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Redox titrations

Presented By;-

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What is Oxidation?

According to Classical or earlier concept **oxidation** is a process which involves the addition of oxygen or any electronegative element or the removal of hydrogen or any electropositive element.

According to electronic concept **oxidation** is defined as the process in which an atom or ion loses one or more electrons.

What is Reduction?

According to Classical or earlier concept **reduction** is a process which involves the addition of hydrogen or any electropositive element or the removal of oxygen or any electronegative element.

According to electronic concept **reduction** is defined as the process in which an atom or ion gains one or more electrons.

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Oxidation Reactions

1. **Addition of oxygen:**

$C + O_2 \rightarrow CO_2$

(oxidation of carbon)

2. **Addition of electronegative element:**

$Fe + S \rightarrow FeS$

(oxidation of Iron)

3. **Removal of hydrogen:**

$H_2S + Br_2 \rightarrow 2\ HBr + S$

(oxidation of sulphide)

4. **Removal of electropositive elements:**

$2\ KI + H_2O_2 \rightarrow I_2 + 2\ KOH$

(oxidation of iodide)

Oxidising agent is a substance which brings about oxidation. In the above examples O_2, S, Cl_2, Br_2, and H_2O_2 are **oxidising agents.**

Reduction Reactions

1. **Addition of hydrogen:**

$N_2 + 3\ H_2 \rightarrow 2NH_3$

(reduction of nitrogen)

2. **Addition of electropositive element:**

$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$

(reduction of mercuric chloride)

3. **Removal of oxygen**

$ZnO + C \rightarrow Zn + CO$

(reduction of zinc oxide)

4. **Removal of electronegative element**

$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$

(reduction of ferric chloride)

Reducing agent is a substance which brings about reduction. In the above examples H2, HgCl2 and C **are Reducing agents.**

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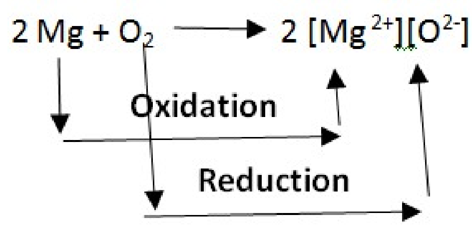
Oxidation and Reduction in terms of Electron Transfer

This is the most commonly used definition of oxidation and reduction and most widely applicable.

In this case, **Oxidation** is the loss of electrons and **Reduction** is the gain of electrons.

Oxidation is loss   Reduction is gain

Oxidation and Reduction reactions are always interlinked. **Because** electrons are neither created nor destroyed in a chemical reaction, oxidation and reduction always occur in pairs, it is impossible to have one without the other. In the below reaction Magnesium gets oxidized by losing two electrons to oxygen which gets reduced by accepting two electrons from magnesium.



Since oxidation and reduction cannot occur individually, they as a whole are called **'Redox Reactions'.** The reactant that oxidizes the other reactants is called as the **Oxidizing agent** and reactant that reduces is called **Reducing agent.**

Redox titrations

Definition:-Redox titrations are a type of volumetric analysis based on **oxidation-reduction (redox) reactions**, where one substance undergoes **oxidation** (loses electrons) and the other undergoes **reduction** (gains electrons).

Example:- **Reaction between Zinc and Copper**

This is a type of metal displacement reaction in which copper metal is obtained when zinc displaces the Cu^{2+}ion in the copper sulphate solution, as shown in the reaction below.

$$Zn\ (s) + CuSO_4\ (aq) \rightarrow ZnSO_4\ (aq) + Cu\ (s)$$

- The oxidation half-reaction can be written as $Zn \rightarrow Zn^{2+} + 2e^{-}$
- The reduction half-reaction can be written as $Cu^{2+} + 2e^{-} \rightarrow Cu$

Types of Redox Reactions

The different types of redox reactions are

1. Decomposition Reaction
2. Combination Reaction
3. Displacement Reaction
4. Disproportionation Reactions

1. Decomposition Reaction

- **This kind of reaction involves the breakdown of a compound into different compounds**.

  Examples of these types of reactions are,

  - $2NaH \rightarrow 2Na + H_2$
  - $2H_2O \rightarrow 2H_2 + O_2$
  - $Na_2CO_3 \rightarrow Na_2O + CO_2$

- All the above reactions result in the breakdown of smaller chemical compounds in the form of AB → A + B
- But, there is a special case that confirms that all the decomposition reactions are not redox reactions.

  For example, $CaCO_3 \rightarrow CaO + CO_2$

2. Combination Reaction

These reactions are the **opposite of decomposition reactions** and hence, involve the **combination of two compounds to form a single compound in the form of $A + B \rightarrow AB$.**

For example,

- $H_2 + Cl_2 \rightarrow 2HCl$
- $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

3. Displacement Reaction

In this kind of reaction, an atom or an ion in a compound is replaced by an atom or an ion of another element.
It can be represented in the form of **$X + YZ \rightarrow XZ + Y$.**

Further displacement reactions can be categorised into:-

1. Metal Displacement

In this type of reaction, a metal present in the compound is displaced by another metal. These types of reactions find their application in metallurgical processes where pure metals are obtained from their ores.

For example, $CuSO_4 + Zn \rightarrow Cu + ZnSO_4$

2. Non-metal Displacement

In this type of reaction, we can find a hydrogen displacement and, sometimes, rarely occurring reactions involving oxygen displacement.

4. Disproportionation Reactions

Disproportionation reactions are known as reactions in which a single reactant is oxidized and reduced.

For example, $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

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Applications of Redox Titrations

Redox titrations are widely used in **analytical chemistry**, **pharmaceutical analysis**, **environmental monitoring**, and **industrial processes** to determine the concentration of oxidizing or reducing agents.

S.No.	Application Area	Details / Examples
1	Pharmaceutical Analysis	Estimation of drugs like ascorbic acid (Vitamin C), sulfa drugs, and iron preparations
2	Water and Wastewater Testing	Determination of iron, manganese, and hydrogen peroxide in water samples
3	Food Industry	Measuring antioxidant levels (e.g., Vitamin C in juices)
4	Industrial Chemistry	Analysis of reducing agents (e.g., sodium thiosulfate) or oxidizers (e.g., $KMnO_4$)
5	Metallurgy	Determination of metal ions like Fe^{2+}, Cr^{3+}, Cu^{2+} in ores and alloys
6	Environmental Analysis	Monitoring pollutants like chlorine and peroxides in air and water
7	Agriculture	Estimation of trace metals in fertilizers and soils
8	Bleaching Agents	Estimation of available chlorine in bleaching powder

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1. Cerimetry
2. Iodimetry
3. Iodometry
4. Bromatometry
5. Dichrometry

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1. Cerimetry

Introduction:

Cerimetry is a redox titration method that uses **ceric ammonium sulfate (Ce^{4+})** as a **strong oxidizing agent**. It is widely used in acidic media and is a **direct titration method**.

Principle:

Ceric ions (Ce^{4+}) act as oxidizing agents and are reduced to cerous ions (Ce^{3+}) in an acidic medium:

$$Ce^{4+} + e^- \rightarrow Ce^{3+}$$

The change in color from **yellow (Ce^{4+})** to **colorless (Ce^{3+})** helps identify the endpoint (self-indicating) or can be detected using external indicators like ferroin.

Applications:

1. Estimation of reducing agents such as:
    - Ferrous salts (Fe^{2+})
    - Oxalic acid
    - Arsenic trioxide (As_2O_3)
    - Stannous chloride (Sn^{2+})
2. Widely used in pharmaceutical and industrial analysis.

2. Iodimetry

Introduction:

Iodimetry is a direct redox titration method that uses **elemental iodine (I_2)** as an **oxidizing agent**. It is used for analyzing substances that act as reducing agents.

Principle:

Iodine reacts directly with reducing agents and gets reduced to iodide (I^-):

$$I_2 + 2e^- \rightarrow 2I^-$$

The endpoint is detected using **starch indicator**, which forms a **blue complex** with iodine that disappears once all iodine is reduced.

Applications:

1. Estimation of:
    - Sodium thiosulfate
    - Arsenic trioxide
    - Hydrogen sulfide
    - Antimony salts
2. Used in both pharmaceutical and environmental testing.

3. Iodometry

Introduction:

Iodometry is an indirect redox titration method. In this, an **oxidizing agent** reacts with excess **potassium iodide (KI)** to **liberate iodine**, which is then titrated with **sodium thiosulfate**.

Principle:

The oxidizing agent oxidizes iodide to iodine: $\text{Oxidant} + 2I^- \rightarrow I_2$

The liberated iodine is then titrated with sodium thiosulfate: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

The endpoint is detected by **starch**, which turns **blue** in the presence of iodine.

Applications:

1. Estimation of oxidizing agents like:
    - Copper(II) sulfate ($CuSO_4$)
    - Chlorine in bleaching powder
    - Hydrogen peroxide
    - Potassium permanganate ($KMnO_4$)
2. Used in pharmaceutical analysis, water testing, and bleaching agents

4. Bromatometry

Introduction:

Bromatometry is a redox titration that involves **potassium bromate ($KBrO_3$)** as an **oxidizing agent**. It generates **bromine (Br_2)** in an acidic medium, which reacts with the analyte.

Principle:

In acidic conditions: $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

The generated bromine reacts with the analyte. The endpoint is detected using indicators like **methyl orange** or **starch (via liberated iodine).**

Applications:

1. Estimation of:
   - Phenol
   - Aniline
   - Some dyes and organic compounds
2. Used in pharmaceutical assays for certain APIs.

5. Dichrometry

Introduction:

Dichrometry is a redox titration method using **potassium dichromate ($K_2Cr_2O_7$)** as a **powerful oxidizing agent** in acidic solution.

Principle:

Dichromate oxidizes Fe^{2+} to Fe^{3+} while itself being reduced to Cr^{3+}:

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

Indicators used include **diphenylamine sulfonate** or **N-phenylanthranilic acid**.

Applications:

1. Estimation of reducing agents like:
   - Ferrous sulfate ($FeSO_4$)
   - Mohr's salt
   - Stannous chloride
2. Used in pharmaceutical and metallurgical industries.

Titration with potassium iodate

- Link:- https://pharmrecord.com/bp108p/

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