Chapter 6: Equilibrium

Comprehensive Study Notes
Class 11 Chemistry - NCERT Based
EXAM SPRINT - Complete Coverage for NEET and Board Examinations

Introduction

Chemical equilibria play crucial roles in biological and environmental processes. The transport of O_2 by hemoglobin, the toxicity of CO, and numerous industrial processes all depend on equilibrium principles. When a liquid evaporates in a closed container, an equilibrium establishes between liquid and vapor phases where the rate of evaporation equals the rate of condensation.

Key Concept: Equilibrium is dynamic - there is continuous molecular activity at the boundary between phases, but no net change occurs.

6.1 Equilibrium in Physical Processes

Basic Characteristics:

- **Dynamic Nature**: Opposing processes occur simultaneously at equal rates
- **Closed System Required**: Equilibrium possible only in closed systems
- **Constant Properties**: All measurable properties remain constant
- **Temperature Dependent**: Equilibrium position varies with temperature

6.1.1 Solid-Liquid Equilibrium

Example: Ice-water equilibrium at 273K and 1 atm

Key Features:

- Mass of ice and water remain constant
- Continuous molecular exchange at interface
- Normal melting/freezing point: Temperature where solid-liquid phases coexist at 1 atm

Representation: $H_2O(s) \rightleftharpoons H_2O(l)$

6.1.2 Liquid-Vapor Equilibrium

Experimental Setup: Water in closed container with manometer

Observations:

- Mercury level rises initially, then becomes constant
- Water volume decreases until equilibrium
- Rate of evaporation = Rate of condensation

Key Concepts:

- **Vapor Pressure**: Constant pressure exerted by vapor at equilibrium
- **Volatility**: Higher vapor pressure = more volatile = lower boiling point
- **Normal Boiling Point**: Temperature where liquid-vapor equilibrium exists at 1 atm

Representation: $H_2O(l) \rightleftharpoons H_2O(g)$

6.1.3 Solid-Vapor Equilibrium (Sublimation)

Example: Iodine sublimation

- Solid $I_2 \rightarrow I_2$ vapor (violet color)
- Intensity becomes constant at equilibrium

Other Examples:

- Camphor(s) ⇌ Camphor(g)
- $NH_4Cl(s) \rightleftharpoons NH_4Cl(g)$

Representation: $I_2(s) \rightleftharpoons I_2(g)$

6.1.4 Dissolution Equilibria

Solids in Liquids:

Saturated Solution: No more solute can dissolve at given temperature

Dynamic Process: Sugar(solution) ⇌ Sugar(solid)

- Rate of dissolution = Rate of crystallization
- Confirmed by radioactive tracer experiments

Gases in Liquids:

Example: CO_2 in soda water

- $CO_2(g) \rightleftharpoons CO_2(solution)$
- Governed by **Henry's Law**: Mass of dissolved gas ∝ pressure of gas
- Explains fizzing when bottle opened (pressure decrease)

Summary of Physical Equilibria

Process	Equilibrium Condition
Liquid ⇌ Vapor	Constant vapor pressure at given T
Solid ⇌ Liquid	Fixed melting point at constant P
Solute(s) ⇌ Solute(solution)	Constant solubility at given T
Gas(g) ⇌ Gas(aq)	[gas(aq)]/[gas(g)] = constant at given T

6.2 Chemical Equilibrium - Dynamic Equilibrium

Definition:

When rates of forward and reverse reactions become equal, concentrations of reactants and products remain constant - this is **chemical equilibrium**.

General Reaction:

$A + B \rightleftharpoons C + D$

Key Features:

1. **Reversible**: Can be approached from either direction
2. **Dynamic**: Forward and reverse reactions continue
3. **Constant Composition**: No net change in concentrations
4. **Rate Equality**: Rate(forward) = Rate(reverse)

Demonstration: Haber Process

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Isotope Evidence:

- Using D_2 instead of H_2 shows scrambling of isotopes
- Formation of NH_3, NH_2D, NHD_2, ND_3 proves dynamic nature

Classification by Extent:

1. **Nearly Complete**: Negligible reactants remain
2. **Minimal Conversion**: Small product formation
3. **Appreciable**: Comparable reactant and product concentrations

6.3 Law of Chemical Equilibrium and Equilibrium Constant

Historical Background:

Guldberg and Waage (1864): Proposed Law of Mass Action

For General Reaction:

$aA + bB \rightleftharpoons cC + dD$

Equilibrium Constant Expression:

```
Kc = [C]^c[D]^d / [A]^a[B]^b
```

Where:

Kc = equilibrium constant (concentration basis)
☐ = molar concentration at equilibrium
Superscripts = stoichiometric coefficients

Experimental Verification: $H_2 + I_2 \rightleftharpoons 2HI$

Temperature: 731K

Data Analysis:

- Various initial concentrations tested
- Equilibrium expression: $Kc = [HI]^2/[H_2][I_2]$
- Constant value obtained: Kc = 54.8

Important Relationships:

1. **Reverse Reaction**: K'c = 1/Kc

2. **Multiplied Equation**: If equation multiplied by n, then $K''c = (Kc)^n$
3. **General Rule**: For net reaction from adding multiple reactions: $K_{net} = K_1 \times K_2 \times K_3$...

6.4 Homogeneous Equilibria

Definition:

All reactants and products in same phase

Examples:

1. **Gaseous**: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
2. **Aqueous**: $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

6.4.1 Equilibrium Constant in Gaseous Systems

Relationship between Kp and Kc:

For ideal gas: $p = cRT$ (where c = concentration in mol/L)

General Derivation: For $aA + bB \rightleftharpoons cC + dD$

```
Kp = Kc(RT)^Δn
```

Where:

- Δn = (moles of gaseous products) - (moles of gaseous reactants)
- $R = 0.0831$ bar L mol^{-1} K^{-1}
- T = temperature in Kelvin

Special Cases:

- If $\Delta n = 0$: $Kp = Kc$ (Example: $H_2 + I_2 \rightleftharpoons 2HI$)

- If $\Delta n \neq 0$: $K_p \neq K_c$

Example: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

- $\Delta n = 2 - (1 + 3) = -2$
- $K_p = K_c(RT)^{-2}$

Units of Equilibrium Constants:

Reaction Type	**Kc Units**	**Kp Units**
$\Delta n = 0$	Dimensionless	Dimensionless
$\Delta n = 1$	mol/L	bar
$\Delta n = -1$	L/mol	bar^{-1}

6.5 Heterogeneous Equilibria

Definition:

Equilibrium involving more than one phase

Key Principle:

Concentrations of pure solids and liquids are constant and incorporated into equilibrium constant

Examples:

1. $CaCO_3$ Decomposition:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Equilibrium Expression:

- Full expression: $K_c = [CaO][CO_2]/[CaCO_3]$

- Since [$CaCO_3$] and [CaO] are constant:
- **Modified**: $K'c = [CO_2]$ or $Kp = pCO_2$

2. Metal-Gas Equilibrium:

$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

Equilibrium Expression: $Kc = [Ni(CO)_4]/[CO]^4$

3. Salt Hydrolysis:

$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$

Equilibrium Expression: $Kc = [AgNO_3]^2/[HNO_3]^2$

Important Note:

Pure solids/liquids must be present for equilibrium to exist, but their concentrations don't appear in Kc expression.

6.6 Applications of Equilibrium Constants

Key Features of Equilibrium Constants:

1. **Temperature Dependent**: Unique value for each temperature
2. **Independent of Initial Concentrations**
3. **Composition Independent**: Value doesn't change with amounts
4. **Reaction Specific**: Different for forward vs reverse reactions
5. **Stoichiometry Dependent**: Changes with equation coefficients

6.6.1 Predicting Extent of Reaction

Magnitude Guidelines:

Kc Value	Interpretation	Example
$Kc > 10^3$	Products predominate	$H_2 + Cl_2 \rightleftharpoons 2HCl$ ($Kc = 4.0\times10^{31}$)
$10^{-3} < Kc < 10^3$	Appreciable amounts of both	$H_2 + I_2 \rightleftharpoons 2HI$ ($Kc = 57.0$)
$Kc < 10^{-3}$	Reactants predominate	$N_2 + O_2 \rightleftharpoons 2NO$ ($Kc = 4.8\times10^{-31}$)

6.6.2 Predicting Direction of Reaction

Reaction Quotient (Qc):

Definition: Expression identical to Kc but using non-equilibrium concentrations

For: $aA + bB \rightleftharpoons cC + dD$

```
Qc = [C]^c[D]^d / [A]^a[B]^b
```

Direction Prediction:

Comparison	Direction	Explanation
$Qc < Kc$	Forward →	More products needed
$Qc > Kc$	Reverse ←	More reactants needed
$Qc = Kc$	Equilibrium	No net reaction

6.6.3 Calculating Equilibrium Concentrations

Systematic Approach (ICE Method):

Step 1: Write balanced equation **Step 2**: Create ICE table

- **I**nitial concentrations
- **C**hange in concentrations

- **E**quilibrium concentrations

Step 3: Substitute into Kc expression **Step 4**: Solve for unknown **Step 5**: Calculate final concentrations **Step 6**: Verify by substituting back

Example Problem Setup:

```
      A    +    B    ⇌    C    +    D
I:   [A]₀      [B]₀       0        0
C:    -x        -x        +x       +x
E:   [A]₀-x    [B]₀-x      x        x
```

6.7 Relationship between K, Q, and Gibbs Energy

Thermodynamic Relationship:

General Expression:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At Equilibrium:

When $\Delta G = 0$ and $Q = K$:

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{(-\Delta G^\circ/RT)}$$

Spontaneity Interpretation:

$\Delta G°$	K Value	Reaction Tendency
$\Delta G° < 0$	$K > 1$	Spontaneous forward
$\Delta G° > 0$	$K < 1$	Non-spontaneous forward
$\Delta G° = 0$	$K = 1$	At equilibrium

Important Constants:

- $R = 8.314$ J mol^{-1} K^{-1}
- T in Kelvin

6.8 Factors Affecting Equilibria

Le Chatelier's Principle:

"If a system at equilibrium is disturbed, the system shifts to counteract the disturbance"

6.8.1 Effect of Concentration Changes

Rules:

1. **Adding Reactant/Product**: Equilibrium shifts to consume added substance
2. **Removing Reactant/Product**: Equilibrium shifts to replenish removed substance

Example: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Adding H_2:

- $Q_c < K_c$ (temporarily)
- Equilibrium shifts right
- More HI formed until $Q_c = K_c$ again

Industrial Applications:

- **Ammonia Production**: NH_3 continuously removed (liquefaction)
- **CaO Production**: CO_2 continuously removed from kiln

Demonstration: $Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$

- **Add Fe^{3+}**: Red color intensifies
- **Add SCN^-**: Red color intensifies
- **Add oxalic acid**: Removes Fe^{3+}, red color fades
- **Add $HgCl_2$**: Removes SCN^-, red color fades

6.8.2 Effect of Pressure Changes

Applicable to Gaseous Reactions:

Rule: Pressure increase favors side with fewer gas molecules

Example: $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

- **Reactants**: 4 moles gas
- **Products**: 2 moles gas
- **Pressure increase**: Shifts right (fewer gas molecules)

Reasoning:

- Volume decrease → Pressure increase
- Concentrations increase
- Qc changes
- System shifts to reduce pressure

Cases Where Pressure Has No Effect:

Equal moles of gas on both sides: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

6.8.3 Effect of Inert Gas Addition

At Constant Volume:

No effect - partial pressures and concentrations unchanged

At Constant Pressure:

Effect possible - volume increases, concentrations decrease

6.8.4 Effect of Temperature Changes

Key Principle:

Temperature change actually changes K value

Rules:

1. **Exothermic Reaction** ($\Delta H < 0$):
   - Temperature increase: K decreases
   - Temperature decrease: K increases
2. **Endothermic Reaction** ($\Delta H > 0$):
   - Temperature increase: K increases
   - Temperature decrease: K decreases

Examples:

Ammonia Synthesis: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta H = -92.38$ kJ/mol)

- **Exothermic**: Low temperature favors products
- **Industrial compromise**: Moderate temperature with catalyst

NO_2 Dimerization: $2NO_2(g) \rightleftharpoons N_2O_4(g)$ ($\Delta H = -57.2$ kJ/mol)

- **Low temperature**: Less brown color (more N_2O_4)
- **High temperature**: More brown color (more NO_2)

Endothermic Example: $[Co(H_2O)_6]^{3+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

- **Room temperature**: Blue (products favored)
- **Low temperature**: Pink (reactants favored)

6.8.5 Effect of Catalyst

Key Points:

1. **No effect on equilibrium position**
2. **Increases rate of both forward and reverse reactions equally**
3. **Reduces activation energy for both directions by same amount**
4. **Helps reach equilibrium faster**
5. **Does not appear in equilibrium expression**

Industrial Importance:

- **Haber Process**: Iron catalyst at 500°C, 200 atm
- **Contact Process**: V_2O_5 or Pt catalyst for SO_3 formation

6.9 Ionic Equilibrium in Solution

Electrolytes vs Non-electrolytes:

Non-electrolytes:

- **Example**: Sugar solution

- **Conductivity**: No electrical conduction
- **Reason**: No ion formation

Electrolytes:

- **Example**: NaCl solution
- **Conductivity**: Conduct electricity
- **Reason**: Ion formation

Classification of Electrolytes:

Strong Electrolytes:

- **Ionization**: Nearly 100% dissociated
- **Examples**: NaCl, HCl, NaOH
- **Representation**: $NaCl \rightarrow Na^+ + Cl^-$

Weak Electrolytes:

- **Ionization**: Partially dissociated (< 5%)
- **Examples**: CH_3COOH, NH_4OH
- **Equilibrium**: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Ionic Equilibrium:

Equilibrium between ions and unionized molecules in weak electrolyte solutions.

6.10 Acids, Bases, and Salts

Natural Occurrence:

- **Gastric juice**: HCl (1.2-1.5 L/day)

- **Vinegar**: CH_3COOH
- **Citrus fruits**: Citric acid, ascorbic acid
- **Tamarind**: Tartaric acid

Etymology:

- **"Acid"**: Latin "acidus" = sour
- **Characteristic properties**: Sour taste, turn blue litmus red, react with metals

6.10.1 Arrhenius Concept

Definitions:

- **Acid**: Substance that produces H^+ ions in water
- **Base**: Substance that produces OH^- ions in water

Ionization Equations:

Acid: $HX(aq) \rightarrow H^+(aq) + X^-(aq)$ **Base**: $MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$

Hydronium Ion:

- **Reality**: H^+ cannot exist alone in water
- **Actual form**: H_3O^+ (hydronium ion)
- **Representation**: $H^+(aq)$ and $H_3O^+(aq)$ used interchangeably

Limitations:

1. **Solvent restriction**: Applicable only to aqueous solutions
2. **Base definition**: Cannot explain basicity of NH_3 (no OH^- group)

6.10.2 Brönsted-Lowry Concept

Definitions:

- **Acid**: Proton (H^+) donor
- **Base**: Proton (H^+) acceptor

Example: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

- **H_2O**: Acts as acid (proton donor)
- **NH_3**: Acts as base (proton acceptor)

Conjugate Acid-Base Pairs:

Definition: Pair differing by one proton

Examples:

- NH_3/NH_4^+: NH_3 (base), NH_4^+ (conjugate acid)
- H_2O/OH^-: H_2O (acid), OH^- (conjugate base)

Strength Relationship:

- **Strong acid → Weak conjugate base**
- **Strong base → Weak conjugate acid**

Amphoteric Substances:

Can act as both acid and base:

- H_2O, HCO_3^-, HSO_4^-, NH_3

6.10.3 Lewis Concept

Definitions:

- **Lewis Acid**: Electron pair acceptor
- **Lewis Base**: Electron pair donor

Example: $BF_3 + NH_3 \rightarrow BF_3{:}NH_3$

- **BF_3**: Lewis acid (accepts electron pair)
- **NH_3**: Lewis base (donates electron pair)

Lewis Acids:

- Electron deficient species: BF_3, $AlCl_3$
- Cations: Co^{3+}, Mg^{2+}, H^+

Lewis Bases:

- Species with lone pairs: H_2O, NH_3, OH^-, F^-

6.11 Ionization of Acids and Bases

Strong vs Weak Acids/Bases:

Strong Acids:

Examples: $HClO_4$, HCl, HBr, HI, HNO_3, H_2SO_4 **Characteristic**: Nearly 100% ionized **Conjugate bases**: Very weak (ClO_4^-, Cl^-, Br^-, I^-, NO_3^-)

Strong Bases:

Examples: $LiOH$, $NaOH$, KOH, $CsOH$, $Ba(OH)_2$ **Characteristic**: Nearly 100% ionized

Weak Acids:

Examples: HNO_2, HF, CH_3COOH **Characteristic**: Partially ionized **Conjugate bases**: Relatively strong

Weak Bases:

Examples: NH_3, amines **Characteristic**: Partially ionized

6.11.1 Ionization Constant of Water

Autoionization:

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

Equilibrium Expression:

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 298K)

Pure Water:

- $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M
- **Neutral solution**: $[H^+] = [OH^-]$

Solution Types:

- **Acidic**: $[H^+] > [OH^-]$, $[H^+] > 10^{-7}$ M
- **Basic**: $[H^+] < [OH^-]$, $[H^+] < 10^{-7}$ M
- **Neutral**: $[H^+] = [OH^-] = 10^{-7}$ M

6.11.2 pH Scale

Definition:

$pH = -\log[H^+] = -\log aH^+$

pOH Definition:

$pOH = -\log[OH^-]$

Water Equilibrium:

$pH + pOH = pKw = 14$ (at 298K)

pH Scale:

- **Acidic**: pH < 7
- **Neutral**: pH = 7
- **Basic**: pH > 7

Common pH Values:

Substance	pH
Concentrated HCl	~-1.0
Gastric juice	~1.2
Lemon juice	~2.2
Soft drinks	~3.0
Black coffee	5.0
Human saliva	6.4
Pure water	7.0
Human blood	7.4
Sea water	7.8
Milk of magnesia	10.0
0.1 M NaOH	13.0

pH Measurement:

1. **pH paper**: Accuracy ±0.5 units
2. **pH meter**: Accuracy ±0.001 units

6.11.3 Ionization Constants of Weak Acids

General Equilibrium:

$HX + H_2O \rightleftharpoons H_3O^+ + X^-$

ICE Table:

	HX	H_3O^+	X^-
Initial:	c	0	0
Change:	$-c\alpha$	$+c\alpha$	$+c\alpha$
Equilibrium:	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Acid Ionization Constant:

$$Ka = [H_3O^+][X^-]/[HX] = c\alpha^2/(1-\alpha)$$

Important Values:

Acid	Formula	Ka (298K)
Hydrofluoric	HF	3.5×10^{-4}
Nitrous	HNO_2	4.5×10^{-4}
Formic	$HCOOH$	1.8×10^{-4}
Acetic	CH_3COOH	1.74×10^{-5}
Hypochlorous	$HClO$	3.0×10^{-8}
Hydrocyanic	HCN	4.9×10^{-10}

Relationship:

$$pKa = -\log Ka$$

Stronger acid → Larger Ka → Smaller pKa

6.11.4 Ionization of Weak Bases

General Equilibrium:

$B + H_2O \rightleftharpoons BH^+ + OH^-$

Base Ionization Constant:

$Kb = [BH^+][OH^-]/[B]$

Important Values:

Base	Formula	Kb (298K)
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}
Ammonia	NH_3	1.77×10^{-5}
Pyridine	C_5H_5N	1.77×10^{-9}
Aniline	$C_6H_5NH_2$	4.27×10^{-10}

Relationship:

$pKb = -\log Kb$

6.11.5 Relation between Ka and Kb

For Conjugate Acid-Base Pair:

$Ka \times Kb = Kw = 1.0 \times 10^{-14}$ (at 298K)

In Terms of pK:

$pKa + pKb = pKw = 14$ (at 298K)

Strength Correlation:

- **Strong acid → Weak conjugate base** (small Kb)
- **Strong base → Weak conjugate acid** (small Ka)

6.11.6 Polyprotic Acids

Definition:

Acids with more than one ionizable proton

Stepwise Ionization:

Example: H_2X (diprotic)

First step: $H_2X \rightleftharpoons H^+ + HX^-$; $K_{a1} = [H^+][HX^-]/[H_2X]$

Second step: $HX^- \rightleftharpoons H^+ + X^{2-}$; $K_{a2} = [H^+][X^{2-}]/[HX^-]$

Important Pattern:

Ka1 > Ka2 > Ka3 (successive ionization becomes harder)

Common Examples:

Acid	**Ka1**	**Ka2**	**Ka3**
H_2CO_3	4.2×10^{-7}	4.8×10^{-11}	-
H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	-
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

6.11.7 Factors Affecting Acid Strength

Key Factors:

1. **Bond Strength**: Weaker H-A bond → Stronger acid

2. **Bond Polarity**: More polar H-A bond → Stronger acid

Periodic Trends:

Within Group (bond strength dominates):

- Size increases → Bond strength decreases → Acid strength increases
- **Example**: $HF < HCl < HBr < HI$

Within Period (polarity dominates):

- Electronegativity increases → Polarity increases → Acid strength increases
- **Example**: $CH_4 < NH_3 < H_2O < HF$

6.11.8 Common Ion Effect

Definition:

Shift in equilibrium when substance providing common ion is added

Example: Acetic Acid + Sodium Acetate

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Adding CH_3COONa:

- Increases $[CH_3COO^-]$
- Equilibrium shifts left
- $[H^+]$ decreases
- pH increases

Calculation:

For 0.05 M CH_3COOH + 0.05 M CH_3COONa:

$$Ka = [H^+][CH_3COO^-]/[CH_3COOH] = x(0.05)/0.05 = x$$

Therefore: $[H^+] = Ka = 1.8\times10^{-5}$ M

6.11.9 Hydrolysis of Salts

Types of Salts:

1. Salt of Strong Acid + Strong Base:

Example: NaCl **Hydrolysis**: None **pH**: 7 (neutral) **Reason**: Neither Na^+ nor Cl^- hydrolyze

2. Salt of Weak Acid + Strong Base:

Example: CH_3COONa **Hydrolysis**: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ **pH**: > 7 (basic) **Reason**: Acetate ion accepts protons

3. Salt of Strong Acid + Weak Base:

Example: NH_4Cl
Hydrolysis: $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ **pH**: < 7 (acidic) **Reason**: Ammonium ion donates protons

4. Salt of Weak Acid + Weak Base:

Example: CH_3COONH_4 **Hydrolysis**: Both ions hydrolyze **pH formula**: $pH = 7 + ½(pKa - pKb)$

Interpretation:

- If pKa > pKb: pH > 7 (basic)
- If pKa < pKb: pH < 7 (acidic)
- If pKa = pKb: pH = 7 (neutral)

6.12 Buffer Solutions

Definition:

Buffer solutions resist change in pH upon dilution or addition of small amounts of acid or base

Importance:

- Body fluids (blood, urine) maintain specific pH
- Industrial processes require pH control
- Medical and cosmetic formulations

Types:

1. Acidic Buffer:

Composition: Weak acid + Salt of weak acid with strong base **Example**: $CH_3COOH + CH_3COONa$ (pH ≈ 4.75)

2. Basic Buffer:

Composition: Weak base + Salt of weak base with strong acid
Example: $NH_3 + NH_4Cl$ (pH ≈ 9.25)

6.12.1 Henderson-Hasselbalch Equation

For Acidic Buffer:

$$pH = pKa + \log([A^-]/[HA])$$

or

$$pH = pKa + \log([Salt]/[Acid])$$

For Basic Buffer:

$$pOH = pKb + \log([BH^+]/[B])$$

or

$$pH = pKa + \log([Base]/[Salt])$$

Buffer Design:

- **Equal concentrations**: pH = pKa (for acidic buffer)
- **Best buffering**: When pH ≈ pKa ± 1
- **Dilution effect**: pH remains constant (ratio unchanged)

6.13 Solubility Equilibria of Sparingly Soluble Salts

Classification by Solubility:

Category	Solubility	Examples
Soluble	> 0.1 M	$CaCl_2$, NaCl
Slightly Soluble	0.01-0.1 M	$Ca(OH)_2$
Sparingly Soluble	< 0.01 M	AgCl, $BaSO_4$

6.13.1 Solubility Product Constant (Ksp)

General Equilibrium:

$MpXq(s) \rightleftharpoons pM^{n+}(aq) + qX^{m-}(aq)$

Solubility Product:

```
Ksp = [M^n+]^p[X^m-]^q
```

Note: Concentration of solid is constant, incorporated into Ksp

Examples:

1. $BaSO_4$: $BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$$Ksp = [Ba^{2+}][SO_4^{2-}] = 1.1\times10^{-10}\ (298K)$$

If molar solubility = S:

- $[Ba^{2+}] = S$, $[SO_4^{2-}] = S$
- $Ksp = S^2 \rightarrow S = \sqrt{Ksp} = 1.05\times10^{-5}$ M

2. General Formula MxXy:

If molar solubility = S:

- [M^p+] = xS, [X^q-] = yS
- Ksp = (xS)^x(yS)^y = x^x·y^y·S^(x+y)
- S = (Ksp/x^x·y^y)^(1/(x+y))

Common Ksp Values (298K):

Salt	**Ksp**
AgCl	1.8×10^{-10}
AgBr	5.0×10^{-13}
AgI	8.3×10^{-17}
$BaSO_4$	1.1×10^{-10}
CaF_2	3.9×10^{-11}
$PbCl_2$	1.9×10^{-4}

6.13.2 Common Ion Effect on Solubility

Principle:

Adding common ion decreases solubility of sparingly soluble salt

Example: AgCl in presence of NaCl

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

Adding NaCl:

- Increases $[Cl^-]$
- Equilibrium shifts left
- $[Ag^+]$ decreases
- Solubility decreases

Quantitative Treatment:

If solubility of AgCl in pure water = S_0
If solubility in 0.1 M NaCl = S

$K_{sp} = [Ag^+][Cl^-] = S(0.1 + S) \approx S(0.1)$

$S = K_{sp}/0.1 << S_0$

Applications:

1. **Purification**: NaCl purified by HCl gas treatment
2. **Gravimetric analysis**: Complete precipitation using excess precipitating agent
3. **Qualitative analysis**: Selective precipitation

pH Effect on Solubility:

For salts of weak acids, solubility increases at lower pH due to protonation of anion.

Example: $CaF_2 + H^+ \rightarrow Ca^{2+} + HF$

- Lower pH → More HF formation
- Removes F^- ions → Increases solubility

NEET-Specific Important Points

High-Yield Topics:

1. Equilibrium Constant Calculations:

- Kc and Kp relationships
- ICE table method
- Reaction quotient (Q) vs equilibrium constant (K)

2. Le Chatelier's Principle:

- Effect of concentration, pressure, temperature
- Industrial applications (Haber process, Contact process)

3. Acid-Base Equilibria:

- Ka, Kb, and Kw relationships
- pH calculations for weak acids/bases
- Buffer calculations using Henderson-Hasselbalch equation

4. Salt Hydrolysis:

- pH predictions based on salt type
- Hydrolysis constant calculations

5. Solubility Product:

- Ksp calculations and solubility predictions
- Common ion effect applications

Common NEET Question Patterns:

1. Numerical Problems:

- Equilibrium constant calculations
- pH of weak acid/base solutions
- Buffer pH calculations
- Solubility from Ksp

2. Conceptual Questions:

- Predicting reaction direction using Q vs K
- Effect of various factors on equilibrium
- Classification of salts and pH predictions

3. Graph Interpretation:

- Equilibrium composition vs time
- pH titration curves
- Solubility vs temperature

Memory Aids and Mnemonics

Le Chatelier's Principle:

"HEAT" - Higher Energy Always Taken

- Endothermic: Higher temperature increases K
- Exothermic: Higher temperature decreases K

Acid-Base Strength:

"Strong acid, weak conjugate base" "Strong base, weak conjugate acid"

pH Scale:

"pH + pOH = 14" (at 298K) **"pKa + pKb = 14"** (for conjugate pairs)

Buffer Types:

"WAR" - Weak Acid + salt of weak acid with stRong base **"WBS"** - Weak Base + Salt of weak base with strong acid

Solubility Rules:

"Like dissolves like" "Common ion decreases solubility"

Practice Questions for NEET

Multiple Choice Questions:

1. For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, if Kc = 0.04 at 250°C, what is Kp? a) 0.04 × RT b) 0.04/(RT) c) 0.04 d) 0.04 + RT
2. The pH of 0.1 M CH_3COOH solution (Ka = 1.8×10^{-5}) is approximately: a) 1 b) 2.9 c) 4.8 d) 7
3. Which salt undergoes anionic hydrolysis? a) NaCl b) NH_4Cl c) CH_3COONa d) KBr

Short Answer Questions:

1. Explain why Kp = Kc for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.
2. Calculate the pH of a buffer containing 0.1 M CH_3COOH and 0.1 M CH_3COONa.
3. Why does AgCl precipitate when NaCl is added to $AgNO_3$ solution?

Long Answer Questions:

1. Derive the relationship between Kp and Kc for gaseous equilibria.
2. Explain buffer action with a suitable example and derive Henderson-Hasselbalch equation.
3. Discuss the common ion effect on solubility with quantitative treatment.

Summary Tables

Equilibrium Constants:

Type	Expression	Units	Temperature Effect
Kc	[Products]/[Reactants]	(mol/L)^Δn	Changes with T
Kp	(P_products)/(P_reactants)	(bar)^Δn	Changes with T
Ka	$[H^+][A^-]/[HA]$	mol/L	Changes with T
Kb	$[BH^+][OH^-]/[B]$	mol/L	Changes with T

Type	Expression	Units	Temperature Effect
Ksp	[M^n+]^x[X^m-]^y	(mol/L)^(x+y)	Changes with T

Acid-Base Classification:

Concept	Acid	Base	Limitations
Arrhenius	H^+ producer	OH^- producer	Aqueous only
Brönsted-Lowry	H^+ donor	H^+ acceptor	Proton transfer only
Lewis	e^- pair acceptor	e^- pair donor	Most general

Salt Hydrolysis Summary:

Salt Type	Example	Hydrolysis	pH	Reason
SA + SB	NaCl	None	7	No hydrolysis
WA + SB	CH_3COONa	Anionic	>7	$A^- + H_2O \rightarrow HA + OH^-$
SA + WB	NH_4Cl	Cationic	<7	$BH^+ + H_2O \rightarrow B + H^+$
WA + WB	CH_3COONH_4	Both	Depends on Ka,Kb	Both ions hydrolyze

EXAM SPRINT - Master Equilibrium

Key Success Strategy:

- Focus on understanding equilibrium as dynamic process
- Master ICE table method for calculations
- Practice pH calculations for all types of solutions
- Understand Le Chatelier's principle applications
- Memorize important Ka, Kb, and Ksp values

- Practice buffer and solubility problems regularly

Common Mistakes to Avoid:

- Confusing Q with K
- Forgetting to account for stoichiometry in equilibrium expressions
- Mixing up Kp and Kc relationships
- Incorrect application of common ion effect
- Wrong pH predictions for salt solutions

Final Tips:

- Always check units in calculations
- Use logarithm properties correctly in pH problems
- Remember temperature dependence of equilibrium constants
- Practice graphical questions involving equilibrium

Source: NCERT Chemistry Class 11, Chapter 6 - Comprehensive coverage for NEET preparation