

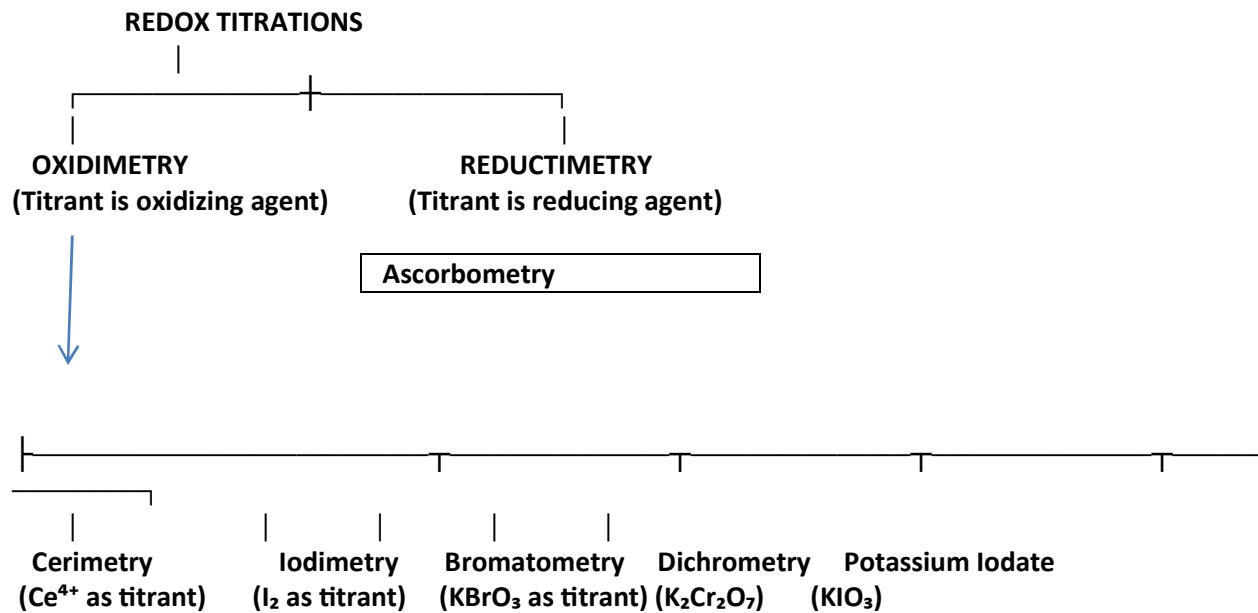
Redox Titrations: Principles and Applications-

Introduction-Redox titrations are a type of volumetric analysis that involve the transfer of electrons between an analyte and a titrant. These titrations are widely used in various fields, including chemistry, biology, and pharmaceuticals.

The **oxidizing agent** (oxidant) accepts electrons and is reduced, while the **reducing agent** (reductant) donates electrons and is oxidized.



Type	Titrant Used	Analyte (Substance Estimated)	Indicator / Detection	Example Reaction	Applications
1. Cerimetry	Ceric ammonium sulphate (Ce^{4+})	Reducing agents (e.g., Fe^{2+} , oxalic acid, ascorbic acid)	Ferroin or self-indicating (yellow \rightarrow colorless)	$\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}$	Estimation of Fe^{2+} , Vitamin C
2. Iodimetry	Iodine (I_2)	Reducing agents (thiosulphate, ascorbic acid)	Starch (blue complex at end point)	$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	Estimation of ascorbic acid, sulphites
3. Iodometry	Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)	Oxidizing agents (e.g., Cu^{2+} , Cl_2 , KMnO_4) after liberating I_2	Starch indicator	$2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$	Estimation of Cu, KMnO_4 , Cl_2
4. Bromatometry	Potassium bromate (KBrO_3)	Reducing agents (phenol, aniline, arsenic compounds)	Methyl orange / Acid medium	$\text{KBrO}_3 + 6\text{H}^+ + 6e^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$	Estimation of phenol, aniline
5. Dichrometry	Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)	Reducing agents (Fe^{2+} , Sn^{2+} , Cu^+)	Diphenylamine / N-phenylanthranilic acid	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Estimation of Fe^{2+} , SnCl_2
6. Potassium Iodate Titration	KIO_3	Reducing agents (Ascorbic acid, arsenites)	Starch indicator	$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	Estimation of iodides, ascorbic acid

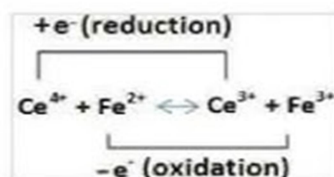


Cerimetry

- **Principle:** Utilizes the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple in acidic medium. The half-reaction is simple:
 $\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$.
- The high stability and simplicity of the reduction make Ce^{4+} a superior titrant in some cases compared to KMnO_4 .
- **Application:** Assay of FeSO_4 (Ferrous sulfate), TiO_2 (Titanium dioxide), and pharmaceutical substances like Ascorbic Acid (Vitamin C).

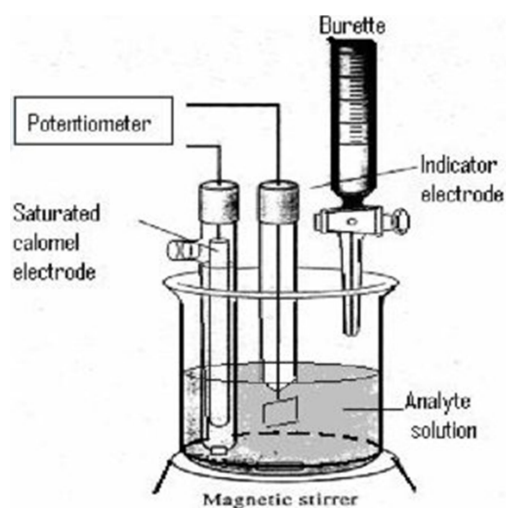
- **Principle:** Based on oxidation by *ceric ammonium sulphate* ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$).
- **Medium:** Acidic (usually H_2SO_4).
- **Indicator:** Ferroin or internal color change (yellow \rightarrow colorless).
- **Applications:**
Assay of Fe^{2+} salts.
Determination of ascorbic acid, oxalic acid, and hydrogen peroxide.

Cerimetry Titration



Ceric ion + Ferric ion \rightarrow Cerium ion + Ferrous ion

yellow \rightarrow colourless soln



NOTE-

oxidations with cerium sulphate solution is called cerimetry.

- Cerium sulphate is a powerful oxidising agent; its reduction potential in 0.5-4.0M sulphuric acid at 25°C is 1.43 ± 0.05 volts.
- It can be used only in acid solution, best in 0.5M or higher concentrations: as the solution is neutralised, cerium(IV) hydroxide [or basic salts precipitate.
- The solution has an intense yellow colour, and in hot solutions which are not too dilute the end point may be detected without an indicator.

Key Applications of Cerimetry Titration

Pharmaceutical Analysis: Cerimetry is used to determine the concentration or purity of various pharmaceutical substances

- **Quantitative Analysis of Metals and Ions:** It is widely used to estimate the concentration of various metal ions in samples: **Iron(II) ion**
- Estimation of other metals like **chromium, copper, nickel, and manganese**.
- Determining metallic **aluminum** in ultra-fine powders and related products.
- **Environmental Monitoring and Industrial Testing:** Cerimetry plays a role in environmental and industrial applications:
 - Estimation of **chemical oxygen demand (COD)** in water and wastewater analysis.
 - Quantifying antioxidants (like Vitamin C) in the **food industry**.
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