Chapter 7: Electrochemistry

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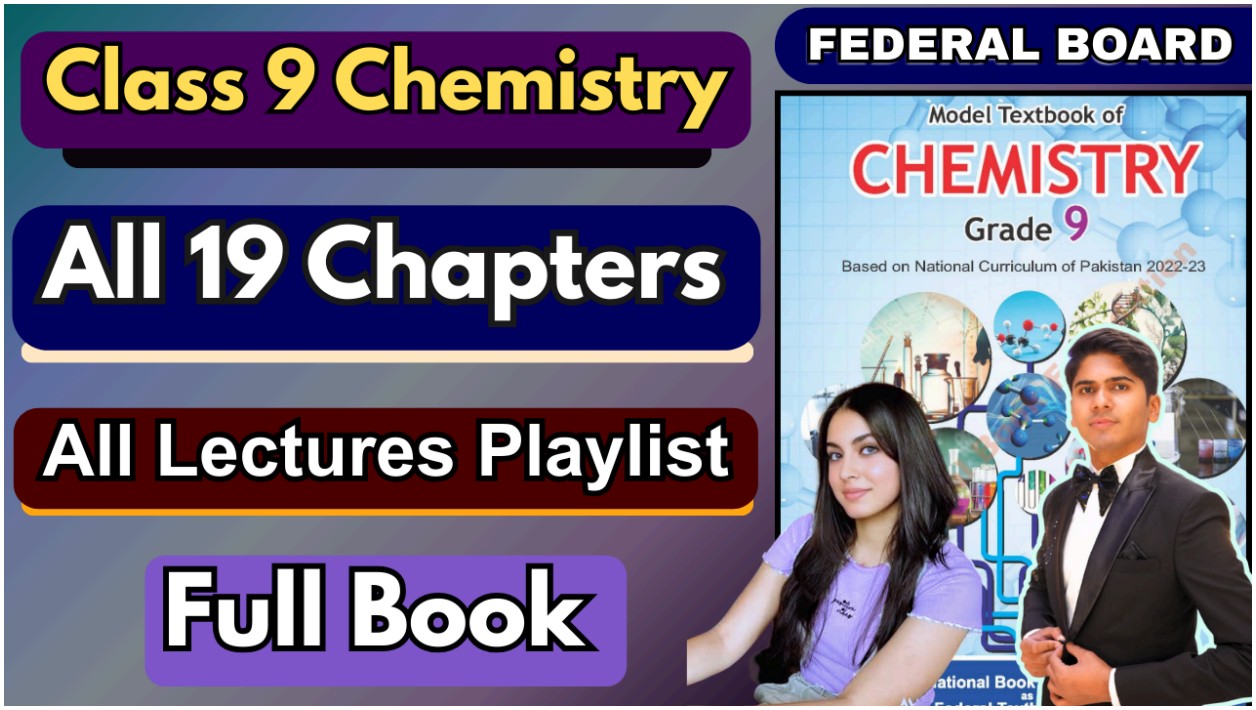


Redox reactions are fundamental chemical processes involved in many natural and industrial activities.

Examples in daily life:

- o **Rusting** of iron objects.
- o **Burning** of fuel in car engines and forest fires.
- o **Metabolism** of food in our bodies.

Industrial Importance:

- o Production of electricity in **batteries and fuel cells**.
- o Decolorizing substances with **household bleaches**.

o Industrial production of metals and chemicals.

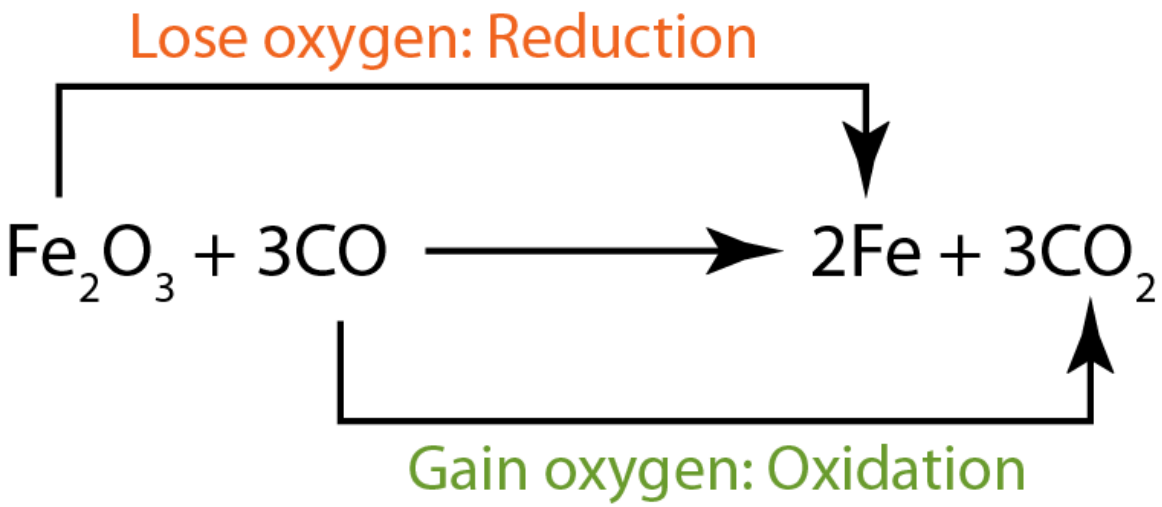
7.1. OXIDATION AND REDUCTION (REDOX)

Oxidation and reduction always occur **simultaneously** in a reaction. Such reactions are called **redox reactions**.

They can be defined in three ways:

1. Transfer of **Oxygen**
2. Transfer of **Hydrogen**
3. Transfer of **Electrons**

In Terms of Transfer of OXYGEN



· **Oxidation = Gain of Oxygen**

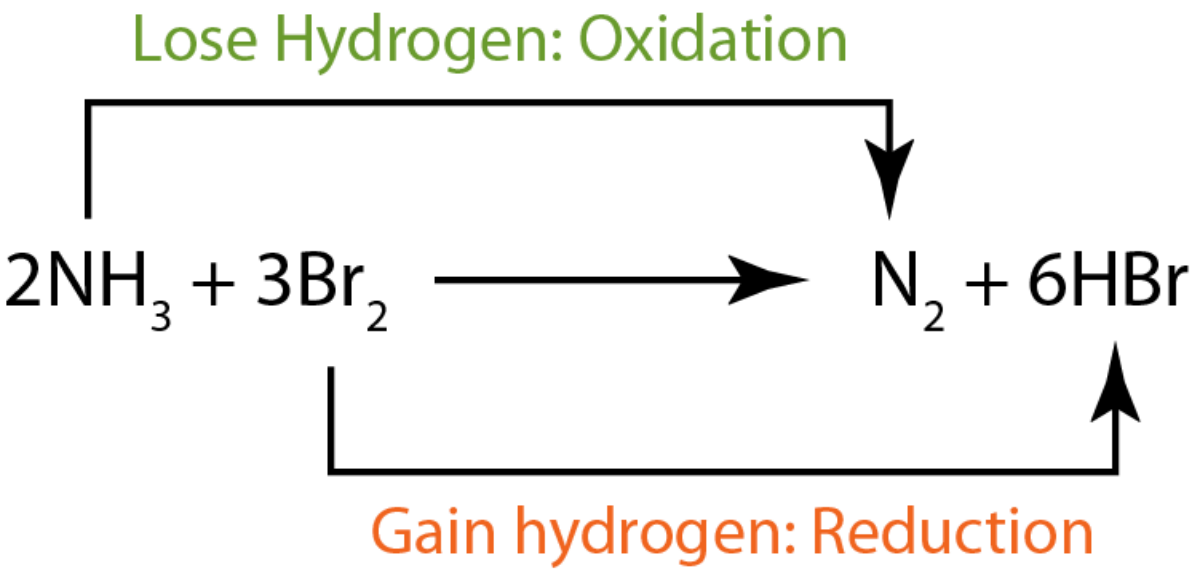
· **Reduction = Loss of Oxygen**

Example from Industry: Extraction of Iron

Reaction: **$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$**

o **Carbon Monoxide (CO)** gains oxygen to become **CO_2**. So, **CO is oxidized**. o **Iron Oxide (Fe_2O_3)** loses oxygen to become **Fe**. So, **Fe_2O_3 is reduced**.

In Terms of Transfer of HYDROGEN



· **Oxidation = Loss of Hydrogen**

· **Reduction = Gain of Hydrogen**

Example: Combustion of Acetylene (for welding)

Reaction: **$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$**

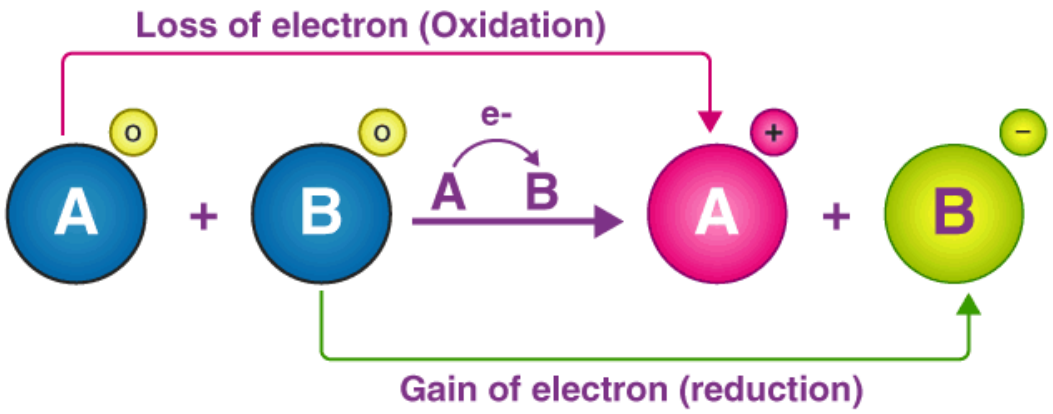
o **Acetylene (C_2H_2)** loses all its hydrogen atoms. So, **C_2H_2 is oxidized**. o **Oxygen (O_2)** gains hydrogen atoms to form water **(H_2O)**. So, **O_2 is reduced**.

Another Example: Burning of Sui Gas (Methane)

Reaction: **$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$**

o **Carbon (C)** in CH_4 loses hydrogen atoms and gains oxygen atoms. So, it is **oxidized**. o **Oxygen (O_2)** gains hydrogen atoms. So, it is **reduced**.

In Terms of Transfer of ELECTRONS



· **Oxidation = Loss of Electrons**

· **Reduction = Gain of Electrons**

Example: Reaction between Copper Oxide and Zinc

Molecular Equation: **$CuO + Zn \rightarrow Cu + ZnO$**

Ionic Equation: Rewriting to show the ions:

o $Cu^{2+} + O^{2-} + Zn \rightarrow Cu + Zn^{2+} + O^{2-}$

Net Ionic Equation: Remove the spectator ion (O^{2-}, which doesn't change).

o **$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$**

Zinc (Zn):

- o Loses 2 electrons to form Zn^{2+}.
- o **Oxidation state** changes from **0 to +2** (increase).
- o So, **Zn is oxidized**.

Copper ion (Cu^{2+}):

- o Gains 2 electrons to form Cu metal.
- o **Oxidation state** changes from **+2 to 0** (decrease).
- o So, **Cu^{2+} is reduced**.

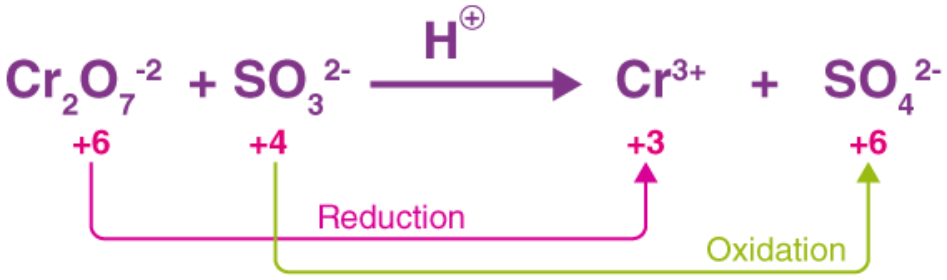
Oxidation	Reduction
1. gain of oxygen	1. Loss of oxygen
2. loss of hydrogen	2. Gain of hydrogen
3. loss of electrons	3. Gain of electrons
4. increase in oxidation number	4. Decrease in oxidation number

7.2. OXIDATION STATES AND RULES FOR ASSIGNING OXIDATION STATES

7.2.1. Oxidation States (Oxidation Numbers)

Definition: The oxidation state or oxidation number is the **hypothetical charge** an atom would have if all its bonds in a molecule or compound were 100% ionic (as if electrons were completely transferred).

Primary Use: It is the most reliable method for identifying oxidation and reduction in a reaction.



- **An increase in oxidation number = Oxidation**
- **A decrease in oxidation number = Reduction**

Summary Table of Redox Processes:

Oxidation	Reduction
Gain of Oxygen	Loss of Oxygen
Loss of Hydrogen	Gain of Hydrogen
Loss of Electrons	Gain of Electrons

7.2.2. Rules for Assigning Oxidation States/Numbers

To assign oxidation numbers correctly, you must follow a set of official rules. **The Main Rules:**

1. **Free Elements:** The oxidation state of any pure, uncombined element is always **0**.

   Examples: Zn (metal), Na (metal), O_2 (gas), H_2 (gas), S_8 (solid). In all these, each atom has an oxidation number of **0**.

2. **Simple Ions:** The oxidation state of a simple ion is equal to its **ionic**

charge. *Examples:* In Na^+, the oxidation number is **+1**. In Ca^{2+}, it is **+2**. In Cl^-, it is **-1**.

3. **Complex/Polyatomic Ions:** The sum of the oxidation numbers of all the atoms in a polyatomic ion must equal the **charge on the ion**.

   Example: In the carbonate ion, CO_3^{2-}, the sum of the oxidation numbers of one C atom and three O atoms must equal **-2**.

4. **Neutral Compounds:** The sum of the oxidation numbers of all the atoms in a neutral molecule is **0**.

   Example: In HCl, the sum of the oxidation numbers of H and Cl is **0**. In CO_2, the sum of one C and two O atoms is **0**.

Common, Fixed Oxidation States (Memorize these!):

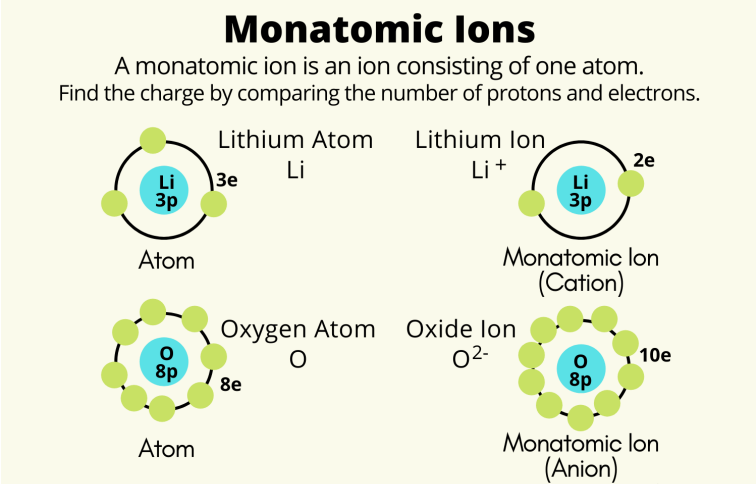
- Element / Group Typical Oxidation State Important Exceptions Group 1 (IA) **+1** Always
- Group 2 (IIA) **+2** Always
- Hydrogen (H) **+1 -1** in metal hydrides (e.g., NaH)
- Oxygen (O) **-2 -1** in peroxides (e.g., H_2O_2), **+2** in OF_2 Group 17
- (VIIA) **-1** Always in binary compounds

Applying the Rules: Monatomic vs. Polyatomic Ions

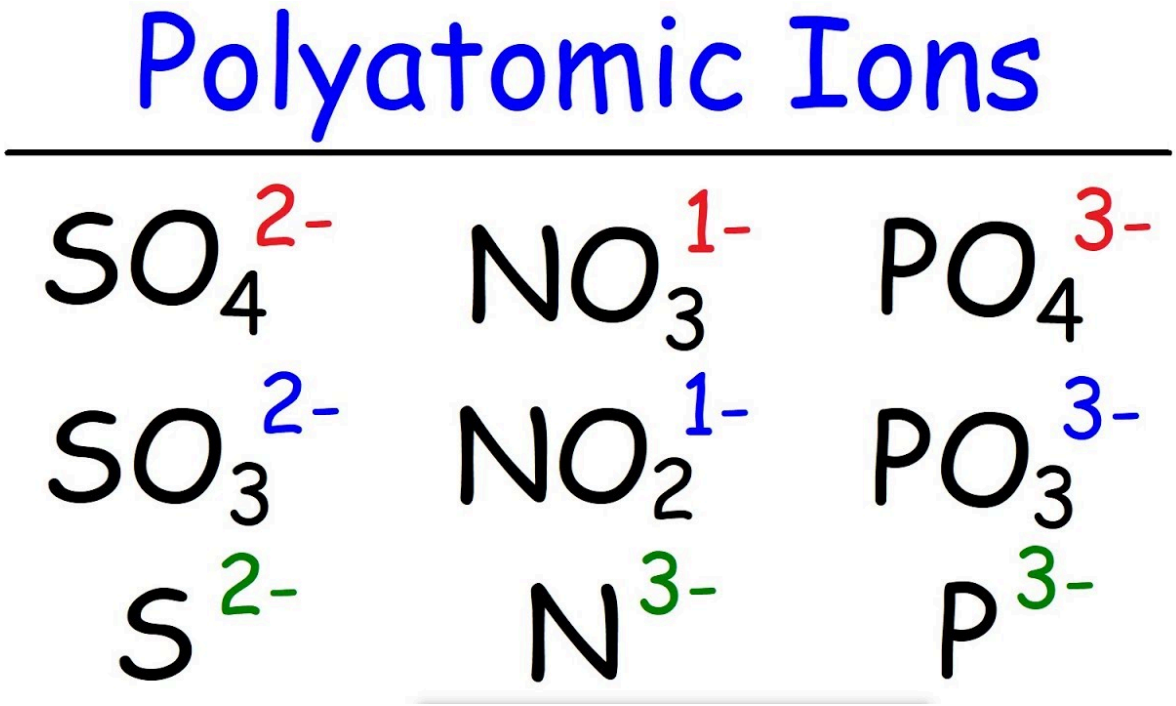
· **Monatomic Ions:** A single atom with a charge.

Its oxidation number **is** its charge.

Example: A sodium **atom** (Na) has an oxidation



number of 0. A sodium **ion** (Na^+) has an oxidation number of **+1**. A chloride **ion** (Cl^-) has an oxidation number of **-1**.



· **Polyatomic Ions:** A group of atoms with a collective charge.

The **sum** of all oxidation numbers in the ion equals the ion's charge.

Example: **Carbonate Ion (CO_3^{2-})**

Overall Charge = **-2**

Oxygen's oxidation state = **-2** (Rule: Common State)

7.3. FORMULA OF AN IONIC COMPOUND

Key Principle: All ionic compounds are **electrically neutral**. This means the **total positive charge** from the cations must exactly balance the **total negative charge** from the anions.

To write a correct formula, follow these three steps:

Step 1: Identify the Ions and Their Charges.

· Figure out what the positive ions (cation) and negative ions (anion) are, and know their charges (e.g., from the periodic table or from a polyatomic ion chart).

Step 2: Determine the Ratio for Neutrality.

· Find the simplest whole-number ratio of cations to anions that makes the total charge zero.

Step 3: Write the Formula.

· Write the cation first, then the anion.

· Use subscripts to show the ratio determined in Step 2.

· **Crucial Rule:** If a polyatomic ion needs a subscript greater than 1, you **must put it in parentheses**.

Worked Examples:

Example 1: Calcium Chloride

1. **Ions & Charges:** Ca^{2+} and Cl^{-}

2. **Ratio:** One +2 charge needs two -1 charges to cancel out. Ratio is **1 Ca^{2+} to 2 Cl^{-}**. 3. **Formula: $CaCl_2$**

Example 2: Magnesium Oxide

1. **Ions & Charges:** Mg^{2+} and O^{2-}

2. **Ratio:** One +2 charge balances one -2 charge. Ratio is **1:1**.

3. **Formula: MgO**

Example 3: Aluminum Sulfate

1. **Ions & Charges:** Al^{3+} and SO_4^{2-}
2. **Ratio:**

   Total positive charge needed: +6 (LCM of 3 and 2).

   Number of Al^{3+} ions: 2 (2 × +3 = +6)

   Number of SO_4^{2-} ions: 3 (3 × -2 = -6)

   Ratio is **2 Al^{3+} to 3 SO_4^{2-}**.

3. **Formula:** Since we need more than one sulfate ion, we use parentheses: **$Al_2(SO_4)_3$**

7.3.1. Use of Roman Numerals as Oxidation Number

Why? Some metals, especially **transition metals** (like Iron, Copper), can form ions with **different charges**.

Purpose: Roman numerals in a compound's name explicitly state the **oxidation state** (charge) of the metal ion. This avoids confusion.

Examples:

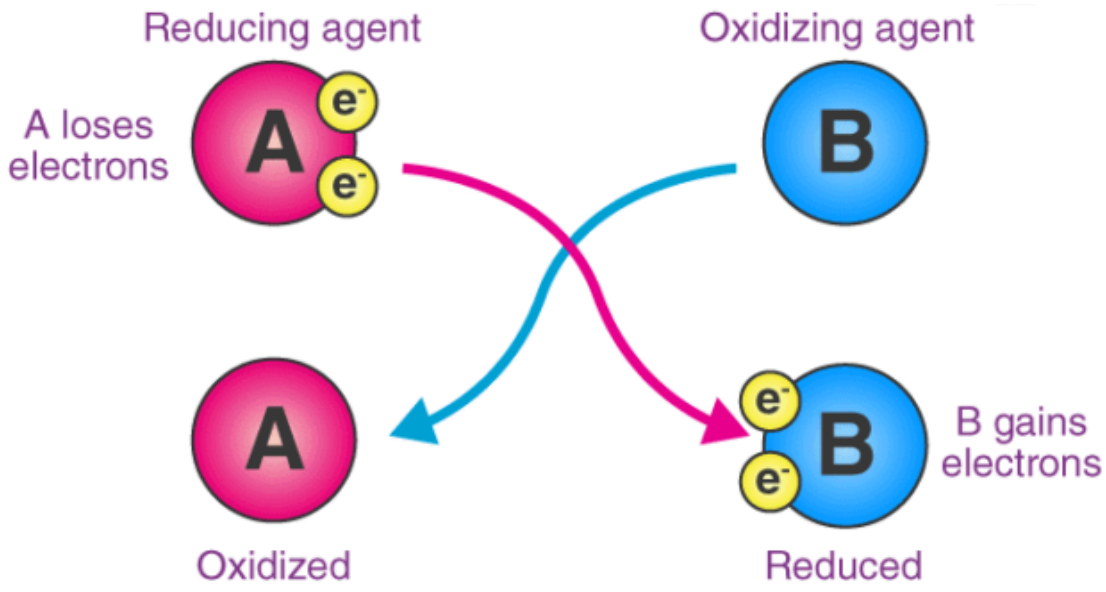
- **$CuSO_4$:** Copper can be +1 or +2. In this compound, it's +2. So, the name is **Copper(II) sulphate**.
- **$FeCl_2$:** The iron ion has a +2 charge. Name: **Iron(II) chloride**.
- **$FeCl_3$:** The iron ion has a +3 charge. Name: **Iron(III) chloride**.

7.4. OXIDIZING AND REDUCING AGENTS

Definitions:

Oxidizing Agent (Oxidant):

- o A substance that **accepts electrons** from another substance.
- o It **causes oxidation** to happen to another substance.
- o **Itself, it is REDUCED.**
- o *Common Examples:* Oxygen (O_2), Chlorine (Cl_2), Hydrogen Peroxide (H_2O_2), Potassium Permanganate ($KMnO_4$).



Reducing Agent (Reductant):

- o A substance that **donates electrons** to another substance.
- o It **causes reduction** to happen to another substance.
- o **Itself, it is OXIDIZED.**
- o *Common Examples:* Hydrogen Gas (H_2), Reactive Metals (Zn, Al), Carbon Monoxide (CO).

Simple Rule: OIL RIG for agents:

· **Oxidizing Agent** Is **Reduced** (and gains electrons).

· **Reducing Agent** Is **Oxidized** (and loses electrons).

Example Reaction: $2Na + Cl_2 \rightarrow 2NaCl$

· Sodium (Na) is oxidized (loses an electron). Therefore, **Na is the Reducing Agent**. · Chlorine (Cl_2) is reduced (gains an electron). Therefore, **Cl_2 is the Oxidizing Agent**.

7.4.2. How to Identify Oxidizing and Reducing Agents?

The most reliable method is to track changes in **oxidation numbers**.

Example Reaction from Steel Manufacturing:

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

1. **Assign Oxidation Numbers:**

   In Fe_2O_3: O is -2, so Fe must be **+3**.

   In CO: O is -2, so C must be **+2**.

   In Fe: Pure element, so Fe is **0**.

   In CO_2: O is -2, so C must be **+4**.

2. **Identify Oxidation and Reduction:**

   Carbon (C): Changes from **+2** in CO to **+4** in CO_2. (Increase = **Oxidation**) **Iron (Fe):** Changes from **+3** in Fe_2O_3 to **0** in Fe. (Decrease = **Reduction**

3. **Identify the Agents:**

The substance that **contains the atom being oxidized** is the **Reducing Agent**. Here, **CO** contains the carbon that is oxidized, so **CO is the Reducing Agent**.

The substance that **contains the atom being reduced** is the **Oxidizing Agent**. Here, **Fe_2O_3** contains the iron that is reduced, so **Fe_2O_3 is the Oxidizing Agent**.

7.5. CORROSION AND ITS PREVENTION

7.5.1. Corrosion

Corrosion is a **natural electrochemical process** where a metal reacts with its environment (especially oxygen and moisture) and gets converted into a more stable compound, usually an oxide.

The Common Example: The **rusting of iron** is the most familiar form of corrosion. **Essential Requirements for Rusting: Oxygen** and **Water** are both necessary.

The Electrochemistry of Rusting (How it works):

Rusting is a redox reaction that sets up a tiny **electrochemical cell** on the surface of the iron.

1. **Anode (Site of Oxidation - Less Moist Area):**

   Here, iron metal **loses electrons** and is oxidized.

   Reaction: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

2. **Cathode (Site of Reduction - More Moist Area):**

   The electrons released at the anode travel to this area.

   Here, atmospheric oxygen **gains those electrons** and is reduced.

   Reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

3. **Formation of Rust:**

The Fe^{2+} ions (from the anode) and OH^- ions (from the cathode) meet in the water film.

They react to form ferrous hydroxide, which is then further oxidized by oxygen to form **rust**, a hydrated iron(III) oxide with the formula **$Fe_2O_3 \cdot xH_2O$**.

7.5.2. Prevention of Corrosion

Preventing corrosion is crucial to protect infrastructure, vehicles, and equipment, and to conserve metal resources. Here are the main methods:

1. Coating with Paint or Epoxy:

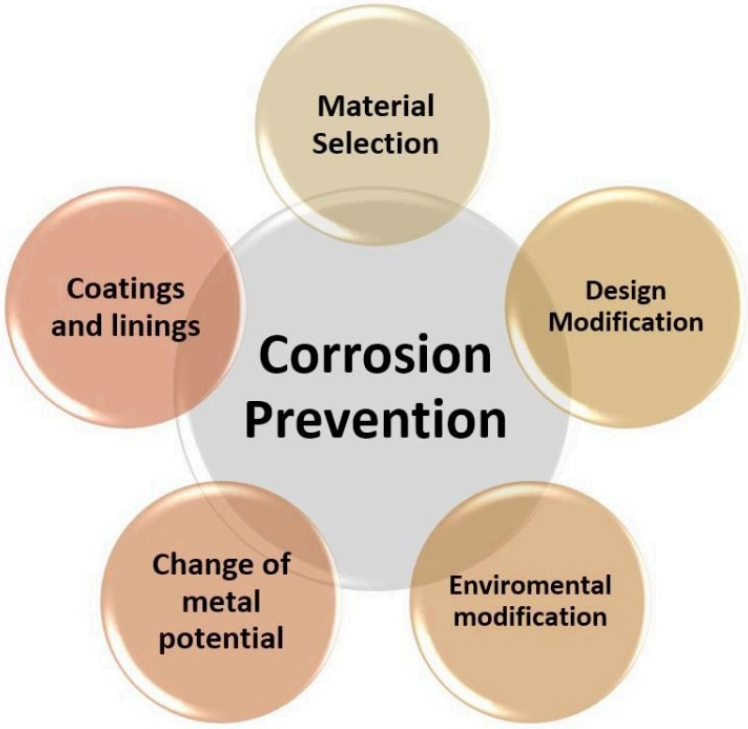
· **How it works:** Creates a simple **physical barrier** that prevents oxygen and moisture from reaching the metal surface.

· **Use:** Very common and cost-effective. Used on cars, bridges, ships, and many other steel structures. It also improves appearance.

2. Alloying:

· **How it works:** Mixing the base metal with other elements to create a new material with superior corrosion resistance.

· **Example: Stainless Steel.** Adding **Chromium** to iron makes stainless steel. Chromium forms a tough, invisible oxide layer that protects the iron underneath from further attack.



3. Coating with a Thin Layer of Another Metal:

This method provides a protective metal layer. The protection mechanism depends on the metal used:

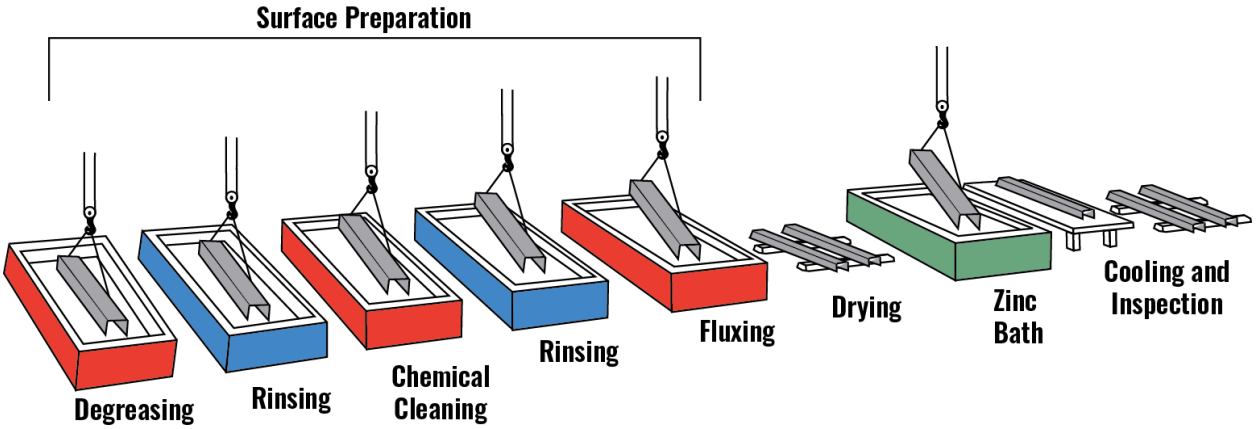
(a) Tinning:

o **Process:** Coating iron with a layer of **tin** (Sn).

- **Protection Mechanism:** Tin is **less reactive** and provides a **physical barrier**. It is non toxic, which is why it's used for **food cans**.
- **Drawback:** If the tin coating is scratched, the iron underneath will corrode *faster* because tin is less active.

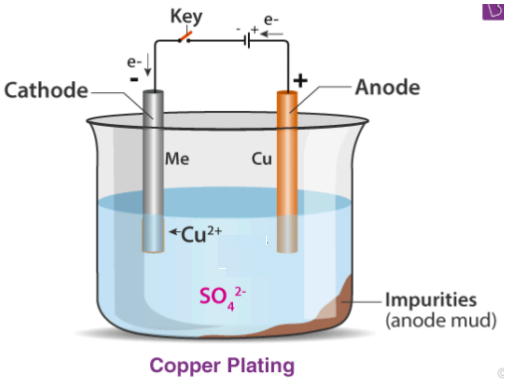
(b) Galvanizing:

- **Process:** Coating iron with a layer of **zinc** (Zn).
- **Protection Mechanism:** Zinc provides a barrier AND acts as a **sacrificial anode**. Even if the coating is scratched, the more reactive zinc will corrode *instead* of the iron. This is why galvanized steel is used for roofing, nails, and fences.



(c) Electroplating:

- **Process:** Using electricity to deposit a thin, decorative, and protective layer of a metal (like chromium or nickel) onto the surface of another metal.



4. Cathodic Protection (Sacrificial Protection):

How it works: This method forces the iron structure to become the **cathode** in an electrochemical cell, thus preventing it from oxidizing.

Process: A block of a **more reactive metal** (like **Magnesium** or **Zinc**) is connected

electrically to the iron structure. This block acts as the **sacrificial anode**.

- The more active metal (Mg/Zn) willingly **oxidizes** and corrodes.
- It supplies electrons to the iron, forcing the iron to be the cathode where reduction (of oxygen) occurs.
- The iron is saved while the sacrificial anode is "sacrificed" and needs to be replaced periodically.

Use: Ideal for large, buried, or submerged structures like **underground pipelines, ship hulls, and water tanks**. The diagram shows magnesium blocks attached to a ship's hull for this purpose.

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