluconate

**Calcium Gluconate injection:** An accurately measured volume of the injection, equivalent to 0.8gm of Calcium gluconate is taken in a titration flask and proceeded as above.

**Calcium Gluconate tablet:** 20 Tablets are finely powdered. An accurately weighed amount of the powder, equivalent to 0.8gm of Calcium gluconate is transferred to a crucible and proceeded as described under Calcium lactate tablets.

**References**

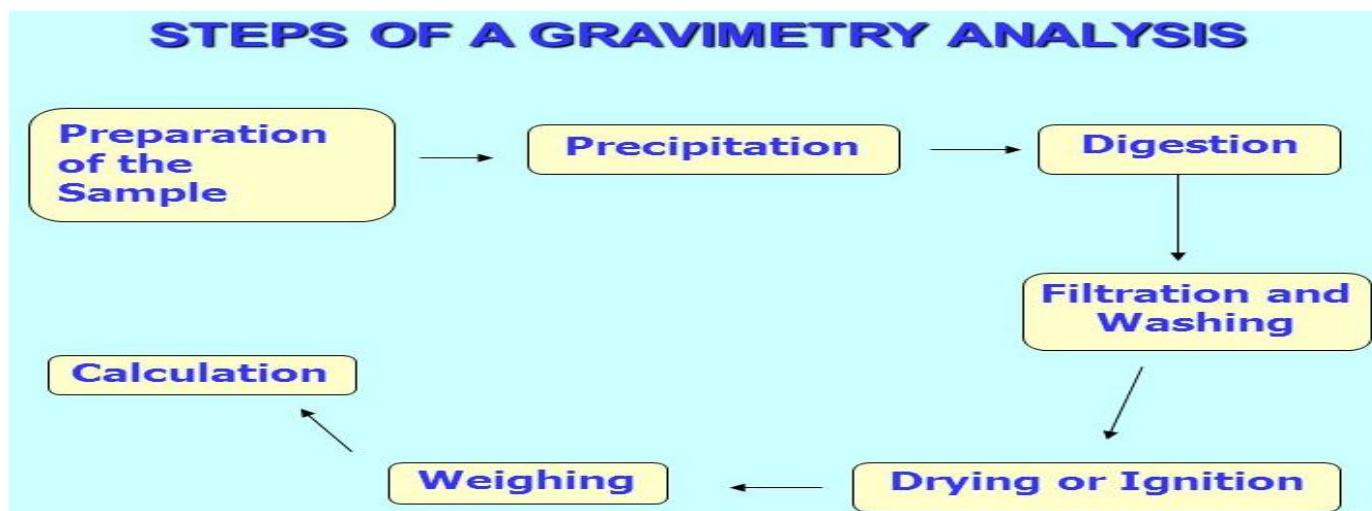
1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Gravimetry****Subtopic: Principle and steps involved in gravimetric analysis****Objective: To Study about Principle and steps involved in gravimetric analysis****Topic Outcomes:** At the end of topic you will

1. Learn Principle involved in gravimetric analysis
  2. Learn steps involved in gravimetric analysis
- 

Gravimetric analysis is a technique through which the amount of an analyte (the ion being analyzed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte. The principle behind gravimetric analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound. In order for the analysis to be accurate, certain conditions must be met:

1. The ion being analyzed must be completely precipitated.
2. The precipitate must be a pure compound.
3. The precipitate must be easily filtered.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Gravimetry

Subtopic: Purity of the precipitate

Objective: To Study about Purity of the precipitate

Topic Outcomes: At the end of topic you will

1. Learn Purity of the precipitate

2. Learn steps of purification

---

## WASHING & FILTERING THE PRECIPITATE

- ✓ Co-precipitate impurities, especially these on the substance can be removed by washing the precipitate after filtering
- ✓ Precipitate will be wet by mother liquid that can also be removed by washing
- ✓ Many precipitate cannot be washed with pure water because peptization occurs (reverse of coagulation)
- ✓ Eg:  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$  is used for washing  $\text{AgCl}$  precipitate

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Topic Outcomes: At the end of topic you will

1. Learn the concept **Co-precipitation**
  2. Learn the concept **post precipitation**
- 

## Difference between co-precipitation and post precipitation:

1. The contamination or impurities is ↑ in post precipitate.
2. But co-precipitate ↓
3. The contamination increases in post precipitate by (mechanical or thermal process.) digestion but in co-precipitate-contamination is ↓
4. The magnitude of contamination by post precipitate much be greater in co-precipitate.

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
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**Name of topic/lesson – Gravimetry**

**Subtopic: Estimation of Barium sulphate I. P.**

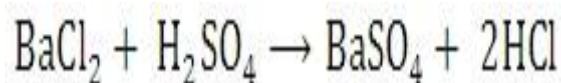
**Objective: To Study about Estimation of Barium sulphate I. P.**

**Topic Outcomes:** At the end of topic you will

1. Learn the monograph of Barium sulphate I. P.
  2. Learn the estimation of barium sulphate IP
- 

**The Gravimetric Estimation of Barium:**

The given barium chloride solution is made up to a definite volume. A measured volume of it is then treated with dilute sulphuric acid and then treated with dilute sulphuric acid and barium precipitated as barium sulphate.



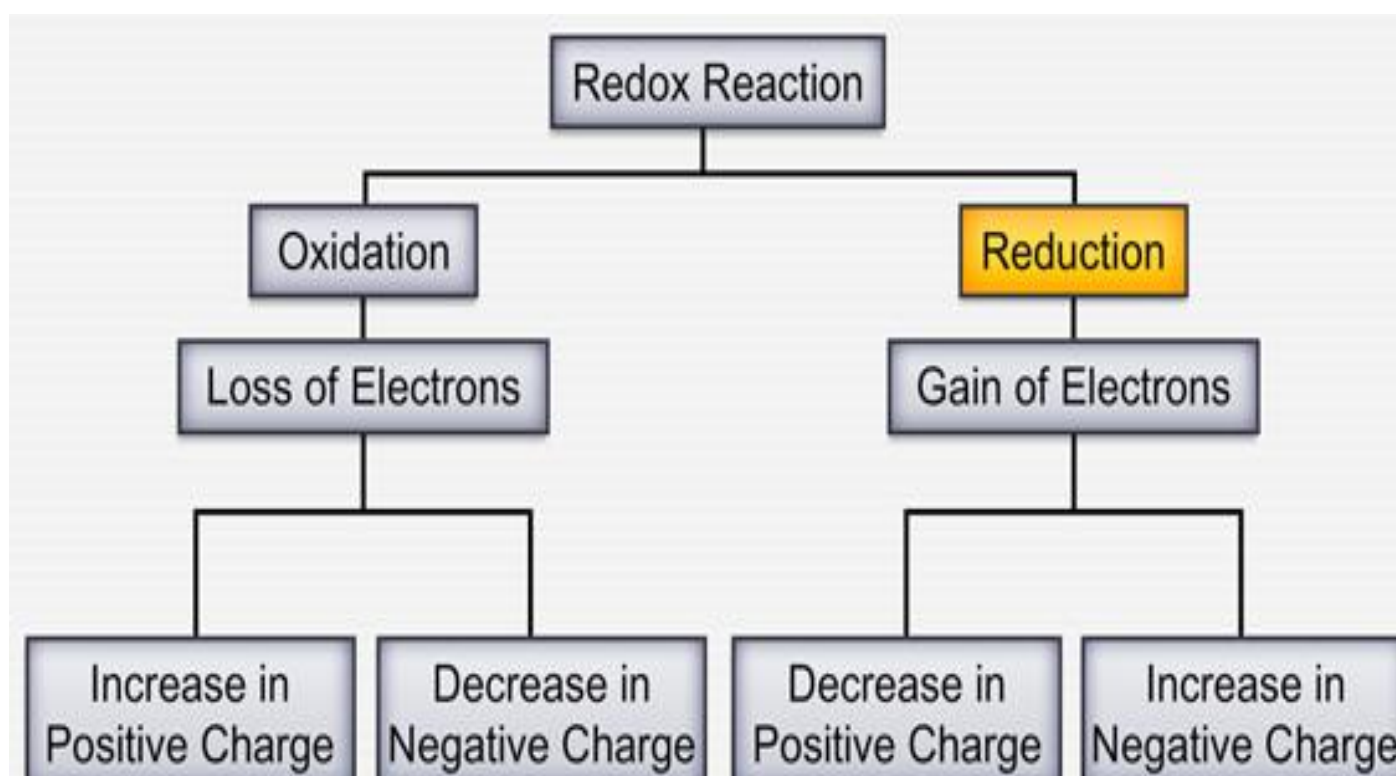
The precipitated barium sulphate is separated and weighed. The mass of Barium in the whole of the given solution is calculated knowing that 233.36 g of barium sulphate contains 137.36 g of barium.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Redox Titration****Subtopic:** Concepts of oxidation and reduction**Objective:** To Study about Concepts of oxidation and reduction**Topic Outcomes:** At the end of topic you will

1. Understand the meaning of oxidation
2. Understand the meaning of reduction



The process in which any substance (atom, ion or molecule) loses one or more electrons is called oxidation. Thus, it is a deelectronation process. The substance which loses electrons is said to be oxidised.

E. g.



The process in which any substance (atom, ion or molecule) gains one or more electrons is called reduction. Thus it is an electronation process. The substance which gains electrons is said to be reduced.

E. g.



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Redox Titration****Subtopic: Preparation and standardization of Potassium Permanganate I. P****Objective: To Study about Preparation and standardization of Potassium Permanganate I. P**

**Topic Outcomes:** At the end of topic you will

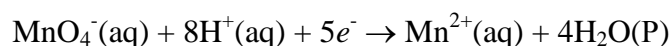
1. Learn **Preparation of Potassium Permanganate I. P**
2. Learn **standardization of Potassium Permanganate I. P**

**Potassium Permanganate Solution Preparation**

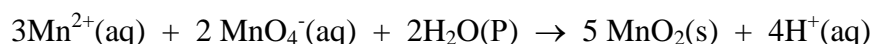
1. Dissolve 3.2 g of **potassium permanganate** in 1000 ml of water.
2. Heat on a water-bath for 1 hour.
3. Allow to stand for 2 days and filter through glass wool.
4. Standardize the **solution** in the following manner.

**Standardization of a KMnO<sub>4</sub> solution.**

Titration involving permanganate are normally carried out in acidic solutions, and the half reaction for permanganate under these conditions is:

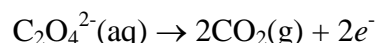


There is one problem with using permanganate ion in titrations, and that is it is able to *autocatalyze* its own destruction. This is because as  $\text{Mn}^{2+}$  is produced during the titration, the  $\text{Mn}^{2+}$  can actually react with additional  $\text{MnO}_4^-$ , producing solid  $\text{MnO}_2$  as a result:

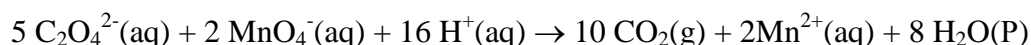


The unfortunate result of this side reaction is that you overestimate the amount of analyte that is being consumed because you must add more titrant to reach the endpoint. There are several methods that have been developed to overcome this difficulty, and we will use the *McBride method* where the titration is carried out at an elevated temperature. This speeds up the reaction with oxalate ion, and since the reaction of  $\text{Mn}^{2+}$  with  $\text{MnO}_4^-$  is relatively slower, the titration error can be minimized.

The oxidation half reaction in the titration occurs when oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ , is oxidized to carbon dioxide:



The combination of half-reactions yields the overall reaction -



An additional advantage of permanganate titrations is that it serves as its own indicator due to its deep purple color. The titration is stopped at the first persistent light pink color.

**Part I: Determining the Concentration of  $\text{KMnO}_4$  Using Primary Standard Sodium Oxalate**

1. Prime a clean buret with the permanganate solution by rinsing it with approx. 2-3 mL of  $\text{KMnO}_4$  into a beaker.
2. Fill the buret with permanganate to approx. 0.0 mL (it doesn't have to be exact), and make sure there are no air bubbles in the buret tip by dispensing a small portion into a beaker.
3. Record the initial volume of permanganate in the data sheet.
4. Using a 20-mL pipet, transfer 20 mL of sodium oxalate solution into the two Erlenmeyer flasks. To each flask add 50 mL of distilled water and 20 mL of 3M  $\text{H}_2\text{SO}_4$ .
5. Heat the contents of the first flask to about 80 °C, and then turn off the Bunsen burner.
6. Now titrate *slowly* while stirring until a permanent faint pink coloration is attained. You will see a brown solid forming that quickly disappears, which is completely normal. If the solution changes completely to brown, then you'll need to do a another sample.
7. Record the volume used in the first titration.
8. Repeat steps 5 and 6 for the second flask.
9. In the data sheet calculate the molarity of the permanganate and average the results.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Redox Titration

Subtopic: Preparation and standardization of Ceric Ammonium Sulphate I. P./B. P

Objective: To Study about Preparation and standardization of Ceric Ammonium Sulphate I. P./B. P

Topic Outcomes: At the end of topic you will

1. Learn Preparation of Ceric Ammonium Sulphate I. P./B. P
2. Learn standardization of Ceric Ammonium Sulphate I. P./B. P

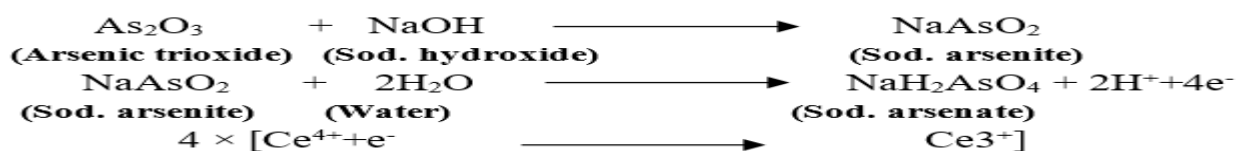
**Preparation of 0.1N ceric ammonium sulphate**

1. 66gm of ceric ammonium sulphate was dissolved with gentle heat in a mixture of 30 ml of sulphuric acid and 500 ml of water
2. The mixture was cooled and filtered
3. The resulting solution was diluted to 1000ml with water

**Standardisation of 0.1 N Ceric Ammonium Sulphate**

1. About 0.2 gm of Arsenic trioxide which was previously dried for about an hour was accurately weighed and transferred into a 500 ml conical flask.
2. The inner walls of the flask were washed with 100 ml of water and mixed thoroughly
3. Then 300 ml of dil. sulphuric acid , 0.15 ml of osmic acid, 0.1 ml of ferroin sulphate indicator were added
4. Titration was carried out until pink colour of solution changed to pale blue or yellowish green colour

**Each ml of 0.1 N ceric ammonium sulphate ~ 0.6326 gm of ceric ammonium sulphate ~ 4.946 grams of arsenic trioxide**



**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

## Name of topic/lesson – Redox Titration

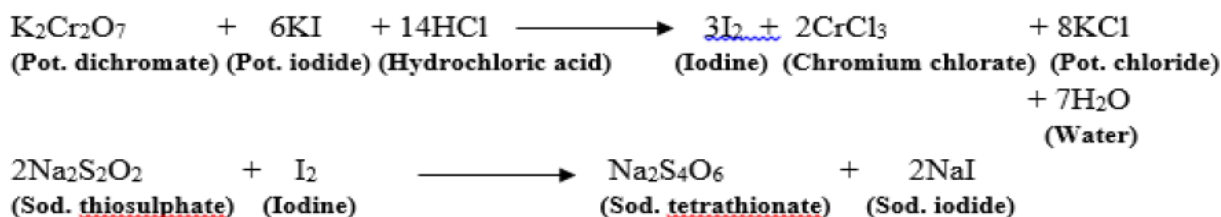
## Subtopic: Preparation and standardization of Sodium Thiosulphate I. P./B. P.

## Objective: To Study about Preparation and standardization of Sodium Thiosulphate I. P./B. P.

## Topic Outcomes: At the end of topic you will

1. Learn Preparation of Sodium Thiosulphate I. P./B. P.
  2. Learn standardization of Sodium Thiosulphate I. P./B. P.
- 

Sodium thiosulphate solution is standardized against potassium dichromate in presence of hydrochloric acid and potassium iodide. Potassium dichromate oxidizes the iodide ion in acidic medium to equivalent amount of iodine. The iodine formed in the reaction oxidizes sodium thiosulphate giving sodium tetrathionate ion and the end point is detected by starch solution.

***Preparation of sodium thiosulphate solution***

Dissolve 25 g of sodium thiosulphate in CO<sub>2</sub> free water and make the volume upto 1000 ml. Keep the solution aside and filter to remove any cloudiness, if appears.

***Preparation of starch solution***

Add one gram of starch to few ml of water, prepare slurry and add gradually to 100 ml of boiling water till a translucent solution will be obtained.

***Standardization of sodium thiosulphate***

Dissolve 0.125 g of accurately weighed potassium dichromate in 25 ml of water present in a 250 ml erlenmeyer flask. Add 10 ml of hydrochloric acid and 2 g of potassium iodide, stopper, shake and keep in dark for 15 min. Add 100 ml of water to the above mixture and titrate with sodium thiosulphate using starch as the indicator. Near end point the color will be changed from dark blue to bottle green. Each ml of 0.1 M sodium thiosulphate is equivalent to 0.04904 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.



**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Redox Titration****Subtopic: Types of redox titrations (Principles and applications)****Objective: To Study about Types of redox titrations (Principles and applications)****Topic Outcomes:** At the end of topic you will

1. Learn **Types of redox titrations**
  2. Learn **Principles and applications of redox**
- 

**PRINCIPLE:**

The principle involved in the oxidation-reduction titrations is that the oxidation process involves the loss of electrons whereas the reduction process involves the gain of electrons.

Oxidation	Reduction
gain in oxygen	loss of oxygen
loss of hydrogen	gain in hydrogen
loss of electrons	gain of electrons

## *Oxidising and Reducing agent*

- An **oxidising agent** is a chemical species that causes the other reactant in a redox reaction to be oxidised, and it is always reduced in the process.
- A **reducing agent** is a chemical species that causes the other reactant in a redox reaction to be reduced, and it is always oxidised in the process.

## Types of Redox Titrations

Redox titrations are named according to the [titrant](#) that is used:

- Bromometry uses a bromine ( $\text{Br}_2$ ) titrant.
- Cerimetry employs cerium(IV) salts.
- Dichrometry uses potassium dichromate.
- Iodometry uses iodine ( $\text{I}_2$ ).
- Permanganometry uses potassium permanganate.

### Applications:

#### **4. Determination of Anions**

A. Determination of soluble oxalates

B. Determination of sulphide, sulphite, thiosulphate, sulphate & persulphates.

C. Determination of halides, chlorate and hypochlorite.

D. Determination of nitrite and nitrate

5. Determination of aldehydes.

6. Determination of moisture content (Karl-Fischer reagent)

7. Bromometric determination of phenolic compounds.

8. Determination of organic pharmaceutical compounds

9. 9- Analysis of mixtures.

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

1. Learn Permanganometry
  2. Learn Principles of Permanganometry
- 

## Permanganate titration

- **Permanganometry** is one of the techniques used in quantitative analysis in Chemistry.
- It is a redox titration and involves the use of permanganates and is used to measure the amount of analyte present in unknown chemical samples.
- It involves two steps, namely the titration of the analyte with potassium permanganate solution and then the standardization of potassium permanganate solution with standard sodium oxalate solution.



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan



Name of topic/lesson – Redox Titration

Subtopic: Cerimetry, Iodimetry, Iodometry

Objective: To Study about Cerimetry, Iodimetry, Iodometry

Topic Outcomes: At the end of topic you will

1. Learn Cerimetry,
2. Learn Principles of Iodimetry, Iodometry

Titration involving with Iodine	
IODIMETRIC DIRECT METHOD	IODOMETRIC INDIRECT METHOD
Analysing strong reducing species	Analysing strong oxidising species
Titration of analyte with std. I <sub>2</sub> soln. (I <sub>3</sub> <sup>-</sup> )	Titration of I <sub>2</sub> produced by analyte against sod. thiosulfate
Titration in acidic/weakly alkaline solution	Add Xs of I <sup>-</sup> to soln of analyte. I <sub>2</sub> is produced in amount equivalent to oxi. agent
Red. Power of red. Agents is increased in neutral solution	Lib I <sub>2</sub> is titrated against Sod. Thio sulfate
pH is maintained neutral by adding NaHCO <sub>3</sub>	$\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^-(\text{Xs}) \rightarrow 14\text{H}^+ + 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$ $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$
$\text{AsO}_3^{3-} + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{3-} + 2\text{I}^- + 2\text{H}^+$	Sodium thio sulfate is universal titrant for iodine in neutral/acidic solution.
In neutral solution, at low acid: equilibrium is shifted to right	Titration occurs in acidic solutions
Potential of As(V)/As(III) couple is decreased sufficiently that As(III) will reduce I <sub>2</sub> and increase reducing power of AsO <sub>3</sub> <sup>3-</sup>	Acidity promotes oxidising agent- iodide reaction
$\text{AsO}_4^{3-} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{AsO}_3^{3-} + \text{H}_2\text{O}$	Lib I <sub>2</sub> is titrated against Sod. Thio sulfate
	How? Equilibrium is shifted to right.
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{AsO}_3 + 4\text{H}_2\text{O}$

**Cerimetry** or **cerimetric** titration, also known as cerate oximetry, is a method of volumetric chemical analysis developed by Ion Atanasiu. It is a redox titration in which a Fe<sup>2+</sup>-1,10-phenanthroline complex (ferroin) color change indicates the end point.

References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and Stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Redox Titration**

**Subtopic: Bromatometry, Dichrometry, Titrations with Potassium Iodate I. P.**

**Objective: To Study about Bromatometry, Dichrometry, Titrations with Potassium Iodate I. P.**

**Topic Outcomes:** At the end of topic you will

1. Learn principle of **Bromatometry**
  2. Learn **Principles of Dichrometry, Titrations with Potassium Iodate I. P.**
- 

- Definition of bromometry. : Quantitative analysis by the use of bromine compares iodometry. Bromatometry is a titration process in which the bromination of a chemical indicator is observed.
- Permanganometry and **Dichrometry** are most significant techniques used in qualitative analysis in Chemistry. It is a redox titration and involves the use of permanganates and dichromates which are used to estimate the amount of analyze present in unknown chemical samples.
- The amount of iodine liberated from iodide (i.e., **KI**) is equivalent to the quantity of the oxidizing agent ( $\text{CuSO}_4$ ) present. On the other hand, when the standard iodine solution is directly **titrated** by a reducing agent (such as sodium thiosulphate), then the **titration** is called as iodimetry **titration**.

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Conductometry

Subtopic: Introduction, Conductivity cell

Objective: To Study about Introduction, Conductivity cell

Topic Outcomes: At the end of topic you will

1. Learn principle of **Conductometry**
  2. Functions of conductivity cell
- 

**Conductometry** is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. **Conductometry** has notable application in analytical chemistry, where **conductometric** titration is a standard technique.

**Principle** of the **conductometric** titrations theory states that for dilutions that are infinite, ions act independently and in the process contribute toward conductance of the solution. The **principle** behind this theory states that anions and cations have different conductance values.

The conductivity of solutions depends on: • the number of ions. The more ions a solution contain, the higher its conductivity. The ionic mobility in a general way. The mobility in turn depends on

– The type of ion: the smaller an ion, the more mobile it is and the better it conducts electrical current. Ions of very high conductivity are  $H_3O^+$  ,  $OH^-$  ,  $K^+$  und  $Cl^-$  . If an ion is surrounded by water molecules (hydratization) and therefore becomes larger, its conductivity decreases.

– The solvent: the more polar a solvent, the more completely ionized are the compounds dissolved in it. Water is an ideal solvent for ionic compounds. In alcohols the ionization decreases with increasing chain length (methanol >ethanol >propanol). In non-polar organic solvents, e.g. chlorinated and non-chlorinated hydrocarbons, there is practically no ionization.

– The temperature: in contrast to what is found with solids, the conductivity of solutions increases with increasing temperature at a rate that ranges from 1 to 9% per Kelvin, depending on the ion.

– The viscosity: the ionic mobility decreases with increasing viscosity, which means that the conductivity also decreases.



The two **electrode cell** is the most commonly **used conductivity cell** Glass **cells** have **electrodes** made of platinum. Epoxy **cells** have easy to clean graphite plates.

Conductivity is the measurement of the electrolytes in a solution. It is defined as the conductance in a given volume of sample. Conductance is the ability of the solution to conduct electric current. Conductivity = Conductance x Probes cell constant (K) OR Conductivity = Electrical Current/Voltage x Distance/Area.

#### Measurement:-

- The instrument used to measure conductance is called conductance bridge or conductometer
- Classical circuit employed for measurement is wheatstone bridge
- All other work on this principle
- Various types are:
  1. Kohlrausch conductance bridge
  2. Direct reading conductance bridge
  3. Phillips conductance bridge
  4. Mullard's conductance bridge
  5. Pye's conductance bridge

#### Ohm's law-

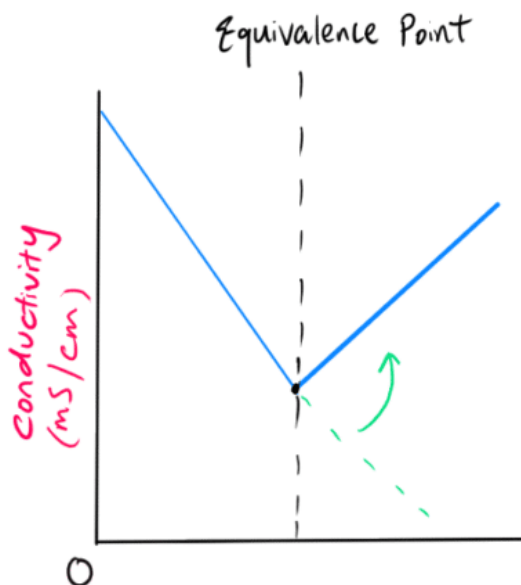
The resistance R in ohms ( $\Omega$ ) is equal to the voltage V in volts (V) divided by the current I in amps (A): Since the current is set by the values of the voltage and resistance, the Ohm's law formula can show that: If we increase the voltage, the current will increase.

#### References

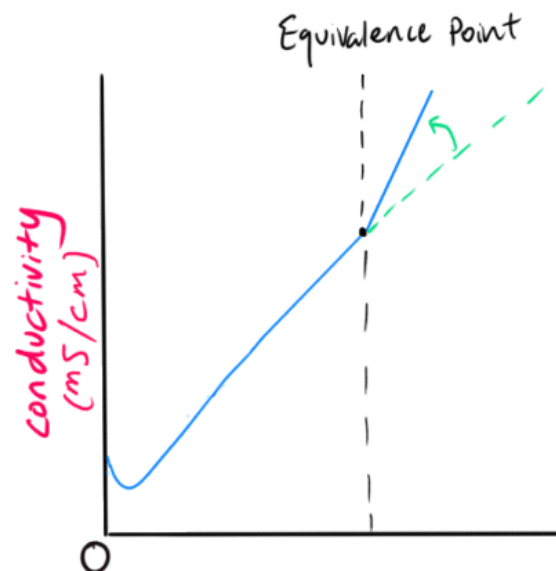
1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

1. Learn principle of Conductometry
2. Understand Conductometric titration

### STRONG ACID w/ STRONG BASE



### WEAK ACID w/ STRONG BASE



#### Strong Acid with a Strong Base

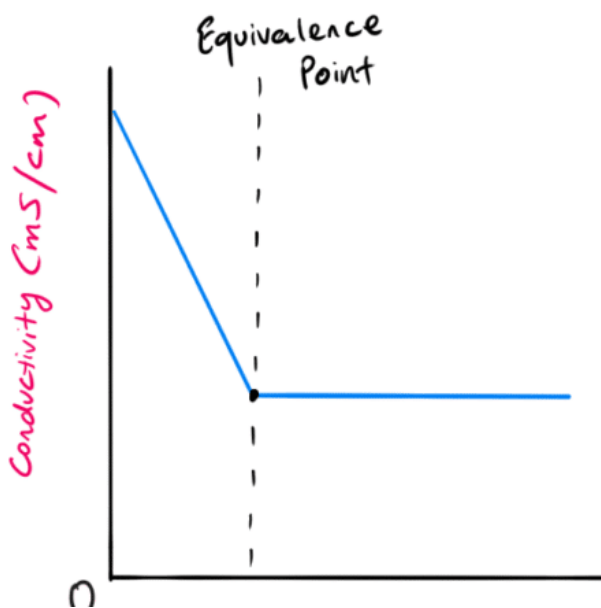
e.g. HCl with NaOH: Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as  $H^+$  ions react with  $OH^-$  ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of  $OH^-$  ions.

#### Weak Acid with a Strong Base,

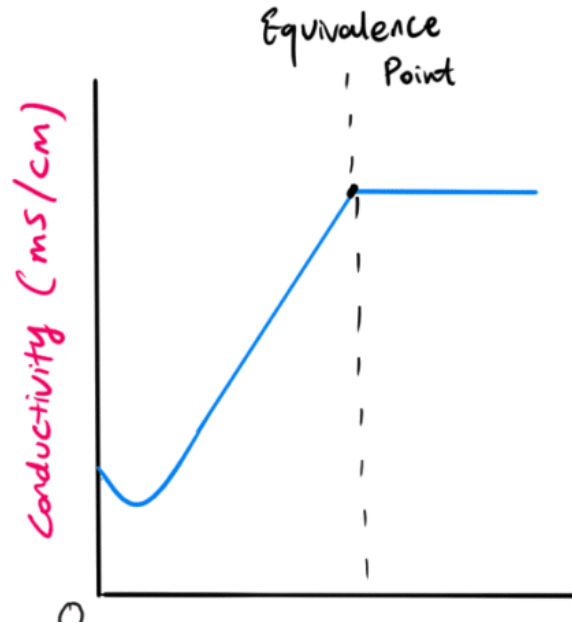
e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of  $H^+$  by  $Na^+$  but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated  $CH_3COOH$  to  $CH_3COONa$  which is the strong

electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt  $\text{CH}_3\text{COONa}$ . Beyond the equivalence point, conductance increases more rapidly with the addition of  $\text{NaOH}$  due to the highly conducting  $\text{OH}^-$  ions

### STRONG ACID w/ WEAK BASE



### WEAK ACID w/ WEAK BASE



### Strong Acid with a Weak Base

E.g. sulphuric acid with dilute ammonia: Initially the conductance is high and then it decreases due to the replacement of  $\text{H}^+$ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate

### Weak Acid with a Weak Base:

The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
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### • ADVANTAGE OF CONDUCTOMETRIC TITRATIONS:

1. Does not require indicators since change in conductance is measured by conductometer
2. Suitable for coloured solutions
3. Since end point is determined by graphical means accurate results are obtained with minimum error
4. Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak & strong acids

## APPLICATIONS OF CONDUCTOMETRY

It can be used for the determination of:-

- Solubility of sparingly soluble salts
- Ionic product of water
- Basicity of organic acids
- Salinity of sea water (oceanographic work)
- Chemical equilibrium in ionic reactions
- Conductometric titration

### References

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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Lecture No: 39

Name of topic/lesson –Potentiometry

Subtopic: Electrochemical cell, construction and working of reference (Standard Hydrogen Electrode)

Objective: To Study about Electrochemical cell, construction and working of reference (Standard Hydrogen Electrode)

Topic Outcomes: At the end of topic you will

1. Learn Principle of potentiometer
2. To Study about Electrochemical cell, construction and working of reference (Standard Hydrogen Electrode)

**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.

## Principle

Emf of a cell depends on the concentration of the electrolytes with which the electrodes are in contact. Therefore, the electrode reaction is,



As the concentration of  $M^{n+}$  changes, the emf of the cell also changes correspondingly.

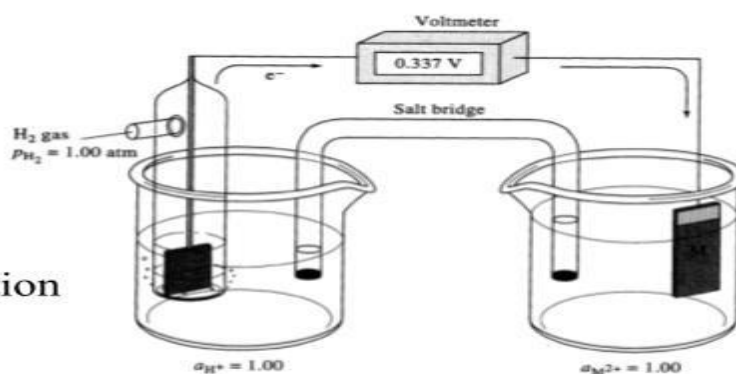


## Standard Reference Electrode Standard Hydrogen Electrode (SHE)



### SHE:

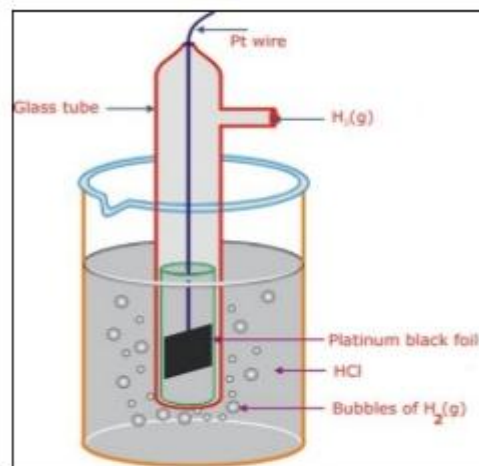
- Assigned 0.000 V
- Can be anode or cathode
- Pt does not take part in reaction
- Difficult to operate



### Standard Conditions:

**1 atm for gases, 1.0M for solutions, 25 °C for all (298 K)**

It consists of a platinum wire in a inverted glass tube. Hydrogen gas is passed through the tube at 1 atm. A platinum foil is attached at the end of the wire. The electrode is immersed in 1M H<sup>+</sup> ion solution at 25°C. The electrode potential of SHE is zero at all temperatures.



### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Potentiometry

Subtopic: Silver Chloride Electrode and Calomel Electrode) and Indicator Electrodes (Metal electrodes and Glass Electrode),

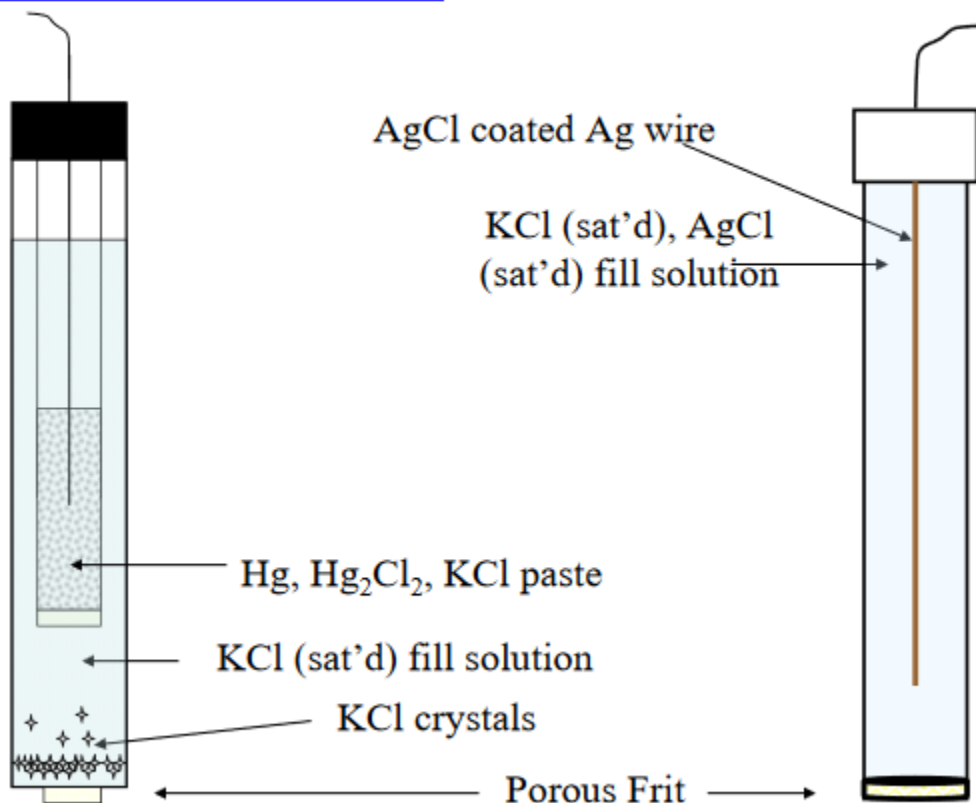
Objective: To Study about Silver Chloride Electrode and Calomel Electrode) and Indicator Electrodes (Metal electrodes and Glass Electrode),

Topic Outcomes: At the end of topic you will

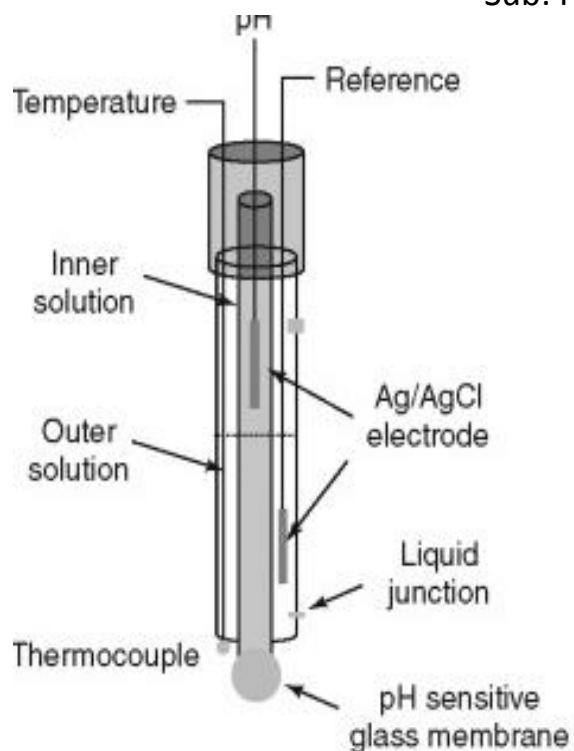
1. Learn principle and working of Silver Chloride Electrode and Calomel Electrode
  2. Understand Indicator Electrodes (Metal electrodes and Glass Electrode)
- 

### Saturated Calomel Electrode

### Ag/AgCl Electrode







### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

Name of topic/lesson – Potentiometry

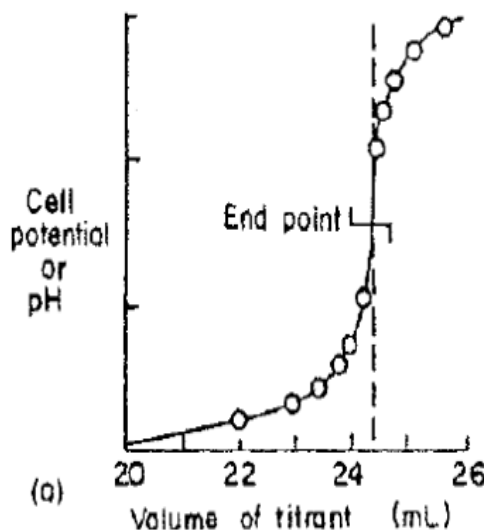
Subtopic: Methods to determine end point of potentiometric titration and applications

Objective: To Study about Methods to determine end point of potentiometric titration and applications

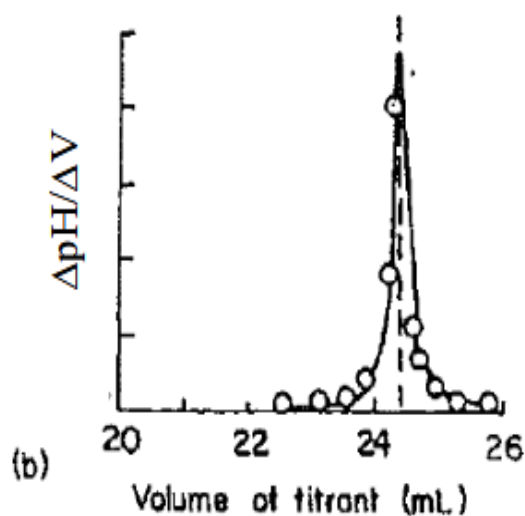
Topic Outcomes: At the end of topic you will

1. Learn principle and working of about **Methods to determine end point of potentiometric titration**
2. Understand **applications of potentiometry.**

End-Point Detection with Potentiometric Titrations Several methods can be used to determine the end point of a Potentiometric titrations. The most straight forward one involves a direct plot of potential as a function of reagent volume.



The second approach to end-point detection is to plot the derivative curves: 1. Plotting first derivative curve by calculating the change in potential or pH per unit volume of titrant (that is,  $\Delta E/\Delta V$  or  $\Delta pH/\Delta V$ ). A plot of  $\Delta E/\Delta V$  or  $\Delta pH/\Delta V$  as a function of corresponding reagent volume produces a curve with a maximum that corresponds to the point of inflection.



### Application of potentiometric titration in

- a) Neutralization reactions:** glass / calomel electrode for determination of Ph
- b) Precipitation reactions:** Membrane electrodes for the determination of the halogens using silver nitrate reagent
- c) Complex formation titration:** metal and membrane electrodes for determination of many cations (mixture of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  using EDTA)
- d) Redox titration:** platinum electrode For example for reaction of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  with  $\text{Ce}^{4+}/\text{Ce}^{3+}$

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Niral Prakashan

## Lecture No42

## Name of topic/lesson – Polarography

## Subtopic: Principle

**Objective:** To Study about Principle of Polarography

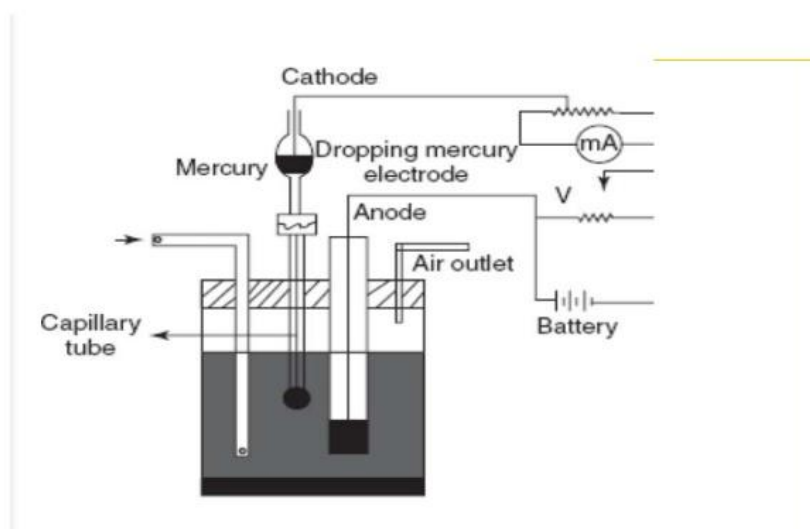
**Topic Outcomes:** At the end of topic you will

1. Learn principle Principle of Polarography
  2. Understand concept of **Polarography**
- 

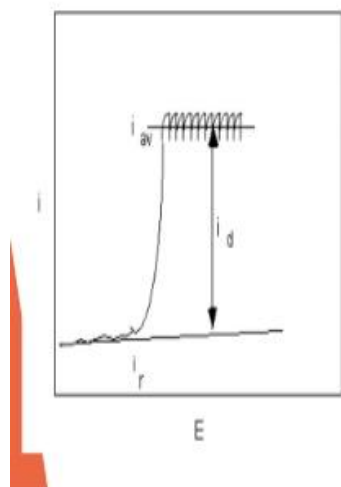
Polarography is a type of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which are useful for their wide cathodic ranges and renewable surfaces. It was invented in 1922 by Czech chemist Jaroslav Heyrovský, for which he won the Nobel prize in 1959.

Polarography is a voltammetric measurement whose response is determined by only diffusion mass transport. The simple principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from a capillary tube. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical sigmoidal shape.

## polarography apparatus:



## POLAROGRAM



- ▶  $i_r$  (residual current) which is the current obtained when no electrochemical change takes place.
- ▶  $i_{av}$  (average current/limiting current) is the current obtained by averaging current values throughout the life time of the drop while
- ▶  $i_d$  (diffusion current) which is the current resulting from the diffusion of electroactive species to the drop surface.

## References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

## Lecture No43

## Name of topic/lesson – Polarography

**Subtopic:** Ilkovic Equation.

**Objective:** To Study about Ilkovic Equation.

**Topic Outcomes:** At the end of topic you will

1. Learn principle Ilkovic Equation.
2. Understand concept of Ilkovic Equation.

## 6. Quantitative analysis: The Ilkovic Equation

It relates the **diffusion current,  $i_d$** , the **concentration** of the analyte and the characteristics of Hg drop :

$$i_d = 607 n D^{1/2} m^{2/3} t^{1/6} C \quad \longrightarrow \quad i_d = k C$$

$i_d$  : max value of the diffusion current in the life of the drop

$n$  : number of electrons involved

$C$  : concentration of ion in bulk, mmol/L

$D$  : diffusion coefficient of the ion ( $\text{cm}^2/\text{s}$ ) [temperature dependent]

$m$  : flow rate of Hg in (mg/s)

$t$  : drop life time (s)

- Ilkovic equation is applicable in the given form only if the migration of the analyte ions (mass transport of ions due to the electric field) is suppressed by addition of inert supporting electrolyte (usually 1 M KCl).
- In this case **diffusion** remains essentially the **only** kind of mass transport of analyte ions in the redox process. *Note that polarographic measurements are conducted in unstirred solution (no convection current).*
- Furthermore, the supporting electrolyte enhances conductivity of the solution.
- The supporting electrolyte may also contain buffer to adjust the pH at a suitable value and chelating agents to mask the interfering ions.

### References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Refractometry**

**Subtopic:** Introduction, refractive index, specific and molar refraction

**Objective:** To Study about Introduction, refractive index, specific and molar refraction

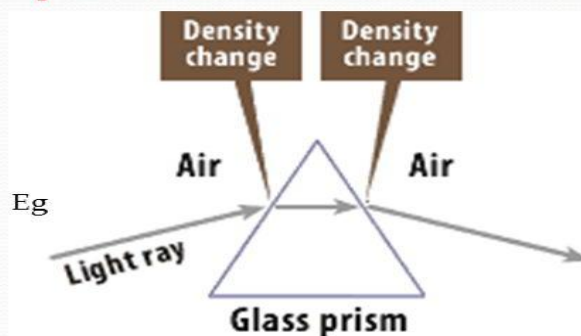
**Topic Outcomes:** At the end of topic you will

1. Learn principle of RefractometryIntroduction.
  2. Understand concept of refractive index, specific and molar refraction
- 

**Refractometry** is the analytical method of measuring substances' refractive index (one of their fundamental physical properties) in order to, for example, assess their composition or purity. A refractometer is the instrument used to measure refractive index ("RI").

## Definition of refraction

- Refraction is the **bending of light** as it passes from one substance to another. The bending is caused by the **differences in density between the two substances.**



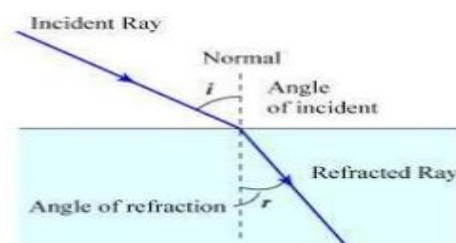
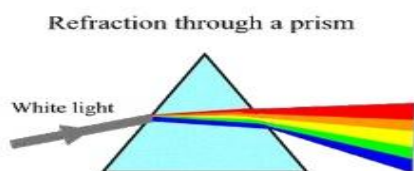
A **refractometer** is a scientific machine that measures the amount that light is bent (or refracted) when it moves from the air into a sample. **Refractometers** are typically used to determine the refractive index of a liquid sample.



## PRINCIPLE



Measurement of RI of unknown substance by measuring angle of refraction made when the substance is brought into contact with the medium (prism) of a known refractive index

**Molecular Refraction.**

**Molecular refraction** is often represented as the sum of the “refractions” of certain constituents that can be either atoms or groups of atoms making a **molecule** of a complex compound, or bonds of the atoms in such a **molecule**.

**Specific Refraction.** a parameter characterizing the electronic polarizability of a unit mass of a substance in the high-frequency electromagnetic field of a light wave. The **specific refraction**  $r$  of a substance is equal to the substance's molecular **refraction**  $R$  divided by its molecular weight  $M$ .

**References**

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
2. Instrumental Methods of Chemical Analysis by Bekette and stenlake, 4th edition.
3. Pharmaceutical Analysis by Waloda, Nirali Prakashan

**Name of topic/lesson – Refractometry**

**Subtopic:** Measurement of RI, Abbe's refractometer and applications

**Objective:** To Study about Measurement of RI, Abbe's refractometer and applications

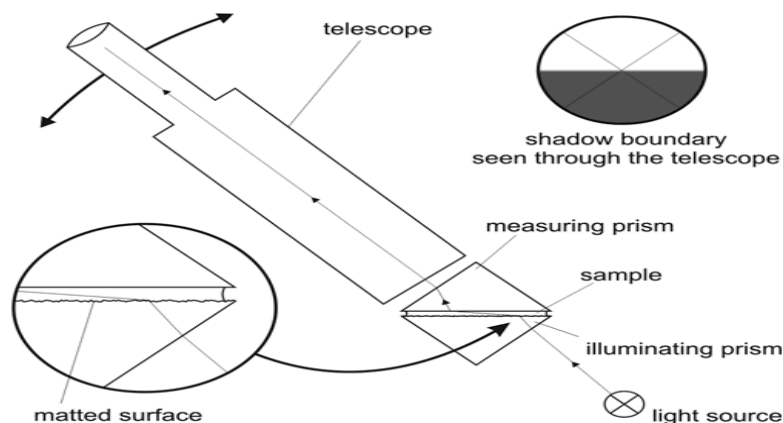
**Topic Outcomes:** At the end of topic you will

1. Learn principle of Abbe's refractometer
2. Learn Measurement of RI, and applications

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## I.) ABBE REFRACTOMETER

- Light refraction through liquids to determine the amount of dissolved solids in liquids by passing light through a sample and showing the refracted angle on a scale.
- RI of the prism should be greater than that of the sample
- In abbe refractometer, the RI can be read directly, only a few drop of the liquid are needed, and either white or monochromatic light can be used.
- This refractometer consist, mainly a telescope and two matched right angle prisms.



## APPLICATIONS & USES



- 1) It is used in the examination of organic compounds (oils, solvents, etc.), solutions, food products, serum protein concentration.
- 2) In veterinary medicine, a refractometer is used to measure the total plasma protein in a blood sample and urine specific gravity.
- 3) In gemmology, a refractometer is used to help identify gem materials by measuring their refractive index.
- 4) Since the index of refraction of a pure substance is constant at constant temperature and pressure, it can be used as a means of identification.
- 5) It is used to determine the purity of oils, fats, and waxes.
- 6) It is used to determine the amount of sugar in sugar solutions and in general, for determining total solids in fruit juices, tomato products, honey, syrups and soda water



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## References

1. Instrumental Methods of Analysis by Willard Merit, Dean Settle, 7th edition, CBS Publisher & Distributor
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3. Pharmaceutical Analysis by Waloda, Nirali Prakashan