UNIT-IV

Redox titrations

(a) Concepts of oxidation and reduction
(b) Types of redox titrations (Principles and applications)
Cerimetry, Iodimetry, Iodometry, Bromatometry, Dichrometry, Titration with potassium iodate

Oxidising Agent → Oxidised other & reduce Itself.

Reducing Agent → Reduce other & Oxidised Itself.

Redox Titration

Oxidation & Reduction both takes place Simmentaneously.

Oxidation → Addition of Oxygen.
→ Removal of H_2.
→ e^- donate.

Reduction → Removal of O_2.
→ Addition of H_2 / e^- Accept.

★ Redox Titration is a laboratory method of determining the concentration of a given analyte by causing a redox reaction between the titrant and the analyte.

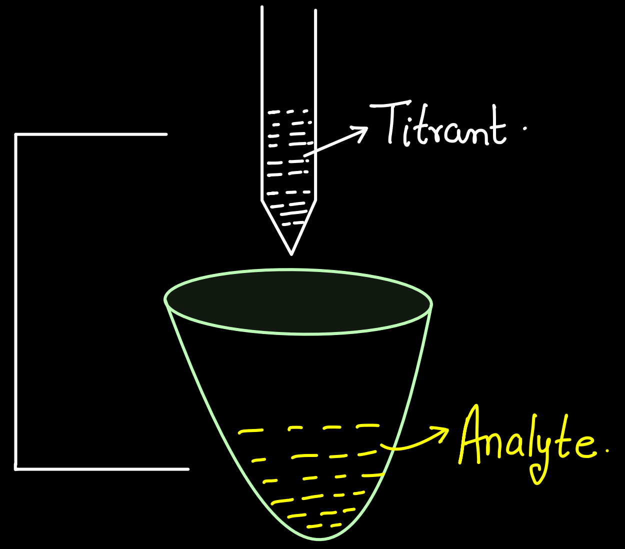
These types of titrations sometimes require the use of a potentiometer or a redox indicator.

Redox Titration

Redox titration is a type of titration where the analyte (the substance being analyzed) undergoes a redox reaction with the titrant (a solution of known concentration).

Redox titration is based on an oxidation-reduction reaction between the titrant and the analyte. It is one of the most common laboratory methods to identify the concentration of unknown analytes

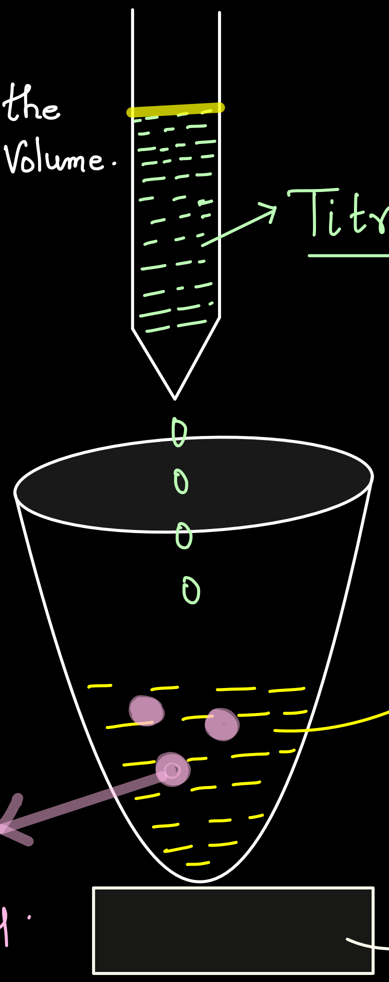
Oxid. & redo. reaction takes Place b/w Titrant & Analyte.



$KMnO_4$ } Oxidised ↓ H_2O_2

End point.
↓
Pink Colour Obtained.

Record the Initial Volume.



Titrant. (Potassium Permanganate). ($KMnO_4$).
→ Self Indicator.

H_2O_2 (Hydrogen Peroxide).

Add few drop of H_2SO_4.
(for Acidic Enviroment).
}
Required for Redox Titration.

White Tile.
→ To observe any Colour Change.

swirling the flask continuously.

Procedure:

Prepare the Titrant:

Ensure the potassium permanganate solution is of known concentration.

Prepare the Analyte:

Pipette a measured volume (e.g., 10 mL) of the hydrogen peroxide solution into a clean conical flask.

Acidify the Solution:

Add a few drops of sulfuric acid (H_2SO_4) to the hydrogen peroxide solution to create an acidic environment, which is required for the redox reaction to proceed properly.

Set Up the Burette:

Fill the burette with the potassium permanganate solution (titrant) and record the initial volume.

Titration:

Place the conical flask with the hydrogen peroxide solution on a white tile to observe any color change clearly.

Begin adding the potassium permanganate solution from the burette to the conical flask drop by drop, swirling the flask continuously.

As you approach the endpoint, the pink color from the permanganate will begin to persist for a few seconds, indicating that the reaction has gone to completion.

Determine the Endpoint:

The endpoint is reached when a faint pink color persists for about 30 seconds. This indicates that all the hydrogen peroxide has been oxidized, and any excess potassium permanganate is present in the solution.

Record the Final Volume:

Note the final volume of the potassium permanganate solution in the burette.

Redox Reaction.

Oxidation.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$$

Reduction.

Oxidation:

Oxidation is the process in which an atom, ion, or molecule loses electrons.

When a substance is oxidized, its oxidation state increases because the loss of electrons makes it more positively charged.

In simple terms, oxidation is the loss of electrons.

Reduction:

Reduction is the process in which an atom, ion, or molecule gains electrons.

When a substance is reduced, its oxidation state decreases because the gain of electrons makes it more negatively charged.

In simple terms, reduction is the gain of

Classification of redox indicators

1. Self-indicating Redox Indicators:

These are redox indicators that *themselves undergo a color change due to their own oxidation-reduction reactions. They are directly involved in the redox process and do not require an external device to detect the endpoint.

Characteristics:

The indicator undergoes a visible color change at the endpoint.

The color change occurs due to the change in the oxidation state of the indicator.

Examples:

Potassium Permanganate (MnO_4^-): It serves as its own indicator in acidic media, changing from purple (oxidized) to colorless (reduced to Mn^{2+}).

Iodine (I_2): In iodine titrations, iodine can serve as its own indicator, and the endpoint is reached when the blue color (due to starch-iodine complex) disappears.

Ferroin: Used in the titration of ferric ions (Fe^{3+}), changes from colorless (Fe^{2+}) to red (Fe^{3+}).

Diphenylamine: Used in the titration of iron(III) to iron(II), changes from colorless to blue upon reduction.

2. External Potentiometric (Electrochemical) Redox Indicators:

These are indicators that are not directly involved in the redox reaction but are used with a potentiometer or an electrode to detect the endpoint of the titration. They rely on measuring the change in the electrode potential (voltage) rather than a visible color change.

Characteristics:

The endpoint is determined by monitoring the voltage (electrode potential) between the solution and a reference electrode.

A potentiometer or an electrochemical cell is used to monitor this potential change.

Examples of Methods:

Platinum Electrode: Used to measure the potential in redox titrations where no visual color change is observed, and the endpoint is determined by a significant potential shift. For example, during titrations of strong oxidizing agents like permanganate.

Silver/Silver Chloride Electrode: Can be used in titrations of halides or other reactions where a potential difference is observed as the analyte is titrated.

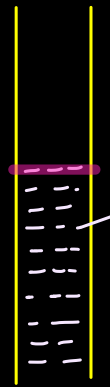
Cerimetry

Titrant.

↑

Cerimetry, or cerimetric titration, is a redox titration method that uses cerium(IV) salts as the oxidizing agent to determine the concentration of reducing agents in a sample.

Record the Initial Volume.



Ce^{+4} (Ceric Ion).

[No bubble during filling]

→ Powerful Oxidising Agent.

→ Source = Ceric Ammonium Sulphate.

→ Slight Yellowish Colour.

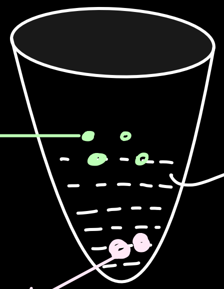
→ Self Indicator, But in Dil form we need Indicator. like ferroin Sulphate.

Ce^{+4}

Oxidised

Oxalic Acid.

few drop of H_2SO_4



Oxalic Acid. (Reducing Agent).

ferroin Indicator.

Procedure:

Preparation:

Prepare a cerium(IV) sulfate solution of known concentration (e.g., 0.1 M).

Pipette a known volume (e.g., 25 mL) of the reducing agent (e.g., oxalic acid or iron(II)) into a clean conical flask.

Add sulfuric acid (H_2SO_4) to the conical flask to ensure the solution is acidic (typically a few drops of concentrated H_2SO_4). This ensures proper oxidation-reduction conditions.

Optionally, add a few drops of a redox indicator (like diphenylamine or ferroin) to the flask. The indicator helps detect the endpoint by changing color.

Filling the Burette:

Fill the burette with the cerium(IV) sulfate solution. Make sure there are no air bubbles in the burette or the tip.

Record the initial volume of cerium(IV) sulfate in the burette.

Titration:

Slowly titrate the reducing agent solution in the conical flask with the cerium(IV) sulfate solution from the burette.

Swirl the conical flask continuously to mix the solutions as the titrant is added.

Watch for the color change (if an indicator is used) or monitor the electrode potential (if using a potentiometer).

As you approach the endpoint, the color change becomes more noticeable (e.g., a faint pink color may persist if using diphenylamine).

End Point:

The endpoint is reached when the color change persists for about 30 seconds (indicating that all the reducing agent has been oxidized).

If using a potentiometer, the endpoint is reached when there is no further change in potential.

Record the Final Volume:

Once the endpoint is reached, record the final volume of cerium(IV) sulfate in the burette.

Applications of Cerimetry

1. Determination of Oxalic Acid Concentration
2. Determination of Ascorbic Acid (Vitamin C)
3. Cerimetry is used to titrate solutions containing ferrous ions (Fe^{2+}).
4. Cerimetry is used for determining the concentration of hydrogen peroxide in solutions.
5. Cerimetry can be used to determine the concentration of manganese(II) (Mn^{2+}) ions in solution.
6. Organic compounds that act as reducing agents (e.g., glucose, glycerol) can also be analyzed using cerimetry.
7. Cerimetry can be used in pharmaceuticals, food chemistry, and biochemical analysis to assess the concentration of organic reducing agents in various samples.

DEPTH OF BIOLOGY

Pharmaceuticals: Determining vitamin C (ascorbic acid) or organic reducing agents.

Food industry: Analyzing vitamin C content and other reducing agents.

Environmental analysis: Testing for iron, manganese, copper, and hydrogen peroxide concentrations.

Chemical industries: For analyzing reducing agents in raw materials or final products.

Biochemistry: Measuring the concentration of reducing agents in biological samples.

Iodimetry vs Iodometry

Iodimetry- Indicator – Starch & done in Acidic Medium (HCl, H_2SO_4).

Iodimetry is a type of redox titration in which iodine (I_2) is used as the titrant to determine the concentration of a reducing agent in a sample. In this method, the reducing agent in the sample reacts with the iodine, reducing it to iodide ions (I^-), and itself gets oxidized.

The basic principle of iodimetry is that iodine, in the presence of a suitable medium, reacts with a reducing agent to form iodide ions (I^-).

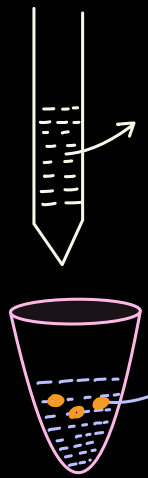
$I_2 \xrightarrow{R.A} I^-$

free I_2 + Starch → Blue Complex.

$\xrightarrow{\cancel{RA}} \cancel{I^-}$

I_2 + Reducing Agent $\longrightarrow I^-$

Oxidizing Agent.



I_2 (Titrant).

Sample Contain Reducing Agent.

1. Principle of Iodimetry:

Iodimetry is based on redox reactions, where iodine (I_2) acts as an oxidizing agent and the analyte (usually a reducing agent) reduces iodine to iodide ions (I^-). The general equation for this reaction is:

$$\left[\text{Reducing Agent} + I_2 \longrightarrow \text{Oxidized form of } R + 2I^- \right]$$

In this reaction, iodine (I_2) is reduced to iodide ions (I^-), and the reducing agent is oxidized.

2. Reagents Used in Iodimetry:

Starch Solution: Starch is often used as an indicator because it forms a blue complex with iodine. This complex appears when free iodine is present in the solution and disappears when iodine is reduced to iodide ions.

Acidic Medium: Most iodimetric titrations require an acidic medium, usually achieved by using dilute hydrochloric acid (HCl) or sulfuric acid (H_2SO_4).

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$$

Procedure of Iodimetry:

The procedure involves titrating a solution containing a reducing agent with a standard iodine solution. The steps are:

Preparation of the Sample:

The sample to be analyzed, which contains the reducing agent, is placed in a flask. If necessary, the solution is diluted to an appropriate volume.

If the sample contains interfering substances, these may need to be removed or neutralized. For example, in the analysis of vitamin C, the sample is often acidified.

Titration:

The iodine solution is titrated against the sample. If the reducing agent is present, it will reduce iodine to iodide ions.

Add a few drops of starch solution towards the end of the titration. Starch forms a blue complex with iodine, making it easy to detect the endpoint.

Endpoint Detection:

The endpoint is reached when the blue starch-iodine complex disappears, indicating that all the iodine has reacted with the reducing agent, and there is no free iodine left in solution.

Alternatively, the endpoint can be identified by the disappearance of the brownish color of iodine.

Calculation:

The volume of iodine solution required to reach the endpoint is recorded.

The amount of reducing agent in the sample is calculated based on the stoichiometry of the reaction and the concentration of the iodine solution.

Applications of Iodimetry:

Iodimetry is used in various fields, including:

Analysis of Reducing Agents: It is commonly used to determine the concentration of reducing agents in solutions, such as in the analysis of ascorbic acid (vitamin C), sulfur dioxide, and hydrogen peroxide.

Chlorine Content in Water: Iodimetry can be used to estimate chlorine content in drinking water or pool water. The chlorine reduces iodine to iodide, and the iodine solution is titrated to determine the chlorine concentration.

Pharmaceutical Industry: It is used in the pharmaceutical industry to assay the purity of substances like vitamin C, or drugs containing reducing agents.

Food Industry: Iodimetry can be used to determine the content of antioxidants in food products.

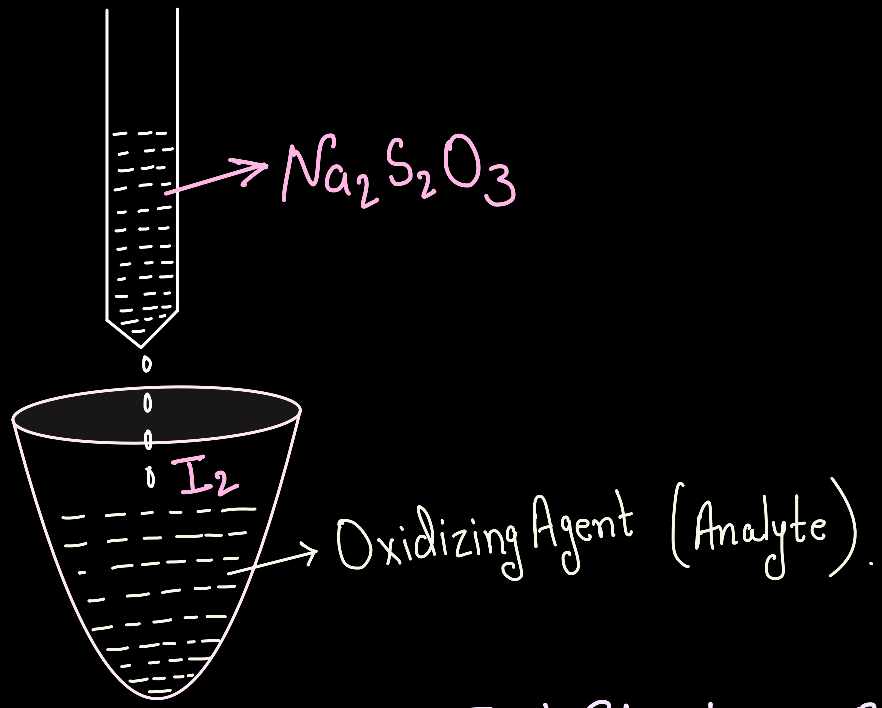
Iodometry → Determine the Conc. of Oxidizing Agent.

Iodometry is an indirect titration method where an oxidizing agent (the analyte) reacts with iodide ions (KI) to liberate iodine (I2). The liberated iodine is then titrated with a standard solution of a reducing agent, typically sodium thiosulfate (Na2S2O3).

Oxidizing Agent + KI

↓

I_2 Liberated.



$Na_2S_2O_3 + I_2$

↓

I^-

$I_2 + \text{Starch} \longrightarrow \text{Blue}.$

$I^- + \text{Starch} \rightarrow \text{Colorless}$

General Procedure of Iodometry:

Preparation of the Sample:

The sample containing the substance to be analyzed (e.g., chlorine, hydrogen peroxide, or other oxidizing agents) is prepared.

Iodine Liberation:

A known amount of an oxidizing agent (like potassium iodide, KI) is added to the sample, and iodine (I_2) is generated from iodide ions (I^-) by the oxidizing agent. This step may involve adding a specific amount of acid, depending on the nature of the reaction.

Titration with Sodium Thiosulfate:

The liberated iodine (I_2) is then titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3$), which reduces iodine (I_2) back to iodide (I^-).

The endpoint is typically determined using starch solution, which forms a blue complex with iodine. The endpoint is reached when the blue color disappears, indicating that all iodine has been reduced to iodide.

Calculation:

The amount of sodium thiosulfate required to reach the endpoint is noted, and based on the stoichiometry of the reactions, the concentration of the oxidizing agent in the sample can be determined.

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Applications of Iodometry:

Analysis of Chlorine in Water: Iodometry is often used to determine the concentration of chlorine in drinking water or wastewater. The chlorine reacts with iodide ions to liberate iodine, which is then titrated.

Determination of Hydrogen Peroxide: Hydrogen peroxide (H_2O_2) is a strong oxidizer and can be analyzed by iodometric titration. Hydrogen peroxide reacts with potassium iodide to liberate iodine.

Determining Oxidizing Agents: Iodometry can be used to measure other oxidizing agents like bromine, iodine, and chlorine in a variety of substances, including industrial chemicals and pharmaceuticals.

Bromatometry

Bromatometric titrations are particularly useful in the analysis of food and feed materials, as they help determine the concentration of key nutrients (like proteins, fats, carbohydrates) or assess the presence of certain elements (such as acids, bases, or minerals).

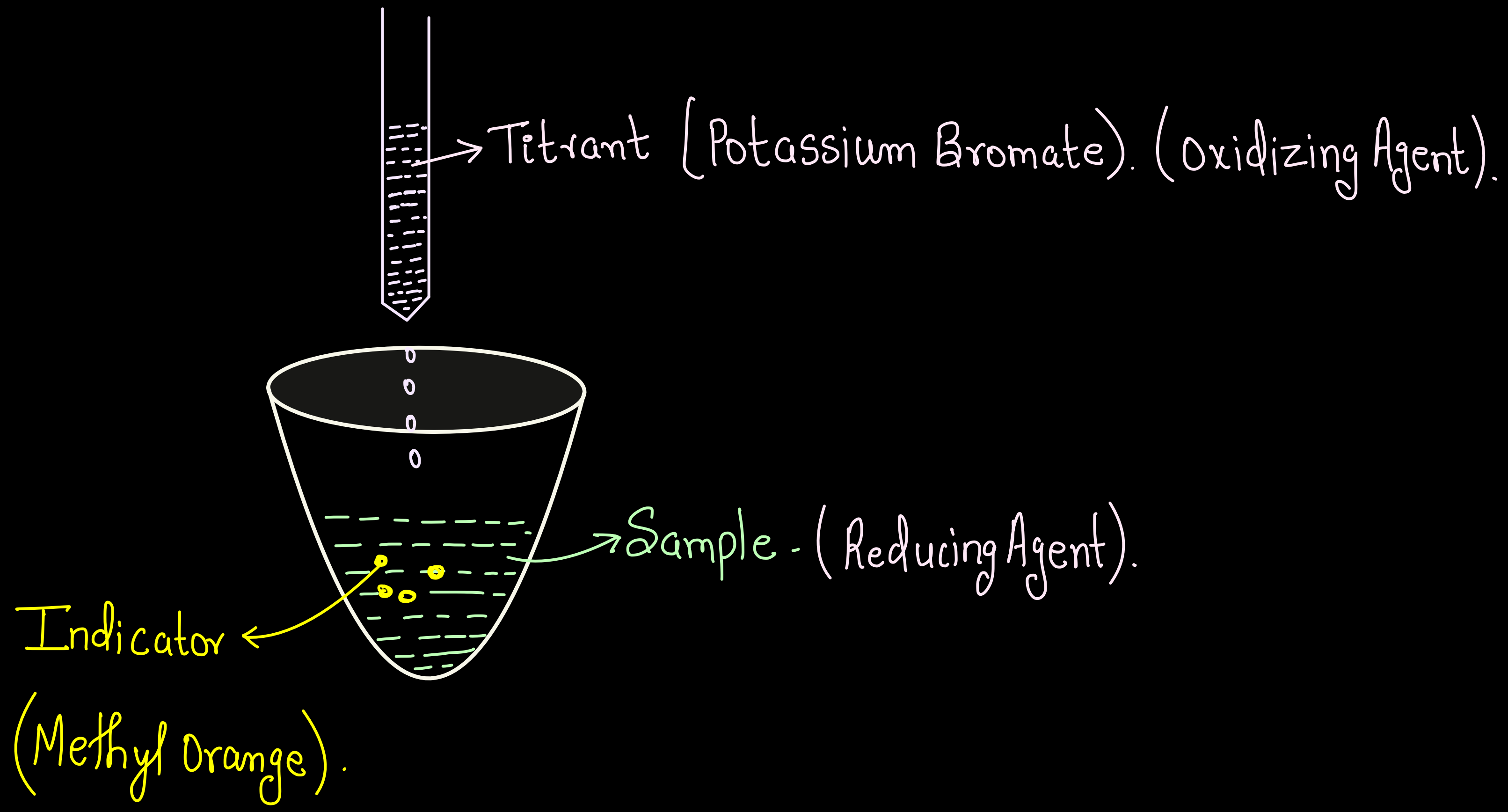
Base

(Neutral).

Acid

(HPh – Indicator).

Base = Pink Colour.



Steps in Bromatometric Titration:

1. Preparation of the Sample:

The sample (whether food, feed, or a liquid) is weighed or measured accurately.

In some cases, the sample might need to be dissolved in a solvent or treated with reagents to break down complex components.

2. Selection of Titrant:

The titrant is a reagent of known concentration that will react with the substance being measured in the sample. Common titrants include acids (e.g., sodium hydroxide for acid-base titrations) or specific reagents for determining the concentration of certain substances (e.g., iodine for determining the presence of unsaturated fats).

3. Addition of Indicator:

Often, an indicator is used to show the endpoint of the titration. The indicator is a substance that changes color when the reaction is complete, signaling that the analyte has been fully reacted.

For example, phenolphthalein is often used in acid-base titrations, where it changes from colorless to pink as the pH goes from acidic to neutral.

4. Titration Process:

The titrant is slowly added to the sample while stirring, and the reaction is allowed to proceed.

The concentration of the substance in the sample can be determined by noting the volume of titrant required to reach the endpoint.

5. Endpoint Detection:
The endpoint is reached when the titrant has completely reacted with the sample, which is often indicated by a color change in the indicator or another measurable change in the system.
The volume of titrant used is recorded.

6. Calculation:
Using the volume of titrant and its concentration, the amount of the substance being analyzed in the sample is calculated using stoichiometric relationships from the balanced chemical equation.
For example, in an acid-base titration, the amount of acid in the sample can be determined based on the volume of base required to neutralize it.

Applications of Bromatometry

1. Nutritional Analysis

Determining Nutritional Content: Bromatometry is widely used to analyze the nutritional components of foods, including proteins, fats, carbohydrates, vitamins, and minerals. This helps in labeling food products with accurate nutritional information.

2. Food Quality Control

Ensuring Consistency: Bromatometric techniques help monitor the consistency and quality of food products during production. For example, determining the sugar or fat content in a food batch ensures that each product meets the required standards.

Detection of Contaminants: Bromatometry helps detect undesirable substances, such as heavy metals (lead, mercury, etc.), pesticides, and toxins, that might be present in food products.

3. Food Safety and Hygiene

Microbial Contaminants: Bromatometry can be used in conjunction with other methods to assess the safety of food by identifying harmful microorganisms or toxins present in food products.

Hygiene in Food Processing: Regular bromatometric analyses help ensure that processed foods meet hygiene and safety standards, reducing the risk of foodborne illnesses.

4. Forensic Applications

Food Poisoning Investigations: Bromatometry can be used in forensic science to analyze food samples in cases of suspected food poisoning or contamination. Identifying the exact cause of illness (e.g., bacterial toxins, improper food handling) can help resolve cases and prevent further incidents.

5. Agricultural Research

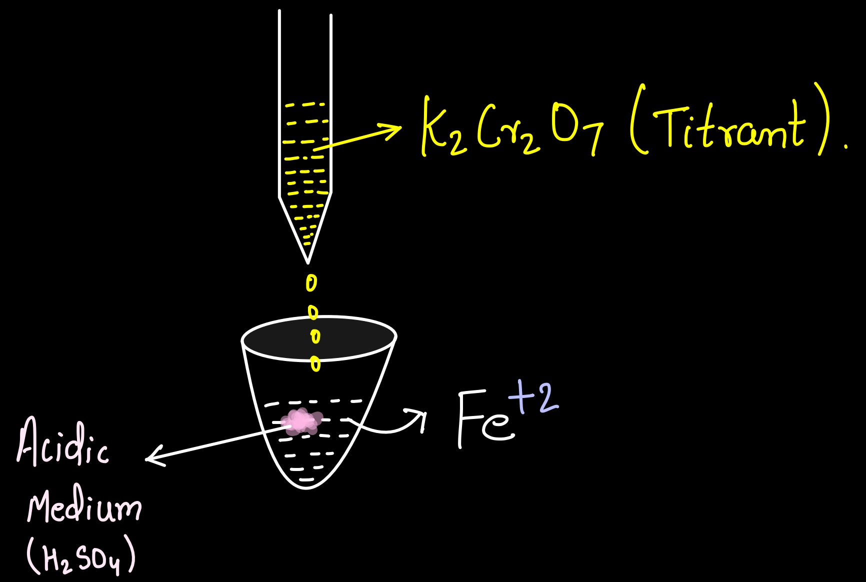
Soil and Crop Nutrient Analysis: Bromatometry aids in the analysis of the nutritional content of crops, which can help optimize agricultural practices and improve crop yields.
Assessing Soil Quality: The study of soil composition (through bromatometric analysis) helps farmers optimize fertilization practices to improve soil health and crop quality.

To determine the Conc. of Fe. ⟵ **Dichrometry** ⟶ Indicator (Diphenylamine Sulfonate) [Green ↓ Purple.]

Dichrometry is a type of redox titration that uses potassium dichromate ($K_2Cr_2O_7$) as a titrant to determine the amount of a reducing agent in a sample, often used for analyzing ferrous ions, oxalic acid, and other reducing agents

Dichrometry is a redox titration method where potassium dichromate ($K_2Cr_2O_7$) is used as the oxidizing agent to react with a reducing agent in an acidic medium

$$\left[\begin{array}{c} K_2Cr_2O_7 + Fe^{+2} \\ \downarrow \\ Fe^{+3}. \end{array}\right]$$



$K_2Cr_2O_7$ + Ind.

↓

Purple Colour.

How it works:

Potassium dichromate is reduced to chromium (III) ions when it reacts with a reducing agent.

The reaction is typically carried out in an acidic medium, often using sulfuric acid.

The endpoint of the titration is indicated by a color change, often from orange to green, or by using an indicator like diphenylamine.

Applications:

1. Analysis of Reducing Agents

Iron(II) Compounds: One of the most common applications is the determination of iron(II) ions in samples, such as in water, food, or pharmaceuticals. Iron(II) is easily oxidized to iron(III) by dichromate in the titration process.

2. Determination of Biochemical Oxygen Demand (BOD): Dichrometric titration is a key part of the BOD test, which is used to assess the organic matter content in wastewater. The reduction of dichromate ions indicates the level of organic material present that can be oxidized by microorganisms in water.

3. Analysis of Active Pharmaceutical Ingredients (APIs): In the pharmaceutical industry, dichrometric titration is employed to measure the concentration of reducing agents or certain drugs that are capable of undergoing oxidation. For instance, it can be used to quantify ascorbic acid (vitamin C) or oxalic acid in formulations.

4. Determination of Trace Metals: Dichrometric titration can be used to quantify metals that act as reducing agents. For example, it is applied in the analysis of nickel, copper, and other trace metals in ores or industrial products.

5.Fertilizer and Soil Testing: In agriculture, the method can be used to measure the reducing agents in soil samples or fertilizers, such as the presence of nitrates or sulfates, which can affect soil health and plant growth.

6. Detection of Chemical Contaminants: In forensic science, dichrometric titration can be used to identify and quantify reducing agents in chemical substances, such as those involved in toxicology studies or criminal investigations where substances like sodium thiosulfate or cyanides need to be measured.

7.Blood Testing: In clinical diagnostics, dichrometric titration is sometimes used to measure the levels of reducing agentsin blood samples, like glucose or other metabolites, helping in the diagnosis of diseases like diabetes.

Iodatometry or Titration with potassium Iodate → Act as Oxidizing Agent.

Titration with potassium iodate is a type of redox titration used in analytical chemistry to determine the concentration of reducing agents, such as sodium thiosulfate, ascorbic acid, or hydrogen peroxide. The process involves the use of potassium iodate (KIO_3), which acts as an oxidizing agent.

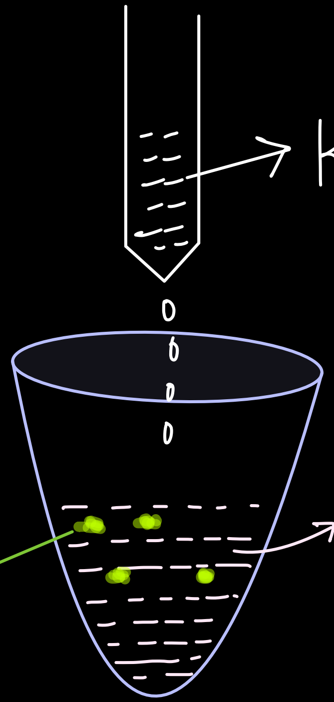
end point → Colorless

$$\left[\text{Titrant} + I_2 \xrightarrow{} I^- \right]$$

$$\left[KIO_3 \rightleftharpoons K^+ + IO_3^- \right]$$

$$\left[KI \rightleftharpoons K^+ + I^- \right]$$

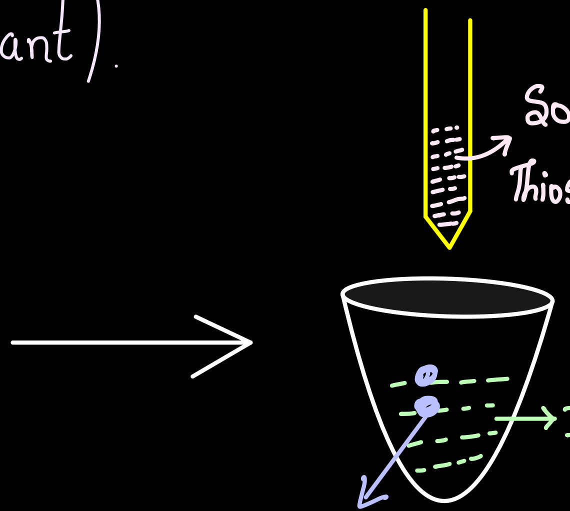
$$\left[IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2\uparrow + 3H_2O. \right]$$



→ KIO_3 (O.A) (Titrant).

Reducing Agent. (Ascorbic Acid).

Acidify the Solution.



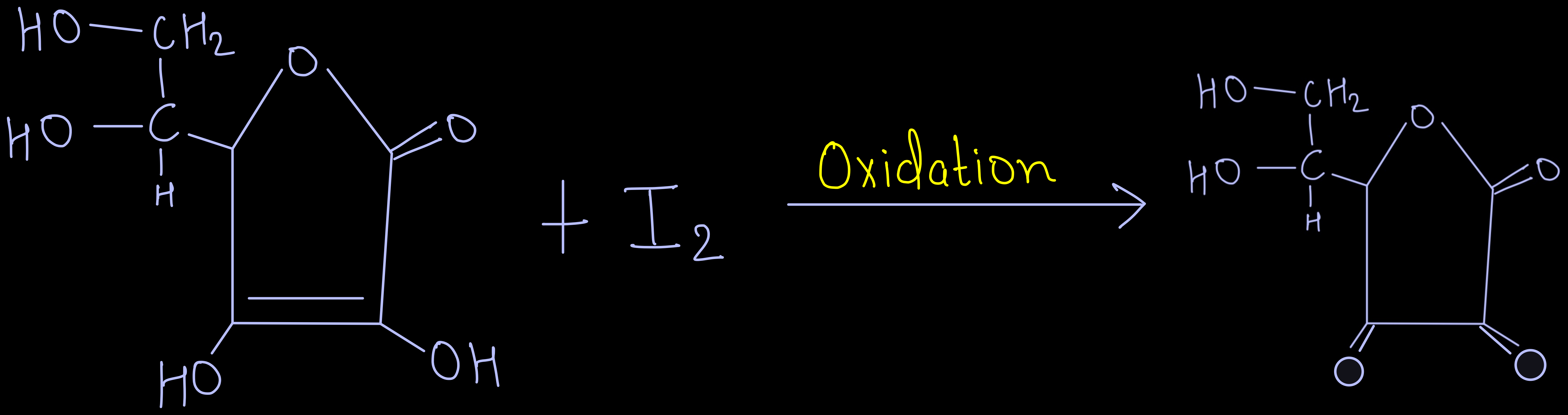
Sod. Thiosulp.

I_2

Starch Ind.

Blue ⟶ I_2+Starch

Ascorbic Acid + I_2 $\xrightarrow{\text{Oxid.}}$ Dehydroascorbic Acid.



Ascorbic Acid.

Dehydro Ascorbic Acid.

Step-by-Step Procedure:

Prepare the sample solution, which contains the reducing agent (e.g., sodium thiosulfate or ascorbic acid).

Add a known excess of potassium iodate (KIO_3) to the solution.

Acidify the solution with an appropriate acid (usually sulfuric acid).

Add excess potassium iodide (KI) to the solution to generate iodine (I_2).

Titrate the free iodine with a standard solution of sodium thiosulfate ($Na_2S_2O_3$) using starch as an indicator.

The endpoint is reached when the blue starch-iodine complex disappears, indicating all iodine has been reduced.

Applications of titration with potassium iodate

1. Determination of Vitamin C (Ascorbic Acid) Concentration

Application: Potassium iodate titration is often used to determine the concentration of vitamin C (ascorbic acid) in food, beverages, or pharmaceutical preparations.

2. Analysis of Hydrogen Peroxide (H_2O_2) Concentration

Application: Potassium iodate titration can be used to determine the concentration of hydrogen peroxide, which is commonly used as a disinfectant, bleach, and in various industrial processes.

3. Determination of Reducing Sugars

Application: The method is used to quantify reducing sugars (e.g., glucose, fructose) in food products or biological samples.

4. Determining Concentrations in Industrial Products (e.g., Bleaching Agents)

Application: Potassium iodate titration is used to monitor the concentration of bleaching agents like sodium hypochlorite in industrial applications, ensuring the proper dosage for effective bleaching.

5. Chemical Analysis of Wine and Beverages

Application: Potassium iodate titration can be applied to wine and other alcoholic beverages to determine the presence and concentration of certain reducing agents or preservatives.

6. Environmental Monitoring

Application: Potassium iodate titration is used for environmental monitoring, especially for analyzing water and soil samples for the presence of reducing agents or pollutants like hydrogen sulfide (H_2S) or organic reducing agents.