Chemical Reactions and Chemical Equilibria

Introduction

- **Chemical equilibrium** is central to quantitative analysis, as most methods (titrations, precipitations, extractions) rely on reactions reaching a stable, measurable state.

- **Equilibrium constants** (K) govern the extent of a reaction, allowing analysts to calculate the precise concentration of species in solution.

- The concepts of **mass balance** and **charge balance** are fundamental tools used to relate the starting components of a system to the final, equilibrium concentrations of all chemical species.

- In high ionic strength solutions, the effective concentration of a species, known as **activity**, must be considered to achieve highly accurate analytical results.

Learning Objectives

By the end of this module, you will be able to:

- Relate changes in **mass balance** to the concentrations of chemical species in equilibrium.
- Apply the concepts of **equilibrium constants** (K), **ionic equilibria**, **activity**, and **activity coefficients** in solving problems in quantitative analysis in the following systems:
  - **Acid-Base equilibria** (pH and titrations).
  - **Solubility equilibria** (precipitation).
  - **Complex ion equilibria** (masking and stability).
  - **Redox equilibria** (electrochemistry and titrations).
  - **Buffers** (resistance to pH change).

Key Concepts and Definitions

Term	Definition
Chemical Equilibrium	The state where the concentrations of reactants and products remain constant over time because the rates of the forward and reverse reactions are equal.
Equilibrium Constant (K)	A numerical value expressing the ratio of product concentrations to reactant concentrations at equilibrium.
Mass Balance	An accounting of matter that states the amount of a substance added to a solution must equal the sum of the concentrations of all its forms at equilibrium.
Activity (α)	The effective concentration of a species in a non-ideal solution, corrected for inter-ionic attractions.
Activity Coefficient (γ)	The factor used to convert concentration (C) to activity (a), where $a = \gamma C$.
Buffer	A solution that resists changes in pH when small amounts of acid or base are added.
Solubility Product (K_{sp})	The equilibrium constant for the dissolution of a sparingly soluble ionic compound.

Detailed Discussion

Mass Balance, Activity, and Non-Ideal Systems

Quantitative analysis relies on solving systems of equations, where mass balance and charge balance are essential components alongside the equilibrium constant expression.

- **Mass Balance:** For any substance in a solution, the total concentration must equal the sum of the concentrations of all species containing that substance. For example, HA is added to water, the mass balance equation for A is:

$$C_{total} \; = \; [\text{HA}] + [\text{A}^-]$$

- **Activity and Ionic Strength:** In concentrated solutions (high **ionic strength**), the electrostatic interactions between ions prevent them from behaving ideally. The effective concentration, or **activity (α)**, is used instead of molar concentration (C).

$$K_{thermodynamic} \; = \; \frac{a_{products}}{a_{reactants}}$$

The **activity coefficient (γ)** accounts for this non-ideality. This is critical for achieving high accuracy in analyses involving complex matrices.

Application of Equilibrium Systems

The equilibrium constant is expressed differently depending on the type of reaction system being analyzed.

- **Acid-Base Equilibria (K_a, K_b)**

These govern the extent of proton transfer reactions and are fundamental to pH measurement and titrimetric analysis.

  - The **acid dissociation constant (K_a)** and **base dissociation constant (K_b)** relate the concentration of the unionized species to its dissociated ions.
  - Titrations, the most common acid-base analytical technique, involve using a known concentration of acid or base (the **titrant**) to react completely with an unknown **analyte**. The equivalence point is calculated using stoichiometry and the relevant K values.

- **Buffers**

Buffers are solutions containing a weak conjugate acid-base pair. They are used to control the pH of a solution during a chemical analysis (e.g., precipitation, enzyme assays).

- Buffer calculations utilize the **Henderson-Hasselbalch equation** (derived from the K_a expression):

$$pH \; = \; pK_a \; + \; log\left(\frac{[A^-]}{[HA]}\right)$$

This formula is used to prepare buffers with a specific pH and to understand their capacity to absorb added acid or base.

- **Solubility Equilibria (K_{sp})**

    These govern the dissolution of sparingly soluble ionic solids. The **Solubility Equilibria (K_{sp})** determines the maximum concentration of ions that can exist in equilibrium in a solution.

    - **Precipitation reactions** are used in gravimetric analysis to separate and quantify analytes. By controlling the solution conditions pH, common ion effects), analysts can ensure quantitative precipitation.

- **Complex Ion Equilibria (K_f, K_d)**
    These involve the formation of stable complex ions between metal ions and ligands (e.g., EDTA titrations).

    - The **Formation Constant (K_f)** or **Stability Constant** measures how readily a metal ion binds to a ligand. Complexation is often used to **mask** interfering ions, increasing the **selectivity** of an analytical method by preventing unwanted side reactions.

- **Redox Equilibria (E^0, Nernst Equation)**

    These involve the transfer of electrons and are the basis of electrochemical methods (potentiometry, voltammetry) and redox titrations.
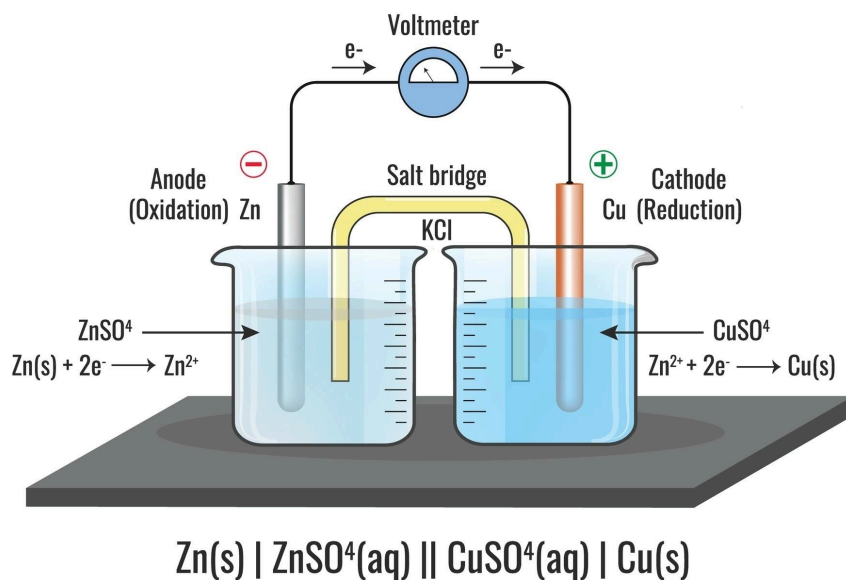   - The position of a redox equilibrium is determined by the **standard reduction potentials (E^0)** of the half-reactions.

- The **Nernst Equation** relates the cell potential (E) to the concentrations (or activities) of the reactants and products, which is critical for measuring concentrations electrochemically:

$$E = E^0 - \frac{RT}{nF} \ln Q$$

  where Q is the reaction quotient, n is the moles of electrons, and T is temperature.

Electrochemical cell

Zn(s) | ZnSO⁴(aq) || CuSO⁴(aq) | Cu(s)

References:

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