AITS Advance Preparatory Guide

Chemical Equilibrium & Redox Equilibrium

Advanced Level for IIT JEE Advanced

All India Test Series (AITS)

May 9, 2025

Contents

1 Introduction

Chemical equilibrium and **redox equilibrium** are foundational to understanding dynamic chemical systems and electrochemical processes, critical for excelling in IIT JEE Advanced. This expanded guide provides exhaustive theoretical insights, advanced examples, rigorous exercises, and JEE-style MCQs, presented in a vibrant format to ensure comprehensive preparation. The content is designed to deepen conceptual understanding and tackle complex, multi-step problems.

2 Chemical Equilibrium: Fundamentals

2.1 Theory

Chemical equilibrium is achieved when the rates of forward and reverse reactions in a reversible process equalize, stabilizing the concentrations of reactants and products. For a reaction:

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

The **equilibrium constant** is expressed as:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \quad K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

The relationship between K_c and K_p is:

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

Key concepts for JEE Advanced:

- **Reaction quotient (Q)**: Q mirrors Ks form but uses initial concentrations. If $Q < K$, the reaction proceeds forward; if $Q > K$, it shifts backward.
- **Equilibrium calculations**: Solving for equilibrium concentrations often involves quadratic or cubic equations, especially in gaseous or complex systems.
- **Degree of dissociation**: For dissociation reactions (e.g., $PCl_5 \rightleftharpoons PCl_3 + Cl_2$), the extent of reaction is quantified.

JEE problems frequently test multi-step equilibria, temperature effects on K, and simultaneous application of K_c and K_p. Understanding the thermodynamic basis of equilibrium ($K = e^{-\Delta G^\circ/RT}$) is also essential.

2.2 Example 1: Equilibrium Constant for Habers Process

For N_2(g) + $3H_2$(g) $\rightleftharpoons$ $2NH_3$(g) at 500 K, equilibrium concentrations are $[N_2]$ = 0.05 M, $[H_2]$ = 0.15 M, $[NH_3]$ = 0.1 M. Calculate K_c and K_p ($R = 0.0821$ Lůatm/(molůK)).

Solution:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.1)^2}{(0.05)(0.15)^3} = \frac{0.01}{0.05 \times 0.003375} \approx 59.26\,\text{M}^{-2}$$

$$\Delta n = 2 - 4 = -2, \quad K_p = K_c(RT)^{\Delta n} = 59.26 \times (0.0821 \times 500)^{-2} \approx 0.0352\,\text{atm}^{-2}$$

3 Le Chateliers Principle

3.1 Theory

Le Chateliers principle predicts how an equilibrium system responds to external changes in concentration, pressure, temperature, or volume. Detailed effects:

- **Concentration**: Adding reactants shifts equilibrium toward products, increasing product concentrations.
- **Pressure**: For gaseous reactions, increased pressure favors the side with fewer moles of gas, reducing Δn.
- **Temperature**: For endothermic reactions ($\Delta H > 0$), increasing temperature shifts equilibrium toward products; for exothermic reactions, it favors reactants.
- **Catalysts**: Do not shift equilibrium but accelerate attainment of equilibrium.

JEE Advanced questions often involve multiple simultaneous changes (e.g., increasing pressure and temperature) or industrial applications like ammonia synthesis, requiring quantitative predictions of equilibrium shifts. The vant Hoff equation ($\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$) explains temperature effects on K.

3.2 Example 2: Effect of Multiple Changes

For $2SO_2$(g) + O_2(g) $\rightleftharpoons$ $2SO_3$(g) ($\Delta H < 0$), predict the effect of simultaneously increasing pressure and decreasing temperature.

Solution: $\Delta n = 2 - 3 = -1$. Increased pressure favors products (SO_3). Decreased temperature favors the exothermic direction (products). Both changes increase SO_3 yield.

4 Acid-Base Equilibria

4.1 Theory

Acid-base equilibria govern proton transfer reactions, described by dissociation constants K_a (acids) and K_b (bases). For a weak acid HA:

$$HA \rightleftharpoons H^+ + A^-, \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

Key concepts:

- **Ionic product of water**: $K_w = [H^+][OH^-] = 10^{-14}$ at 25řC, linking pH and pOH (pH + pOH = 14).
- **Buffer solutions**: Comprise a weak acid and its conjugate base, maintaining pH via the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

- **Hydrolysis**: Conjugate bases of weak acids (e.g., CN^-) react with water, increasing $[OH^-]$ and pH.
- **Polyprotic acids**: Ionize in steps (e.g., H_3PO_4), with $K_{a1} > K_{a2} > K_{a3}$.

JEE Advanced problems often involve complex buffers, hydrolysis of salts, or pH calculations for polyprotic systems, requiring iterative approximations or simultaneous equilibria.

4.2 Example 3: pH of a Buffer with Polyprotic Acid

Calculate the pH of a buffer with 0.1 M NaH_2PO_4 and 0.05 M Na_2HPO_4 (K_{a2} of $H_3PO_4 = 6.2 \times 10^{-8}$).

Solution:

$$\text{pH} = \text{p}K_{a2} + \log\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -\log(6.2\times10^{-8}) + \log\frac{0.05}{0.1} = 7.21 - 0.30 = 6.91$$

5 Solubility Equilibria

5.1 Theory

Solubility equilibria describe the dissolution of sparingly soluble salts, quantified by the **solubility product constant** (K_{sp}). For A_xB_y:

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-}, \quad K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Key aspects:

- **Common ion effect**: Adding a common ion (e.g., Ag^+ to AgCl) reduces solubility.
- **Precipitation**: Occurs when the ion product $Q > K_{sp}$.
- **Complex ion formation**: Ligands (e.g., NH_3 with Ag^+) increase solubility by forming complexes.

JEE Advanced questions often involve calculating solubility under competing equilibria or predicting selective precipitation in mixed solutions.

5.2 Example 4: Solubility with Complex Formation

Calculate the solubility of AgCl ($K_{sp} = 1.8\times10^{-10}$) in 0.1 M NH_3 (K_f for $[Ag(NH_3)_2]^+ = 1.7\times10^7$).

Solution: AgCl dissolves: $AgCl \rightleftharpoons Ag^+ + Cl^-$, then $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$. Total reaction:

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-, \quad K = K_{sp}\cdot K_f = 3.06\times10^{-3}$$

Let solubility = s. $[Ag(NH_3)_2]^+ = s$, $[Cl^-] = s$, $[NH_3] \approx 0.1 - 2s \approx 0.1$. $K = \frac{s\cdot s}{(0.1)^2} \implies s^2 = 3.06\times10^{-5} \implies s \approx 5.53\times10^{-3}$ M.

6 Redox Reactions

6.1 Theory

Redox reactions involve electron transfer, with **oxidation** (electron loss) and **reduction** (electron gain). Key concepts:

- **Oxidation number**: Tracks electron distribution to identify redox processes.
- **Ion-electron method**: Balances redox reactions in acidic or basic media by separating half-reactions.
- **Disproportionation**: A single species is both oxidized and reduced (e.g., $Cl_2 \rightarrow Cl^- + ClO_3^-$).

JEE Advanced problems often require balancing complex redox reactions, identifying redox in organic systems, or analyzing stoichiometry in titrations.

6.2 Example 5: Disproportionation of H_2O_2

Balance: $H_2O_2 \rightarrow H_2O + O_2$ in acidic medium.

Solution: Oxidation: $H_2O_2 \to O_2 + 2H^+ + 2e^-. Reduction: H_2O_2 + 2H^+ + 2e^- \to 2H_2O$. Combine: $2H_2O_2 \to 2H_2O + O_2$.

7 Electrochemical Cells

7.1 Theory

Electrochemical cells convert chemical energy to electrical energy (galvanic) or vice versa (electrolytic). Key components:

- **Standard electrode potential (E°)**: Measures a half-cells reduction tendency (e.g., $E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.34\,\mathrm{V}$).
- **Cell potential**: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- **Gibbs free energy**: $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where $F = 96485\,\mathrm{C/mol}$.
- **Concentration cells**: Generate potential from concentration differences.

JEE Advanced questions involve calculating potentials, predicting spontaneity, or analyzing cells under non-standard conditions.

7.2 Example 6: Concentration Cell Potential

Calculate E_{cell} for Cu | Cu^{2+}(0.001 M) || Cu^{2+}(0.1 M) | Cu at 298 K.

Solution:

$$E = -\frac{0.0592}{2}\log\frac{0.001}{0.1} = -\frac{0.0592}{2}\log 0.01 = 0.0592\,\mathrm{V}$$

8 Nernst Equation

8.1 Theory

The **Nernst equation** adjusts cell potential for non-standard conditions:

$$E = E^\circ - \frac{RT}{nF}\ln Q, \quad \text{at 298 K: } E = E^\circ - \frac{0.0592}{n}\log Q$$

Applications:

- Calculating E_{cell} with varying concentrations or partial pressures.
- Determining equilibrium constants: At $E = 0$, $E^\circ = \frac{0.0592}{n}\log K$.
- Analyzing pH electrodes or redox titrations.

JEE Advanced problems often involve complex Q expressions or multi-electron transfers.

8.2 Example 7: Nernst Equation for Redox Titration

For $Fe^{2+} + Ce^{4+} \to Fe^{3+} + Ce^{3+}$, calculate E at 298 K when [Fe^{2+}] = 0.01 M, [Fe^{3+}] = 0.1 M, [Ce^{4+}] = 0.05 M, [Ce^{3+}] = 0.02 M. Given: $E^\circ_{\mathrm{Ce^{4+}/Ce^{3+}}} = 1.61\,\mathrm{V}$, $E^\circ_{\mathrm{Fe^{3+}/Fe^{2+}}} = 0.77\,\mathrm{V}$.

Solution:

$$E^\circ_{\text{cell}} = 1.61 - 0.77 = 0.84\,\text{V}, \quad Q = \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} = \frac{0.1 \times 0.02}{0.01 \times 0.05} = 4$$

$$E = 0.84 - \frac{0.0592}{1}\log 4 \approx 0.84 - 0.0356 = 0.8044\,\text{V}$$

9 Simultaneous Equilibria

9.1 Theory

Simultaneous equilibria occur when multiple equilibrium processes coexist, such as acid-base and solubility equilibria in a single system. For example, in a solution of AgCN, both K_{sp} ($\text{AgCN} \rightleftharpoons \text{Ag}^+ + \text{CN}^-$) and K_a ($\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$) apply. Solving requires:

- Combining equilibrium expressions.
- Accounting for common ions or competing reactions.
- Iterative approximations for complex systems.

JEE Advanced problems often involve calculating concentrations in such systems or predicting outcomes of mixed equilibria.

9.2 Example 8: Simultaneous Equilibria in AgCN

Calculate the solubility of AgCN ($K_{sp} = 6.0 \times 10^{-17}$, K_a of HCN = 4.9 $\times 10^{-10}$) in a pH 5 buffer.

Solution: $\text{AgCN} \rightleftharpoons \text{Ag}^+ + \text{CN}^-$, $\text{CN}^- + \text{H}^+ \rightleftharpoons \text{HCN}$. $[\text{H}^+] = 10^{-5}$. $[\text{CN}^-] = \frac{K_a[\text{HCN}]}{[\text{H}^+]} \approx \frac{4.9\times10^{-10}\cdot s}{10^{-5}} = 4.9 \times 10^{-5}s$. $K_{sp} = s \cdot (4.9 \times 10^{-5}s) = 6.0 \times 10^{-17} \implies s^2 = 1.224 \times 10^{-12} \implies s \approx 1.11 \times 10^{-6}\,\text{M}$.

10 Redox Titrations

10.1 Theory

Redox titrations quantify analytes via redox reactions, using indicators or potentiometric methods. Common systems include:

- **Permanganate titrations**: MnO_4^- as a self-indicator in acidic medium.
- **Iodometric titrations**: I_2/I^- system for indirect redox analysis.
- Equivalence point calculations: Use stoichiometry and Nernst equation for potential.

JEE Advanced questions involve determining concentrations or balancing titration reactions under specific conditions.

10.2 Example 9: KMnO_4 Titration

Calculate the volume of 0.02 M KMnO_4 required to titrate 25 mL of 0.1 M FeSO_4 in acidic medium.

Solution: Reaction: $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$. Moles of $\text{Fe}^{2+} = 0.1 \times 0.025 = 0.0025$. Moles of $\text{MnO}_4^- = \frac{0.0025}{5} = 0.0005$. Volume = $\frac{0.0005}{0.02} \times 1000 = 25\,\text{mL}$.

11 Electrochemical Series Applications

11.1 Theory

The **electrochemical series** ranks species by their standard reduction potentials, predicting redox spontaneity and corrosion tendencies. Applications:

- **Spontaneity**: A redox reaction is spontaneous if $E^\circ_{\text{cell}} > 0$.
- **Corrosion**: Metals with lower E° (e.g., Zn) act as sacrificial anodes.
- **Electrolysis**: Predicts products based on E° values.

JEE Advanced problems may involve predicting reaction feasibility or analyzing electrolytic processes.

11.2 Example 10: Corrosion Protection

Explain why zinc is used to protect iron from corrosion.

Solution: Zinc ($E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\,\text{V}$) has a lower reduction potential than iron ($E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\,\text{V}$), making Zn more reactive. Zn oxidizes preferentially, acting as a sacrificial anode.

12 Exercises

12.1 Exercise 1

Calculate K_c for CO(g) + Cl_2(g) $\rightleftharpoons$ CO comparative to Cl_2(g) at 600 K, given $K_p = 0.8\,\text{atm}^{-1}$.

Solution: $\Delta n = 1 - 2 = -1$. $K_c = K_p(RT)^{\Delta n} = 0.8 \times (0.0821 \times 600)^{-1} \approx 0.0162\,\text{M}^{-1}$.

12.2 Exercise 2

Predict the effect of adding NaCl to AgCl(s) $\rightleftharpoons$ Ag^+ + Cl^-.

Solution: NaCl increases [Cl^-], shifting equilibrium left, reducing AgCl solubility.

12.3 Exercise 3

Calculate the pH of 0.02 M $NaHCO_3$ (K_{a1} of $H_2CO_3 = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$).

Solution: HCO_3^- acts as both acid and base. pH $\approx \frac{\text{p}K_{a1}+\text{p}K_{a2}}{2} = \frac{6.37+10.25}{2} = 8.31$.

12.4 Exercise 4

Calculate the solubility of $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) in 0.05 M Na_2SO_4.

Solution: $s \cdot 0.05 = 1.1 \times 10^{-10} \implies s = 2.2 \times 10^{-9}\,\text{M}$.

12.5 Exercise 5

Balance: I_2 + HNO_3 $\rightarrow$ HIO_3 + NO_2 (acidic).

Solution: Oxidation: $I_2 + 6H_2O \rightarrow 2HIO_3 + 10H^+ + 10e^-$. Reduction: $HNO_3 + H^+ + e^- \rightarrow NO_2 + H_2O$. Combine: $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$.

12.6 Exercise 6

Calculate E°_{cell} for Mg | Mg^{2+} || Pb^{2+} | Pb ($E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37\,\text{V}$, $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.13\,\text{V}$).

Solution: $E^\circ_{\text{cell}} = -0.13 - (-2.37) = 2.24\,\text{V}$.

12.7 Exercise 7

Calculate the pH of 0.1 M H_3PO_4 ($K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$).

Solution: $[H^+] \approx \sqrt{7.5 \times 10^{-3} \cdot 0.1} \approx 0.0274$. pH = 1.56.

13 Multiple Choice Questions

13.1 MCQ 1

K_p for $2NO_2 \rightleftharpoons N_2O_4$ at 300 K is 0.6 atm^{-1}. What is K_c? 0.0246 M^{-1}, 0.6 M^{-1}, 14.61 M^{-1}, 0.0246 atm^{-1}
A. 0.0246 M^{-1} **B.** 0.6 M^{-1} **C.** 14.61 M^{-1} **D.** 0.0246 atm^{-1}

Answer: C

Solution: $\Delta n = 1 - 2 = -1$. $K_c = 0.6 \times (0.0821 \times 300)^{-1} \approx 14.61\,\text{M}^{-1}$.

13.2 MCQ 2

Effect of increasing volume on $PCl_5 \rightleftharpoons PCl_3 + Cl_2$? Shifts right, Shifts left, No effect, Increases K
A. Shifts right **B.** Shifts left **C.** No effect **D.** Increases K

Answer: A

Solution: Increasing volume decreases pressure, favoring products ($\Delta n = 1$).

13.3 MCQ 3

pH of 0.05 M $(NH_4)_2SO_4$ (K_b of $NH_3 = 1.8 \times 10^{-5}$)? 5.28, 7.00, 8.72, 4.92
A. 5.28 **B.** 7.00 **C.** 8.72 **D.** 4.92

Answer: A

Solution: NH_4^+ hydrolysis: $K_h = \frac{10^{-14}}{1.8 \times 10^{-5}} \approx 5.56 \times 10^{-10}$. $[H^+] = \sqrt{5.56 \times 10^{-10} \cdot 0.1} \approx 5.27 \times 10^{-6}$. pH = 5.28.

13.4 MCQ 4

Which precipitates first in 0.01 M Ca^{2+}, 0.01 M F^-? (K_{sp} $CaF_2 = 3.9 \times 10^{-11}$, $CaCO_3 = 3.8 \times 10^{-9}$) CaF_2, $CaCO_3$, Both, Neither
A. CaF_2 **B.** $CaCO_3$ **C.** Both **D.** Neither

Answer: A

Solution: For CaF_2: $Q = 0.01 \cdot (0.01)^2 = 10^{-6} > K_{sp}$. For $CaCO_3$: $Q = 10^{-4} < K_{sp}$. CaF_2 precipitates first.

13.5 MCQ 5

E°_{cell} for Al | Al^{3+} || Ni^{2+} | Ni? ($E^\circ_{Al^{3+}/Al} = -1.66\,V$, $E^\circ_{Ni^{2+}/Ni} = -0.25\,V$) 1.41 V, -1.41 V, 0.25 V, 1.91 V
A. 1.41 V **B.** -1.41 V **C.** 0.25 V **D.** 1.91 V

Answer: A

Solution: $E^\circ_{\text{cell}} = -0.25 - (-1.66) = 1.41\,V$.

13.6 MCQ 6

Effect of adding NaOH to $NH_4^+ \rightleftharpoons NH_3 + H^+$? Shifts right, Shifts left, No effect, Decreases K
A. Shifts right **B.** Shifts left **C.** No effect **D.** Decreases K

Answer: A

Solution: NaOH reduces $[H^+]$, shifting equilibrium right.

13.7 MCQ 7

Solubility of Ag_2SO_4 ($K_{sp} = 1.4 \times 10^{-5}$) in 0.1 M $AgNO_3$? 1.4 $\times 10^{-3}$ M, 7.0 $\times 10^{-4}$ M, 3.5 $\times 10^{-4}$ M, 1.4 $\times 10^{-5}$ M
A. 1.4 $\times 10^{-3}$ M **B.** 7.0 $\times 10^{-4}$ M **C.** 3.5 $\times 10^{-4}$ M **D.** 1.4 $\times 10^{-5}$ M

Answer: C

Solution: $(0.2)^2 \cdot s = 1.4 \times 10^{-5} \implies s = 3.5 \times 10^{-4}\,M$.

13.8 MCQ 8

E_{cell} for Zn | Zn^{2+}(0.01 M) || Zn^{2+}(1 M) | Zn? 0.0592 V, -0.0592 V, 0.0296 V, 0 V
A. 0.0592 V **B.** -0.0592 V **C.** 0.0296 V **D.** 0 V

Answer: A

Solution: $E = -\frac{0.0592}{2} \log \frac{0.01}{1} = 0.0592\,V$.

14 Conclusion

This expanded guide, with its exhaustive theory, advanced problems, and vibrant design, equips JEE Advanced aspirants to master **chemical equilibrium** and **redox equilibrium**. Rigorous practice will ensure exam excellence.