Equilibrium

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Chemical and ionic Equilibrium

In this Session :

- ✓ Weightage of concepts
- ✓ Revision of Entire chapter
- ✓ Revising important formula
- ✓ Solving previous year questions

Average Weightage:

- JEE Main: 12-16 marks per year (15-20% of chemistry paper)
- JEE Advanced: 8-12 marks per year (15-18% of chemistry paper)
- Questions per paper: 2-3 questions

Main Topic Distribution:

1. Chemical Equilibrium (45%)
   - ○ Focus on equilibrium constants, shifts, and applications
2. Ionic Equilibrium (55%)
   - ○ Emphasis on pH, buffers, and solubility products

1. Dynamic Equilibrium in Reversible Reactions

$\rightleftharpoons$

Key Concepts:

- A reversible reaction reaches equilibrium when forward reaction rate (rf) equals backward reaction rate (rb)
- At equilibrium: $\boxed{rf = rb}$
- Equilibrium is dynamic in nature (both reactions continue but at equal rates)

Law of Chemical Equilibrium

For a reversible reaction: $aA(g) + bB(g) \rightleftharpoons xX(g) + yY(g)$

Equilibrium Constant (Kc) = $[X]^x[Y]^y/[A]^a[B]^b$

pro reactant

$K_c =$

Significance of K value:

K > 1: Products are favored (reaction goes forward)

K < 1: Reactants are favored (reaction goes backward)

K = 1: Equal amounts of products and reactants

Properties of Equilibrium Constant (Kc)

ⓧ

Properties of Equilibrium Constant (Kc)

1. Temperature dependent but concentration independent
2. Independent of catalyst presence

Audience

3. Depends on stoichiometry of reactants and products

Important Cases:

a) For reversed reaction: $K' = 1/K$

When reaction direction is reversed, Kc becomes inverse

$A + B \rightleftharpoons C + D$

$K = 1.1 \times 10^{-10}$

$\frac{1}{1.1 \times 10^{-10}}$

b) For divided equation: $K' = \sqrt[n]{K}$

When equation is divided by factor 'n'
New equilibrium constant becomes nth root

$K' = \sqrt[2]{1.1 \times 10^{-10}}$

c) For multiplied equation: $K' = K^n$

$K = 2^2 = 4$

When equation is multiplied by factor 'n'
New equilibrium constant becomes K^n

d) For multi-step equations: $K = K_1 \times K_2 \times K_3 \times \ldots \times K_n$

Overall equilibrium constant is product of individual step constants

Effect of Temperature

Given by van't Hoff equation:

$\log(K_2/K_1) = [\Delta H°/2.303R][T_2 - T_1/T_1T_2]$

For endothermic reaction ($\Delta H° > 0$):

K increases with temperature ✓

For exothermic reaction ($\Delta H° < 0$):

K decreases with temperature

Effect of Changing Conditions (Le Chatelier's Principle)

Change	Effect on Equilibrium
Increase in reactant concentration	Shifts forward
Increase in product concentration	Shifts backward
Temperature increase	Favors endothermic reaction
Temperature decrease	Favors exothermic reaction

$A + B \rightleftharpoons C + D$

Endothermic

$T \uparrow \Rightarrow$ forward.

$T \downarrow \Rightarrow$ Backward.

Exotheimic

$T \uparrow \Rightarrow$ backward

Temperature increase	Favors endothermic reaction
Temperature decrease	Favors exothermic reaction
Pressure increase	Shifts toward fewer moles of gas
Pressure decrease	Shifts toward more moles of gas
Catalyst addition	No effect on equilibrium
Inert gas addition	No effect

Exothermic

T ↑ ⇒ backward

T ↓ ⇒ forward.

$\overset{④}{1N_2 + 3H_2} \rightleftharpoons \overset{②}{2NH_3}$

P ↑ forward.

P ↓ backward.

2. Reaction Quotient (Q)

- $Q = \overset{\text{Product}}{[C]^c[D]^d}/\overset{\text{Reactant}}{[A]^a[B]^b}$ (at any instant) ✓
- When Q = Kc: System at equilibrium
- When Q < Kc: Reaction proceeds forward ✓
- When Q > Kc: Reaction proceeds backward

$\Delta G = 0$

$\Delta S = 0$

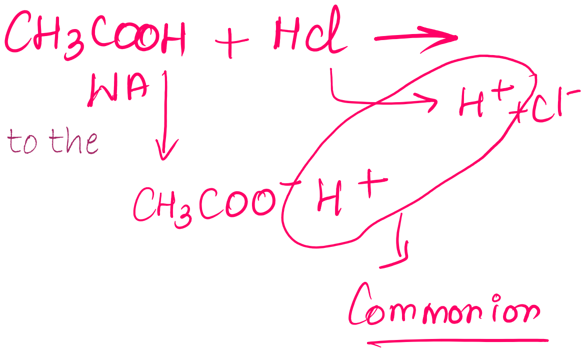
Important Relations

1. $\Delta G = \Delta G^\circ + RT \ln Q$
2. At equilibrium: $\Delta G = 0$, $Q = K_c$ ✓
3. $\Delta G^\circ = -2.303RT \log K_c$ (van't Hoff isotherm)

Common Ion Effect

Definition

- Suppression of ionization of a weak electrolyte due to the presence of a common ion from another electrolyte
- Follows Le Chatelier's principle ✓



Key Points:

1. Decreases degree of dissociation
2. Decreases solubility of sparingly soluble salts
3. Used in buffer solutions

Mathematical Treatment:

For weak acid $HA \rightleftharpoons H^+ + A^-$

- With added salt containing A^-: $[H^+] = K_a \times [HA]/[A^-]$
- Degree of dissociation decreases as $[A^-]$ increases

Applications:

1. Buffer solutions
2. Precipitation control
3. Solubility reduction
4. pH control in industrial processes

Degree of Dissociation (α)

Definition

- Fraction of total solute molecules that dissociate into ions
- α = Number of molecules dissociated/Total number of molecules initially present ⊛

Characteristics:

1. $0 \leq \alpha \leq 1$
2. Strong electrolytes: $\alpha \approx 1$
3. Weak electrolytes: $\alpha << 1$
4. Depends on:
    - Concentration
    - Temperature
    - Common ions
    - Nature of solvent

Calculations:

1. For weak acid: $\alpha = \sqrt{(Ka/C)}$ [for dilute solutions]
2. For weak base: $\alpha = \sqrt{(Kb/C)}$ [for dilute solutions]

Effect of Factors:

1. Concentration (C):
    α decreases as C increases
2. Temperature:
    α increases with temperature
3. Common ion:
    Decreases α

Ostwald's Dilution Law

Statement

- The degree of dissociation of a weak electrolyte increases with dilution

Mathematical Form:

$Ka = C\alpha^2/(1-\alpha)$

$$Ka = \frac{C\alpha^2}{(1-\boxed{\alpha})}$$

Where:

- Ka = Dissociation constant
- C = Concentration
- α = Degree of dissociation

$$\boxed{C\alpha^2}$$

$$\alpha = \sqrt{\frac{Ka}{C}}$$

Special Cases:

1. For very weak electrolytes (α << 1):

Special Cases:

1. For very weak electrolytes ($\alpha << 1$):
   - $K_a = C\alpha^2$ ✓
2. For moderate dilution:
   - $\alpha = \sqrt{(K_a/C)}$

3. Ionic Equilibrium

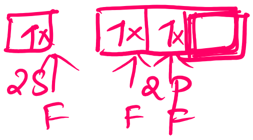
Acid-Base Concepts

Concept	Acid Definition	Base Definition
Arrhenius	H^+ producer in aqueous solution (HCl, H_2SO_4)	OH^- producer in aqueous solution ($NaOH$, KOH)
Brønsted-Lowry	Proton donor (CH_3COOH, HCl)	Proton acceptor ($\ddot{N}H_3$)
Lewis ✓	Electron pair acceptor (BF_3, $AlCl_3$)	Electron pair donor ($\ddot{N}H_3$, $H_2\ddot{O}$, F^-)

✓

NH_4^+

$BF_3 - 1s^2 2s^2 2p^1$



Salt Hydrolysis

1. Weak Acid + Strong Base Salt:
   - Anion hydrolysis
   - pH > 7 (alkaline)
   - $K_h = K_w/K_a$

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$

$$K_h = \frac{k_w}{K_a}.$$

2. Strong Acid + Weak Base Salt:
   - Cation hydrolysis
   - pH < 7 (acidic)
   - $K_h = K_w/K_b$

$$K_h = \frac{k_w}{k_b}$$

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

3. Weak Acid + Weak Base Salt:
   - Both anion and cation hydrolyze
   - pH = 7 if $K_a = K_b$
   - $K_h = K_w/(K_a \times K_b)$ ✓

$$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$$

Solubility Product (Ksp)

Types of Electrolytes and Their Ksp Relations:

Binary Electrolyte (1:1)

Example: $AgCl$, $BaSO_4$

s – molar Solubility (mol/L)

$$Ca_3(PO_4)_2.$$
$$\rightleftharpoons$$
$$3Ca^{2+} + 2PO_4^{3-}$$

$$K_{sp} = (3s)^3 (2s)^2$$ ✓

Binary Electrolyte (1:1)

Example: AgCl, $BaSO_4$
$s = \sqrt{Ksp}$
$Ksp = s^2$ ✓

$$Ksp = (3s)^3 (2s)^2 \checkmark$$
$$= 27s^3 . 4s^2$$
$$\boxed{Ksp = 108s^5}$$

Ternary Electrolyte (1:2)

Example: $PbCl_2$, $Ca(OH)_2$
$s = \sqrt[3]{(Ksp/4)}$
$Ksp = 4s^3$ ✓

Ternary Electrolyte (2:1)

Example: Ag_2CrO_4, Ag_2CO_3
$s = \sqrt[3]{(Ksp/4)}$
$Ksp = 4s^3$ ✓

Quaternary Electrolyte (1:3)

Example: $Fe(OH)_3$, $Al(OH)_3$
$s = \sqrt[4]{(Ksp/27)}$
$Ksp = 27s^4$ ✓

Complex Salts (3:2)

Example: $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$
$s = \sqrt[4]{(Ksp/108)}$
$Ksp = 108s^5$ ✓

Important Points:

- Higher Ksp means higher solubility
- Precipitation occurs when ion product > Ksp ✗
- Common ion effect reduces solubility
- Temperature generally increases solubility and Ksp

Buffer Solutions :

1. Types:
   - Simple buffers (weak acid + weak base)
   - Mixed buffers
   - Acidic buffers (weak acid + its salt)
   - Basic buffers (weak base + its salt)

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  - Basic buffers (weak base + its salt)

2. Henderson Equation:
  - For acidic buffer: pH = pKa + log([Salt]/[Acid]) ✓
  - For basic buffer: pOH = pKb + log([Base]/[Salt]) ✓

$\boxed{p^H + p^{OH} = 14}$

Buffer Capacity

Definition

Buffer capacity (β) is the resistance of a buffer solution to pH change

Mathematically: $\beta = \Delta n/\Delta pH$

Δn = moles of acid/base added

ΔpH = change in pH

Factors Affecting Buffer Capacity:

- Concentration of buffer components

Higher concentration → Higher capacity ✓

- Relative concentrations of acid/base and salt

Maximum when [acid] = [salt]

- pH of solution

Maximum when pH = pKa

Henderson-Hasselbalch Equation Application:

For acidic buffer:

pH = pKa + log([salt]/[acid])
Maximum capacity when [salt] = [acid]

For basic buffer:

pOH = pKb + log([base]/[salt])
Maximum capacity when [base] = [salt]

1. At a given temperature, the equilibrium constant (Kc) for the reaction N2O4(g) ⇌ 2NO2(g) is 0.0625. If the initial concentration of N2O4 is 2.0 M and initial concentration of

NO2 is zero, calculate the equilibrium concentration of NO2.

a) ✓ 0.5 M
b) 0.25 M
c) 0.125 M
d) 0.707 M

$K_c = 0.0625$ $\quad N_2O_4 \rightleftharpoons 2NO_2$

Initial $\quad 2.0 \quad\quad 0$

Eqm $\quad 2-x \quad\quad 2x$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0625$$

$$= \frac{(2x)^2}{(2-x)} = 0.0625 \Rightarrow x = 0.5M$$

2. The pH of a 0.1 M CH3COOH solution is 2.87. Calculate the ionization constant (Ka) of CH3COOH. $\longrightarrow CH_3COO^- + H^+$

a) ✓ 1.8 × 10⁻⁵
b) 1.8 × 10⁻⁴
c) 1.8 × 10⁻³
d) 1.8 × 10⁻²

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{(1.35\times10^{-3})^2}{0.1}$$

$$K_a = 1.8\times10^{-5}$$

$pH = 2.87$

$pH = -\log_{10}[H^+]$

$[H^+] = 1.35\times10^{-3}$

$[CH_3COO^-] = 1.35\times10^{-3}$

3. For the reaction PCl5(g) ⇌ PCl3(g) + Cl2(g), Kp = 1.8 atm at 250°C. If the partial pressure of PCl5 at equilibrium is 0.5 atm, what is the partial pressure of Cl2?

a) ✓ 0.95 atm
b) 1.34 atm
c) 0.85 atm
d) 1.80 atm

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

$$K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$$

$$1.8 = \frac{x \cdot x}{0.5}$$

$$1.8 = \frac{x^2}{0.5}$$

$$x = 0.95$$

4. Calculate the pH of a buffer solution prepared by mixing 0.2 M ~~NH4~~Cl and 0.1 M NH4OH. Given: Kb for NH4OH = 1.8 × 10⁻⁵

a) ✓ 8.74

$$p^{OH} = -\log[OH^-] = -\log\left(\frac{K_b \times [NH_4OH]}{[NH_4Cl]}\right)$$

$\times 10^{-5} \times 0.1$

$p = -\log$ $[NH_4Cl]$

[✓ a) 8.74]
b) 9.26
c) 4.74
d) 5.26

$= -\log\left(\frac{1.8\times10^{-5}\times0.1}{0.2}\right)$

$pOH = 5.26.$

$pH + pOH = 14$

$pH - 5.26 = 14$

$pH = 8.74.$

5. The solubility product (Ksp) of AgCl is 1.8×10^{-10}. Calculate its solubility in 0.1 M NaCl solution.

[✓ a) 1.8×10^{-9} M]
b) 1.8×10^{-10} M
c) 1.8×10^{-11} M
d) 1.8×10^{-8} M

$K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10}.$

$[Cl^-] = 0.1M.$

$[Ag^+] = \frac{1.8\times10^{-10}}{0.1} = 1.8\times10^{-9} M.$

6. For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, what is the relationship between Kp and Kc?

a) $K_p = K_c(RT)^2$
[✓ b) $K_p = K_c(RT)^{-2}$]
c) $K_p = K_c(RT)$
d) $K_p = K_c$

$K_p = K_c(RT)^{\Delta n}$ $\Delta n = (c+d) - (a+b)$

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

$= 2 - 4 = -2$

7. A solution contains both NH_4Cl and NH_4OH. What happens to the pH when HCl is added?

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

a) pH decreases significantly
b) pH increases significantly
[✓ c) pH decreases slightly]
d) pH remains almost constant

8. The value of Kc for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 4 at 300K. If 2 moles each of CO and H2O are mixed in a 1L vessel, what is the equilibrium concentration of $\underline{CO_2}$?

$K_c = 4 \quad T = 300K \quad V = 1L$

- a) 1.17 M
- [✓ b) 1.33 M]
- c) 1.50 M
- d) 1.67 M

	CO +	H_2O ⇌	CO_2 +	H_2
Initial	2	2	–	–
At eqm	2-x	2-x	x	x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{x^2}{(2-x)^2} = $$

$$x = 1.33M.$$

9. The Ksp of Mg(OH)2 is $\underline{1.2}$ X 10^{-11}. What is the pH of a saturated solution of Mg(OH)2?

- a) 9.97
- [✓ b) 10.32]
- c) 10.68
- d) 11.03

$$K_{sp} = [Mg^{2+}][OH^-]^2 \Rightarrow s \cdot (2s)^2$$

$$K_{sp} = 4s^3 \Rightarrow s = 1.44 \times 10^{-4}$$

$$2s = [OH^-] = 1.44 \times 10^{-4} \times 2$$

$$pOH = -\log(2.88 \times 10^{-4}) = 3.54$$

$$pH = 10.32.$$

10. In which of the following cases will the equilibrium constant NOT change?

- a) Change in temperature
- [✓ b) Addition of catalyst]
- c) Change in pressure
- d) Change in concentration

11. For the dissociation of water, H2O $\rightleftharpoons$ H^+ + OH^-, Kw = 1.0×10^{-14} at 25°C. What is $[H^+]$ in a solution of pH = 8.5?

a) 3.16×10^{-9} M
b) 3.16×10^{-8} M
c) 3.16×10^{-7} M
d) 3.16×10^{-6} M