

# 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:**  $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}$

### 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:**  $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$

### 6.1.3 Solid-Vapor Equilibrium (Sublimation)

**Example:** Iodine sublimation

- Solid  $\text{I}_2 \rightarrow \text{I}_2$  vapor (violet color)
- Intensity becomes constant at equilibrium

**Other Examples:**

- Camphor(s)  $\rightleftharpoons$  Camphor(g)
- $\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_4\text{Cl(g)}$

**Representation:**  $\text{I}_2\text{(s)} \rightleftharpoons \text{I}_2\text{(g)}$

### 6.1.4 Dissolution Equilibria

#### Solids in Liquids:

**Saturated Solution:** No more solute can dissolve at given temperature

**Dynamic Process:** Sugar(solution)  $\rightleftharpoons$  Sugar(solid)

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

#### Gases in Liquids:

**Example:**  $\text{CO}_2$  in soda water

- $\text{CO}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(solution)}$
- Governed by **Henry's Law:** Mass of dissolved gas  $\propto$  pressure of gas
- Explains fizzing when bottle opened (pressure decrease)

### Summary of Physical Equilibria

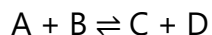
Process	Equilibrium Condition
Liquid $\rightleftharpoons$ Vapor	Constant vapor pressure at given T
Solid $\rightleftharpoons$ Liquid	Fixed melting point at constant P
Solute(s) $\rightleftharpoons$ Solute(solution)	Constant solubility at given T
Gas(g) $\rightleftharpoons$ Gas(aq)	$[\text{gas(aq)}]/[\text{gas(g)}]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

## 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**.

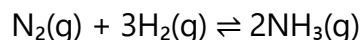
### General Reaction:



### 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



### Isotope Evidence:

- Using D<sub>2</sub> instead of H<sub>2</sub> shows scrambling of isotopes
- Formation of NH<sub>3</sub>, NH<sub>2</sub>D, NHD<sub>2</sub>, ND<sub>3</sub> proves dynamic nature

### Classification by Extent:

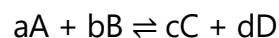
1. **Nearly Complete:** Negligible reactants remain
2. **Minimal Conversion:** Small product formation
3. **Appreciable:** Comparable reactant and product concentrations

## 6.3 Law of Chemical Equilibrium and Equilibrium Constant

### Historical Background:

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

### For General Reaction:



### Equilibrium Constant Expression:

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

### Where:

$K_c$  = 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:  $K_c = \frac{[HI]^2}{[H_2][I_2]}$
- Constant value obtained:  $K_c = 54.8$

### Important Relationships:

1. **Reverse Reaction:**  $K'_c = 1/K_c$

2. **Multiplied Equation:** If equation multiplied by  $n$ , then  $K'^c = (Kc)^n$

3. **General Rule:** For net reaction from adding multiple reactions:  $K_{\text{net}} = K_1 \times K_2 \times K_3 \dots$

## 6.4 Homogeneous Equilibria

### Definition:

All reactants and products in same phase

### Examples:

1. **Gaseous:**  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

2. **Aqueous:**  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$

### 6.4.1 Equilibrium Constant in Gaseous Systems

#### Relationship between $K_p$ and $K_c$ :

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

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

$$K_p = K_c(RT)^{\Delta n}$$

#### Where:

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

#### Special Cases:

- If  $\Delta n = 0$ :  $K_p = K_c$  (Example:  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ )

- 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	$K_c$ Units	$K_p$ Units
$\Delta n = 0$	Dimensionless	Dimensionless
$\Delta n = 1$	mol/L	bar
$\Delta n = -1$	L/mol	bar <sup>-1</sup>

## 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:

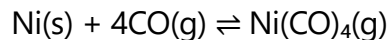


### Equilibrium Expression:

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

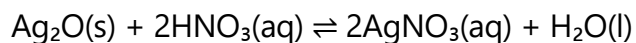
- Since  $[\text{CaCO}_3]$  and  $[\text{CaO}]$  are constant:
- **Modified:**  $K'_c = [\text{CO}_2]$  or  $K_p = p\text{CO}_2$

## 2. Metal-Gas Equilibrium:



**Equilibrium Expression:**  $K_c = [\text{Ni(CO)}_4]/[\text{CO}]^4$

## 3. Salt Hydrolysis:



**Equilibrium Expression:**  $K_c = [\text{AgNO}_3]^2/[\text{HNO}_3]^2$

## Important Note:

Pure solids/liquids must be present for equilibrium to exist, but their concentrations don't appear in  $K_c$  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
$K_c > 10^3$	Products predominate	$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$ ( $K_c = 4.0 \times 10^{31}$ )
$10^{-3} < K_c < 10^3$	Appreciable amounts of both	$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ ( $K_c = 57.0$ )
$K_c < 10^{-3}$	Reactants predominate	$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ ( $K_c = 4.8 \times 10^{-31}$ )

## 6.6.2 Predicting Direction of Reaction

### Reaction Quotient (Qc):

**Definition:** Expression identical to  $K_c$  but using non-equilibrium concentrations

**For:**  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

$$Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

### Direction Prediction:

Comparison	Direction	Explanation
$Q_c < K_c$	Forward $\rightarrow$	More products needed
$Q_c > K_c$	Reverse $\leftarrow$	More reactants needed
$Q_c = K_c$	Equilibrium	No net reaction

## 6.6.3 Calculating Equilibrium Concentrations

### Systematic Approach (ICE Method):

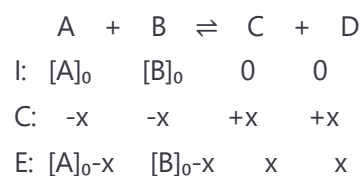
**Step 1:** Write balanced equation **Step 2:** Create ICE table

- Initial concentrations
- Change in concentrations

- Equilibrium 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:**



## 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:**

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

### Important Constants:

- $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
- 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:**  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

#### Adding $\text{H}_2$ :

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

### Industrial Applications:

- **Ammonia Production:**  $\text{NH}_3$  continuously removed (liquefaction)
- **CaO Production:**  $\text{CO}_2$  continuously removed from kiln

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

- **Add  $\text{Fe}^{3+}$ :** Red color intensifies
- **Add  $\text{SCN}^-$ :** Red color intensifies
- **Add oxalic acid:** Removes  $\text{Fe}^{3+}$ , red color fades
- **Add  $\text{HgCl}_2$ :** Removes  $\text{SCN}^-$ , red color fades

## 6.8.2 Effect of Pressure Changes

**Applicable to Gaseous Reactions:**

**Rule:** Pressure increase favors side with fewer gas molecules

**Example:**  $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$

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

**Reasoning:**

- Volume decrease  $\rightarrow$  Pressure increase
- Concentrations increase
- $Q_c$  changes
- System shifts to reduce pressure

**Cases Where Pressure Has No Effect:**

Equal moles of gas on both sides:  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

### 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:**  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  ( $\Delta H = -92.38 \text{ kJ/mol}$ )

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

**NO<sub>2</sub> Dimerization:**  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$  ( $\Delta H = -57.2 \text{ kJ/mol}$ )

- **Low temperature:** Less brown color (more N<sub>2</sub>O<sub>4</sub>)
- **High temperature:** More brown color (more NO<sub>2</sub>)

**Endothermic Example:**  $[\text{Co}(\text{H}_2\text{O})_6]^{3+} + 4\text{Cl}^- \rightleftharpoons [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O}$

- **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<sub>2</sub>O<sub>5</sub> or Pt catalyst for SO<sub>3</sub> 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:**  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

##### **Weak Electrolytes:**

- **Ionization:** Partially dissociated (< 5%)
- **Examples:**  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{OH}$
- **Equilibrium:**  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

#### **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:**  $\text{CH}_3\text{COOH}$
- **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  $\text{H}^+$  ions in water
- **Base:** Substance that produces  $\text{OH}^-$  ions in water

### Ionization Equations:

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

### Hydronium Ion:

- **Reality:**  $\text{H}^+$  cannot exist alone in water
- **Actual form:**  $\text{H}_3\text{O}^+$  (hydronium ion)
- **Representation:**  $\text{H}^+(\text{aq})$  and  $\text{H}_3\text{O}^+(\text{aq})$  used interchangeably

### Limitations:

1. **Solvent restriction:** Applicable only to aqueous solutions
2. **Base definition:** Cannot explain basicity of  $\text{NH}_3$  (no  $\text{OH}^-$  group)



## 6.10.2 Brönsted-Lowry Concept

### Definitions:

- **Acid:** Proton ( $\text{H}^+$ ) donor
- **Base:** Proton ( $\text{H}^+$ ) acceptor

**Example:**  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

- **$\text{H}_2\text{O}$ :** Acts as acid (proton donor)
- **$\text{NH}_3$ :** Acts as base (proton acceptor)

### Conjugate Acid-Base Pairs:

**Definition:** Pair differing by one proton

### Examples:

- $\text{NH}_3/\text{NH}_4^+$ :  $\text{NH}_3$  (base),  $\text{NH}_4^+$  (conjugate acid)
- $\text{H}_2\text{O}/\text{OH}^-$ :  $\text{H}_2\text{O}$  (acid),  $\text{OH}^-$  (conjugate base)

### Strength Relationship:

- **Strong acid**  $\rightarrow$  **Weak conjugate base**
- **Strong base**  $\rightarrow$  **Weak conjugate acid**

### Amphoteric Substances:

Can act as both acid and base:

- $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{NH}_3$

### 6.10.3 Lewis Concept

#### Definitions:

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

**Example:**  $\text{BF}_3 + \text{NH}_3 \rightarrow \text{BF}_3:\text{NH}_3$

- **BF<sub>3</sub>:** Lewis acid (accepts electron pair)
- **NH<sub>3</sub>:** Lewis base (donates electron pair)

#### Lewis Acids:

- Electron deficient species:  $\text{BF}_3$ ,  $\text{AlCl}_3$
- Cations:  $\text{Co}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$

#### Lewis Bases:

- Species with lone pairs:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ ,  $\text{F}^-$

## 6.11 Ionization of Acids and Bases

### Strong vs Weak Acids/Bases:

#### Strong Acids:

**Examples:**  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  **Characteristic:** Nearly 100% ionized **Conjugate bases:** Very weak ( $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ )

#### Strong Bases:

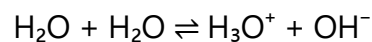
**Examples:**  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{CsOH}$ ,  $\text{Ba}(\text{OH})_2$  **Characteristic:** Nearly 100% ionized

**Weak Acids:**

**Examples:**  $\text{HNO}_2$ ,  $\text{HF}$ ,  $\text{CH}_3\text{COOH}$  **Characteristic:** Partially ionized **Conjugate bases:** Relatively strong

**Weak Bases:**

**Examples:**  $\text{NH}_3$ , amines **Characteristic:** Partially ionized

**6.11.1 Ionization Constant of Water****Autoionization:****Equilibrium Expression:**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at 298K)}$$

**Pure Water:**

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

**Solution Types:**

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

**6.11.2 pH Scale****Definition:**

$$\text{pH} = -\log[\text{H}^+] = -\log a\text{H}^+$$

**pOH Definition:**

$$\text{pOH} = -\log[\text{OH}^-]$$

**Water Equilibrium:**

$$\text{pH} + \text{pOH} = \text{pK}_w = 14 \text{ (at 298K)}$$

**pH Scale:**

- **Acidic:**  $\text{pH} < 7$
- **Neutral:**  $\text{pH} = 7$
- **Basic:**  $\text{pH} > 7$

**Common pH Values:**

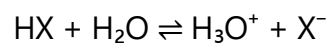
Substance	pH
Concentrated HCl	~-1.0
Gastric juice	~1.2
Lemon juice	~2.2
Soft drinks	~3.0
Black coffee	5.0
Human saliva	6.4
Pure water	7.0
Human blood	7.4
Sea water	7.8
Milk of magnesia	10.0
0.1 M NaOH	13.0

#### pH Measurement:

1. **pH paper:** Accuracy  $\pm 0.5$  units
2. **pH meter:** Accuracy  $\pm 0.001$  units

### 6.11.3 Ionization Constants of Weak Acids

#### General Equilibrium:



#### ICE Table:

	HX	H <sub>3</sub> O <sup>+</sup>	X <sup>-</sup>
Initial:	c	0	0
Change:	-cα	+cα	+cα
Equilibrium:	c(1-α)	cα	cα

### Acid Ionization Constant:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} = \frac{c\alpha^2}{(1-\alpha)}$$

### Important Values:

Acid	Formula	K <sub>a</sub> (298K)
Hydrofluoric	HF	3.5×10 <sup>-4</sup>
Nitrous	HNO <sub>2</sub>	4.5×10 <sup>-4</sup>
Formic	HCOOH	1.8×10 <sup>-4</sup>
Acetic	CH <sub>3</sub> COOH	1.74×10 <sup>-5</sup>
Hypochlorous	HClO	3.0×10 <sup>-8</sup>
Hydrocyanic	HCN	4.9×10 <sup>-10</sup>

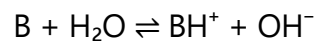
### Relationship:

$$\text{p}K_a = -\log K_a$$

**Stronger acid → Larger K<sub>a</sub> → Smaller pK<sub>a</sub>**

## 6.11.4 Ionization of Weak Bases

### General Equilibrium:

**Base Ionization Constant:**

$$K_b = [\text{BH}^+][\text{OH}^-]/[\text{B}]$$

**Important Values:**

Base	Formula	K <sub>b</sub> (298K)
Dimethylamine	(CH <sub>3</sub> ) <sub>2</sub> NH	5.4 × 10 <sup>-4</sup>
Ammonia	NH <sub>3</sub>	1.77 × 10 <sup>-5</sup>
Pyridine	C <sub>5</sub> H <sub>5</sub> N	1.77 × 10 <sup>-9</sup>
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	4.27 × 10 <sup>-10</sup>

**Relationship:**

$$\text{p}K_b = -\log K_b$$

**6.11.5 Relation between K<sub>a</sub> and K<sub>b</sub>****For Conjugate Acid-Base Pair:**

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \text{ (at 298K)}$$

**In Terms of pK:**

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ (at 298K)}$$

**Strength Correlation:**

- **Strong acid** → **Weak conjugate base** (small  $K_b$ )
- **Strong base** → **Weak conjugate acid** (small  $K_a$ )

### 6.11.6 Polyprotic Acids

#### Definition:

Acids with more than one ionizable proton

#### Stepwise Ionization:

**Example:**  $H_2X$  (diprotic)

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

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

#### Important Pattern:

**$K_{a1} > K_{a2} > K_{a3}$**  (successive ionization becomes harder)

#### Common Examples:

Acid	$K_{a1}$	$K_{a2}$	$K_{a3}$
$H_2CO_3$	$4.2 \times 10^{-7}$	$4.8 \times 10^{-11}$	-
$H_2SO_3$	$1.5 \times 10^{-2}$	$1.0 \times 10^{-7}$	-
$H_3PO_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.2 \times 10^{-13}$

### 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:**  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

**Within Period** (polarity dominates):

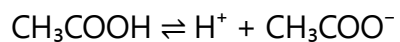
- Electronegativity increases → Polarity increases → Acid strength increases
- **Example:**  $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$

### 6.11.8 Common Ion Effect

**Definition:**

Shift in equilibrium when substance providing common ion is added

**Example: Acetic Acid + Sodium Acetate**



**Adding  $\text{CH}_3\text{COONa}$ :**

- Increases  $[\text{CH}_3\text{COO}^-]$
- Equilibrium shifts left
- $[\text{H}^+]$  decreases
- pH increases

**Calculation:**

For 0.05 M  $\text{CH}_3\text{COOH}$  + 0.05 M  $\text{CH}_3\text{COONa}$ :

$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = x(0.05)/0.05 = x$$

Therefore:  $[\text{H}^+] = K_a = 1.8 \times 10^{-5} \text{ M}$

### 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  $\text{Na}^+$  nor  $\text{Cl}^-$  hydrolyze

##### 2. Salt of Weak Acid + Strong Base:

**Example:**  $\text{CH}_3\text{COONa}$  **Hydrolysis:**  $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$  **pH:**  $> 7$  (basic) **Reason:** Acetate ion accepts protons

##### 3. Salt of Strong Acid + Weak Base:

**Example:**  $\text{NH}_4\text{Cl}$

**Hydrolysis:**  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$  **pH:**  $< 7$  (acidic) **Reason:** Ammonium ion donates protons

##### 4. Salt of Weak Acid + Weak Base:

**Example:**  $\text{CH}_3\text{COONH}_4$  **Hydrolysis:** Both ions hydrolyze **pH formula:**  $\text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$

#### Interpretation:

- If  $\text{p}K_a > \text{p}K_b$ :  $\text{pH} > 7$  (basic)
- If  $\text{p}K_a < \text{p}K_b$ :  $\text{pH} < 7$  (acidic)
- If  $\text{p}K_a = \text{p}K_b$ :  $\text{pH} = 7$  (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:**  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$   
(pH  $\approx$  4.75)

**2. Basic Buffer:**

**Composition:** Weak base + Salt of weak base with strong acid

**Example:**  $\text{NH}_3 + \text{NH}_4\text{Cl}$  (pH  $\approx$  9.25)

**6.12.1 Henderson-Hasselbalch Equation****For Acidic Buffer:**

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

or

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

**For Basic Buffer:**

$$\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{BH}^+]}{[\text{B}]}\right)$$

or

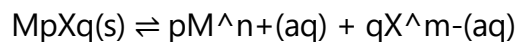
$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Base}]}{[\text{Salt}]}\right)$$

**Buffer Design:**

- **Equal concentrations:**  $\text{pH} = \text{pK}_a$  (for acidic buffer)
- **Best buffering:** When  $\text{pH} \approx \text{pK}_a \pm 1$
- **Dilution effect:** pH remains constant (ratio unchanged)

**6.13 Solubility Equilibria of Sparingly Soluble Salts****Classification by Solubility:**

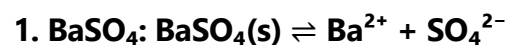
Category	Solubility	Examples
Soluble	> 0.1 M	$\text{CaCl}_2$ , $\text{NaCl}$
Slightly Soluble	0.01-0.1 M	$\text{Ca}(\text{OH})_2$
Sparingly Soluble	< 0.01 M	$\text{AgCl}$ , $\text{BaSO}_4$

**6.13.1 Solubility Product Constant (K<sub>sp</sub>)****General Equilibrium:****Solubility Product:**

$$K_{sp} = [M^{n+}]^p [X^{m-}]^q$$

**Note:** Concentration of solid is constant, incorporated into  $K_{sp}$

**Examples:**



$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} \text{ (298K)}$$

If molar solubility =  $S$ :

- $[Ba^{2+}] = S$ ,  $[SO_4^{2-}] = S$
- $K_{sp} = S^2 \rightarrow S = \sqrt{K_{sp}} = 1.05 \times 10^{-5} \text{ M}$

**2. General Formula  $M_xX_y$ :**

If molar solubility =  $S$ :

- $[M^{p+}] = xS$ ,  $[X^{q-}] = yS$
- $K_{sp} = (xS)^x (yS)^y = x^x y^y S^{(x+y)}$
- $S = (K_{sp}/x^x y^y)^{1/(x+y)}$

**Common  $K_{sp}$  Values (298K):**

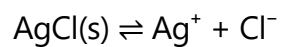
Salt	K <sub>sp</sub>
AgCl	$1.8 \times 10^{-10}$
AgBr	$5.0 \times 10^{-13}$
AgI	$8.3 \times 10^{-17}$
BaSO <sub>4</sub>	$1.1 \times 10^{-10}$
CaF <sub>2</sub>	$3.9 \times 10^{-11}$
PbCl <sub>2</sub>	$1.9 \times 10^{-4}$

### 6.13.2 Common Ion Effect on Solubility

#### Principle:

Adding common ion decreases solubility of sparingly soluble salt

#### Example: AgCl in presence of NaCl



#### Adding NaCl:

- Increases  $[\text{Cl}^-]$
- Equilibrium shifts left
- $[\text{Ag}^+]$  decreases
- Solubility decreases

#### Quantitative Treatment:

If solubility of AgCl in pure water =  $S_0$

If solubility in 0.1 M NaCl =  $S$

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

$$S = K_{sp}/0.1 \ll S_0$$

### 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  $\rightarrow$  More HF formation
- Removes  $F^-$  ions  $\rightarrow$  Increases solubility

## NEET-Specific Important Points

### High-Yield Topics:

#### 1. Equilibrium Constant Calculations:

- $K_c$  and  $K_p$  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:**

- $K_a$ ,  $K_b$ , and  $K_w$  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:**

- $K_{sp}$  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  $K_{sp}$

### **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  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , if  $K_c = 0.04$  at  $250^\circ\text{C}$ , what is  $K_p$ ? a)  $0.04 \times RT$  b)  $0.04/(RT)$  c)  $0.04$  d)  $0.04 + RT$
2. The pH of 0.1 M  $\text{CH}_3\text{COOH}$  solution ( $K_a = 1.8 \times 10^{-5}$ ) is approximately: a) 1 b) 2.9 c) 4.8 d) 7
3. Which salt undergoes anionic hydrolysis? a)  $\text{NaCl}$  b)  $\text{NH}_4\text{Cl}$  c)  $\text{CH}_3\text{COONa}$  d)  $\text{KBr}$

### Short Answer Questions:

1. Explain why  $K_p = K_c$  for the reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ .
2. Calculate the pH of a buffer containing 0.1 M  $\text{CH}_3\text{COOH}$  and 0.1 M  $\text{CH}_3\text{COONa}$ .
3. Why does  $\text{AgCl}$  precipitate when  $\text{NaCl}$  is added to  $\text{AgNO}_3$  solution?

### Long Answer Questions:

1. Derive the relationship between  $K_p$  and  $K_c$  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
$K_c$	$[\text{Products}]/[\text{Reactants}]$	$(\text{mol/L})^{\Delta n}$	Changes with T
$K_p$	$(P_{\text{products}})/(P_{\text{reactants}})$	$(\text{bar})^{\Delta n}$	Changes with T
$K_a$	$[\text{H}^+][\text{A}^-]/[\text{HA}]$	mol/L	Changes with T
$K_b$	$[\text{BH}^+][\text{OH}^-]/[\text{B}]$	mol/L	Changes with T

Type	Expression	Units	Temperature Effect
K <sub>sp</sub>	$[M^{n+}]^x[X^{m-}]^y$	$(\text{mol/L})^{(x+y)}$	Changes with T

### Acid-Base Classification:

Concept	Acid	Base	Limitations
Arrhenius	H <sup>+</sup> producer	OH <sup>-</sup> producer	Aqueous only
Brønsted-Lowry	H <sup>+</sup> donor	H <sup>+</sup> acceptor	Proton transfer only
Lewis	e <sup>-</sup> pair acceptor	e <sup>-</sup> pair donor	Most general

### Salt Hydrolysis Summary:

Salt Type	Example	Hydrolysis	pH	Reason
SA + SB	NaCl	None	7	No hydrolysis
WA + SB	CH <sub>3</sub> COONa	Anionic	>7	$A^- + H_2O \rightarrow HA + OH^-$
SA + WB	NH <sub>4</sub> Cl	Cationic	<7	$BH^+ + H_2O \rightarrow B + H^+$
WA + WB	CH <sub>3</sub> COONH <sub>4</sub>	Both	Depends on K <sub>a</sub> , K <sub>b</sub>	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 K<sub>a</sub>, K<sub>b</sub>, and K<sub>sp</sub> 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  $K_p$  and  $K_c$  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