

UNIT 2: ELECTROCHEMISTRY

Oxidation-Reduction Reactions

Oxidation-Reduction (Redox) Reactions are chemical processes where electrons are transferred between substances, leading to changes in oxidation states of the elements involved.

Oxidation

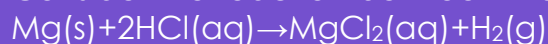
- **Definition:** Oxidation originally referred to the addition of oxygen to a compound. Today, it has a broader meaning:
 - **Oxidation** is the process where an atom or element **loses electrons**.
 - This leads to an **increase in the oxidation number** of the element.

Reduction

- **Definition:** Reduction initially described the extraction of metals from ores. It now includes:
 - **Reduction** is the process where an atom or element **gains electrons**.
 - This results in a **decrease in the oxidation number** of the element.

Example of Redox Reaction

Consider the reaction between magnesium and hydrochloric acid:



- **Oxidation:** Magnesium (Mg) is oxidized because it loses electrons, going from 0 to +2 oxidation state.
- **Reduction:** Hydrogen ions (H⁺) are reduced, gaining electrons and forming hydrogen gas (H₂).

Note: Oxidation and reduction reactions always occur together in pairs, as one substance loses electrons (oxidation), another gains them (reduction). These combined reactions are known as **Redox Reactions**.

Balancing Redox Reactions

Law of Conservation of Mass

- **Scientific Law:** Atoms are neither created nor destroyed in chemical reactions. Therefore, in any chemical equation, the number of atoms of each element on the reactant side must equal the number on the

product side. Additionally, the total charge should be balanced on both sides.

Methods to Balance Redox Reactions

1. Change in Oxidation-Number Method

- Useful for reactions not occurring in aqueous solutions or those not involving ions.
- **Steps:**
 1. Write the unbalanced chemical equation.
 2. Assign oxidation numbers to all elements in the reaction.
 3. Identify the oxidized and reduced species based on changes in oxidation numbers.
 4. Calculate the number of electrons lost (oxidation) and gained (reduction).
 5. Multiply by appropriate factors to equalize electrons lost and gained, then balance the equation by inspection.
- **Example:** Balance the equation: $\text{PbS (s)} + \text{O}_2\text{(g)} \rightarrow \text{PbO(s)} + \text{SO}_2\text{(g)}$
 - **Oxidation:** S in PbS is oxidized from -2 to +4.
 - **Reduction:** O_2 is reduced from 0 to -2.
 - Balance the number of electrons by multiplying and adding coefficients, ensuring the equation is balanced in terms of both atoms and charge.

Half-Reaction Method

Involves dividing the overall reaction into oxidation and reduction half-reactions, which are balanced separately before combining.

Steps:

- 1 Separate the equation into oxidation and reduction half-reactions.
- 2 Balance atoms and charges in each half-reaction.
 - Atoms other than oxygen (O) and hydrogen (H) are balanced first.
 - In acidic solutions, balance O by adding H_2O and H by adding H^+ .
 - Balance charges by adding electrons.
- 3 Multiply the half-reactions by appropriate factors to equalize the electrons lost and gained.

4 Add the half-reactions and ensure the final equation is balanced in terms of atoms and charge.

Example: Balance the redox reaction in a basic medium:
 $\text{MnO}_4^- + \text{I}^- \rightarrow \text{MnO}_2 + \text{I}_2$

- Write and balance the half-reactions for oxidation and reduction.
- Combine the half-reactions, add OH^- to balance H^+ , and ensure the final equation is balanced.

Electrolytic Cells

Electrolytic Cells are devices that use electrical energy to drive chemical reactions, specifically the decomposition of compounds into their elements. This process, known as electrolysis, involves passing a direct electric current through an ionic compound, usually in an aqueous solution. In an electrolytic cell, the positively charged ions (cations) move towards the negatively charged electrode (cathode), where they gain electrons (reduction). Meanwhile, the negatively charged ions (anions) move towards the positively charged electrode (anode), where they lose electrons (oxidation).

Preferential Discharge

Preferential Discharge refers to the phenomenon where, during electrolysis, when multiple ions are present, not all of them will be discharged at the electrodes. Instead, the ions that are more easily discharged, based on several factors, are preferentially discharged.

Factors Affecting Preferential Discharge

1. **Position in the Electrochemical Series:** The electrochemical series ranks ions based on their tendency to gain or lose electrons. Ions lower in the series are more likely to be discharged at the electrodes. For example, in a solution containing potassium ions (K^+) and copper ions (Cu^{2+}), copper ions are preferentially discharged because they are lower in the series.
2. **Concentration of Ions:** The concentration of an ion in the solution affects its likelihood of being discharged. A higher concentration increases the probability of that ion being discharged. For example, in a solution of sodium chloride (NaCl) in water, chloride ions (Cl^-) might be discharged first if their concentration is significantly higher than that of hydroxide ions (OH^-), even though hydroxide ions are lower in the electrochemical series.
3. **Nature of Electrode:** The material of the electrode also influences which ions are discharged. If the electrode is inert (e.g., graphite or platinum), it

does not participate in the reaction, and the ions are discharged based on their position in the electrochemical series and concentration. However, if the electrode is active (e.g., copper or silver), it can take part in the reaction, affecting which ions are discharged. For example, during the electrolysis of copper sulfate (CuSO_4) using copper electrodes, the copper anode dissolves, and copper ions are deposited at the cathode.

Electrolysis of Different Solutions

1. **Electrolysis of Brine (Concentrated Sodium Chloride Solution):** In the electrolysis of brine, the Na^+ , Cl^- , H^+ , and OH^- ions compete for discharge. Hydrogen ions (H^+) are reduced at the cathode because they have a less negative reduction potential than sodium ions. Chloride ions (Cl^-) are oxidized at the anode, producing chlorine gas, while hydrogen gas is produced at the cathode.
 - **Cathode Reaction:** $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
 - **Anode Reaction:** $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
 - **Overall Reaction:** $2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$
2. **Electrolysis of Dilute Sulfuric Acid (H_2SO_4):** In the electrolysis of dilute sulfuric acid, the ions present include H^+ , OH^- , and SO_4^{2-} . The hydrogen ions are reduced at the cathode, producing hydrogen gas, while the hydroxide ions are oxidized at the anode, producing oxygen gas.
 - **Cathode Reaction:** $4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2(\text{g})$
 - **Anode Reaction:** $4\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 4\text{e}^-$
 - **Overall Reaction:** $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
3. **Electrolysis of Copper(II) Sulfate (CuSO_4) Using Inert Electrodes:** When using inert electrodes, copper ions (Cu^{2+}) are reduced at the cathode, and hydroxide ions (OH^-) are oxidized at the anode.
 - **Cathode Reaction:** $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
 - **Anode Reaction:** $4\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 4\text{e}^-$
 - **Overall Reaction:** $\text{Cu}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
4. **Electrolysis of Copper(II) Sulfate Using Copper Electrodes:** In this case, the copper anode dissolves, and copper ions are deposited at the cathode. This process is used in the refining of copper.
 - **Anode Reaction:** $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$
 - **Cathode Reaction:** $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

In summary, electrolytic cells involve the decomposition of ionic compounds through electrolysis, where the preferential discharge of ions is influenced by factors like their position in the electrochemical series, concentration, and the nature of the electrode. Understanding these principles is crucial for predicting the products of electrolysis in various scenarios.

Quantitative Aspects of Electrolysis

Faraday's First Law of Electrolysis

Faraday's First Law states that the mass of a substance (m) deposited or dissolved at the electrodes is directly proportional to the quantity of electricity (Q) passed through the electrolyte.

Mathematically:

$$m \propto Q$$

or

$$m = z \times Q$$

where z is the electrochemical equivalent.

Since:

$$z = \frac{E}{F} \text{ and } Q = I \times t$$

We can rewrite the equation as:

$$m = \frac{E \times I \times t}{F}$$

Where:

- E is the equivalent weight of the substance.
- F is the Faraday constant (96,500 Coulombs).
- I is the current in amperes.
- t is the time in seconds.

The equivalent weight (E) of a substance is given by:

$$E = \frac{M}{n}$$

Where M is the molecular mass and n is the valence (number of electrons exchanged).

Example Problem

1. Electrolysis of Molten NaCl:

- To reduce 1 mole of Na^+ ions, 1 mole of electrons is needed.
- The cathode reaction:



Faraday's Second Law of Electrolysis

Faraday's Second Law states that the masses of different substances liberated or dissolved by the same amount of electricity are proportional to their equivalent masses.

Mathematically:

$$\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3} = \text{constant}$$

Where m_1, m_2, m_3 are the masses of different substances, and E_1, E_2, E_3 are their respective equivalent masses.

Industrial Applications of Electrolysis

1. Extraction of Metals:

- Metals like aluminum are extracted from their ores using electrolysis. For example, aluminum is extracted from aluminum oxide (Al_2O_3) using an electrolytic cell. The aluminum ions (Al^{3+}) are reduced at the cathode to form aluminum metal.

2. Electrolytic Refining of Metals:

- Metals like copper are purified by making impure copper the anode and pure copper the cathode. The copper ions move from the anode to the cathode, where they deposit as pure metal.

3. Electroplating:

- Electroplating involves coating a metal object with a thin layer of another metal using electrolysis. For instance, an iron key can be coated with copper to prevent corrosion.

4. Electrosynthesis of Nonmetals and Compounds:

- Chlorine and sodium hydroxide are produced by the electrolysis of brine (NaCl solution), with chlorine gas being released at the anode and sodium hydroxide being formed at the cathode.

Voltaic Cells (Zn-Cu Voltaic Cell)

Introduction

A voltaic cell, also known as a galvanic cell, is a device that converts chemical energy into electrical energy through spontaneous redox reactions. The Zn-Cu voltaic cell is a classic example of this type of cell.

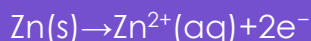
Construction of a Voltaic Cell

Components:

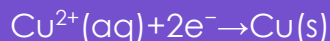
- Electrodes:**
 - Zinc Electrode (Anode):** This is where oxidation occurs. Zinc metal (Zn) loses electrons and forms zinc ions (Zn^{2+}).
 - Copper Electrode (Cathode):** This is where reduction occurs. Copper ions (Cu^{2+}) gain electrons to form copper metal (Cu).
- Solutions:**
 - Zinc Sulfate Solution (ZnSO_4):** Contains Zn^{2+} ions.
 - Copper Sulfate Solution (CuSO_4):** Contains Cu^{2+} ions.
- Salt Bridge:**
 - A salt bridge is a tube filled with an inert electrolyte (e.g., KCl) that maintains electrical neutrality by allowing ions to move between the two solutions, completing the circuit.
- External Circuit:**
 - A conductive wire that allows electrons to flow from the anode to the cathode.

Chemical Reactions:

- Oxidation Reaction (Anode):** Zinc metal loses electrons:



- Reduction Reaction (Cathode):** Copper ions gain electrons:



- Overall Reaction:**



Operation:

1. **Electrons Flow:** Electrons are released from the zinc electrode (anode) and travel through the external wire to the copper electrode (cathode).
2. **Ions Movement:** Zinc ions (Zn^{2+}) enter the solution, and copper ions (Cu^{2+}) are reduced to copper metal and deposit on the cathode.
3. **Salt Bridge Function:** The salt bridge maintains charge balance by allowing ions to migrate between the two half-cells, preventing charge buildup that would stop the reaction.

Cell Diagram (Cell Notation)

The cell notation for the Daniell cell is written as:



Conventions:

- **Single Vertical Line:** Indicates a phase boundary, e.g., solid electrode | solution.
- **Double Vertical Line:** Represents the salt bridge.

Measuring Standard Electrode Potentials

Electrode Potential Measurement:

1. **Reference Electrode:** The Standard Hydrogen Electrode (SHE) is used as a reference. It has a potential of 0.00 V by definition.
2. **Cell Potential Calculation:** The cell potential (E°) is determined by:
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Example:

For the Daniell cell:

- **Standard Reduction Potential of Zn^{2+}/Zn :** -0.76 V
- **Standard Reduction Potential of Cu^{2+}/Cu :** +0.34 V

Thus,

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

Electromotive Force (EMF) and Concentration Cells

Electromotive Force (EMF)

Every galvanic (or voltaic) cell is constructed from two half-cells: the oxidation half-cell (anode) and the reduction half-cell (cathode). The key concept in a galvanic cell is the difference in electrode potential between these two electrodes. One electrode has a higher electrode potential, meaning it has a greater tendency to lose electrons compared to the other. This difference creates a potential difference, causing electrons to flow from the electrode with the higher potential (anode) to the electrode with the lower potential (cathode).

The electromotive force (EMF) or cell potential is the driving force behind this electron flow. It is calculated using the electrode potentials of the two half-cells:

1. When oxidation potentials are used:

$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$$

2. When reduction potentials are used:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Dependence of EMF on Concentration

The cell potential depends on the concentrations of ions and gas pressures in the cell. This relationship can be described by the Nernst equation, which adjusts the standard electrode potentials for non-standard conditions:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Where:

- E is the cell potential under non-standard conditions.
- E° is the standard cell potential.
- R is the universal gas constant (8.314 J/mol·K).
- T is the temperature in Kelvin.
- n is the number of moles of electrons transferred.
- F is the Faraday constant (96,485 C/mol).
- Q is the reaction quotient, which depends on the concentrations of the reactants and products.

At 25°C (298 K), the equation simplifies to:

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

Concentration Cells

A concentration cell uses two half-cells with the same electrode material but differing ion concentrations. The cell potential in such cells is derived solely from the concentration difference. The Nernst equation applies here as well, showing that the cell potential decreases as the concentrations of the reactants and products approach equilibrium:

$$E = \frac{0.0592}{n} \log \frac{[\text{Concentrated}]}{[\text{Dilute}]}$$

Examples

1. **Equilibrium Constant Calculation:** For the reaction:

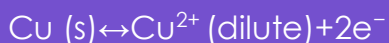


The equilibrium constant K is computed using:

$$K = \frac{[\text{Cd}^{2+}]}{[\text{H}^+]^2}$$

with concentrations converted from gas pressures if necessary.

2. **Cell Potential with Concentration Variations:** For a concentration cell with Cu electrodes:



The potential is calculated based on the difference in concentrations.

3. **Determining pH:** To determine pH from cell potential:



Using:

$$\text{pH} = \frac{0.76 - E_{\text{cell}}}{0.0592}$$

Summary

Galvanic Cells:

- Convert chemical energy into electrical energy.
- Anode is negative; cathode is positive.

Electrolytic Cells:

- Convert electrical energy into chemical energy.
- Anode is positive; cathode is negative.

Batteries and Fuel Cells

Batteries

Definition:

A battery is a device that stores chemical energy and converts it into electrical energy through electrochemical reactions. It consists of one or more galvanic cells connected in series.

Types of Batteries:

1. **Primary Batteries:** These are single-use batteries that cannot be recharged once depleted. Examples include:
 - **Dry Cell Batteries:** Use a paste electrolyte (e.g., AA, AAA batteries).
 - **Alkaline Batteries:** Use an alkaline electrolyte (e.g., AA, AAA alkaline batteries).
2. **Secondary Batteries:** These are rechargeable batteries. Examples include:
 - **Lead-Acid Batteries:** Common in cars, use a liquid electrolyte.
 - **Nickel-Metal Hydride (NiMH) Batteries:** Often used in rechargeable electronics.
 - **Lithium-Ion Batteries:** Used in many modern electronics like laptops and smartphones.

Battery Components:

- **Electrodes:** The positive (cathode) and negative (anode) electrodes that participate in the electrochemical reactions.
- **Electrolyte:** The substance that conducts electricity between the electrodes (can be liquid, paste, or solid).

Electrochemical Reactions:

- In a battery, chemical reactions occur at the electrodes, generating electric current. The anode undergoes oxidation (loses electrons), and the cathode undergoes reduction (gains electrons).

Fuel Cells

Definition:

A fuel cell is similar to a battery but operates with a continuous supply of reactants (fuel) rather than relying on stored chemicals.

Example - Hydrogen-Oxygen Fuel Cell:

1. Basic Structure:

- **Anode:** Hydrogen gas is oxidized here.
- **Cathode:** Oxygen gas is reduced here.
- **Electrolyte:** Conducts ions between the anode and cathode (can be acidic like phosphoric acid or alkaline like potassium hydroxide).

2. Reactions:

- **Anode Reaction (Hydrogen Oxidation):**
$$\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$$
- **Cathode Reaction (Oxygen Reduction):**
$$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$$
- **Overall Reaction:**
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$$

Applications: Fuel cells are used in various fields, including power generation, transportation (e.g., hydrogen-powered cars), and emergency power systems.

Corrosion of Metals

Definition:

Corrosion is the deterioration of metals through electrochemical reactions with their environment.

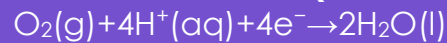
Iron Corrosion (Rusting):

- **Conditions for Rusting:**
 - **Moisture:** Required for the corrosion process.
 - **Oxygen:** Reacts with iron to form rust.
- **Process:**

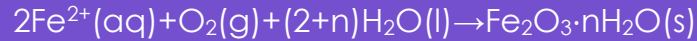
1. **Anodic Reaction (Oxidation):**



2. **Cathodic Reaction (Reduction):**



3. **Rust Formation:**



Prevention Methods:

- **Coating:** Paint or other coatings to block moisture and oxygen.
- **Alloying:** Adding other metals like chromium (e.g., stainless steel).
- **Galvanizing:** Coating with zinc, which corrodes instead of iron (sacrificial protection).

Summary:

- Batteries are devices that store and convert chemical energy into electrical energy.
- Fuel cells generate electricity through continuous reactions of fuel and oxidant.
- Corrosion is an electrochemical process causing metal deterioration, which can be mitigated through various protective measures.