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## Equilibrium

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### Equilibrium State

Equilibrium is a state of a system where its observable properties remain constant over time under a given set of conditions. At equilibrium, the forward and backward reactions occur at the same rate, resulting in no net change in the composition of the system.

### Physical and Chemical Equilibrium

Physical equilibrium involves reversible physical processes such as phase changes or dissolution, where different phases coexist without net change. Examples include solid-liquid, liquid-vapour, and solid-vapour equilibria. Chemical equilibrium occurs in chemical reactions where the rate of the forward reaction equals the rate of the backward reaction, maintaining constant concentrations of reactants and products.

### Henry's Law

Henry's Law states that the mass of a gas dissolved in a given mass of solvent at a constant temperature is directly proportional to the pressure of the gas above the solvent.

Mathematically,  $m \propto P$ , where  $m$  is the mass of gas dissolved and  $P$  is the pressure.

## Law of Mass Action

This law states that at constant temperature, the rate of a chemical reaction is proportional to the product of the molar concentrations of the reactants, each raised to the power of their stoichiometric coefficients in the balanced chemical equation.

## Equilibrium Constant

The equilibrium constant expresses the ratio of the product of concentrations of products to that of reactants, each raised to the power of their stoichiometric coefficients. It is denoted as  $K_c$  when expressed in terms of concentrations and  $K_p$  when expressed in terms of partial pressures for gaseous systems.

## Homogeneous and Heterogeneous Equilibria

Homogeneous equilibrium involves reactants and products in the same phase, for example, gases reacting together. Heterogeneous equilibrium involves reactants and products in different phases, such as a solid in equilibrium with its vapor.

## Le Chatelier's Principle

This principle states that if a system at equilibrium experiences a change in concentration, pressure, or temperature, the system adjusts to counteract the change and restore a new equilibrium.

## Factors Affecting Equilibrium

- **Concentration:** Changing the concentration of reactants or products shifts the equilibrium to minimize the change.

- **Pressure:** Increasing pressure favors the side with fewer moles of gas; decreasing pressure favors the side with more moles.
- **Temperature:** Increasing temperature favors the endothermic direction; decreasing temperature favors the exothermic direction.
- **Inert Gas Addition:** Adding an inert gas at constant volume does not affect equilibrium.
- **Catalyst:** Catalysts speed up the attainment of equilibrium but do not change its position.

## Solved Examples

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### Example 1: Calculating Equilibrium Constant $K_C$

Consider the reaction:  $2NO_2(g) \rightleftharpoons N_2O_4(g)$ . At equilibrium, the concentration of  $NO_2$  is 0.04 mol/L and  $N_2O_4$  is 0.06 mol/L. Calculate the equilibrium constant  $K_C$ .

**Solution:**

Write the expression for  $K_C$ :

$$K_C = [N_2O_4] / [NO_2]^2$$

Substitute the values:

$$K_C = 0.06 / (0.04)^2 = 0.06 / 0.0016 = 37.5$$

Therefore, the equilibrium constant  $K_C$  is 37.5.

### Example 2: Effect of Pressure on Equilibrium

For the reaction  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ , predict the effect of increasing pressure on the position of equilibrium.

## Solution:

The reaction involves 4 moles of gas on the reactant side and 2 moles on the product side. Increasing pressure favors the side with fewer moles of gas. Therefore, the equilibrium shifts towards the formation of ammonia ( $\text{NH}_3$ ).

## Practice Set

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- **Level 1 (Easy):** Define dynamic equilibrium and give an example.
- **Level 2 (Moderate):** Write the expression for the equilibrium constant  $K_c$  for the reaction:  $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$ .
- **Level 3 (Challenging):** For the reaction  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ , if the equilibrium constant  $K_c$  is 500 at a certain temperature, calculate the concentration of  $\text{SO}_3$  when the concentrations of  $\text{SO}_2$  and  $\text{O}_2$  are 0.1 mol/L and 0.05 mol/L respectively.

## Answer Key

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- **Level 1:** Dynamic equilibrium is a state where the forward and backward reactions occur at the same rate, resulting in no net change in concentrations. Example: Liquid water in equilibrium with its vapor.
- **Level 2:**  $K_c = [\text{COCl}_2] / ([\text{CO}][\text{Cl}_2])$
- **Level 3:** Using  $K_c = [\text{SO}_3]^2 / ([\text{SO}_2]^2[\text{O}_2])$ , substitute values:  
$$500 = [\text{SO}_3]^2 / (0.1^2 \times 0.05) = [\text{SO}_3]^2 / 0.0005$$
Therefore,  $[\text{SO}_3]^2 = 500 \times 0.0005 = 0.25$ 
$$[\text{SO}_3] = \sqrt{0.25} = 0.5 \text{ mol/L}$$

## Ionic Equilibrium

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### Electrolytes and Ionization

Electrolytes are substances that conduct electricity when dissolved in water due to the presence of ions formed by dissociation. Strong electrolytes completely dissociate into ions, while weak electrolytes partially dissociate establishing an equilibrium between ions and undissociated molecules.

## Acids and Bases

An acid is a substance that donates  $H^+$  ions in aqueous solution (Arrhenius concept), acts as a proton donor (Bronsted concept), and accepts electron pairs (Lewis concept). Acids turn blue litmus paper red and react with metals to liberate hydrogen gas.

A base furnishes  $OH^-$  ions in aqueous solution (Arrhenius concept), accepts protons (Bronsted concept), and donates electron pairs (Lewis concept). Bases turn red litmus paper blue and have a bitter taste and soapy feel.

## Neutralization and Conjugate Acid-Base Pairs

Neutralization involves the combination of  $H^+$  and  $OH^-$  ions to form water. A conjugate acid-base pair differs by one proton; a strong acid has a weak conjugate base and vice versa.

## pH and pOH

pH is the negative logarithm of the hydronium ion concentration:  $pH = -\log[H_3O^+]$ . pOH is the negative logarithm of hydroxide ion concentration:  $pOH = -\log[OH^-]$ . At 25°C,  $pH + pOH = 14$ .

## Strength of Acids and Bases

Acid strength depends on bond strength and polarity. Weaker H-A bonds and greater polarity increase acid strength. The dissociation constants  $K_a$  and  $K_b$  measure acid and

base strengths respectively, with larger  $K_a$  or smaller  $pK_a$  indicating stronger acids.

## Common Ion Effect and Hydrolysis

The common ion effect suppresses the dissociation of weak electrolytes in the presence of a common ion. Hydrolysis is the reverse of neutralization, where ions react with water to produce acidic or basic solutions. Salts of strong acids and bases do not hydrolyze and are neutral, while salts of strong acids with weak bases or vice versa hydrolyze to give acidic or basic solutions.

## Solved Examples

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### Example 1: Calculating pH of a Strong Acid

Calculate the pH of a 0.01 M HCl solution.

**Solution:**

HCl is a strong acid and dissociates completely, so  $[H^+] = 0.01$  M.

$$\text{pH} = -\log(0.01) = 2.$$

### Example 2: Effect of Common Ion

Explain the effect of adding NaCl to a solution of HCl.

**Solution:**

NaCl provides  $Cl^-$  ions, a common ion with HCl. This suppresses the dissociation of HCl, reducing the concentration of  $H^+$  ions and increasing the pH slightly.

## Practice Set

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- **Level 1 (Easy):** Define an acid and a base according to Arrhenius theory.
- **Level 2 (Moderate):** Calculate the pH of a solution with  $[\text{OH}^-] = 1 \times 10^{-4} \text{ M}$ .
- **Level 3 (Challenging):** Explain the common ion effect with an example.

## Answer Key

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- **Level 1:** Acid: Substance that increases  $\text{H}^+$  ions in aqueous solution. Base: Substance that increases  $\text{OH}^-$  ions in aqueous solution.
- **Level 2:**  $\text{pOH} = -\log(1 \times 10^{-4}) = 4$ ;  $\text{pH} = 14 - 4 = 10$ .
- **Level 3:** The common ion effect is the suppression of ionization of a weak electrolyte by the addition of a common ion. Example: Adding NaCl to acetic acid solution reduces acetic acid ionization.

## Buffer and Solubility

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### Buffer Solutions

A buffer solution resists changes in pH upon dilution or addition of small amounts of acid or base. The pH of an acidic buffer is given by the Henderson–Hasselbalch equation:  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right)$ . For basic buffers,  $\text{pOH} = \text{p}K_b + \log\left(\frac{[\text{Salt}]}{[\text{Base}]}\right)$ .

### Solubility Product

When a sparingly soluble salt dissolves in water, an equilibrium is established between the undissolved solid and its ions in solution. The solubility product constant,  $K_{\text{sp}}$ , is the product of the molar concentrations of the ions, each raised to the power of their stoichiometric coefficients.

## Common Ion Effect on Solubility

The presence of a common ion decreases the solubility of a salt. The solubility of salts of weak acids increases with decreasing pH due to increased  $\text{H}_3\text{O}^+$  concentration.

## Predicting Precipitation

Using the ionic product  $Q$  and solubility product  $K_{sp}$ , precipitation occurs if  $Q > K_{sp}$ , dissolution if  $Q < K_{sp}$  and equilibrium if  $Q = K_{sp}$ .

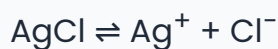
## Solved Examples

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### Example 1: Calculating Solubility Product

Calculate the solubility product of AgCl if its solubility is  $1.3 \times 10^{-5}$  mol/L.

**Solution:**



$$\text{Solubility, } S = 1.3 \times 10^{-5} \text{ mol/L}$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = S \times S = S^2 = (1.3 \times 10^{-5})^2 = 1.69 \times 10^{-10}$$

### Example 2: Buffer pH Calculation

Calculate the pH of a buffer solution containing 0.1 M acetic acid ( $\text{p}K_a = 4.76$ ) and 0.1 M sodium acetate.

**Solution:**

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right) = 4.76 + \log(0.1/0.1) = 4.76 + 0 = 4.76$$

## Practice Set

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- **Level 1 (Easy):** Define a buffer solution.
- **Level 2 (Moderate):** Calculate the solubility product of  $\text{BaSO}_4$  if its solubility is  $1.0 \times 10^{-4}$  mol/L.
- **Level 3 (Challenging):** Explain how the common ion effect influences the solubility of a salt.

## Answer Key

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- **Level 1:** A buffer solution resists changes in pH when small amounts of acid or base are added.
- **Level 2:**  $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$   
 $K_{\text{sp}} = S \times S = (1.0 \times 10^{-4})^2 = 1.0 \times 10^{-8}$
- **Level 3:** The common ion effect decreases the solubility of a salt by shifting the equilibrium towards the solid, reducing ionization in solution.

## Quick Reference Table

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## Common Mistakes and Misconceptions

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## Glossary

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