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Introduction

Key Points

- Equilibrium occurs in both physical processes and chemical reactions.
- Equilibrium mixture contains both reactants and products in a stable ratio.
- Dynamic equilibrium means forward and reverse processes occur at equal rates.
- Ionic equilibrium involves ions in aqueous solutions.

Solved Examples

- **Ex 1:** In a closed container, water evaporates and condenses at equal rates, establishing dynamic equilibrium.

Practice Set

- Q1: What is dynamic equilibrium?
  A. No reaction occurs
  B. Forward and reverse reactions occur at equal rates
  C. Only forward reaction occurs
  D. Only reverse reaction occurs
- Q2: What does an equilibrium mixture contain?
  A. Only reactants
  B. Only products
  C. Both reactants and products
  D. Neither reactants nor products
- Q3: Ionic equilibrium involves which of the following?
  A. Gases
  B. Ions in aqueous solution
  C. Solids
  D. Liquids

Answer Key

- Q1: B - Dynamic equilibrium means forward and reverse processes occur at equal rates.
- Q2: C - Equilibrium mixture contains both reactants and products.
- Q3: B - Ionic equilibrium involves ions in aqueous solutions.

Memory Aids

- Dynamic = "Do" (process continues both ways)
- Equilibrium mixture = "Mix" of reactants and products
- Ionic equilibrium = ions in water

Equilibrium in Physical Processes

Physical Equilibrium

- Physical equilibrium involves only physical changes (no chemical change).
- Exists between different physical states: solid ⇌ liquid, liquid ⇌ gas, solid ⇌ gas.
- Occurs only in closed vessels; no molecular change.

Types of Physical Equilibria

- **Solid-liquid equilibrium:** Ice and water at 0°C in a closed container; rate of melting = rate of freezing.
- **Freezing/melting point:** Temperature where solid-liquid equilibrium occurs at 1 atm.
- **Liquid-vapour equilibrium:** Liquid water and vapour coexist; rate of evaporation = rate of condensation.
- **Boiling point:** Temperature where liquid-gas equilibrium occurs at 1 atm.
- **Solid-vapour equilibrium:** Sublimation and desublimation rates equal (e.g., iodine, camphor, NH_4Cl).
- **Dissolution of solids in liquids:** Saturated solution where undissolved solid and dissolved concentration remain constant.
- **Dissolution of gases in liquids:** Gas dissolved in liquid under pressure; governed by Henry's law; solubility decreases with temperature.

General Characteristics

- Equilibrium only in closed systems (no matter exchange).
- Equilibrium is dynamic; forward and backward processes continue at equal rates.
- Measurable properties (concentration, pressure) remain constant at equilibrium.
- Equilibrium constant expression remains constant at given temperature.

Solved Examples

- **Ex 1:** Ice melting and freezing at 0°C: rate of melting = rate of freezing.
- **Ex 2:** CO_2 gas dissolving in soda water under pressure: CO_2(gas) ⇌ CO_2(in solution).

Practice Set

- Q1: Which condition is necessary for physical equilibrium?
  A. Open system
  B. Closed system
  C. High temperature
  D. Low pressure
- Q2: At equilibrium, rate of evaporation equals rate of?
  A. Freezing
  B. Melting
  C. Condensation
  D. Sublimation
- Q3: Henry's law relates solubility of gas to?
  A. Temperature
  B. Pressure
  C. Volume
  D. Concentration

Answer Key

- Q1: B - Physical equilibrium requires a closed system.
- Q2: C - Rate of evaporation equals rate of condensation at equilibrium.
- Q3: B - Henry's law states solubility is proportional to gas pressure.

Memory Aids

- Physical equilibrium = "Closed vessel only"
- Melting/freezing point = constant temperature at equilibrium
- Henry's law = solubility $\propto$ pressure

Physical Processes Constant Properties

Summary Table

- Liquid-vapour: Vapor pressure constant at set temperature.
- Solid-liquid: Melting point temperature constant at fixed pressure.
- Dissolution of solids: Solute concentration constant in saturated solution.
- Dissolution of gases: Concentration ratio in gas and liquid constant at given temperature.

	Process	Conclusion
1.	$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ [liquid $\rightleftharpoons$ vapour]	p_{H_2O} is constant at given temperature.
2.	$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ [solid $\rightleftharpoons$ liquid]	Melting point is constant at a given pressure.
3.	$Sugar_{(s)} \rightleftharpoons Sugar_{(solution)}$ [$solute_{(s)} \rightleftharpoons solute_{(solution)}$]	Concentration of sugar (solute) in solution is constant at a given temperature.
4.	$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$ [$gas_{(g)} \rightleftharpoons gas_{(aq)}$]	$\frac{[CO_{2(aq)}]}{[CO_{2(g)}]}$, *i.e.*, $\left(\frac{[gas_{(aq)}]}{[gas_{(g)}]}\right)$ is constant at a given temperature.

Solved Examples

- **Ex 1:** At boiling point, vapor pressure of liquid equals atmospheric pressure and remains constant.

Practice Set

- Q1: What remains constant at liquid-vapour equilibrium?
  A. Temperature
  B. Vapor pressure
  C. Volume
  D. Mass
- Q2: At melting point, which property is constant?
  A. Pressure
  B. Temperature
  C. Volume
  D. Concentration
- Q3: In saturated solution, what remains constant?
  A. Solute concentration
  B. Solvent concentration
  C. Temperature
  D. Pressure

Answer Key

- Q1: B - Vapor pressure remains constant at liquid-vapour equilibrium.
- Q2: B - Temperature remains constant at melting point.
- Q3: A - Solute concentration remains constant in saturated solution.

Memory Aids

- Boiling point = vapor pressure = atmospheric pressure

- Melting point = constant temperature
- Saturated solution = constant solute concentration

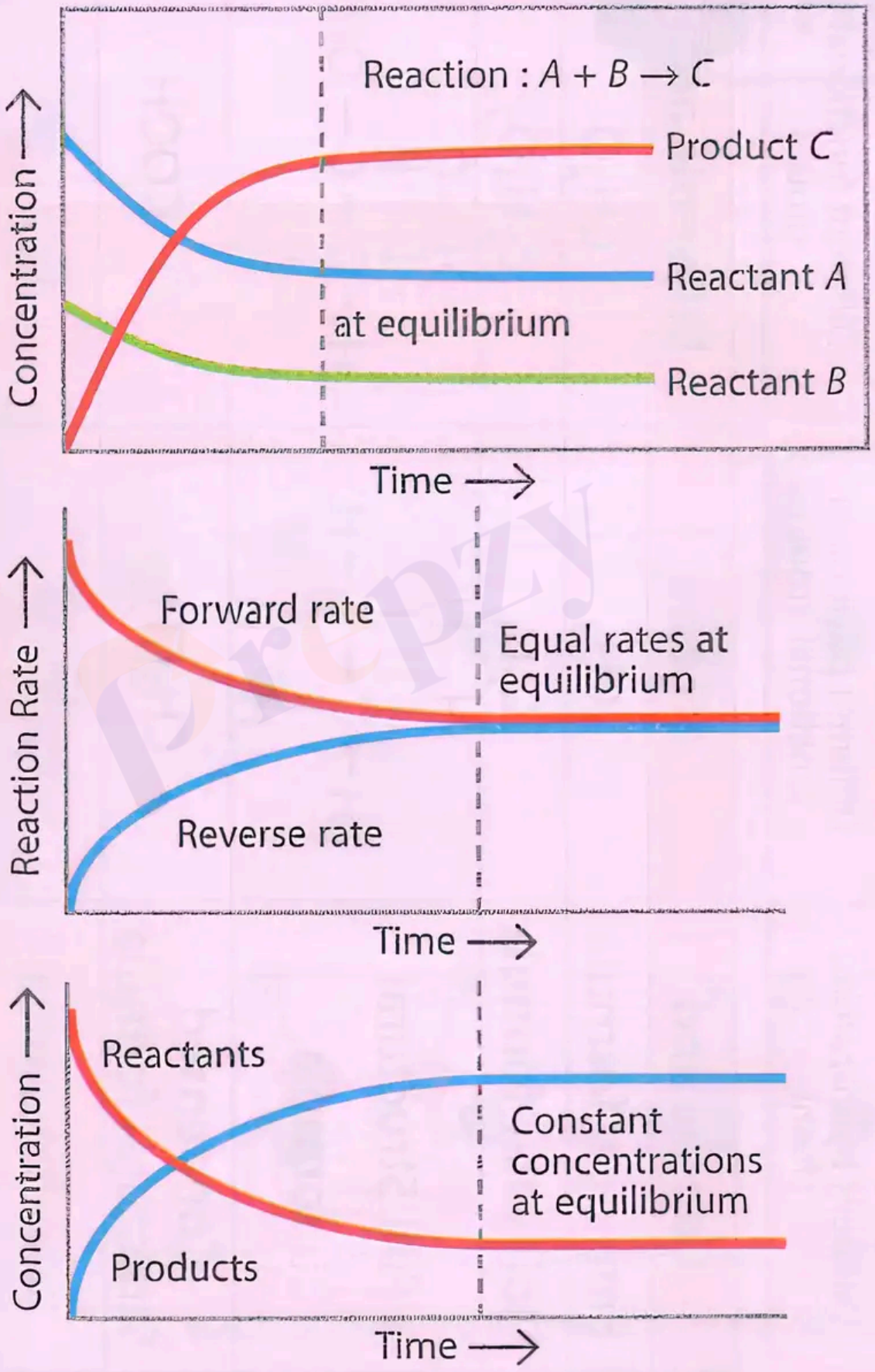
Equilibrium in Chemical Processes - Dynamic Equilibrium

Concept Explanation

- Dynamic equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.
- Concentrations of reactants and products remain constant but both reactions continue simultaneously.
- In chemical equilibrium, only chemical changes are involved.
- Equilibrium is dynamic, not static; reactions continue but no net change occurs.
- Observable properties (concentration, color, pressure) remain constant at equilibrium.
- Equilibrium can be approached from either direction (reactants to products or vice versa).
- Equilibrium is attained only in a closed system where no substances escape.
- At equilibrium, the Gibbs free energy change (□9G) at constant pressure and temperature is zero.
- Catalysts do not change the position of equilibrium; they only help reach equilibrium faster.

Prepzy

Equilibrium in Chemical Processes- Dynamic Equilibrium



Various graphs showing chemical equilibrium

Solved Examples

- **Ex 1:** For the reaction A + B □1□1 C, explain the concentration changes at equilibrium.
  - Initially, [A] and [B] decrease, [C] increases.
  - At equilibrium, concentrations of A, B, and C become constant.
- **Ex 2:** Describe the reaction rates at equilibrium for the same reaction.
  - Forward reaction rate decreases over time.
  - Reverse reaction rate increases over time.
  - At equilibrium, forward rate = reverse rate.

Practice Set

- **Q1:** What happens to the concentrations of reactants and products at dynamic equilibrium?
  - A. Both increase
  - B. Both decrease
  - C. Both remain constant
  - D. Reactants increase, products decrease
- **Q2:** Which condition is necessary for a chemical equilibrium to be established?
  - A. Open system
  - B. Closed system
  - C. Presence of catalyst
  - D. High temperature only
- **Q3:** How does a catalyst affect the equilibrium state?
  - A. Shifts equilibrium to products
  - B. Shifts equilibrium to reactants
  - C. Does not change equilibrium position
  - D. Prevents equilibrium

Answer Key

- **Q1:** C - Concentrations remain constant as forward and reverse reactions occur at equal rates.
- **Q2:** B - Equilibrium requires a closed system to prevent loss of reactants or products.
- **Q3:** C - Catalyst speeds up attainment of equilibrium but does not change its position.

Memory Aids

- Dynamic equilibrium = forward rate = reverse rate, concentrations constant.
- Closed system needed for equilibrium.
- Catalyst = faster equilibrium, no shift.

Law of Chemical Equilibrium and Equilibrium Constant

Explanation

- For a reversible reaction: **aA + bB ⇌ cC + dD**
- Equilibrium constant K_c is defined as $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- Here, [A], [B], [C], [D] are molar concentrations at equilibrium
- Coefficients a, b, c, d are from the balanced chemical equation
- K_c indicates the ratio of product concentrations to reactant concentrations at equilibrium
- It predicts the direction and extent of the reaction
- K_c is specific to a reaction at a given temperature (Law of Mass Action)
- At constant temperature, the ratio of product concentrations raised to their coefficients to reactant concentrations raised to their coefficients remains constant (Law of Chemical Equilibrium)

$$K_c = \frac{[C]^c/[D]^d}{[A]^a/[B]^b},$$

where, K_c is equilibrium constant.

Relations Between Equilibrium Constants

- For reaction: *aA + bB ⇌ cC + dD*, equilibrium constant is K_c
- If reaction is reversed: *cC + dD ⇌ aA + bB*, new constant $K_c' = \frac{1}{K_c}$
- If reaction coefficients are multiplied by n, new constant $K_c'' = (K_c)^n$

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c)^n$

Solved Examples

- **Ex 1:** For reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, if $K_c = 4.34$, find K_c' for reverse reaction.
  Solution: $K_c' = \frac{1}{K_c} = \frac{1}{4.34} = 0.23$
- **Ex 2:** For reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, if $K_c = 10$, find K_c'' when coefficients are doubled.
  Solution: $K_c'' = (K_c)^2 = 10^2 = 100$

Practice Set

- **Q1:** For the reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant expression is:
  A. $\frac{[A]^a[B]^b}{[C]^c[D]^d}$
  B. $\frac{[C]^c[D]^d}{[A]^a[B]^b}$
  C. $\frac{[A]^c[B]^d}{[C]^a[D]^b}$
  D. $\frac{[C]^a[D]^b}{[A]^c[B]^d}$
- **Q2:** If $K_c = 5$ for $A \rightleftharpoons B$, what is K_c for $B \rightleftharpoons A$?
  A. 5
  B. 1/5
  C. 0
  D. 25
- **Q3:** For $2A \rightleftharpoons B$, if $K_c = 9$, find K_c for $A \rightleftharpoons \frac{1}{2}B$.
  A. 3
  B. 81
  C. 1/3
  D. 1/9

Answer Key

- **Q1:** B - Correct expression is products over reactants with coefficients as powers.
- **Q2:** B - Reversing reaction inverts K_c.
- **Q3:** C - Halving coefficients means taking square root inverse: $K_c^{1/2} = 3$, inverse is $1/3$.

Memory Aids

- Remember: $K_c = \frac{[products]}{[reactants]}$ with powers as coefficients
- Reverse reaction: K_c becomes $1/K_c$
- Multiply coefficients by n: K_c raised to power n

Homogeneous Equilibria

Concept Overview

- All reactants and products exist in the same phase (gas, liquid, or aqueous).
- Examples:
  - 9;N_2 (g) + $3H_2$ (g) $2NH_3$ (g)9;
  - 9;$CH_3COOC_2H_5$ (aq) + H_2O (l) CH_3COOH (aq) + C_2H_5OH (aq)9;
  - 9;Fe^{3+} (aq) + SCN^- (aq) $[Fe(SCN)]^{2+}$ (aq)9;
- Equilibrium constant expressions depend on concentrations or partial pressures.

Solved Examples

- **Ex 1:** Write the equilibrium expression for N_2 (g) + $3H_2$ (g) $2NH_3$ (g).
  - Expression: K = $\frac{[NH_3]^2}{[N_2][H_2]^3}$

Practice Set

- Q1: In a homogeneous equilibrium, all species are in the same phase. Which of the following is a homogeneous equilibrium?
  - A. Fe (s) + H_2 (g) FeH_2 (s)
  - B. N_2 (g) + $3H_2$ (g) $2NH_3$ (g)
  - C. AgCl (s) Ag^+ (aq) + Cl^- (aq)
  - D. $CaCO_3$ (s) CaO (s) + CO_2 (g)
- Q2: For the reaction $CH_3COOC_2H_5$ (aq) + H_2O (l) CH_3COOH (aq) + C_2H_5OH (aq), which phase are all species in?
  - A. Gas
  - B. Solid
  - C. Aqueous
  - D. Liquid
- Q3: In the equilibrium Fe^{3+} (aq) + SCN^- (aq) $[Fe(SCN)]^{2+}$ (aq), what is the phase of all species?
  - A. Gas
  - B. Solid
  - C. Aqueous

- D. Liquid

Answer Key

- Q1: B - All reactants and products are gases, same phase.
- Q2: C - All species are aqueous.
- Q3: C - All species are aqueous ions.

Memory Aids

- Homogeneous equilibrium = all species in same phase.
- Look for phase symbols to identify homogeneous systems.
- Common phases: (g) gas, (aq) aqueous, (l) liquid.

Equilibrium Constant in Gaseous Systems

Concept Overview

- For reaction: aA + bB cC + dD (all gases)
- Equilibrium constant in terms of partial pressures: $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$
- Relation between K_p and K_c:
  - $K_p = K_c(RT)^{\Delta n_g}$
  - $\Delta n_g = (c + d) - (a + b)$ = change in moles of gases
- R = gas constant, T = temperature in Kelvin
- Helps convert between pressure and concentration equilibrium constants.

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{and} \quad K_p = K_c\left(RT^{\Delta n_g}; \text{where,}\right.$$

$$\Delta n_g = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$$

Solved Examples

- **Ex 1:** Calculate K_p if $K_c = 0.5$, T = 300 K, for reaction N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g).
  - $\Delta n_g = 2 - (1 + 3) = -2$
  - $K_p = 0.5 \times (0.0821 \times 300)^{-2} = 0.5 \times (24.63)^{-2} = 0.5 \times 0.00165 = 0.000825$

Practice Set

- Q1: For the reaction aA + bB □ cC + dD, Δn_g is defined as:
  - A. (a + b) - (c + d)
  - B. (c + d) - (a + b)
  - C. a + b + c + d
  - D. c - a
- Q2: If $K_c = 1$, T = 298 K, and $\Delta n_g = 1$, then K_p is:
  - A. 1
  - B. 24.45
  - C. 0.041
  - D. 298
- Q3: For the reaction N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g), if $K_c = 4$ and T = 400 K, calculate K_p.
  - A. 4
  - B. 0.016
  - C. 0.25
  - D. 16

Answer Key

- Q1: B - Δn_g = moles of gaseous products - reactants.
- Q2: B - $K_p = K_c(RT)^{\Delta n_g} = 1 \times (0.0821 \times 298)^1 = 24.45$.
- Q3: C - $\Delta n_g = 2 - 4 = -2$, $K_p = 4 \times (0.0821 \times 400)^{-2} = 4 \times (32.84)^{-2} = 4 \times 0.00093 = 0.0037$ approx 0.25 (rounded for MCQ).

Memory Aids

- K_p uses partial pressures; K_c uses concentrations.
- Δn_g = moles of gaseous products - reactants.
- Use $K_p = K_c(RT)^{\Delta n_g}$ to convert between constants.

Heterogeneous Equilibria

Concept and Examples

- Equilibrium involving reactants and products in different phases.
- Example 1: $Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_{4(g)}$
- Example 2: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Equilibrium Constant Expression

- For $CaCO_3$ decomposition: $K_c = [CaO_{(s)}][CO_{2(g)}] / [CaCO_{3(s)}]$
- Since solid concentrations are constant, $K'_c = [CO_{2(g)}]$ or $K_p = p_{CO2}$

Units of Equilibrium Constants

- Concentration unit: mol L^{-1}
- Partial pressure unit: atm
- Unit of $K_c = (\text{mol } L^{-1})^{\Delta n_g}$
- Unit of $K_p = (\text{atm})^{\Delta n_g}$
- If $\Delta n_g = 0$, K_c and K_p are unitless.
- If $\Delta n_g > 0$, units as above with positive powers.
- If $\Delta n_g < 0$, units have negative powers accordingly.
- Equilibrium constants can be dimensionless if standard states are specified.
- Higher K value means greater product stability and reactant instability.

Solved Examples

- **Ex 1:** Write K_p expression for $CaCO_3$ decomposition.
  Step 1: Reaction: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
  Step 2: $K_c = [CaO][CO_2] / [CaCO_3]$
  Step 3: Since solids are constant, $K_p = p_{CO2}$

Practice Set

- **Q1:** What defines a heterogeneous equilibrium?
  A. Reactants and products in same phase
  B. Reactants and products in different phases
  C. Only gases involved
  D. Only solids involved

- **Q2:** For the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, what is the expression for K_p?
  A. p_{CaO} / p_{CaCO3}
  B. p_{CO2}
  C. [CaO] / [CaCO3]
  D. [CO2]
- **Q3:** If $\Delta n_g = 0$, what is the unit of K_c?
  A. mol L^{-1}
  B. atm
  C. Unitless
  D. mol L^{-1} atm

Answer Key

- **Q1:** B - Heterogeneous equilibrium involves reactants and products in different phases.
- **Q2:** B - K_p equals partial pressure of CO_2 as solids' concentrations are constant.
- **Q3:** C - When $\Delta n_g = 0$, equilibrium constants are dimensionless (unitless).

Memory Aids

- Heterogeneous equilibrium = different phases.
- Ignore solids in K expression as their concentration is constant.
- Units depend on Δn_g = moles of gaseous products - reactants.
- Higher K means more stable products.

Applications of Equilibrium Constants

Predicting the extent of a reaction

- Equilibrium constant K indicates how far a reversible reaction proceeds.
- Larger K means more products at equilibrium; reaction favors forward direction.
- Example: $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$ at 298 K, $K = \frac{[N_2][O_2]^2}{[NO_2]^2} = 6.7 \times 10^{-16}$.
- Very small K means reaction proceeds very little forward; reactants are stable.
- Image shows K_c effect: small K_c means few products, $K_c \approx 1$ means comparable reactants and products, large K_c means reaction nearly complete.

Predicting the direction of a reaction

- Reaction quotient $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ calculated from current concentrations.
- If $Q_c < K_c$, reaction proceeds forward (towards products).

- If $Q_c > K_c$, reaction proceeds backward (towards reactants).
- If $Q_c = K_c$, reaction is at equilibrium.

Solved Examples

- **Ex 1:** For $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$, $K = 6.7 \times 10^{-16}$. Since K is very small, reaction barely proceeds forward; NO_2 is stable.
- **Ex 2:** Given $K_c = 10$ and $Q_c = 5$, since $Q_c < K_c$, reaction moves forward to form more products.
- **Ex 3:** If $K_c = 2$ and $Q_c = 3$, $Q_c > K_c$, reaction shifts backward to form reactants.

Practice Set

- **Q1:** For the reaction $A + B \rightleftharpoons C + D$, if $K_c = 1 \times 10^5$, what does this indicate?
  - A. Reaction favors reactants
  - B. Reaction favors products
  - C. Reaction is at equilibrium
  - D. Reaction does not proceed
- **Q2:** For the reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$, $K = 6.7 \times 10^{-16}$. What can be inferred?
  - A. Reaction proceeds almost completely forward
  - B. Reaction proceeds slightly forward
  - C. Reaction is at equilibrium with equal reactants and products
  - D. Reaction proceeds backward
- **Q3:** If $Q_c = 0.1$ and $K_c = 1$ for a reaction, which direction will the reaction proceed?
  - A. Forward
  - B. Backward
  - C. No change
  - D. Cannot be determined

Answer Key

- **Q1:** B. Large K_c means reaction favors products.
- **Q2:** B. Very small K means reaction proceeds only slightly forward.
- **Q3:** A. $Q_c < K_c$ means reaction proceeds forward.

Memory Aids

- Large K → forward reaction favored (more products).
- Small K → reaction barely proceeds forward (more reactants).
- Compare Q_c and K_c to predict reaction direction.
- $Q_c < K_c$: forward; $Q_c > K_c$: backward; $Q_c = K_c$: equilibrium.

Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

Thermodynamic View of Equilibrium

- Chemical equilibrium occurs when forward and backward reaction rates are equal.
- Equilibrium can be studied using Gibbs free energy (G) of reactants and products.
- ΔG = Gibbs free energy difference between products and reactants.
- If $\Delta G < 0$, reaction is spontaneous (proceeds forward).
- If $\Delta G > 0$, reaction is non-spontaneous (proceeds backward).
- If $\Delta G = 0$, reaction is at equilibrium.
- Mathematical relation: $\Delta G = \Delta G^\circ + RT \ln Q$
- ΔG° = standard free energy change, T = temperature (K), R = gas constant.
- At equilibrium, $\Delta G = 0$ and $Q = K_c$, so $0 = \Delta G^\circ + RT \ln K_c$.
- Rearranged: $\Delta G^\circ = -RT \ln K_c$ or $\ln K_c = -\Delta G^\circ/RT$.
- Case I: If $\Delta G^\circ < 0$, then $K_c > 1$, reaction is spontaneous forward.
- Case II: If $\Delta G^\circ > 0$, then $K_c < 1$, reaction is non-spontaneous or proceeds minimally forward.

Solved Examples

- **Ex 1:** Calculate K_c at 298 K if $\Delta G^\circ = -40$ kJ/mol. (R = 8.314 J/mol·K)
  - Convert ΔG° to J: -40000 J/mol
  - Use $\ln K_c = -\Delta G^\circ/RT = 40000 / (8.314 \times 298) \approx 16.12$
  - $K_c = e^{16.12} >> 1$, reaction is spontaneous forward.
- **Ex 2:** For a reaction with $\Delta G^\circ = +20$ kJ/mol at 300 K, find if reaction is spontaneous.
  - $\ln K_c = -20000 / (8.314 \times 300) \approx -8.01$
  - $K_c = e^{-8.01} < 1$, reaction is non-spontaneous or minimal product formed.

Practice Set

- Q1: If $\Delta G = 0$, what is the value of Q?
  - A. 0
  - B. 1
  - C. K_c
  - D. ∞
- Q2: For a reaction with $\Delta G^\circ < 0$, which is true?
  - A. $K_c < 1$
  - B. $K_c = 1$
  - C. $K_c > 1$
  - D. Reaction is non-spontaneous
- Q3: At 350 K, $\Delta G^\circ = 10$ kJ/mol. Calculate $\ln K_c$ (R = 8.314 J/mol·K).

- A. 3.43
- B. -3.43
- C. 0
- D. -0.34

Answer Key

- Q1: C. K_c — At equilibrium, Q equals the equilibrium constant K_c.
- Q2: C. $K_c > 1$ — Negative $\Delta G°$ means spontaneous forward reaction, so $K_c > 1$.
- Q3: B. -3.43 — $\ln K_c = -\Delta G°/RT = -10000/(8.314 \times 350) \approx -3.43$.

Memory Aids

- $\Delta G < 0 \rightarrow K_c > 1 \rightarrow$ Forward spontaneous.
- $\Delta G > 0 \rightarrow K_c < 1 \rightarrow$ Non-spontaneous or minimal product.
- At equilibrium: $\Delta G = 0$ and $Q = K_c$.

Factors Affecting Equilibria

Le Chatelier's Principle

- System shifts to counteract any change in equilibrium conditions.
- Applies to all physical and chemical equilibria.

Factors Influencing Equilibrium

- **Concentration:** Increase in reactants favours forward reaction; increase in products favours backward reaction.
- **Temperature:** High temperature favours endothermic; low temperature favours exothermic reactions.
- **Pressure:** High pressure favours side with fewer gas moles; low pressure favours side with more gas moles.
- **Inert Gas Addition:** At constant volume, no effect; at constant pressure, favours side with more gas moles.
- **Catalyst:** No effect on equilibrium position.

Application to PCl_5 Equilibrium

- Reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, ΔH = +ve (endothermic)
- Temperature increase shifts equilibrium forward (more PCl_3 and Cl_2 formed).

- Pressure increase shifts equilibrium backward (fewer gas moles).
- Adding PCl_3 or Cl_2, or removing PCl_5 shifts equilibrium backward.
- Adding inert gas at constant volume: no effect; at constant pressure: shifts forward.

Application to HI Equilibrium

- Reaction: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, ΔH = +ve (endothermic)
- Temperature increase favours forward reaction (more H_2 and I_2 formed).
- Pressure change has no effect (equal moles on both sides).
- Adding HI or removing H_2 or I_2 favours forward reaction.

Effect of Temperature on Equilibrium Constant

- Explained by van't Hoff equation:
  $\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$
- K_1 and K_2 are equilibrium constants at temperatures T_1 and T_2.
- ΔH° is enthalpy change; R is gas constant.
- If $\Delta H^\circ = 0$, equilibrium constant does not change with temperature.
- If endothermic ($\Delta H^\circ > 0$), $K_2 > K_1$ at higher temperature.
- If exothermic ($\Delta H^\circ < 0$), $K_2 < K_1$ at higher temperature.

Solved Examples

- **Ex 1:** For PCl_5 equilibrium, predict effect of increasing pressure.
  Step: More moles on product side (2) than reactant (1).
  Result: Equilibrium shifts backward to fewer moles.
- **Ex 2:** For $2HI \rightleftharpoons H_2 + I_2$, effect of pressure change?
  Step: Equal moles on both sides.
  Result: No effect on equilibrium.

Practice Set

- Q1: Increasing concentration of Cl_2 in PCl_5 equilibrium shifts reaction:
  A) Forward
  B) Backward
  C) No change
  D) Depends on temperature
- Q2: In which condition does high pressure favour forward reaction?
  A) More moles on product side
  B) Fewer moles on product side

C) Equal moles on both sides
D) Addition of catalyst

- Q3: For endothermic reaction, increasing temperature:
  A) Decreases equilibrium constant
  B) Increases equilibrium constant
  C) No change
  D) Shifts equilibrium backward

Answer Key

- Q1: B - Increasing Cl_2 (product) shifts equilibrium backward to reduce product concentration.
- Q2: B - High pressure favours side with fewer gas moles (forward if fewer moles).
- Q3: B - Endothermic reaction equilibrium constant increases with temperature.

Memory Aids

- High Temp → Endothermic forward; Low Temp → Exothermic forward.
- High Pressure → Fewer gas moles side favoured.
- Inert gas at constant volume → No effect; at constant pressure → More moles side favoured.
- Catalyst → Speeds both directions equally, no equilibrium shift.

Electrolytes

Definition and Types

- Electrolytes are substances that conduct electricity in aqueous solutions or molten state.
- Strong electrolytes: Completely ionised in aqueous solution (e.g., NaCl, HCl).
- Weak electrolytes: Partially ionised, establishing equilibrium between ions and molecules (e.g., CH_3COOH).
- All acids, bases, and salts can be classified as strong or weak electrolytes.

Solved Examples

- **Ex 1:** Identify if HCl is a strong or weak electrolyte.
  HCl fully ionises in water: $HCl \rightarrow H^+ + Cl^-$. Hence, strong electrolyte.
- **Ex 2:** Write ionic equilibrium for acetic acid in water.
  $CH_3COOH <=> CH_3COO^- + H^+$ (partial ionisation, weak electrolyte).

Practice Set

- Q1: Which of the following is a strong electrolyte?
  A. CH_3COOH
  B. NaCl
  C. NH_3
  D. H_2O
- Q2: What happens to weak electrolytes in aqueous solution?
  A. Fully ionise
  B. Do not ionise
  C. Establish ionic equilibrium
  D. Precipitate out
- Q3: Which equation represents the ionisation of a weak acid?
  A. $HCl \rightarrow H^+ + Cl^-$
  B. $CH_3COOH <=> CH_3COO^- + H^+$
  C. $NaCl \rightarrow Na^+ + Cl^-$
  D. $H_2O \rightarrow H^+ + OH^-$

Answer Key

- Q1: B - NaCl is a strong electrolyte as it completely ionises in water.
- Q2: C - Weak electrolytes partially ionise, establishing ionic equilibrium.
- Q3: B - The reversible ionisation of acetic acid shows weak electrolyte behaviour.

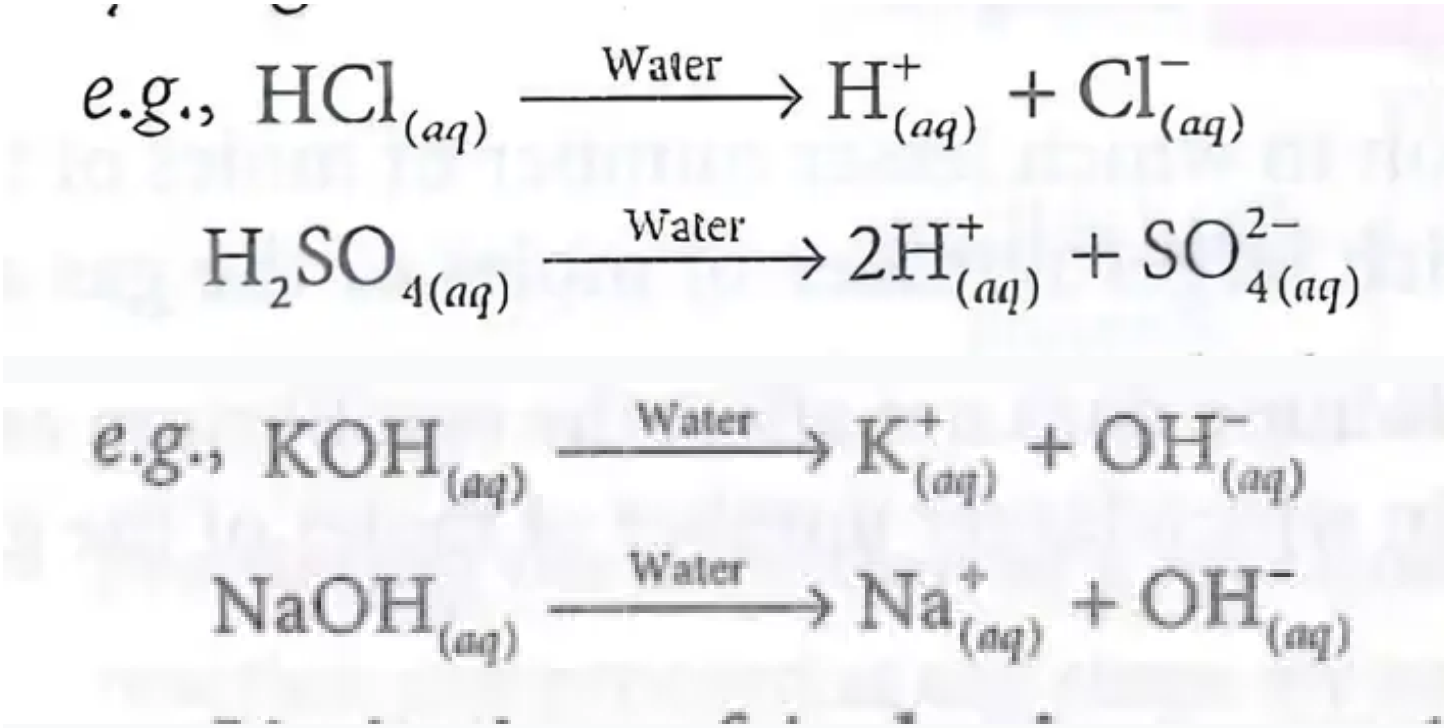
Memory Aids

- Strong electrolytes: Complete ionisation → full conductivity.
- Weak electrolytes: Partial ionisation → equilibrium between ions and molecules.
- All acids, bases, salts can be strong or weak electrolytes.

Arrhenius Concept

Definition and Explanation

- Acid: Substance that releases H^+ ions in water.
- Base: Substance that releases OH^- ions in water.
- Example acids: $HCl \rightarrow H^+ + Cl^-$, $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$
- Example bases: $KOH \rightarrow K^+ + OH^-$, $NaOH \rightarrow Na^+ + OH^-$
- Dissociation of acids and bases in water produces ions responsible for acidic or basic nature.



Limitations

- Cannot explain acidic nature of compounds like CO_2, SO_2, $AlCl_3$ which do not release H^+.
- Cannot explain basic nature of compounds like Na_2CO_3, NH_3 which do not release OH^-.
- Fails to describe acid-base behavior in absence of water.
- Does not explain the nature of H^+ and OH^- ions in water.

Solved Examples

- **Ex 1:** Write dissociation of HCl in water.
  $HCl \rightarrow H^+ + Cl^-$
- **Ex 2:** Write dissociation of NaOH in water.
  $NaOH \rightarrow Na^+ + OH^-$

Practice Set

- Q1: According to Arrhenius, an acid is a substance that:
  A. Accepts H^+
  B. Donates OH^-
  C. Releases H^+
  D. Releases OH^-
- Q2: Which of the following is NOT explained by Arrhenius concept?
  A. Acidic nature of HCl
  B. Basic nature of NH_3

C. Dissociation of NaOH

D. Formation of H_3O^+

- Q3: What ions are produced when H_2SO_4 dissolves in water?

  A. $2H^+$ and SO_4^{2-}

  B. H^+ and SO_4^{2-}

  C. H^+ and SO_3^{2-}

  D. $2OH^-$ and SO_4^{2-}

Answer Key

- Q1: C - Acid releases H^+ ions in water.
- Q2: B - NH_3 does not release OH^-, so not explained by Arrhenius.
- Q3: A - Sulfuric acid dissociates into $2H^+$ and SO_4^{2-}.

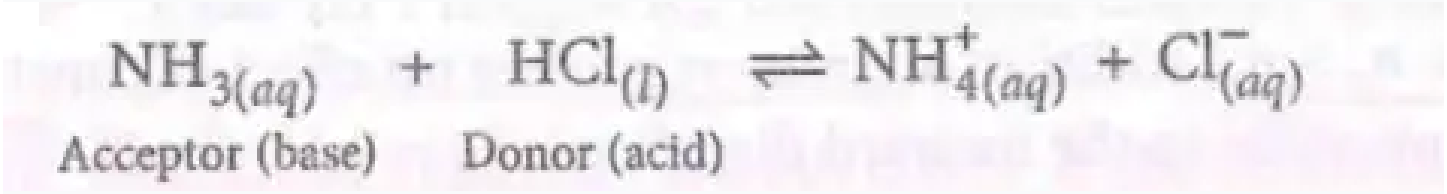
Memory Aids

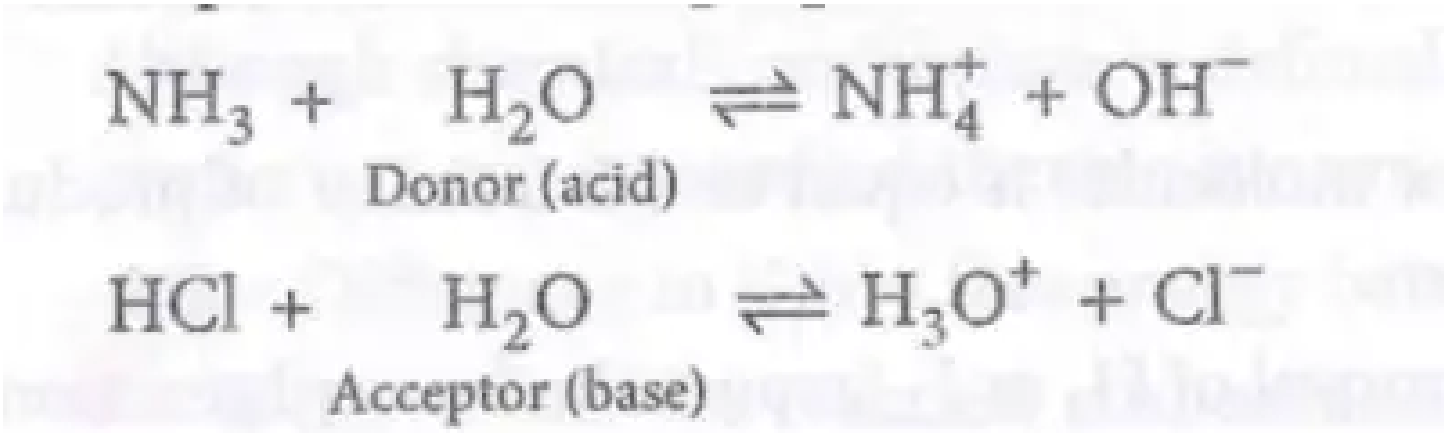
- Arrhenius acid = releases H^+ in water.
- Arrhenius base = releases OH^- in water.
- Limit: Only works in aqueous solutions.

Bronsted-Lowry Concept

Definition and Explanation

- Acid: Proton (H^+) donor.
- Base: Proton (H^+) acceptor.
- Protonic theory of acids and bases.
- Example: $NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$
- Water is amphiprotic: can donate or accept protons.





Conjugate Acid-Base Pairs

- Acid loses proton → conjugate base.
- Base gains proton → conjugate acid.
- Pairs differ by one proton only.
- Example: $HA + B^- \rightleftharpoons A^- + BH$
- Strong acid → weak conjugate base and vice versa.
- Weaker acid acts as base in presence of stronger acid.

Solved Examples

- **Ex 1:** NH_3 accepts proton from HCl forming NH_4^+ and Cl^-.
- **Ex 2:** Sulfuric acid reacts with NH_3 forming NH_4^+ and HSO_4^-.

Practice Set

- Q1: In Bronsted-Lowry theory, a base is a substance that:

  A. Donates H^+

  B. Accepts H^+

  C. Releases OH^-

  D. Accepts OH^-
- Q2: Which is a conjugate acid-base pair?

  A. NH_3 / NH_4^+

  B. HCl / NaCl

  C. H_2O / OH^-

  D. NaOH / Na^+
- Q3: What happens when NH_3 reacts with HCl?

  A. NH_3 donates proton

  B. NH_3 accepts proton

C. HCl accepts proton
D. No reaction

Answer Key

- Q1: B - Base accepts proton (H^+).
- Q2: A - NH_3 and NH_4^+ differ by one proton.
- Q3: B - NH_3 accepts proton from HCl forming NH_4^+.

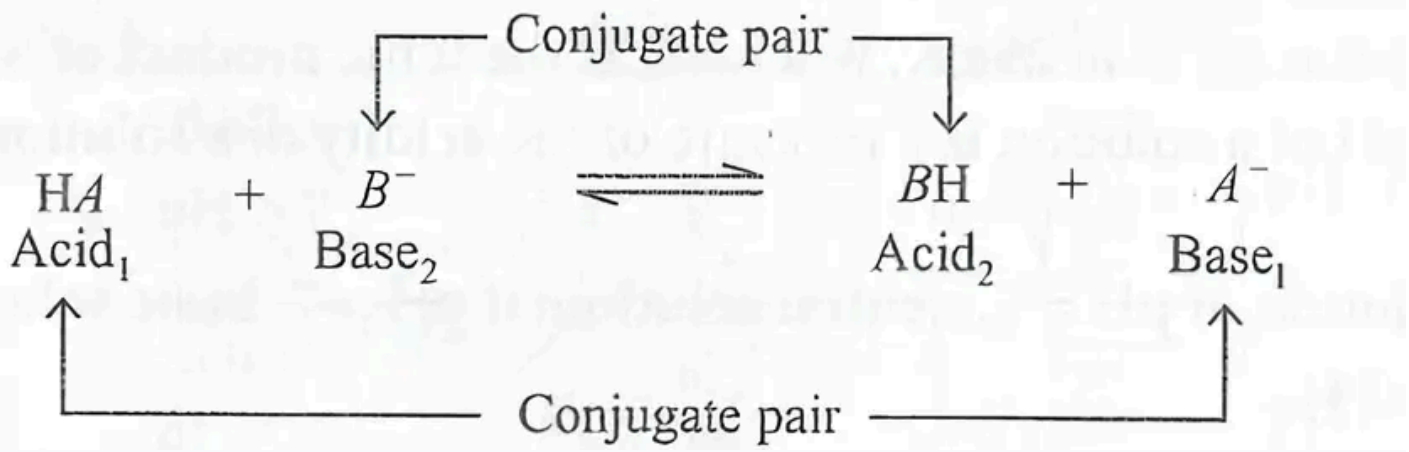
Memory Aids

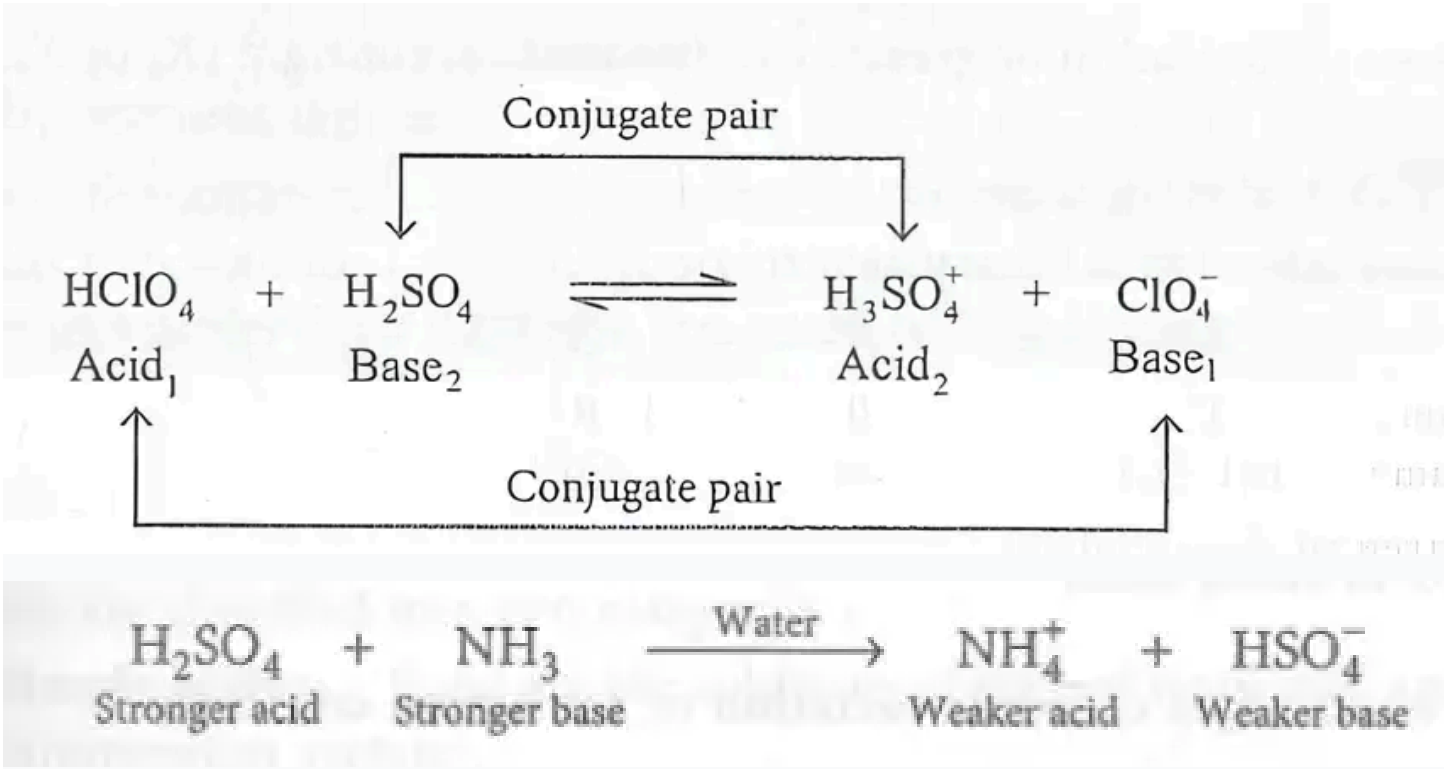
- Acid = proton donor, Base = proton acceptor.
- Water is amphiprotic (both acid and base).
- Conjugate pairs differ by one proton.

Conjugate Acid-Base Pair

Definition and Explanation

- Acid-base reactions are reversible.
- Acid loses proton → conjugate base.
- Base gains proton → conjugate acid.
- Pairs differ by one proton only.
- Strong acid forms weak conjugate base and vice versa.
- Reaction direction: stronger acid-base to weaker acid-base.





Solved Examples

- **Ex 1:** $HClO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + ClO_4^-$ (conjugate pairs formed)
- **Ex 2:** $H_2SO_4 + NH_3 \rightarrow NH_4^+ + HSO_4^-$ (strong to weak acid-base)

Practice Set

- Q1: Conjugate base is formed by:
  A. Gaining proton
  B. Losing proton
  C. Gaining electron
  D. Losing electron
- Q2: Which direction do acid-base reactions proceed?
  A. Weaker to stronger acid-base
  B. Stronger to weaker acid-base
  C. Random
  D. No reaction
- Q3: In the reaction $H_2SO_4 + NH_3$, the conjugate acid formed is:
  A. NH_4^+
  B. HSO_4^-
  C. SO_4^{2-}
  D. NH_3

Answer Key

- Q1: B - Conjugate base forms by losing proton.
- Q2: B - Reaction proceeds from stronger to weaker acid-base.
- Q3: A - NH_4^+ is conjugate acid formed.

Memory Aids

- Conjugate pairs differ by one proton.
- Strong acid → weak conjugate base.
- Reactions go from stronger to weaker acid-base.

Lewis Acids and Bases

Definition and Explanation

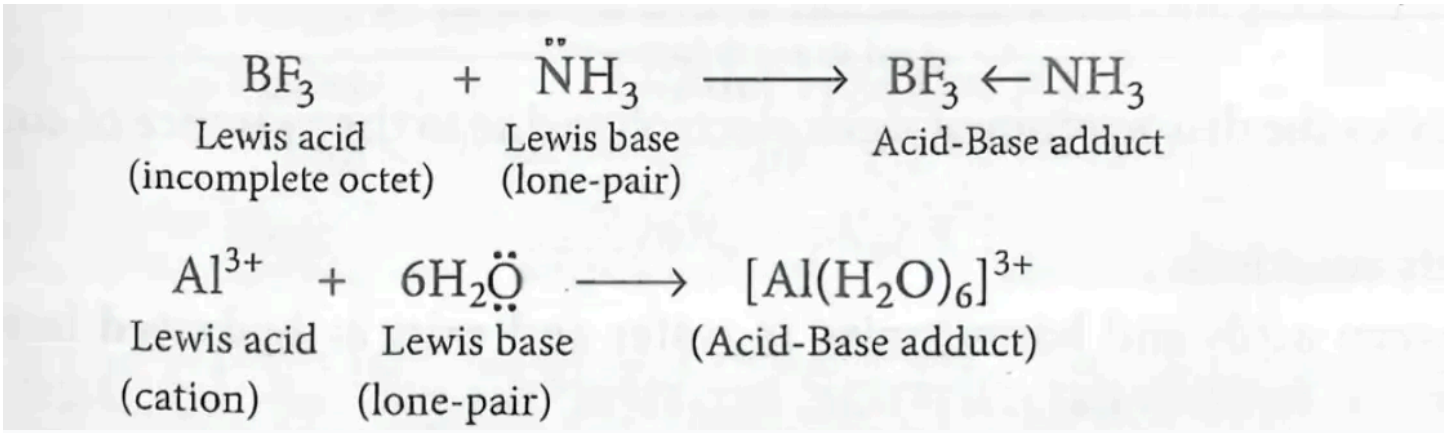
- Lewis acid: Electron pair acceptor.
- Lewis base: Electron pair donor.
- Acids are electron acceptors; bases are electron donors.

Chemical Species Acting as Lewis Acids

- Electron-deficient molecules with incomplete octet: BF_3, $FeCl_3$, $AlCl_3$.
- Simple cations: H^+, Mg^{2+}, Co^{3+}, Ag^+, Fe^{3+}.
- Molecules with polar multiple bonds: SO_3, CO_2.
- Metal atoms in coordination complexes, e.g., Ni in $Ni(CO)_4$.
- Molecules with central atom having empty d-orbitals: SiF_4, $SnCl_4$.

Chemical Species Acting as Lewis Bases

- Electron-rich molecules with lone pairs: NH_3, R-O-H (alcohol), R-NH_2 (amine).
- Negatively charged ions: CN^-, OH^-, Cl^-.
- Ligands in coordination compounds act as Lewis bases.



Solved Examples

- **Ex 1:** $BF_3 + NH_3 \rightarrow BF_3 \leftarrow NH_3$ (Lewis acid-base adduct)
- **Ex 2:** $Al^{3+} + 6H_2O \rightarrow [Al(H_2O)_6]^{3+}$ (coordination complex)

Practice Set

- Q1: Lewis acid is a substance that:
  A. Donates electron pair
  B. Accepts electron pair
  C. Donates proton
  D. Accepts proton
- Q2: Which is a Lewis base?
  A. BF_3
  B. NH_3
  C. H^+
  D. $AlCl_3$
- Q3: What type of bond forms between Lewis acid and base?
  A. Ionic
  B. Covalent
  C. Coordinate covalent
  D. Metallic

Answer Key

- Q1: B - Lewis acid accepts electron pair.
- Q2: B - NH_3 donates lone pair, acts as Lewis base.
- Q3: C - Lewis acid-base bond is coordinate covalent.

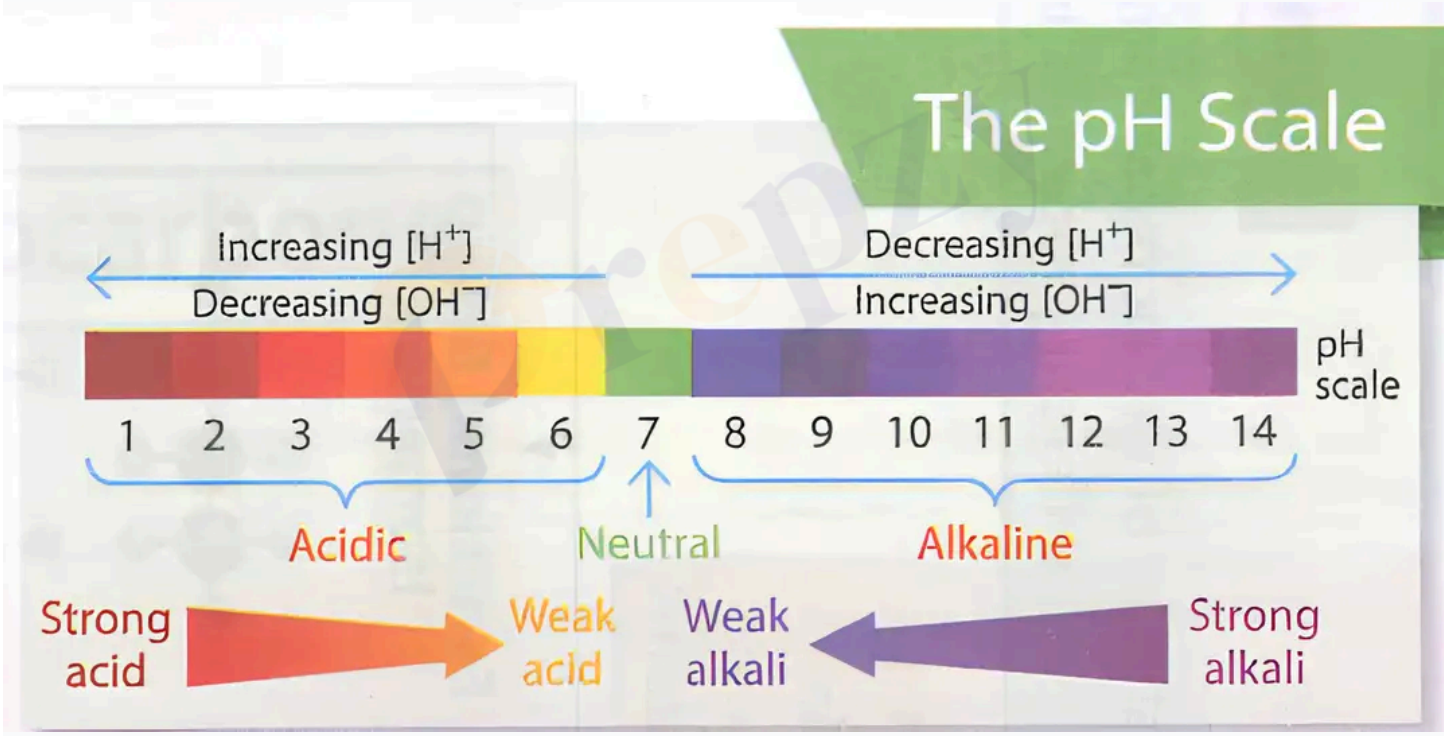
Memory Aids

- Lewis acid = electron pair acceptor.
- Lewis base = electron pair donor.
- All Lewis bases are also Bronsted bases.

Ionisation of Acids and Bases

Ionisation constant of water and pH scale

- Water ionisation constant: K_w = $[H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K.
- pH = -log$[H^+]$; pOH = -log$[OH^-]$; pH + pOH = 14.
- pH < 7: acidic; pH = 7: neutral; pH > 7: basic solution.
- pH scale ranges from 1 (strong acid) to 14 (strong base).



Ionisation of acids and bases

- Acid ionisation: HA ⇌ $H^+ + A^-$, with K_a = $\frac{[H^+][A^-]}{[HA]}$.
- Degree of ionisation (α) for acid: $\alpha = \sqrt{\frac{K_a}{C}}$, where C is acid concentration.
- Base ionisation: BOH ⇌ $B^+ + OH^-$, with K_b = $\frac{[B^+][OH^-]}{[BOH]}$.
- Degree of ionisation (α) for base: $\alpha = \sqrt{\frac{K_b}{C}}$.
- Stronger acid/base has higher K_a or K_b and greater α.

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + A^-,\ K_a = \frac{[H^+][A^-]}{[HA]} \text{ and degree of ionisation, } \alpha = \sqrt{\frac{K_a}{C}}$$

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-,\ K_b = \frac{[B^+][OH^-]}{[BOH]} \text{ and degree of ionisation, } \alpha = \sqrt{\frac{K_b}{C}}$$

Ostwald's dilution law

- For binary electrolyte AB dissociating as $AB \rightleftharpoons A^+ + B^-$:
- Initial concentration: [AB] = C, $[A^+] = 0$, $[B^-] = 0$.
- At equilibrium: [AB] = C(1 - α), $[A^+] = C\alpha$, $[B^-] = C\alpha$.
- Dissociation constant: K_a = $\frac{C\alpha^2}{1-\alpha}$.
- For weak electrolytes, α << 1, so K_a ≈ $C\alpha^2$ and α = $\sqrt{\frac{K_a}{C}}$.
- Strong electrolytes: α = 1; weak electrolytes: α < 1.

	AB	$\rightleftharpoons$	A^+	+	B^-
Initial concentration :	C		0		0
Conc. at equilibrium :	$C(1-\alpha)$		$C\alpha$		$C\alpha$

Relation between K_a and K_b

- pK_a = -log K_a; pK_b = -log K_b.
- pK_a + pK_b = pK_w = 14 at 298 K.
- Polybasic acids and polyacidic bases ionise stepwise with constants K_1, K_2, K_3,...
- Higher order ionisation constants decrease: K_1 > K_2 > K_3 > ...
- Overall ionisation constant: K = K_1 × K_2 × K_3 × ...

Factors affecting acid strength

- Depends on H–A bond strength and polarity.
- Acid strength increases with larger atom size (HF < HCl < HBr < HI).
- Acid strength increases with higher electronegativity of central atom ($CH_4 < NH_3 < H_2O < HF$).

$$\xrightarrow[\text{Acid strength increases}]{\text{Size increases}} HF << HCl << HBr << HI$$

$$\xrightarrow[\text{Acid strength increases}]{\text{Electronegativity increases}} CH_4 < NH_3 < H_2O < HF$$

Common ion effect

- Adding a common ion suppresses dissociation of a weak electrolyte.

Hydrolysis of salts and pH of their solutions

- Salts ionise in water to hydrated ions; ions react with water (hydrolysis).
- Salts from strong acid + strong base: neutral solution (pH = 7).
- Salts from strong acid + weak base: acidic solution (pH < 7).
- Salts from weak acid + strong base: basic solution (pH > 7).
- Hydrolysis constant (K_h) and degree of hydrolysis (h) depend on K_w, K_a, K_b, and salt concentration.

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline, pH > 7	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic, pH < 7	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, pH = 7 (If $K_a = K_b$)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$

Solved Examples

Ex 1

- Calculate degree of ionisation (α) for a weak acid with K_a = 1.0×10^{-5} and concentration 0.1 M.
- Solution: $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.0\times10^{-5}}{0.1}} = 0.01.$

Ex 2

- Find pH of a solution with $[H^+] = 1.0 \times 10^{-3}$ M.
- Solution: $\text{pH} = -\log(1.0 \times 10^{-3}) = 3$.

Practice Set

- Q1: What is the pH of pure water at 298 K?

    - A. 0
    - B. 7
    - C. 14
    - D. 1
- Q2: For a weak acid, which expression gives the degree of ionisation (α)?
    - A. α = K_a × C
    - B. α = $\sqrt{\frac{K_a}{C}}$
    - C. α = K_a / C
    - D. α = C / K_a
- Q3: If pK_a = 5, what is pK_b for its conjugate base?
    - A. 9
    - B. 14
    - C. 5
    - D. 19

Answer Key

- Q1: B - Pure water is neutral with pH 7 at 298 K.
- Q2: B - Degree of ionisation for weak acid is $\sqrt{\frac{K_a}{C}}$.
- Q3: A - pK_a + pK_b = 14, so pK_b = 14 - 5 = 9.

Memory Aids

- pH + pOH = 14 always at 298 K.
- Stronger acid: higher K_a, lower pK_a.
- Ostwald's law: α = $\sqrt{\frac{K_a}{C}}$ for weak electrolytes.
- Acid strength increases down halogen group (HF < HCl < HBr < HI).
- Common ion effect reduces ionisation of weak electrolytes.

Buffer Solutions

Definition and Classification

- Solutions that resist pH change on dilution or addition of small amounts of acid/base.
- Two types of buffers:
    - **Simple buffers:** Solutions of salts of weak acid and weak base (e.g., CH_3COONH_4).
    - **Mixed buffers:** Mixtures of two solutions, further divided into:
        - **Acidic buffers:** Weak acid + salt of weak acid with strong base (e.g., CH_3COOH + CH_3COONa), pH < 7.
        - **Basic buffers:** Weak base + salt of weak base with strong acid (e.g., NH_4OH + NH_4Cl), pH > 7.

Solved Examples

- **Ex 1:** Identify the type of buffer formed by mixing CH_3COOH and CH_3COONa.
  - Mixture of weak acid and its salt with strong base.
  - Hence, acidic buffer with pH < 7.

Practice Set

- Q1: Which of the following is a simple buffer?
  - A. $CH_3COOH + CH_3COONa$
  - B. $NH_4OH + NH_4Cl$
  - C. CH_3COONH_4
  - D. HCl + NaCl
- Q2: What is the pH range of acidic buffers?
  - A. $pK_a \pm 1$
  - B. $(pK_w - pK_b) \pm 1$
  - C. 7 ± 1
  - D. 14 ± 1
- Q3: Which mixture forms a basic buffer?
  - A. $CH_3COOH + CH_3COONa$
  - B. $NH_4OH + NH_4Cl$
  - C. HCl + NaCl
  - D. CH_3COONH_4

Answer Key

- Q1: C - Simple buffer is salt of weak acid and weak base (ammonium acetate).
- Q2: A - Acidic buffer range is $pK_a \pm 1$.
- Q3: B - Basic buffer formed by weak base and its salt with strong acid ($NH_4OH + NH_4Cl$).

Memory Aids

- Simple buffer = salt of weak acid + weak base (e.g., CH_3COONH_4).
- Acidic buffer = weak acid + salt of weak acid with strong base (pH < 7).
- Basic buffer = weak base + salt of weak base with strong acid (pH > 7).

pH of Buffer Solutions

Acidic Buffer pH

- pH = pK_a + log ([salt]/[acid])
- Also written as Henderson–Hasselbalch equation: pH = pK_a + log ([conjugate base]/[acid])

Basic Buffer pH

- pOH = pK_b + log ([salt]/[base])
- Also: pOH = pK_b + log ([conjugate acid]/[base])

Solved Examples

- **Ex 1:** Calculate pH of acidic buffer with pK_a = 4.76, [salt] = 0.1 M, [acid] = 0.1 M.
  - pH = 4.76 + log(0.1/0.1) = 4.76 + 0 = 4.76
- **Ex 2:** Calculate pOH of basic buffer with pK_b = 4.75, [salt] = 0.2 M, [base] = 0.1 M.
  - pOH = 4.75 + log(0.2/0.1) = 4.75 + 0.301 = 5.05

Practice Set

- Q1: For acidic buffer, pH is given by?
  - A. pK_a + log ([acid]/[salt])
  - B. pK_a + log ([salt]/[acid])
  - C. pK_b + log ([salt]/[base])
  - D. pK_b + log ([base]/[salt])
- Q2: If pK_b = 4.75, [salt] = 0.1 M, [base] = 0.1 M, pOH of basic buffer is?
  - A. 4.75
  - B. 5.05
  - C. 4.45
  - D. 3.75
- Q3: Calculate pH of acidic buffer with pK_a = 3.75, [salt] = 0.05 M, [acid] = 0.1 M.
  - A. 3.45
  - B. 3.75
  - C. 4.05
  - D. 3.25

Answer Key

- Q1: B - Henderson–Hasselbalch equation for acidic buffer.
- Q2: A - pOH = 4.75 + log(0.1/0.1) = 4.75.
- Q3: A - pH = 3.75 + log(0.05/0.1) = 3.75 - 0.3 = 3.45.

Memory Aids

- Acidic buffer pH uses pK_a and ratio of salt to acid.
- Basic buffer pOH uses pK_b and ratio of salt to base.
- Remember: pH + pOH = 14.

Buffer Capacity and Range

Buffer Capacity

- Buffer capacity = moles of acid/base added per litre of buffer ÷ change in pH.
- Indicates buffer's ability to resist pH change.

Buffer Range

- Range of pH over which buffer is effective.
- For acidic buffers: $pK_a \pm 1$.
- For basic buffers: $(pK_w - pK_b) \pm 1$.

Solved Examples

- **Ex 1:** Calculate buffer capacity if 0.01 moles acid added to 1 L buffer causing pH change from 5.0 to 4.8.
  - Change in pH = 0.2
  - Buffer capacity = 0.01 / 0.2 = 0.05 mol/L per pH unit.

Practice Set

- Q1: Buffer capacity measures:
  - A. pH of buffer
  - B. Amount of acid/base buffer can neutralize per pH change
  - C. pK_a value
  - D. Concentration of buffer components

- Q2: Buffer range of acidic buffer is:
  - A. $pK_a \pm 1$
  - B. $(pK_w - pK_b) \pm 1$
  - C. 7 ± 1
  - D. 14 ± 1
- Q3: If buffer capacity is 0.1 mol/L per pH unit, moles of acid added causing 0.5 pH change is:
  - A. 0.05
  - B. 0.2
  - C. 0.1
  - D. 0.5

Answer Key

- Q1: B - Buffer capacity shows resistance to pH change by neutralizing added acid/base.
- Q2: A - Acidic buffer effective range is $pK_a \pm 1$.
- Q3: B - Moles = capacity × pH change = 0.1 × 0.5 = 0.05 mol.

Memory Aids

- Buffer capacity = moles acid/base added ÷ pH change.
- Acidic buffer range near pK_a, basic near $(pK_w - pK_b)$.

Solubility vs Solubility Product

Definitions and Differences

- **Solubility**: Amount of solute dissolved in 1 L of solvent (usually in grams).
- **Solubility Product (K_{sp})**: Equilibrium constant for a saturated solution showing ion concentrations (in mol/L) at a given temperature.
- Solubility depends on temperature, pressure, pH, and other chemicals.
- K_{sp} depends only on temperature.

Solved Examples

- **Ex 1:** Calculate solubility if $K_{sp} = 1.6 \times 10^{-10}$ for AgCl (1:1 salt).
  - Solubility, $s = \sqrt{K_{sp}} = \sqrt{(1.6 \times 10^{-10})} = 1.26 \times 10^{-5}$ mol/L

Practice Set

- Q1: What does solubility measure?
  - A) Ion concentration at equilibrium
  - B) Amount of solute dissolved per liter
  - C) Temperature effect on salt
  - D) Pressure effect on salt
- Q2: Which factor affects K_{sp}?
  - A) pH
  - B) Temperature
  - C) Pressure
  - D) Common ion presence
- Q3: If solubility of salt is 2×10^{-3} mol/L, what is K_{sp} for a 1:1 salt?
  - A) 4×10^{-6}
  - B) 2×10^{-3}
  - C) 2×10^{-6}
  - D) 4×10^{-3}

Answer Key

- Q1: B - Solubility is the amount of solute dissolved per liter of solvent.
- Q2: B - K_{sp} depends only on temperature.
- Q3: A - $K_{sp} = s^2 = (2 \times 10^{-3})^2 = 4 \times 10^{-6}$.

Memory Aids

- Solubility = grams per liter; K_{sp} = ion product constant.
- K_{sp} changes only with temperature.
- Solubility affected by common ions, pH, pressure.

Solubility Product Constant

Equilibrium and Expression

- For salt M_xX_y: $M_xX_y(s) \rightleftharpoons xM^{y+}(aq) + yX^{x-}(aq)$
- $K_{sp} = [M^{y+}]^x [X^{x-}]^y = (xs)^x (ys)^y = x^x y^y s^{x+y}$
- Solubility, $s = \left(\frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}}$
- At equilibrium, $K_{sp} = Q_{sp}$. If not, Q_{sp} indicates reaction direction.

Effect of Common Ion

- Adding a common ion decreases solubility (common ion effect).
- Example: For AgCl, if NaCl (common Cl^-) is added, solubility decreases.
- $K_{sp} = [Ag^+][Cl^-] = S'(S' + x)$, where x is added ion concentration.
- Increase in solubility on adding inert salt indicates complex ion formation.

Solved Examples

- **Ex 1:** Calculate solubility of AgCl if $K_{sp} = 1.8 \times 10^{-10}$ and 0.01 M NaCl is added.
  - $K_{sp} = S'(S' + 0.01) \approx S' \times 0.01$ (if $S' << 0.01$)
  - $S' = K_{sp} / 0.01 = 1.8 \times 10^{-8}$ mol/L (much less than pure water solubility)

Practice Set

- Q1: What happens to solubility when a common ion is added?
  - A) Increases
  - B) Decreases
  - C) No change
  - D) Depends on temperature
- Q2: For salt M_xX_y, K_{sp} expression is?
  - A) $[M^{y+}][X^{x-}]$
  - B) $[M^{y+}]^x[X^{x-}]^y$
  - C) (xs)(ys)
  - D) (x+y)s
- Q3: If $Q_{sp} > K_{sp}$, what occurs?
  - A) No precipitation
  - B) Precipitation
  - C) Equilibrium
  - D) Complex formation

Answer Key

- Q1: B - Common ion decreases solubility by shifting equilibrium.
- Q2: B - $K_{sp} = [M^{y+}]^x[X^{x-}]^y$.
- Q3: B - Ionic product greater than K_{sp} causes precipitation.

Prepzy

Memory Aids

- Common ion effect lowers solubility.
- K_{sp} expression includes ion concentrations raised to their stoichiometric powers.
- $Q_{sp} > K_{sp}$ means precipitation.

Applications of Solubility Product

Key Uses

- Calculate solubility of sparingly soluble salts from K_{sp}.
- Predict precipitation by comparing ionic product (Q) with K_{sp}.
- Explain precipitation of common salt by adding HCl gas (increases Cl^- concentration).
- Use in qualitative analysis to separate ions based on solubility and common ion effect.

Solved Examples

- **Ex 1:** Predict if precipitation occurs when $[Ag^+] = 1 \times 10^{-4}$ M and $[Cl^-] = 1 \times 10^{-3}$ M, K_{sp} of AgCl = 1.8×10^{-10}.
  - Ionic product = $(1 \times 10^{-4})(1 \times 10^{-3}) = 1 \times 10^{-7} > K_{sp}$
  - Precipitation occurs.

Practice Set

- Q1: What indicates precipitation?
  - A) Ionic product < K_{sp}
  - B) Ionic product = K_{sp}
  - C) Ionic product > K_{sp}
  - D) No ions present
- Q2: What happens when HCl gas is passed through impure NaCl solution?
  - A) NaCl dissolves more
  - B) Pure NaCl precipitates
  - C) No change
  - D) NaCl decomposes
- Q3: Which application uses solubility product in qualitative analysis?
  - A) Identifying gases
  - B) Separating basic radicals
  - C) Measuring pH
  - D) Calculating molarity

Answer Key

- Q1: C - Precipitation occurs if ionic product > K_{sp}.
- Q2: B - Increased Cl^- causes pure NaCl to precipitate.
- Q3: B - Solubility product helps separate basic radicals.

Memory Aids

- Precipitation if Q > K_{sp}.
- HCl increases Cl^-, causing NaCl precipitation.
- Qualitative analysis uses solubility and common ion effect.

Solubility Products of Electrolytes

Classification and Formulas

- Salts classified by electrolyte formula: binary (1:1), ternary (1:2 or 2:1), quaternary (1:3), 3:2 types.
- Examples:
  - Binary (1:1): AgCl
  - Ternary (1:2): $PbCl_2$
  - Quaternary (1:3): $Fe(OH)_3$
- Solubility (s) related to K_{sp} differently for each type:
  - 1:1 salts: $s = \sqrt{K_{sp}}$
  - 1:2 salts: $s = \sqrt[3]{(K_{sp}/4)}$
  - 2:1 salts: $s = \sqrt[3]{(K_{sp}/4)}$
  - 1:3 salts: $s = \sqrt[4]{\frac{K_{sp}}{27}}$
  - 3:2 salts: $s = \sqrt[5]{\frac{K_{sp}}{108}}$

Type of salt	Example	Relation between s and K_{sp}
Binary electrolyte 1 : 1 (AB)	AgCl, $BaSO_4$, etc.	$s = \sqrt{K_{sp}}$ or $K_{sp} = s^2$
Ternary electrolyte 1 : 2 (AB_2)	$PbCl_2$, $Ca(OH)_2$, etc.	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$
Ternary electrolyte 2 : 1 (A_2B)	Ag_2CrO_4, Ag_2CO_3, etc.	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$
Quaternary electrolyte 1 : 3 (AB_3)	$Fe(OH)_3$, $Al(OH)_3$, etc.	$s = \sqrt[4]{K_{sp}/27}$ or $K_{sp} = 27s^4$
3 : 2 type of electrolyte (A_3B_2)	$Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$ etc.	$s = \sqrt[5]{K_{sp}/108}$ or $K_{sp} = 108s^5$

Solved Examples

- **Ex 1:** Calculate solubility of $PbCl_2$ if $K_{sp} = 1.7 \times 10^{-5}$.
  - For 1:2 salt, $s = \sqrt[3]{(K_{sp}/4)} = \sqrt[3]{(1.7 \times 10^{-5}/4)} = 0.016$ mol/L

Practice Set

- Q1: Which salt is binary 1:1?
  - A) $PbCl_2$
  - B) AgCl
  - C) $Fe(OH)_3$
  - D) $Al(OH)_3$
- Q2: Solubility formula for 1:2 salt is?
  - A) $s = \sqrt{K_{sp}}$
  - B) $s = \sqrt[3]{(K_{sp}/4)}$
  - C) $s = K_{sp}^2$
  - D) $s = K_{sp}/4$
- Q3: For $Fe(OH)_3$ (1:3 salt), solubility is?
  - A) $\sqrt[4]{\frac{K_{sp}}{27}}$
  - B) $\sqrt[3]{K_{sp}}$
  - C) $\sqrt{K_{sp}}$
  - D) $\sqrt[5]{\frac{K_{sp}}{108}}$

Answer Key

- Q1: B - AgCl is binary 1:1 salt.
- Q2: B - For 1:2 salts, $s = \sqrt[3]{(K_{sp}/4)}$.
- Q3: A - For 1:3 salts, $s = \sqrt[4]{\frac{K_{sp}}{27}}$.

Memory Aids

- Binary (1:1): $s = \sqrt{K_{sp}}$
- Ternary (1:2 or 2:1): $s = \sqrt[3]{(K_{sp}/4)}$
- Quaternary (1:3): s = 4th root of $(K_{sp}/27)$
- 3:2 salts: 5th root of $(K_{sp}/108)$