Notes for Exam Preparation: Equilibrium

Introduction

Chemical equilibrium is a fundamental concept in chemistry where reactions occur in both the forward and reverse directions, eventually reaching a state where the rates of the forward and reverse reactions are equal. This equilibrium can be influenced by changes in concentration, pressure, and temperature, and understanding these effects is crucial for predicting and controlling chemical reactions in various industrial processes.

Reversible Reactions and Equilibrium

Reversible Reactions

Reversible reactions are those in which the reactants can form products and the products can revert to reactants simultaneously. These reactions are represented with a double arrow ($\rightleftharpoons$), indicating the forward and reverse reactions.

Characteristics of Equilibrium

Equilibrium is characterized by:

- **Dynamic Nature**: Both forward and reverse reactions occur at the same rate.
- **Constant Concentrations**: The concentrations of reactants and products remain constant over time.
- **Closed System Requirement**: Equilibrium can only be achieved in a closed system where no reactants or products can escape.

Changing the Position of Equilibrium

The position of equilibrium can be shifted by changes in concentration, pressure, and temperature. This shift follows Le Chatelier's principle, which states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

Effect of Concentration on Equilibrium

- **Increasing the concentration of reactants**: Shifts the equilibrium towards the products.
- **Increasing the concentration of products**: Shifts the equilibrium towards the reactants.

Effect of Pressure on Equilibrium

The effect of pressure changes depends on the number of gas molecules on either side of the balanced equation.

- **Increasing Pressure**:
  - If fewer gas molecules are on the right side: Equilibrium shifts towards the products (e.g., $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$)
  - If more gas molecules are on the right side: Equilibrium shifts towards the reactants (e.g., $N_2O_4(g) \rightleftharpoons 2NO_2(g)$)
  - **Decreasing Pressure**:
  - If fewer gas molecules are on the right side: Equilibrium shifts towards the reactants.
  - If more gas molecules are on the right side: Equilibrium shifts towards the products.

Effect of Temperature on Equilibrium

The effect of temperature changes depends on whether the reaction is exothermic or endothermic.

- **Increasing Temperature**:
  - For exothermic reactions (heat is a product): Shifts the equilibrium towards the reactants.
  - For endothermic reactions (heat is a reactant): Shifts the equilibrium towards the products.
- **Decreasing Temperature**:
  - For exothermic reactions: Shifts the equilibrium towards the products.
  - For endothermic reactions: Shifts the equilibrium towards the reactants.

Effect of Catalysts on Equilibrium

Catalysts do not affect the position of equilibrium. They only speed up the rate at which equilibrium is achieved by lowering the activation energy for both the forward and reverse reactions.

Equilibrium Expressions and the Equilibrium Constant, Kc

Equilibrium Constant (Kc)

The equilibrium constant in terms of concentration (Kc) is a measure of the ratio of the concentrations of the products to the reactants at equilibrium.

- For a general reaction $aA+bB \rightleftharpoons cC+dD$
- $K_c=[C]^c[D]^d / [A]^a[B]^b$
- **Effect of Changes on Kc**
- **Concentration**: Changes in concentration do not affect the value of Kc. They only shift the position of equilibrium.

- **Pressure**: Changes in pressure do not affect the value of Kc for reactions involving gases.
- **Temperature**: Changes in temperature can alter the value of Kc. For exothermic reactions, increasing temperature decreases Kc, and for endothermic reactions, increasing temperature increases Kc.

Equilibria in Gas Reactions: The Equilibrium Constant, Kp

Equilibrium Constant (Kp)

The equilibrium constant in terms of partial pressures (Kp) is used for gaseous reactions.

- For the reaction $aA(g)+bB(g)\rightleftharpoons cC(g)+dD(g)a$
- $Kp=(P_C)^c(P_D)^d/ (P_A)^a(P_B)^b$

Units of Kp

The units of Kp depend on the stoichiometry of the reaction and the partial pressures involved. They are typically expressed in terms of atm, kPa, or bar.

Calculations Using Partial Pressures

- Given partial pressures of reactants and products at equilibrium, Kp can be calculated using the equilibrium expression.
- For example, if $P_{N_2}=0.2atm$, $P_{H_2}=0.6atm$, and $P_{NH3}=0.4atm$ for the reaction N2+3H2⇌2NH3N_2 + 3H_2 \rightleftharpoons 2NH_3N2+3H2⇌2NH3:
- $Kp=(PNH3)^2 / (PN_2)(PH_2)^3$

  $=(0.4)2(0.2)(0.6)3$

Industrial Applications of Equilibrium

The Haber Process

The Haber process synthesizes ammonia from nitrogen and hydrogen: $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$

- **Conditions**:
  - High pressure (200 atm): Favors the production of ammonia.
  - Moderate temperature (450°C): Balances rate and yield.
  - Iron catalyst: Speeds up the reaction without affecting the equilibrium position.

The Contact Process

The Contact process produces sulfuric acid from sulfur dioxide: $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$

- **Conditions**:
  - High pressure (2 atm): Favors the production of sulfur trioxide.
  - High temperature (450°C): Increases the reaction rate.
  - Vanadium(V) oxide catalyst: Increases the rate of attainment of equilibrium.

Acid-Base Equilibria

Simple Definitions of Acids and Bases

- **Arrhenius Definition**:
  - Acid: Produces H^+ ions in water.
  - Base: Produces OH^- ions in water.

Brønsted–Lowry Theory

- **Acid**: Proton donor.
- **Base**: Proton acceptor.

Conjugate Acids and Bases

- When an acid donates a proton, it forms its conjugate base.
- When a base accepts a proton, it forms its conjugate acid.

Strong and Weak Acids and Bases

- **Strong Acids/Bases**: Fully dissociate in water.
  - Example: $HCl \rightarrow H^+ + Cl^-$HCl
- **Weak Acids/Bases**: Partially dissociate in water.
  - Example: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
- **pH Values**:
  - Strong acids/bases have extreme pH values (low for acids, high for bases).
  - Weak acids/bases have pH values closer to 7.

Practice Problems

Problem 1: Le Chatelier's Principle

- Given the reaction: $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$

  How will the equilibrium position change if:

  - The concentration of SO_2 is increased?
  - The pressure is increased?
  - The temperature is decreased (exothermic reaction)?

Problem 2: Equilibrium Constant Calculation

- Calculate Kc for the reaction $N_2+3H_2 \rightleftharpoons 2NH_3$

  if $[N_2]=0.2M, [H_2]=0.6M, [NH_3]=0.4M$

Problem 3: Industrial Process Application

- Explain how the principles of Le Chatelier apply to the industrial production of ammonia in the Haber process, considering changes in temperature and pressure.

Problem 4: Strong vs. Weak Acids

- Compare the pH and extent of dissociation of 1M HCl (strong acid) and 1M CH_3COOH (weak acid).

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