Chemical Reactions

Chapter 10: Electrode Potentials, Electrochemical Series, and Electrolysis

This chapter delves into the fascinating world where chemistry meets electricity. We will explore how chemical reactions can produce electricity and how electricity can drive chemical reactions.

10.1 Electrode Potential and Electrochemical Cells

- **Electrode Potential:** When a metal is placed in a solution containing its own ions, a potential difference (voltage) is set up between the metal and the solution. This potential difference is called the electrode potential. It arises due to the tendency of the metal atoms to lose electrons (oxidize) or the metal ions to gain electrons (reduce).
    - It cannot be measured directly, only measured relative to a standard reference electrode.
- **Standard Hydrogen Electrode (SHE):** The reference electrode used to measure standard electrode potentials. It is assigned a standard electrode potential of exactly 0 Volts under standard conditions (1 { M} H^+ ions, 1 { atm} H_2 gas, 25 {°C}).
- **Electrochemical Cells (Voltaic or Galvanic Cells):** Devices that convert chemical energy directly into electrical energy through spontaneous redox reactions.
    - **Components:**
        - **Two half-cells:** Each containing an electrode immersed in an electrolyte solution.
        - **Salt bridge:** Connects the two half-cells, allowing ion flow to maintain electrical neutrality.
        - **External circuit:** Connects the electrodes, allowing electron flow through a wire and often a voltmeter.
    - **Operation:**
        - At the **anode (negative electrode)**: Oxidation occurs (electrons are lost).
        - At the **cathode (positive electrode)**: Reduction occurs (electrons are gained).
        - Electrons flow from the anode to the cathode through the external circuit, creating an electric current.
    - **Example: Daniel Cell (Zinc-Copper Cell):**
        - Anode: Zn(s) ➡️ Zn^{2+}(aq) + 2e^- (Zinc is oxidized)
        - Cathode: Cu^{2+}(aq) + 2e^- ➡️ Cu(s) (Copper ions are reduced)
        - Overall Reaction: Zn(s) + Cu^{2+}(aq) ➡️ Zn^{2+}(aq) + Cu(s)

10.2 Electrochemical Series (Reactivity Series)

- **Definition:** A list of elements (primarily metals) arranged in order of their standard electrode potentials, which reflects their relative tendency to lose electrons (get oxidized) or gain electrons (get reduced). It is also known as the reactivity series of metals.
- **Significant Features of the Series:**
    - **Top of the series (more negative electrode potential):** Elements are stronger reducing agents, more easily oxidized, more reactive, and displace elements lower in the series from their solutions. (e.g., K, Na, Ca, Mg, Al, Zn, Fe, Pb, H, Cu, Ag, Au).
    - **Bottom of the series (more positive electrode potential):** Elements are stronger oxidizing agents, more easily reduced, less reactive.
- **Limitations of the Electrochemical Series:**
    - It predicts reactivity under standard conditions (1 { M} concentration, 25 {°C}). Changes in concentration or temperature can alter the relative electrode potentials.
    - It predicts the *thermodynamic* feasibility of a reaction but not necessarily the *rate* of the reaction.

10.3 Corrosion as an Electrochemical Process

- **Corrosion:** The deterioration of metals due to chemical reactions with their environment. Most commonly, it's the oxidation of metals (rusting of iron).
- **Rusting of Iron:** An electrochemical process involving the oxidation of iron and the reduction of oxygen in the presence of water.
    - **Requirements:** Both **oxygen** and **water** are necessary for rusting.
    - **Process:**
        - At the anode (iron surface): Fe(s) ➡️ Fe^{2+}(aq) + 2e^- (Iron is oxidized)
        - At the cathode (areas with higher oxygen concentration): O2(g) + 2H2O(l) + 4e^- ➡️ 4OH^-(aq) (Oxygen is reduced)
        - Overall: Fe^{2+} ions react with OH^- ions and more oxygen to form hydrated iron(III) oxide (Fe2O3 … xH2O), which is rust.
- **Prevention of Rusting:**
    1. **Barrier Protection:** Coating the iron surface to prevent contact with oxygen and water (e.g., painting, oiling, greasing, plastic coating).
    2. **Galvanizing:** Coating iron with a layer of zinc. Zinc is more reactive than iron, so it corrodes preferentially, protecting the iron (**sacrificial protection**).
        - Zn(s) ➡️ Zn^{2+}(aq) + 2e^- (Zinc acts as the anode)
    3. **Electroplating:** Coating a metal with a thin layer of another metal (e.g., chromium, nickel) using electrolysis.
    4. **Cathodic Protection:** Connecting the iron object to a more reactive metal (a sacrificial anode) that will corrode instead of the iron. This is commonly used for underground pipelines or ships.
    5. **Alloying:** Mixing iron with other metals (e.g., chromium and nickel to make stainless steel), which makes it more resistant to corrosion.

10.4 Electric Charges and Current

- **Electric Charge:** A fundamental property of matter that describes how it interacts with electric fields. Measured in Coulombs (C).
    - Electrons carry a negative charge. Protons carry a positive charge.
- **Electric Current:** The rate of flow of electric charge. Measured in Amperes (A).
    - I = Q/t (Current = Charge / Time)
    - In metals, current is carried by the flow of electrons.
    - In electrolytes, current is carried by the flow of ions.

10.5 Electrolysis

- **Electrolysis:** The process of using electrical energy to drive a non-spontaneous chemical reaction (a redox reaction). It involves passing an electric current through an electrolyte.
- **Ionic Theory (of Electrolysis):** Electrolytes are substances that produce mobile ions when dissolved in water or when molten. These ions are responsible for conducting electricity.
- **Electrolytes and Non-electrolytes:**
    - **Electrolytes:** Substances that conduct electricity when molten or in aqueous solution due to the presence of mobile ions (e.g., acids, bases, salts).
        - **Strong Electrolytes:** Ionize/dissociate completely (e.g., NaCl, HCl, NaOH).
        - **Weak Electrolytes:** Ionize/dissociate partially (e.g., CH3COOH, NH3).
    - **Non-electrolytes:** Substances that do not conduct electricity in any state because they do not contain mobile ions (e.g., sugar solution, pure water, ethanol).
- **Mechanism of Electrolysis:**
    - The electrolyte is contained in an electrolytic cell, with two electrodes connected to a DC power supply.
    - **Anode (positive electrode):** Anions (negative ions) are attracted to the anode and are oxidized (lose electrons).
    - **Cathode (negative electrode):** Cations (positive ions) are attracted to the cathode and are reduced (gain electrons).
    - The movement of ions towards the electrodes and the electron transfer at the electrodes constitute the electric current.
- **Factors Affecting Products of Electrolysis:**
    1. **Position in the Electrochemical Series:** For competing ions, the ion lower in the electrochemical series is preferentially discharged at the cathode (reduced), and the ion higher in the series is preferentially discharged at the anode (oxidized). (For anions, usually OH^- or halide ions are discharged over sulphate/nitrate).
    2. **Concentration:** If an ion is present in high concentration, it might be preferentially discharged even if it's less preferred by the electrochemical series (e.g., concentrated NaCl solution producing Cl2 at anode instead of O2).
    3. **Nature of Electrode:** Inert electrodes (e.g., graphite, platinum) do not participate in the reaction. Reactive electrodes (e.g., copper anode) may be oxidized themselves.
- **Faraday's Laws of Electrolysis:**
    1. **First Law:** The mass of a substance liberated or deposited at an electrode is directly proportional to the quantity of electricity passed. (m 🔀 Q, where Q = I × t).

2. **Second Law:** When the same quantity of electricity is passed through solutions of different electrolytes, the masses of the substances liberated or deposited are proportional to their chemical equivalents (or molar mass/charge).
    - 1 Faraday (F) = 96,500 Coulombs (C) = the charge on 1 mole of electrons.
- **Uses of Electrolysis:**
    1. **Extraction and Purification of Metals:**
        - **Extraction:** Highly reactive metals (e.g., Al, Na, Mg) are extracted by the electrolysis of their molten ores (e.g., aluminium from molten alumina in the Hall-Héroult process).
        - **Purification:** Impure metals (e.g., copper) can be purified by making the impure metal the anode and a pure piece of the metal the cathode.
    2. **Electroplating:** Coating an object with a thin layer of a desired metal (e.g., silver, chromium, gold) to improve appearance, prevent corrosion, or enhance hardness. The object to be plated is made of the cathode.
    3. **Electrolysis of Brine (Concentrated NaCl solution):** Produces important industrial chemicals:
        - At anode: 2Cl^-(aq) ➡️ Cl2(g) + 2e^- (Chlorine gas)
        - At cathode: 2H2O(l) + 2e^- ➡️ H2(g) + 2OH^-(aq) (Hydrogen gas and hydroxide ions)
        - Remaining solution: Sodium hydroxide (NaOH).
        - Overall: 2NaCl(aq) + 2H2O(l) ↔{{electrolysis}} 2NaOH(aq) + H2(g) + Cl2(g)

Chapter 11: Energy and Chemical Reactions

All chemical reactions involve changes in energy. Some reactions release energy, while others absorb it. Understanding these energy changes is crucial in chemistry.

11.1 What is Energy?

- Energy is the ability to do work or produce heat. It exists in various forms: chemical, thermal, electrical, mechanical, light, nuclear, etc.
- **Law of Conservation of Energy (First Law of Thermodynamics):** Energy cannot be created or destroyed, only transformed from one form to another.

11.2 Energy Changes in Reactions: Heat Content and Heat of Reaction

- **Heat Content (Enthalpy, H):** The total energy stored within a chemical system. It includes the kinetic and potential energy of atoms and molecules. We cannot measure absolute enthalpy, only changes in enthalpy.
- **Heat of Reaction (Enthalpy Change, ΔH):** The amount of heat energy absorbed or released during a chemical reaction at constant pressure.
    - ΔH = H{{products}} - H{{reactants}}
- **Exothermic Reactions:**
    - **Definition:** Reactions that **release heat energy** to the surroundings. The surroundings get warmer.
    - **Energy Profile Diagram:** Products have lower energy than reactants.
    - **ΔH value:** Negative (ΔH < 0).
    - Examples: Combustion, neutralization, respiration, freezing.

- **Endothermic Reactions:**
  - **Definition:** Reactions that **absorb heat energy** from the surroundings. The surroundings get colder.
  - **Energy Profile Diagram:** Products have higher energy than reactants.
  - **ΔH value:** Positive (ΔH > 0).
  - Examples: Photosynthesis, melting of ice, thermal decomposition, dissolving some salts (e.g., ammonium nitrate).
- **Representing Energy Changes:**
  - **Thermochemical Equations:** Chemical equations that include the enthalpy change (ΔH).

- Exothermic:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l),$$

$$\Delta H = -286 \text{ kJ/mol}$$

- Endothermic:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g),$$

$$\Delta H = +178 \text{ kJ/mol}$$

11.3 Measurement of the Heat of Reaction (Calorimetry)

- **Calorimetry:** The experimental technique used to measure heat changes during chemical reactions or physical processes. A device called a **calorimeter** is used.
- **Specific Heat Capacity (c):** The amount of heat energy required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or Kelvin).
- **Heat Change Calculation:**

- $Q = mc\Delta T$
  - Q = heat absorbed/released (Joules, J)
  - m = mass of substance (grams, g)
  - c = specific heat capacity ($Jg^{-1}{}^{\circ}C^{-1}$)
  - ΔT = change in temperature ($^{\circ}C$ or K)
    - This calculated heat (Q) can then be related to the moles of reactant to find the molar heat of reaction.

11.4 Specific Heats of Reaction

- **Heat of Formation (ΔH_f):** The enthalpy change when one mole of a compound is formed from its constituent elements in their standard states under standard conditions (25 {°C}, 1 atm).
  - ΔHf of elements in their standard state is 0.
- **Heat of Neutralization (ΔH{neut}):** The enthalpy change when one mole of water is formed from the reaction of an acid with a base under standard conditions.
  - For strong acid-strong base reactions, it's typically around -57.3 { kJ/mol}.
- **Heat of Combustion (ΔHc):** The enthalpy change when one mole of a substance is completely burned in excess oxygen under standard conditions.
- **Heat of Solution (ΔH{sol}):** The enthalpy change when one mole of a substance dissolves in a large amount of solvent to form a solution.

11.5 Hess's Law and the Born-Haber Cycle

- **Hess's Law of Constant Heat Summation:** If a reaction can be expressed as a series of steps (individual reactions), then the enthalpy change (ΔH) for the overall reaction is the sum of the enthalpy changes for each step, regardless of the pathway taken.
  - This is very useful for calculating enthalpy changes for reactions that are difficult to measure directly.
- **Born-Haber Cycle:** A specialized thermochemical cycle that applies Hess's Law to calculate the **lattice energy** of an ionic compound. It relates various energy changes (enthalpy of formation, atomization, ionization, electron affinity) to the lattice energy.
  - **Lattice Energy:** The energy required to separate one mole of an ionic solid into its constituent gaseous ions. It is a measure of the strength of ionic bonds.

11.6 Bond Energy

- **Bond Energy (or Bond Enthalpy):** The average amount of energy required to break one mole of a particular type of covalent bond in the gaseous state.
    - Breaking bonds is an **endothermic** process (requires energy, positive value).
    - Forming bonds is an **exothermic** process (releases energy, negative value).
- **Estimating ΔH from Bond Energies:**
    - ΔH{{reaction}} = Σ{(Bond energies of bonds broken)} - Σ{ (Bond energies of bonds formed)}
    - This is an estimation because bond energies are average values.

11.7 Chemical Thermodynamics (Introduction)

- **The First Law of Thermodynamics:** States that the total energy of an isolated system is constant. It is essentially the law of conservation of energy. $\Delta U = Q + W$ (change in internal energy = heat added + work done).
- **The Second Law of Thermodynamics:** States that the total **entropy** (disorder or randomness) of an isolated system can only increase over time, or remain constant in ideal cases. It never decreases.
    - Processes tend to move towards greater disorder.
- **Conditions for Spontaneity of Reactions Using ΔG (Gibbs Free Energy):**
    - **Gibbs Free Energy (ΔG):** A thermodynamic quantity that predicts the spontaneity of a process at constant temperature and pressure.
    - $\Delta G = \Delta H - T\Delta S$
        - ΔH = enthalpy change (heat)
        - T = absolute temperature (Kelvin)
        - ΔS = entropy change (disorder)
    - **Spontaneous Reaction:**
        - $\Delta G < 0$ (negative)
        - Favored by exothermic reactions ($\Delta H < 0$) and increase in disorder ($\Delta S > 0$).
    - **Non-spontaneous Reaction:**
        - $\Delta G > 0$ (positive)
    - **At Equilibrium:**
        - $\Delta G = 0$