AITS Advance Preparatory Guide

Chemical Kinetics

Advanced Level for IIT JEE Advanced

All India Test Series (AITS)

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Contents

1 Introduction

Chemical kinetics explores the rates of chemical reactions and the factors influencing them, a cornerstone for IIT JEE Advanced preparation. This comprehensive guide offers exhaustive theoretical explanations, advanced examples, rigorous exercises, and JEE-style MCQs, presented in a vibrant format to ensure mastery. The content is designed to tackle complex reaction mechanisms, mathematical modeling, and multi-step problem-solving, equipping aspirants for the exams challenges.

2 Fundamentals of Chemical Kinetics

2.1 Theory

Chemical kinetics studies the speed of chemical reactions and the molecular processes governing them. The **rate of reaction** is defined as the change in concentration of a reactant or product per unit time:

$$\text{Rate} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t}$$

Key concepts:

- **Rate law**: Expresses rate as a function of reactant concentrations: $\text{Rate} = k[A]^m[B]^n$, where k is the rate constant, and m, n are partial orders.
- **Order of reaction**: Sum of partial orders $(m+n)$. May be zero, fractional, or negative.
- **Molecularity**: Number of molecules in the rate-determining step of a mechanism.

For JEE Advanced, determining rate laws experimentally, solving differential rate equations, and analyzing complex orders are critical. The rate constants units depend on the overall order: $\text{M}^{1-n}\text{s}^{-1}$ for an n-th order reaction.

2.2 Example 1: Determining Rate Law

For the reaction 2NO + $O_2 \rightarrow 2NO_2$, the following data is obtained: [NO] = 0.1 M, [O_2] = 0.1 M, rate = 0.02 M/s; [NO] = 0.2 M, [O_2] = 0.1 M, rate = 0.08 M/s; [NO] = 0.1 M, [O_2] = 0.2 M, rate = 0.04 M/s. Find the rate law and k.

Solution: Compare experiments 1 and 2: [NO] doubles, rate quadruples, so order w.r.t. NO = 2. Compare 1 and 3: [O_2] doubles, rate doubles, so order w.r.t. O_2 = 1. Rate law: $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$. Using experiment 1:

$$k = \frac{0.02}{(0.1)^2(0.1)} = 20\,\text{M}^{-2}\text{s}^{-1}$$

3 Integrated Rate Laws

3.1 Theory

Integrated rate laws describe concentration changes over time, derived from differential rate laws. For common orders:

- **Zero-order**: $\text{Rate} = k$, $[A] = [A]_0 - kt$, plot $[A]$ vs. t is linear.
- **First-order**: $\text{Rate} = k[A]$, $\ln[A] = \ln[A]_0 - kt$, plot $\ln[A]$ vs. t is linear.
- **Second-order**: $\text{Rate} = k[A]^2$, $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$, plot $\frac{1}{[A]}$ vs. t is linear.

The **half-life** ($t_{1/2}$) depends on order:

$$t_{1/2} = \frac{[A]_0}{2k} \text{ (zero)}, \quad t_{1/2} = \frac{\ln 2}{k} \text{ (first)}, \quad t_{1/2} = \frac{1}{k[A]_0} \text{ (second)}$$

JEE Advanced problems often involve determining order from experimental data, calculating $t_{1/2}$, or solving for concentrations at specific times.

3.2 Example 2: First-Order Half-Life

A first-order reaction has $k = 2.3 \times 10^{-3}\,\text{s}^{-1}$. Calculate its half-life and the time for 75% completion.

Solution:

$$t_{1/2} = \frac{\ln 2}{2.3 \times 10^{-3}} \approx 301.3\,\text{s}$$

For 75% completion, $[A] = 0.25[A]_0$. $\ln \frac{[A]_0}{0.25[A]_0} = kt \implies \ln 4 = 2.3 \times 10^{-3} \cdot t \implies t \approx 602.6\,\text{s}$.

4 Arrhenius Equation and Activation Energy

4.1 Theory

The **Arrhenius equation** relates the rate constant to temperature and **activation energy** (E_a):

$$k = Ae^{-\frac{E_a}{RT}}$$

Taking the natural logarithm:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Key points:

- **Activation energy**: Energy barrier for the reaction; higher E_a means slower reaction.
- **Pre-exponential factor (A)**: Reflects collision frequency and orientation.
- Temperature dependence: Plot $\ln k$ vs. $\frac{1}{T}$ yields slope $-\frac{E_a}{R}$.

JEE Advanced questions often involve calculating E_a from rate constants at different temperatures or predicting rate changes with temperature.

4.2 Example 3: Calculating Activation Energy

For a reaction, $k = 0.01\,\text{s}^{-1}$ at 300 K and $0.04\,\text{s}^{-1}$ at 310 K. Calculate E_a ($R = 8.314\,\text{J/(molůK)}$).

Solution:

$$\ln \frac{0.04}{0.01} = \frac{E_a}{8.314} \left(\frac{1}{300} - \frac{1}{310} \right)$$

$$\ln 4 = \frac{E_a}{8.314} \cdot \frac{10}{93000} \implies 1.386 = \frac{E_a \cdot 1.075 \times 10^{-4}}{8.314} \implies E_a \approx 107,000\,\text{J/mol} = 107\,\text{kJ/mol}$$

5 Reaction Mechanisms

5.1 Theory

A **reaction mechanism** describes the sequence of elementary steps leading to the overall reaction. Each step has its own rate law, and the **rate-determining step** (slowest) governs the overall rate. Key concepts:

- **Elementary steps**: Have molecularity equal to the number of colliding species.
- **Intermediates**: Formed and consumed within the mechanism.
- **Steady-state approximation**: Assumes intermediates have constant concentrations.

JEE Advanced problems require deriving rate laws from mechanisms, identifying intermediates, or validating mechanisms against experimental rate laws.

5.2 Example 4: Rate Law from Mechanism

For 2A + B $\rightarrow$ C, the mechanism is: (1) A + B $\xrightarrow{k_1}$ X (slow), (2) X + A $\xrightarrow{k_2}$ C (fast). Derive the rate law.

Solution: The slow step determines the rate: Rate $= k_1[A][B]$. X is an intermediate. The rate law is Rate $= k_1[A][B]$.

6 Catalysis

6.1 Theory

Catalysis increases reaction rate by providing an alternative pathway with lower activation energy. Types include:

- **Homogeneous catalysis**: Catalyst in the same phase as reactants (e.g., acid catalysis). **Heterogeneous catalysis**: Catalyst in a different phase (e.g., Pt in hydrogenation).
- **Enzyme catalysis**: Biological catalysts with high specificity.

Catalysts do not affect equilibrium but accelerate attainment. JEE Advanced questions may involve catalytic mechanisms or rate enhancements.

6.2 Example 5: Catalytic Rate Enhancement

A catalyst lowers E_a from 100 kJ/mol to 80 kJ/mol at 298 K. Calculate the rate enhancement ($R = 8.314$ J/(molůK)).

Solution: Rate ratio = $\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{\frac{E_{a,\text{uncat}} - E_{a,\text{cat}}}{RT}} = e^{\frac{100000-80000}{8.314 \cdot 298}} \approx e^{8.06} \approx 3160.$

7 Complex Reaction Kinetics

7.1 Theory

Complex reactions involve multiple pathways, such as:

- **Parallel reactions**: A reactant forms multiple products (e.g., A $\rightarrow$ B, A $\rightarrow$ C).
- **Consecutive reactions**: A $\rightarrow$ B $\rightarrow$ C, with intermediate B.
- **Reversible reactions**: A $\rightleftharpoons$ B, approaching equilibrium.

JEE Advanced problems require solving differential equations or analyzing concentration-time profiles for such systems. For consecutive reactions, the maximum concentration of intermediates is a common focus.

7.2 Example 6: Consecutive Reaction Kinetics

For A $\xrightarrow{k_1}$ B $\xrightarrow{k_2}$ C, with $k_1 = 0.01\,\text{s}^{-1}$, $k_2 = 0.02\,\text{s}^{-1}$, find the time for maximum [B].

Solution: For A → B → C, [B] maximizes at $t_{\text{max}} = \frac{1}{k_1-k_2}\ln\frac{k_1}{k_2} = \frac{1}{0.01-0.02}\ln\frac{0.01}{0.02} \approx \frac{\ln 0.5}{-0.01} \approx 69.3\,\text{s}$.

8 Experimental Methods in Kinetics

8.1 Theory

Experimental methods determine rate laws and constants. Common techniques:

- **Initial rate method**: Measures rate at $t = 0$ for varying initial concentrations.
- **Integrated rate method**: Fits concentration-time data to integrated rate laws.
- **Isolation method**: Keeps all but one reactant in excess to simplify rate law.

JEE Advanced questions may involve interpreting experimental data or designing kinetic experiments.

8.2 Example 7: Initial Rate Method

For A + B → C, data: [A] = 0.1 M, [B] = 0.1 M, rate = 0.01 M/s; [A] = 0.2 M, [B] = 0.1 M, rate = 0.04 M/s; [A] = 0.1 M, [B] = 0.2 M, rate = 0.02 M/s. Find the rate law.

Solution: Order w.r.t. A: $\frac{0.04}{0.01} = \left(\frac{0.2}{0.1}\right)^m \implies m = 2$. Order w.r.t. B: $\frac{0.02}{0.01} = \left(\frac{0.2}{0.1}\right)^n \implies n = 1$. Rate law: Rate $= k[A]^2[B]$.

9 Temperature and Pressure Effects

9.1 Theory

Temperature and **pressure** significantly affect reaction rates. Temperature increases rate via the Arrhenius equation, while pressure affects gaseous reactions by altering concentrations:

$$[\text{A}] = \frac{P_A}{RT}$$

For gaseous reactions, rate $\propto P^m$ for an m-th order reactant. JEE Advanced problems may involve predicting rate changes under varying conditions or analyzing industrial processes.

9.2 Example 8: Pressure Effect on Rate

For $2N_2O$(g) → $2N_2$(g) + O_2(g), the rate law is Rate $= k[N_2O]$. If pressure doubles, how does the rate change?

Solution: $[N_2O] \propto P$. Doubling pressure doubles $[N_2O]$, doubling the rate.

10 Nuclear Kinetics

10.1 Theory

Nuclear kinetics applies first-order kinetics to radioactive decay:

$$\text{Rate} = \lambda N, \quad N = N_0 e^{-\lambda t}, \quad t_{1/2} = \frac{\ln 2}{\lambda}$$

Key applications:

- **Radioactive decay series**: Sequential decays (e.g., U-238 to Pb-206).
- **Carbon dating**: Uses ^{14}C decay ($t_{1/2} = 5730\,\text{years}$).

JEE Advanced questions may involve calculating decay times or activity.

10.2 Example 9: Radioactive Decay

A sample of ^{60}Co ($t_{1/2} = 5.27\,\text{years}$) has initial activity 1000 Bq. Calculate activity after 10 years.

Solution: $\lambda = \frac{\ln 2}{5.27} \approx 0.1316\,\text{year}^{-1}$. Activity = $\lambda N = \lambda N_0 e^{-\lambda t} = 1000 \cdot e^{-0.1316 \cdot 10} \approx 268\,\text{Bq}$.

11 Surface Reactions

11.1 Theory

Surface reactions involve reactions on solid surfaces, common in heterogeneous catalysis (e.g., Langmuir adsorption). The rate depends on surface coverage:

$$\text{Rate} = k\theta, \quad \theta = \frac{KP}{1+KP}$$

JEE Advanced questions may involve analyzing adsorption isotherms or catalytic rates.

11.2 Example 10: Langmuir Adsorption Kinetics

For a surface reaction, rate = $k\theta$, $\theta = \frac{0.1P}{1+0.1P}$. If P increases from 1 atm to 2 atm, calculate the rate ratio.

Solution: At $P = 1$: $\theta = \frac{0.1}{1+0.1} \approx 0.0909$. At $P = 2$: $\theta = \frac{0.2}{1+0.2} \approx 0.1667$. Rate ratio = $\frac{0.1667}{0.0909} \approx 1.83$.

12 Exercises

12.1 Exercise 1

For A → Products, [A] drops from 0.1 M to 0.025 M in 100 s. If first-order, calculate k.

Solution: $\ln \frac{0.1}{0.025} = kt \implies \ln 4 = 100k \implies k \approx 0.01386\,\text{s}^{-1}$.

12.2 Exercise 2

A zero-order reaction has $k = 0.02\,\text{M/s}$. How long for [A] to drop from 0.5 M to 0.1 M?

Solution: $[A] = [A]_0 - kt \implies 0.1 = 0.5 - 0.02t \implies t = 20\,\text{s}$.

12.3 Exercise 3

Calculate E_a if k triples when temperature rises from 298 K to 308 K ($R = 8.314$ J/(molůK)).

Solution: $\ln 3 = \frac{E_a}{8.314}\left(\frac{1}{298} - \frac{1}{308}\right) \implies 1.099 = \frac{E_a \cdot 1.087\times10^{-4}}{8.314} \implies E_a \approx 84,000$ kJ/mol.

12.4 Exercise 4

For A + B → C, mechanism: (1) A → X (slow), (2) X + B → C (fast). Derive rate law.

Solution: Rate = $k_1[A]$ (slow step).

12.5 Exercise 5

A catalyst lowers E_a from 120 kJ/mol to 90 kJ/mol at 300 K. Calculate rate enhancement.

Solution: $\frac{k_{\text{cat}}}{k_{\text{uncat}}} = e^{\frac{120000-90000}{8.314\cdot 300}} \approx e^{12.02} \approx 1.67 \times 10^5$.

12.6 Exercise 6

For A → B → C, $k_1 = 0.05\,\text{s}^{-1}$, $k_2 = 0.1\,\text{s}^{-1}$. Find t_{max} for [B].

Solution: $t_{\text{max}} = \frac{\ln(0.05/0.1)}{0.05-0.1} \approx 13.86\,\text{s}$.

12.7 Exercise 7

For ^{131}I ($t_{1/2} = 8.02$ days), calculate time for 90% decay.

Solution: $\lambda = \frac{\ln 2}{8.02} \approx 0.0864\,\text{day}^{-1}$. $\ln \frac{1}{0.1} = \lambda t \implies t \approx 26.6$ days.

13 Multiple Choice Questions

13.1 MCQ 1

Order of reaction 2A → B if rate doubles when [A] doubles? 1, 2, 0, 1/2
A. 1 **B.** 2 **C.** 0 **D.** 1/2

Answer: A

Solution: Rate ∝ $[A]^m$. $2 = 2^m \implies m = 1$.

13.2 MCQ 2

Half-life of a first-order reaction with $k = 0.0693\,\text{s}^{-1}$? 10 s, 5 s, 20 s, 15 s
A. 10 s **B.** 5 s **C.** 20 s **D.** 15 s

Answer: A

Solution: $t_{1/2} = \frac{\ln 2}{0.0693} \approx 10\,\text{s}$.

13.3 MCQ 3

E_a if k doubles from 300 K to 310 K? 51.2 kJ/mol, 25.6 kJ/mol, 76.8 kJ/mol, 12.8 kJ/mol
A. 51.2 kJ/mol **B.** 25.6 kJ/mol **C.** 76.8 kJ/mol **D.** 12.8 kJ/mol

Answer: A

Solution: $\ln 2 = \frac{E_a}{8.314}\left(\frac{1}{300} - \frac{1}{310}\right) \implies E_a \approx 51,200\,$J/mol.

13.4 MCQ 4

Rate law for mechanism: (1) A + B → X (slow), (2) X → C (fast)? $k[A][B]$, $k[A]$, $k[B]$, $k[A]^2$
A. $k[A][B]$ **B.** $k[A]$ **C.** $k[B]$ **D.** $k[A]^2$

Answer: A

Solution: Rate = $k_1[A][B]$ (slow step).

13.5 MCQ 5

Rate enhancement if E_a drops from 50 kJ/mol to 40 kJ/mol at 298 K? 7.39, 3.70, 14.78, 1.85
A. 7.39 **B.** 3.70 **C.** 14.78 **D.** 1.85

Answer: A

Solution: $e^{\frac{50000-40000}{8.314\cdot 298}} \approx e^2 \approx 7.39.$

13.6 MCQ 6

Time for max [B] in A → B → C, $k_1 = k_2 = 0.01\,$s^{-1}? 100 s, 69.3 s, 50 s, 138.6 s
A. 100 s **B.** 69.3 s **C.** 50 s **D.** 138.6 s

Answer: A

Solution: $t_{\text{max}} = \frac{1}{k_1} = \frac{1}{0.01} = 100\,$s (when $k_1 = k_2$).

13.7 MCQ 7

Activity of ^{90}Sr ($t_{1/2} = 28.8\,$years) after 50 years, initial 1000 Bq? 315 Bq, 500 Bq, 250 Bq, 630 Bq
A. 315 Bq **B.** 500 Bq **C.** 250 Bq **D.** 630 Bq

Answer: A

Solution: $\lambda = \frac{\ln 2}{28.8} \approx 0.0241$. Activity = $1000 \cdot e^{-0.0241\cdot 50} \approx 315\,$Bq.

13.8 MCQ 8

Rate change for A(g) → B(g), Rate $= k[A]^2$, if pressure triples? 9-fold, 3-fold, 27-fold, No change
A. 9-fold **B.** 3-fold **C.** 27-fold **D.** No change

Answer: A

Solution: [A] $\propto P$. Rate $\propto P^2$. Tripling P increases rate 9-fold.

14 Conclusion

This extensive guide, with its detailed theory, advanced problems, and vibrant design, equips JEE Advanced aspirants to excel in **chemical kinetics**. Thorough practice will ensure mastery of this critical chapter.