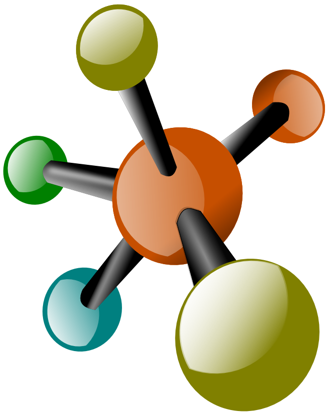
Chapter Name: Electro Chemistry

Oxidation

Oxidation is a process in which an atom, ion, or molecule loses electrons. It results in an increase in oxidation number of the element.

Electronic Concept:

Oxidation involves loss of electrons by a species.



$$A \rightarrow A^{n+} + ne^-$$

Example:

$Fe \rightarrow Fe^{2+} + 2e^-$

Here, iron (Fe) loses two electrons — it gets oxidized.

Common Examples of Oxidation:

- Conversion of metals into oxides:

$$2Mg + O_2 \rightarrow 2MgO$$

- Addition of oxygen or removal of hydrogen in a compound.

Reduction

Reduction is a process in which an atom, ion, or molecule gains electrons. It results in a decrease in oxidation number.

Electronic Concept:

Reduction involves gain of electrons by a species.

$$B^{n+} + ne^- \rightarrow B$$

Example:

$Cu^{2+} + 2e^- \rightarrow Cu$

Here, copper ions gain two electrons — it gets reduced.

Common Examples of Reduction:

- Removal of oxygen or addition of hydrogen:

$$CuO + H_2 \rightarrow Cu + H_2O$$

Redox Reaction

A redox reaction is a chemical reaction in which oxidation and reduction occur simultaneously.

Explanation:

- One species **loses electrons** (oxidized).
- Another species **gains those electrons** (reduced).

Example:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Here:

- $Zn \rightarrow Zn^{2+} + 2e^- \rightarrow$ Oxidation
- $Cu^{2+} + 2e^- \rightarrow Cu \rightarrow$ Reduction

Thus, this is a **redox reaction**.

___ Definitions of Terms ___

Electrolytes

Electrolytes are substances that conduct electricity in their molten state or aqueous solution by producing ions.

Explanation:

When dissolved in water or melted, electrolytes dissociate into cations and anions, which move towards electrodes when electric current is passed.

Examples:

Sodium chloride (NaCl), Sulphuric acid (H_2SO_4), Copper sulphate ($CuSO_4$), Sodium hydroxide (NaOH)

Types of Electrolytes:

- **Strong Electrolytes** – completely dissociate in solution (e.g., HCl, NaOH, NaCl)
- **Weak Electrolytes** – partially dissociate (e.g., CH_3COOH, NH_4OH)

Non-Electrolytes

Substances that do not conduct electricity either in molten or aqueous form are called non-electrolytes.

Explanation:

They do not produce ions in solution; they exist only as neutral molecules.

Examples:

- Sugar ($C_{12}H_{22}O_{11}$)
- Alcohol (C_2H_5OH)
- Urea ($CO(NH_2)_2$)

Difference Between Electrolytes and Non-Electrolytes:

Property	**Electrolytes**	**Non-Electrolytes**
Conductivity	Conduct electricity	Do not conduct electricity
Ion formation	Produce ions in solution	Do not produce ions
Example	NaCl, H_2SO_4, NaOH	Sugar, Alcohol, Urea

___ Faraday's Laws of Electrolysis ___

Electrolysis is the process of chemical decomposition of an electrolyte when an electric current is passed through it.

● First Law of Electrolysis (Faraday's First Law)

Statement:

The **mass (m)** of a substance deposited or liberated at an electrode is directly proportional to the **quantity of electricity (Q)** passed through the electrolyte.

$$m \propto Q$$

Since Q=I×t

$$m = Z \times I \times t$$

Where:

- m = mass of substance (g)
- I = current (ampere)
- t = time (seconds)
- Z = electrochemical equivalent (g/C)

Example:

If 1 ampere current is passed for 965 seconds, the amount of silver deposited can be calculated using its electrochemical equivalent.

● Second Law of Electrolysis (Faraday's Second Law)

Statement:

When the same quantity of electricity is passed through different electrolytes, the masses of substances deposited or liberated are directly proportional to their chemical equivalents.

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

Where:

- m1, m2 = masses of substances deposited
- E1, E2 = equivalent weights of substances

🔷 Important Terms

Faraday (F):

- 1 Faraday = 96500 Coulombs = Charge of 1 mole of electrons.

Electrochemical Equivalent (Z):

- The mass of substance deposited by 1 Coulomb of charge.

$$Z = \frac{E}{96500}$$

Equivalent Weight (E):

$$E = \frac{\text{Atomic or Molecular Weight}}{\text{Valency}}$$

🔷 Simple Numerical Problems

🔴 Example 1:

Calculate the mass of copper deposited when a current of 2 amperes is passed through copper sulphate solution for 30 minutes. (Atomic weight of Cu = 63.5, Valency = 2)

Given:

I = 2 A, t = 30 × 60 = 1800 s

E = 63.5 / 2 = 31.75

Z = E / 96500 = 31.75 / 96500 = 0.000329 g/C

Using formula:

m = Z × I × t

m = 0.000329 × 2 × 1800

m = **1.184 g**

✅ Mass of copper deposited = 1.184 g

🔴 Example 2:

Find the quantity of electricity (in coulombs) required to deposit 27 g of aluminium (Atomic weight = 27, Valency = 3).

Given:

m = 27 g, E = 27 / 3 = 9

We know,

$$Q = \frac{m \times 96500}{E}$$

$$Q = \frac{27 \times 96500}{9} = 2.895 \times 10^5 \text{ C}$$

✅ Required charge = 2.895×10^5 C

🟡 Elementary Concept of pH

Definition of pH

The term pH stands for "power of hydrogen" or "**potential of hydrogen**." It is a measure of the hydrogen ion concentration [H+] in a solution.

Explanation

- The pH scale ranges from 0 to 14.
- It indicates whether a solution is acidic, neutral, or basic.

pH Value	Nature of Solution	Examples
0 – 6.9	Acidic	HCl, Lemon juice
7	Neutral	Pure Water
7.1 – 14	Basic (Alkaline)	NaOH, Soap solution

Key Points

- Lower pH → Higher acidity (more H^+ ions)
- Higher pH → Higher basicity (more OH^- ions)
- Neutral solution (pH = 7): $[H^+] = [OH^-]$

Importance of pH

- In biological systems: Enzyme activity depends on pH.
- In agriculture: Soil pH affects crop growth.
- In industrial processes: Used to control reactions in chemical manufacturing.

Buffer Solutions

A buffer is a solution that resists change in pH when small amounts of acid or base are added.

How it Works

A buffer contains a weak acid and its salt or a weak base and its salt. It maintains the pH by neutralizing added acids or bases.

Types of Buffer

Acidic Buffer:
Contains a weak acid + its salt with a strong base.
Example: Acetic acid + Sodium acetate ($CH_3COOH + CH_3COONa$)
→ $pH < 7$

Basic Buffer:
Contains a weak base + its salt with a strong acid.
Example: Ammonium hydroxide + Ammonium chloride ($NH_4OH + NH_4Cl$)
→ $pH > 7$

Applications of Buffer

- **In blood:** Maintains pH around 7.4
- **In industries:** Used in fermentation, dyeing, and electroplating.
- **In pharmaceuticals:** Stabilizes the pH of medicines.

___ Industrial Applications of Electrolysis ___

Electrolysis has many important uses in industries such as metal extraction, refining, and coating.

● Electrometallurgy (Extraction of Metals)

The process of extracting metals from their ores using electrolysis is called electrometallurgy.

Examples:

Extraction of Aluminium:
From alumina (Al_2O_3) by electrolysis in fused cryolite (Na_3AlF_6).

$$\text{At cathode: } Al^{3+} + 3e^- \rightarrow Al$$

$$\text{At anode: } O^{2-} \rightarrow O_2 + 4e^-$$

Extraction of Sodium:
From molten NaCl by electrolysis (Down's cell).

Importance

Used for highly reactive metals like Al, Mg, Na, Ca, etc.

● Electroplating

Electroplating is the process of depositing a thin layer of one metal over another metal by electrolysis.

Purpose:

- To prevent corrosion
- To improve appearance
- To provide wear resistance

Example:

- Silver plating: On spoons and ornaments
- Nickel plating: On steel to prevent rust
- Chromium plating: On car parts

Explanation:

- Metal to be plated → Cathode
- Solution of salt of coating metal → Electrolyte
- Metal to be deposited → Anode

● Electrolytic Refining

The process of purifying impure metals using electrolysis is called electrolytic refining.

Principle:
The impure metal acts as anode, and the pure metal acts as cathode.

Example:
Refining of Copper:
Anode → Impure Cu
Cathode → Pure Cu strip
Electrolyte → $CuSO_4$ solution + H_2SO_4

Reactions:

$$\text{At anode: } Cu \rightarrow Cu^{2+} + 2e^-$$

$$\text{At cathode: } Cu^{2+} + 2e^- \rightarrow Cu$$

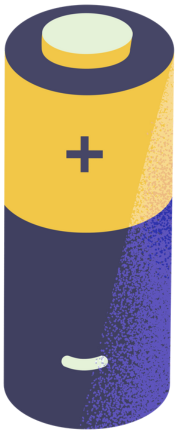
Result:

Pure copper is deposited at the cathode, and impurities settle as anode mud.

_ Application of Redox Reactions in Electrochemical Cells _

Primary Cells (Non-Rechargeable)

Cells in which the redox reaction is irreversible and once exhausted, cannot be recharged.



⚡ **Example:** Dry Cell (Leclanché Cell)

Construction:

Anode: Zinc container
Cathode: Carbon rod surrounded by MnO_2 and carbon powder
Electrolyte: Paste of NH_4Cl and $ZnCl_2$

Reaction

- At anode:

$$Zn \rightarrow Zn^{2+} + 2e^-$$

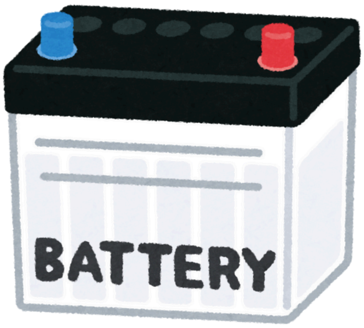
- At Cathode

$$2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$$

Use: Flashlights, radios, clocks, and remotes.

Secondary Cells (Rechargeable)

A secondary cell (also known as a rechargeable cell or accumulator) is a type of electrochemical cell in which the chemical reaction is reversible.



⚡ **Example:** Lead Storage Battery

Construction:

Anode: Lead (Pb) plates
Cathode: Lead dioxide (PbO_2) plates
Electrolyte: Dilute sulphuric acid (H_2SO_4)

Reactions during Discharge:

- At anode:

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$$

- At Cathode

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$$

Recharging: When current is passed in reverse, Pb and PbO_2 are re-formed.

Applications: Used in automobiles, inverters, and backup power systems.

● Fuel Cells

Electrochemical cells that continuously convert chemical energy of fuel (like H_2 or CH_4) into electrical energy.

Example: Hydrogen–Oxygen Fuel Cell

Electrolyte: KOH solution

Reaction

- At anode:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

- At Cathode

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

- **Overall Reaction:**

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Electric energy}$$

Use:

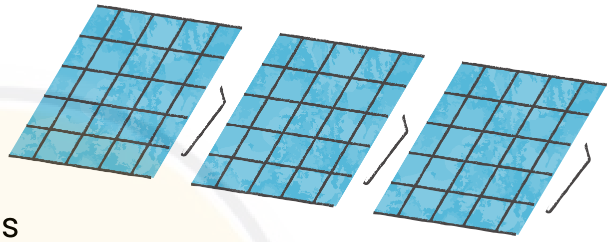
Used in spacecrafts and advanced vehicles.

Solar Cells

Devices that convert solar energy into electrical energy using photovoltaic effect

Construction:
Made of silicon (Si) or gallium arsenide (GaAs) semiconductors.

Working Principle:
When sunlight falls on the semiconductor, electrons are released, generating electric current.



Uses:

- Powering satellites
- Street lights
- Solar panels in homes and industries

Difference Between Primary and Secondary Cell

Basis of Difference	**Primary Cell**	**Secondary Cell**
1. Reversibility	Chemical reaction is irreversible.	Chemical reaction is reversible.
2. Recharging	Cannot be recharged once exhausted.	Can be recharged by passing electric current in the opposite direction.
3. Initial Cost	Low initial cost, but cannot be reused.	High initial cost, but economical in the long run.
4. Examples	Dry cell, Mercury cell.	Lead-acid battery, Nickel-cadmium cell, Lithium-ion battery.

Introduction to Corrosion

Corrosion is the gradual destruction or deterioration of a metal due to its chemical or electrochemical reaction with the surrounding environment (like air, moisture, acids, or salts).

In simple terms —
👉 *Corrosion is the unwanted conversion of a metal into its compound (oxide, hydroxide, or carbonate) due to environmental attack.*

Examples

- Rusting of iron in presence of moisture and oxygen
- Tarnishing of silver
- Green coating on copper ($CuCO_3 \cdot Cu(OH)_2$)

Importance of Studying Corrosion

- Causes damage to structures, machinery, and pipelines.
- Reduces strength, appearance, and efficiency of materials.
- Leads to economic loss in industries.

Types of Corrosion

Corrosion is broadly classified into two main types:

1. Chemical (Dry) Corrosion

Corrosion that occurs in the absence of moisture, mainly due to the direct chemical attack of gases (like O_2, SO_2, CO_2) on metal surfaces at high temperature.

Mechanism:

- In this process, the metal reacts directly with the gas to form a dry oxide layer.
- The rate of corrosion depends on the porosity and stability of the oxide film.

Examples:

- Formation of rust on iron at high temperatures.
- Tarnishing of silver or formation of scale on copper.

2. Electrochemical (Wet) Corrosion

Corrosion that occurs in presence of moisture or electrolyte through the formation of electrochemical cells (anodic and cathodic regions) on the metal surface.

Example:

- Rusting of iron in presence of water and oxygen.

Mechanism:

When a metal surface comes in contact with water containing dissolved oxygen or ions:

- Some parts act as anode and others as cathode.
- At anode, metal undergoes oxidation (loss of electrons).
- At cathode, reduction occurs (gain of electrons).
- These reactions together cause corrosion.

● Factors Affecting Rate of Corrosion

The rate of corrosion depends on several environmental and material factors:

1. Nature of the Metal

- Reactivity: More reactive metals (like Mg, Al, Zn) corrode faster.
- Purity: Impurities create tiny galvanic cells, increasing corrosion.
- Grain Size: Finer grains reduce corrosion rate.
- Electrode Potential: Metals with lower electrode potential corrode easily.

2. Nature of the Environment

- Moisture: Water or humidity accelerates corrosion.
- Oxygen: Presence of dissolved oxygen increases corrosion (especially in Fe).
- pH Value: Acidic conditions (low pH) promote corrosion.
- Temperature: Higher temperature increases rate of chemical reactions.
- Presence of Salts: Chlorides and sulphates increase conductivity, hence faster corrosion.

3. Conductivity of the Medium

- Higher conductivity (due to dissolved ions) → faster electron transfer → faster corrosion.

4. Presence of Oxide Film

- Some metals like Al, Cr, Ni form protective oxide films which slow down corrosion.
- If oxide layer is porous or unstable, corrosion continues beneath it.

5. Difference in Metal Potential (Galvanic Couple)

- When two dissimilar metals are in contact, the more active metal acts as anode and corrodes faster.
- **Example:** Iron and Copper in contact → Iron (anode) corrodes, Copper (cathode) protected.

Design and Surface Conditions

- Rough or uneven surfaces trap moisture and promote corrosion.
- Improper design (like crevices or joints) retains electrolytes and increases local corrosion.

___ Corrosion Preventive Measures ___

● Internal Corrosion Preventive Measures

These measures are applied during or before the manufacturing process of the metal. The main objective is to improve the intrinsic properties of the metal so that it becomes more resistant to corrosion.

a) Purification of Metal

- Impurities in metals (like sulfur, phosphorus, carbon, etc.) act as corrosion centers.
- Removing these impurities during extraction or refining helps in reducing corrosion.
- **Example:** Electrolytic refining of copper produces pure copper, which is more corrosion-resistant than impure copper.

b) Alloying

- Alloying means mixing a base metal with one or more other elements to improve its corrosion resistance, strength, or hardness.
- The added element forms a protective oxide film or alters the metal's structure to resist oxidation and chemical attack.

Examples:

- Stainless steel (Iron + Chromium + Nickel) — resists rust due to the protective chromium oxide film.
- Bronze (Copper + Tin) — more corrosion-resistant than pure copper.

c) Heat Treatment

- Heat treatment involves heating and cooling metals under controlled conditions to change their internal structure.
- This improves grain structure, removes internal stresses, and enhances corrosion resistance.
- **Example:** Annealing of steel makes it more uniform and less prone to localized corrosion.

● External Corrosion Preventive Measures

These methods are applied after the metal is manufactured. They protect the metal surface from coming into direct contact with the corrosive environment.

a) Metallic Coatings

Metallic coatings involve covering the surface of a metal with another metal that is less susceptible to corrosion.

There are two main types of metallic coatings:

A. Anodic Coating (Active Coating):

- The coating metal is more reactive than the base metal.
- It sacrifices itself to protect the base metal by corroding preferentially.
- **Example:** Zinc coating on iron (galvanization). Zinc acts as a sacrificial anode and protects iron from rusting.

B. Cathodic Coating (Inactive Coating):

- The coating metal is less reactive than the base metal.
- It acts as a barrier preventing contact with air and moisture.
- **Example:** Tin coating on iron (tinning). Tin prevents moisture from reaching the iron surface.

b) Organic Inhibitors

- Organic inhibitors are chemical substances that are added in small amounts to the corrosive environment (like water or acid) to reduce the rate of corrosion.
- They work by forming a protective film on the metal surface.
- Common inhibitors include amines, mercaptans, and organic phosphates.
- **Example:** Adding inhibitors in boilers or cooling systems to prevent corrosion of iron pipes.

● Mechanism of Electrochemical Corrosion

There are two common mechanisms:

(a) Hydrogen Evolution Mechanism

Occurs in:

Acidic environments (like H_2SO_4, HCl).

Process:

- Anodic reaction (oxidation):

$M \rightarrow M^{n+} + ne^-$ (Metal dissolves as positive ions.)

- Cathodic reaction (reduction):

$2H^+ + 2e^- \rightarrow H_2 \uparrow$ (Hydrogen gas is liberated.)

Overall Reaction:

$$M + 2H^+ \rightarrow M^{2+} + H_2 \uparrow$$

Example:

- Corrosion of iron in dilute H_2SO_4 or HCl solution.

Observation:

- Metal surface shows pitting and gas bubbles.
- The reaction continues as long as the acid and metal are in contact.

(b) Oxygen Absorption Mechanism

Occurs in:

Neutral or alkaline environments containing dissolved oxygen (e.g., water, moist air).

Example:

Rusting of iron in damp air.

Process:

A. *Formation of anodic and cathodic areas:*

- Due to impurities or differences in oxygen concentration on metal surface.

B. *Anodic reaction (oxidation):*

$Fe \rightarrow Fe^{2+} + 2e^-$ (Iron gets oxidized to ferrous ions.)

C. *Cathodic reaction (reduction):*

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

D. *Formation of rust:*

- The Fe^{2+} ions react with OH^- to form $Fe(OH)_2$.
- Further oxidation forms $Fe(OH)_3$, which dehydrates to $Fe_2O_3 \cdot xH_2O$ (rust).

Overall Reaction:

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3$$