

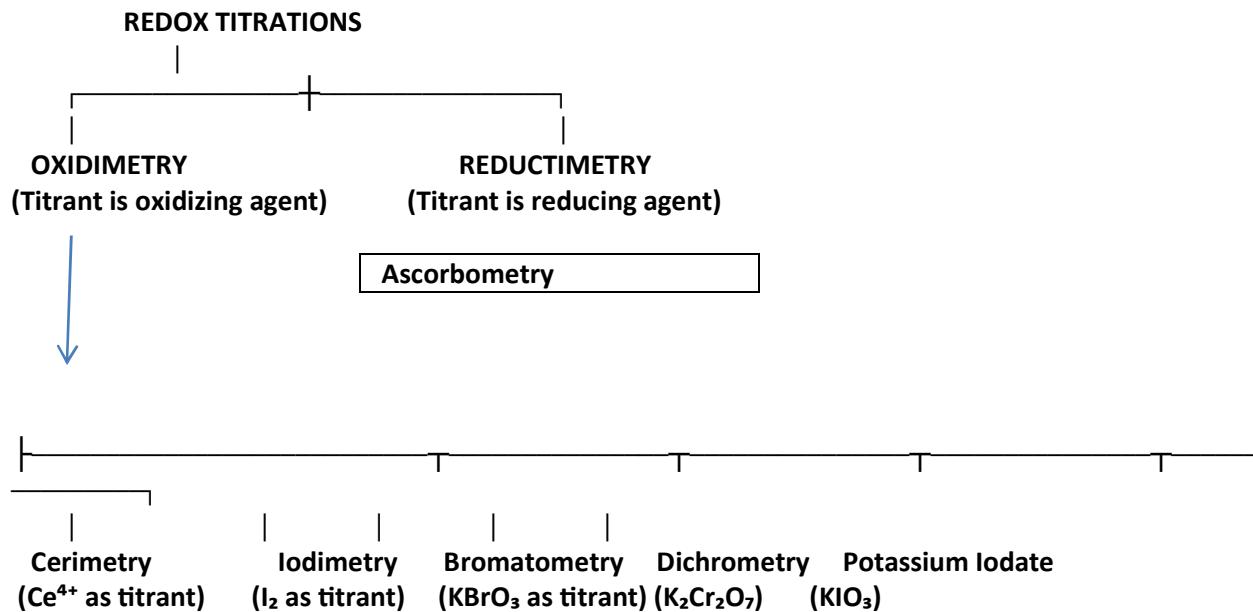
## **Redox Titrations: Principles and Applications-**

**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
<b>1. Cerimetry</b>	Ceric ammonium sulphate ( $\text{Ce}^{4+}$ )	Reducing agents (e.g., $\text{Fe}^{2+}$ , 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 $\text{Fe}^{2+}$ , Vitamin C
<b>2. Iodimetry</b>	Iodine ( $\text{I}_2$ )	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
<b>3. Iodometry</b>	Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ )	Oxidizing agents (e.g., $\text{Cu}^{2+}$ , $\text{Cl}_2$ , $\text{KMnO}_4$ ) after liberating $\text{I}_2$	Starch indicator	$2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$	Estimation of Cu, $\text{KMnO}_4$ , $\text{Cl}_2$
<b>4. Bromatometry</b>	Potassium bromate ( $\text{KBrO}_3$ )	Reducing agents (phenol, aniline, arsenic compounds)	Methyl orange / Acid medium	$\text{KBrO}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$	Estimation of phenol, aniline
<b>5. Dichrometry</b>	Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )	Reducing agents ( $\text{Fe}^{2+}$ , $\text{Sn}^{2+}$ , $\text{Cu}^+$ )	Diphenylamine / N-phenylantranilic acid	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Estimation of $\text{Fe}^{2+}$ , $\text{SnCl}_2$
<b>6. Potassium Iodate Titration</b>	$\text{KIO}_3$	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 Ce<sup>4+</sup>/Ce<sup>3+</sup> couple in acidic medium. The half-reaction is simple:  $\text{Ce}^4 + \text{e}^- \rightarrow \text{Ce}^3+$ .
- The high stability and simplicity of the reduction make Ce<sup>4+</sup> a superior titrant in some cases compared to KMnO<sub>4</sub>.
- **Application:** Assay of FeSO<sub>4</sub> (Ferrous sulfate), TiO<sub>2</sub> (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  $\text{H}_2\text{SO}_4$ ).

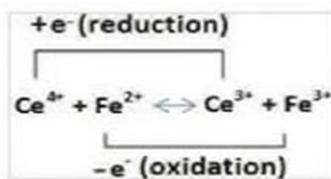
- **Indicator:** Ferroin or internal color change (yellow  $\rightarrow$  colorless).

- **Applications:**

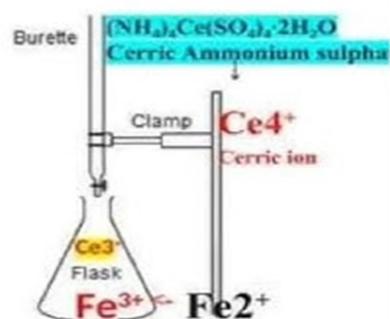
Assay of  $\text{Fe}^{2+}$  salts.

Determination of ascorbic acid, oxalic acid, and hydrogen peroxide.

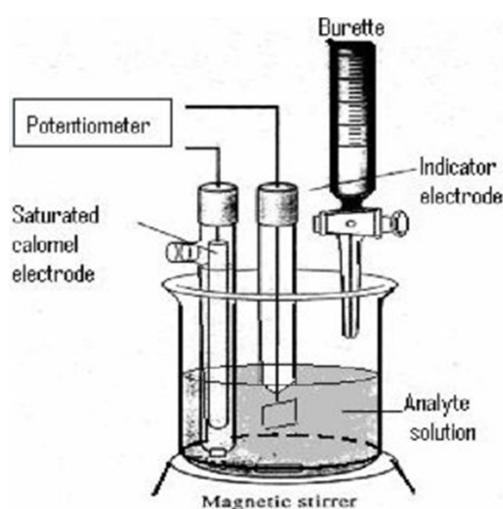
## Cerimetry Titration



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



yellow  $\rightarrow$  colourless soln



NOTE-

oxidations with cerium sulphate solution is called cerimtry.

- Cerium) sulphate is a powerful oxidising agent; its reduction potential in 0.5-4.0M sulphuric acid at 25°C is  $1.43 \pm 0.05$  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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