UNIT 4

Redox titrations

Redox titrations are a class of volumetric titrations that involve **oxidation-reduction reactions**, where electrons are transferred from one species to another. These titrations are widely used for the quantitative determination of reducing and oxidizing agents in pharmaceutical and chemical analysis.

Basic Concepts of Oxidation and Reduction

1. Oxidation

Originally, oxidation referred to the combination of a substance with oxygen. However, in modern chemistry, oxidation is defined as:

- **Loss of electrons** by a substance
- **Increase in oxidation number**
- **Addition of oxygen** or **removal of hydrogen**

Example:

Fe2+→Fe3++e−\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-Fe2+→Fe3++e−

Here, iron (Fe^{2+}) **loses an electron** and is oxidized to Fe^{3+}.

---

2. Reduction

Reduction is the opposite of oxidation:

- **Gain of electrons** by a substance
- **Decrease in oxidation number**
- **Addition of hydrogen** or **removal of oxygen**

Example:

$Cl2+2e^- \rightarrow 2Cl^-$

Chlorine (Cl_2) **gains electrons** and is reduced to Cl^-.

3. Oxidizing Agent

A substance that **accepts electrons** and gets reduced itself.
It causes **oxidation** of the other reactant.

Examples: $KMnO_4$, $K_2Cr_2O_7$, I_2, H_2O_2

4. Reducing Agent

A substance that **donates electrons** and gets oxidized itself.
It causes **reduction** of the other reactant.

Examples: $FeSO_4$, $Na_2S_2O_3$, oxalic acid, $SnCl_2$

5. Redox Reaction

A redox reaction involves simultaneous oxidation and reduction.

Example:

$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ (Reduction)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (Oxidation)

Overall:

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Significance in Titrations

Redox titrations are used to:

- Determine the **oxidizing or reducing strength** of substances
- Analyze **iron salts**, **peroxides**, **sulphides**, **ascorbic acid**, etc.
- Quantify pharmaceutical substances like **hydrogen peroxide**, **potassium permanganate**, **iodine**, and **sodium thiosulphate**

Types of Redox Titrations

Redox titrations may involve:

- **Potassium permanganate titrations (permanganometry)**
- **Potassium dichromate titrations (dichrometry)**
- **Iodine titrations (iodometry and iodimetry)**
- **Ceric sulphate titrations**

Indicators Used

- **Self-indicator**: $KMnO_4$ (purple to colorless)
- **External indicator**: Potassium ferricyanide (in Fe^{2+} titration)
- **Starch indicator**: For iodine-based titrations (blue complex with iodine)

Cerimetry is a type of redox titration that involves the use of **ceric ammonium sulfate (Ce^{4+})** as the oxidizing agent. It is commonly carried out in **acidic medium** (usually dilute H_2SO_4 or HNO_3) where **Ce^{4+} (yellow)** is reduced to **Ce^{3+} (colorless or faint blue-green)**.

Principle of Cerimetry

Ceric ion (Ce^{4+}) acts as a strong **oxidizing agent** and accepts **one electron** to form cerous ion (Ce^{3+}):

Ce4++e−→Ce3+\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}Ce4++e−→Ce3+

During titration, Ce^{4+} oxidizes the analyte (a reducing agent), and itself gets reduced to Ce^{3+}. The titration is usually performed in acidic medium to maintain the stability and reactivity of Ce^{4+} ions.

Standard Cerimetry Reaction Example

1. **With Fe^{2+} (ferrous ions):**

$Ce4^{++}Fe2^{+}$→$Ce3^{+}$+Fe3+

This reaction is fast, stoichiometric, and does not require a catalyst.

Indicators Used in Cerimetry

1. **Self-indicating titration**: The yellow color of Ce^{4+} disappears at end-point as it converts to colorless Ce^{3+}.
2. **External Indicator**: Potassium ferricyanide (for Fe^{2+} estimation).
3. **Internal Indicators**:
    - Ferroin
    - Methylene blue
    - o-Phenanthroline

Applications of Cerimetry

Cerimetry is used for the **quantitative estimation** of a variety of reducing agents. Some common pharmaceutical and chemical applications include:

1. Estimation of Iron (Fe^{2+})

- Ferrous salts such as **ferrous sulfate** or **ferrous fumarate** in pharmaceutical formulations can be titrated with standard ceric ammonium sulfate solution.

2. Estimation of Ascorbic Acid (Vitamin C)

- Ascorbic acid is a reducing agent that is titrated directly with Ce^{4+} in sulfuric acid medium.
- C6H8O6+2Ce4+→C6H6O6+2Ce3++2H+

3. Estimation of Sulphur Dioxide (SO_2)

- Used in food and pharmaceutical preservatives.

4. Estimation of Hydroquinone and Paracetamol

- Compounds having phenolic or reducing groups can also be estimated using cerimetry.

Advantages of Cerimetry

- Ceric ammonium sulfate is **stable in acidic solution**.
- Titrations are **rapid** and **quantitative**.
- Suitable for **colorimetric or potentiometric detection**.
- **One electron transfer** per molecule makes calculations straightforward.

Iodometry and Iodimetry

Overview

Iodimetry and **Iodometry** are two important types of redox titrations that involve **iodine (I_2)** or **iodide (I^-)** as reactants. Both are widely used in pharmaceutical analysis due to the versatility and moderate strength of iodine as a redox agent.

Iodimetry

Definition:

Iodimetry is a **direct titration method** in which a **standard solution of iodine (I_2)** is used as the **oxidizing agent** to titrate reducing substances.

Principle:

Iodine (I_2) acts as a mild oxidizing agent and **accepts electrons** to form iodide (I^-):

I2+2e−→2I−

A reducing agent donates electrons and gets oxidized.

Example Reaction:

Estimation of **ascorbic acid**:

C6H8O6+I2→C6H6O6+2HI

Indicators:

- **Starch solution** is used as an **internal indicator**, forming a **blue complex** with free iodine near the end-point.

Applications of Iodimetry:

- Estimation of **ascorbic acid (vitamin C)**
- Estimation of **arsenites**, **hypophosphorous acid**
- Drugs that act as reducing agents like **phenol**, **quinones**, and **thiols**

Iodometry

Definition:

Iodometry is an **indirect titration method** in which an **oxidizing agent reacts with excess potassium iodide (KI)** to liberate iodine (I_2), which is then **titrated with standard sodium thiosulfate ($Na_2S_2O_3$)** solution.

Principle:

The oxidizing agent oxidizes iodide (I^-) to iodine (I_2), which is then reduced back to iodide by thiosulfate:

Oxidizing Agent+2I−→I2+Reduced Product

Then:

I2+2S2O32−→2I−+S4O62−

Indicators:

- **Starch** is used near the end-point, added **after most of the iodine has reacted**, forming a **blue complex**. Disappearance of blue color indicates end-point.

Applications of Iodometry:

- Estimation of **copper(II) sulfate**
- Estimation of **chloramine-T**, **hydrogen peroxide**
- Estimation of **potassium permanganate** and **potassium dichromate**
- Analysis of **sulphur dioxide**, **hypochlorites**, and **chlorinated water**

Key Differences:

Feature	Iodimetry	Iodometry
Role of iodine	Used as a standard oxidizing agent	Liberated during reaction with oxidant
Type of titration	Direct	Indirect
I_2 reacts with	Reducing agent	Sodium thiosulfate
Example analyte	Ascorbic acid	Copper sulfate, $KMnO_4$, $K_2Cr_2O_7$

Advantages

- Moderate redox potential of iodine makes the reactions selective
- Titrations can be performed under mild conditions
- Applicable to a wide range of pharmaceuticals and water analysis

Precautions

- Iodine is volatile; keep solutions covered and in cool, dark conditions
- Use freshly prepared starch indicator
- Avoid exposure to air to prevent iodine loss by evaporation

Bromatometry

Definition:

Bromatometry is a type of redox titration in which **bromine** acts as the **oxidizing agent**. In practice, bromine is not added directly but is **generated in situ** from a solution of **potassium bromate ($KBrO_3$)** and **potassium bromide (KBr)** in **acidic medium**.

Principle:

When $KBrO_3$ is treated with KBr and an acid like HCl, **bromine is liberated**:

$$KBrO3+5KBr+6HCl \rightarrow 3Br2+3H2O+6KCl$$

The liberated bromine **oxidizes the analyte** (usually organic substances like phenols, anilines, or alkaloids). The reaction involves **electrophilic substitution or oxidation** depending on the substrate.

End Point Detection:

- **Potentiometrically** or

- Using **indicators** like methyl orange or starch (depending on the substrate)
- **External or internal indicators** may be used based on reaction type.

Applications of Bromatometry:

- Estimation of **phenol**, **aniline**, and related compounds.
- Analysis of **alkaloids** such as morphine and codeine.
- Used in assay of **reserpine**, **chlorpromazine**, and **sulphadiazine**.
- Useful in determining compounds that undergo bromination or oxidation.

2. Dichrometry (Potassium Dichromate Titrations)

Definition:

Dichrometry is a redox titration method that employs **potassium dichromate ($K_2Cr_2O_7$)** as a **standard oxidizing agent**.

Principle:

In acidic medium, $K_2Cr_2O_7$ acts as a strong oxidizing agent and **accepts 6 electrons**, getting reduced to **Cr^{3+}**:

Cr2O72−+14H⁺+6e−→2Cr3++7H2O

The analyte (typically **Fe^{2+}**, **Sn^{2+}**, or other reducing agents) donates electrons and gets oxidized.

Reaction with Fe^{2+} (Ferrous ion):

$Cr_2O_7^{2-}+6Fe^{2+}+14H^{+}\rightarrow 2Cr^{3+}+6Fe^{3+}+7H_2O$

Indicators Used:

- **External Indicator**: Potassium ferricyanide – spot test with a drop of reaction mixture
- **Internal Indicator**: Diphenylamine, N-phenylanthranilic acid – change in color at end-point

Applications of Dichrometry:

- Estimation of **iron (Fe^{2+}) salts** (e.g., ferrous sulfate, ferrous fumarate)
- Assay of **hydrogen sulfide**, **tin(II) chloride**
- Standardization of reducing agents like **Mohr's salt** and **sodium thiosulfate**

Advantages of Potassium Dichromate:

- **Primary standard** (highly pure, stable)
- **Sharp end-point** with suitable indicators
- Useful over wide range of redox potentials

TITRATION WITH POTTASIUM IODATE

Definition:

Potassium iodate (KIO_3) is a **strong oxidizing agent** used in **iodometric titrations**. In acidic medium, it oxidizes **potassium iodide (KI)** to liberate **iodine (I_2)**, which is then titrated with **standard sodium thiosulfate ($Na_2S_2O_3$)** solution.

Principle:

In the presence of excess potassium iodide and dilute acid (typically HCl or H_2SO_4), KIO_3 liberates iodine:

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

The liberated iodine is then titrated with sodium thiosulfate:

$I_2 + 2S_2O3^{2-} \rightarrow 2I- + S_4O_6^{2-}$

Thus, KIO_3 indirectly oxidizes reducing substances by generating a known amount of iodine.

Procedure Summary:

1. Add excess KI and acid to the analyte solution.
2. Add standard KIO_3 solution (or allow KIO_3 to react with KI to liberate I_2).
3. Titrate liberated iodine with standard $Na_2S_2O_3$ solution.
4. Use **starch indicator** towards the end point (blue color → colorless).

Indicator:

- **Starch** is used as an **internal indicator**.
- Added near the endpoint, forms a **deep blue complex** with iodine.
- The disappearance of blue color indicates the endpoint.

Applications of KIO_3 Titrations:

1. **Estimation of reducing agents**:
    - Ascorbic acid
    - Sulfur dioxide
    - Hydrazine derivatives
2. **Assay of certain pharmaceuticals**:
    - Potassium iodide (KI)
    - Sodium thiosulfate

        - Sulfites and metabisulfites
3. **Standardization of sodium thiosulfate**:
    - KIO_3 is a **primary standard** and can be used to standardize $Na_2S_2O_3$.
4. **Estimation of chlorine content** in bleaching powders and disinfectants.

Why KIO_3 is preferred:

- It is a **primary standard**: pure, stable, and easily weighed.
- It gives **stoichiometric and reproducible** reactions.
- It allows **accurate indirect iodometric analysis**.

Stoichiometry:

From the reaction:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

1 mole of KIO_3 gives 3 moles of I_2
Which reacts with 6 moles of $Na_2S_2O_3$

So:
1 mole of KIO_3 ≡ 6 moles of $Na_2S_2O_3$