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CHAPTER NOTES

Chemical Kinetics Class 12 Notes — CBSE Chemistry Chapter 4

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Chemical Kinetics Class 12 Notes — CBSE Chemistry

Chapter 4

Chapter 4 of Class 12 Chemistry — **Chemical Kinetics** — answers the question “How fast does a reaction go?” While thermodynamics tells us IF a reaction will happen, kinetics tells us HOW FAST. This chapter is crucial for **5-7 marks** in Boards and is heavily tested in competitive exams. Focus on the integrated rate equations and Arrhenius equation numericals.

Key Concepts

Rate of a Chemical Reaction

For a general reaction: $aA + bB \rightarrow cC + dD$

$$\text{Rate} = -(1/a)(d[A]/dt) = -(1/b)(d[B]/dt) = (1/c)(d[C]/dt) = (1/d)(d[D]/dt)$$

Average rate: $\Delta[\text{concentration}] / \Delta t$ (over a time interval)

Instantaneous rate: $d[\text{concentration}]/dt$ (at a specific moment — slope of tangent)

Factors Affecting Rate of Reaction

- **Concentration:** Higher concentration $\rightarrow$ more collisions $\rightarrow$ faster rate
- **Temperature:** 10°C rise $\approx$ doubles the rate (rough rule)
- **Catalyst:** Lowers activation energy $\rightarrow$ faster rate
- **Nature of reactants:** Ionic reactions are fast; covalent bond-breaking is slow
- **Surface area:** Larger surface area $\rightarrow$ faster rate (powdered vs lump)

Rate Law and Order of Reaction

$$\text{Rate} = k[A]^x[B]^y$$

Where k = rate constant, x = order w.r.t. A, y = order w.r.t. B

$$\text{Overall order} = x + y$$

Important: Order is determined experimentally, NOT from the balanced equation!

Molecularity IS determined from the elementary step.

Order vs Molecularity

Property	Order	Molecularity
Determination	Experimental	Theoretical (from mechanism)
Value	Can be 0, fraction, integer	Always positive integer (1, 2, 3)
Applies to	Overall reaction	Elementary step only
Can be zero?	Yes	No

Integrated Rate Equations

Zero Order Reaction

$$[A] = [A]_0 - kt$$

$$k = [A]_0 / t \text{ (when reaction is complete)}$$

$$t_{1/2} = [A]_0 / 2k \text{ (half-life depends on initial concentration)}$$

Unit of k: $\text{mol L}^{-1} \text{s}^{-1}$

Graph: $[A]$ vs $t \rightarrow$ straight line with slope = $-k$

First Order Reaction

$$k = (2.303/t) \log([A]_0/[A])$$

$$\text{Or: } \ln[A] = \ln[A]_0 - kt$$

$$t_{1/2} = 0.693/k \text{ (half-life is INDEPENDENT of initial concentration!)}$$

Unit of k: s^{-1} (or min^{-1} , time^{-1})

Graph: $\ln[A]$ vs $t \rightarrow$ straight line with slope = $-k$

Key Point: Radioactive decay is always first order! The half-life formula ($t_{1/2} = 0.693/k$) is the same one used in nuclear physics.

Pseudo First Order Reaction

A reaction that is actually second order but behaves as first order because one reactant is in large excess.

- **Hydrolysis of ester:** $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$ (water in excess)
- **Inversion of sugar:** $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$ (water in excess)

Collision Theory

$$\text{Rate} = Z_{AB} \times e^{(-E_a/RT)} \times P$$

Where: Z_{AB} = collision frequency, E_a = activation energy, P = probability/steric factor

For a reaction to occur, collisions must be:

1. **Energetically sufficient** (energy $\geq E_a$)
2. **Properly oriented** (correct geometry)

Arrhenius Equation

$$k = A \times e^{(-E_a/RT)}$$

Taking log: $\log k = \log A - E_a/(2.303RT)$

For two temperatures:

$$\log(k_2/k_1) = (E_a/2.303R) \times [(T_2 - T_1)/(T_1 T_2)]$$

Where: A = frequency factor (pre-exponential), E_a = activation energy (J/mol), $R = 8.314 \text{ J/mol}\cdot\text{K}$

Graph tip: Plot of $\log k$ vs $1/T$ gives a straight line with slope $= -E_a/(2.303R)$. This is how E_a is determined experimentally.

Effect of Catalyst

- Catalyst provides an **alternative pathway** with lower activation energy
- Does NOT change ΔH or ΔG of the reaction
- Does NOT shift equilibrium — it speeds up both forward and reverse reactions equally
- It only helps reach equilibrium faster

Important Definitions

Term	Definition
Rate of Reaction	Change in concentration of reactant or product per unit time
Rate Constant (k)	Proportionality constant in the rate law; rate when all concentrations are unity
Order of Reaction	Sum of powers of concentration terms in the rate law (experimental)
Molecularity	Number of molecules/atoms/ions taking part in an elementary step
Half-life ($t_{1/2}$)	Time for concentration of reactant to fall to half its initial value
Activation Energy (E_a)	Minimum energy that colliding molecules must have for reaction to occur
Catalyst	Substance that increases rate by lowering E_a without being consumed

Solved Examples — NCERT Based

Example 1: First Order Rate Constant

Q: A first order reaction has a rate constant of $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of the reactant take to reduce to 3 g?

Solution:

$$k = (2.303/t) \log([A]_0/[A])$$

$$1.15 \times 10^{-3} = (2.303/t) \log(5/3)$$

$$1.15 \times 10^{-3} = (2.303/t) \times 0.2219$$

$$t = (2.303 \times 0.2219) / (1.15 \times 10^{-3})$$

$$t = 0.5113 / 1.15 \times 10^{-3} = 444.6 \text{ s} \approx 7.4 \text{ min}$$

Example 2: Half-life of First Order Reaction

Q: The half-life of a first order reaction is 60 minutes. What percentage of the reactant will be left after 3 hours?

Solution:

3 hours = 180 minutes = 3 half-lives

After each half-life, amount halves:

After $t_{1/2}$: 50% | After $2t_{1/2}$: 25% | After $3t_{1/2}$: **12.5%**

Example 3: Arrhenius Equation — Finding E_a

Q: The rate constant of a reaction at 300 K is 1.6×10^{-2} and at 310 K is 3.2×10^{-2} . Calculate the activation energy.

Solution:

$$\log(k_2/k_1) = (E_a/2.303R) \times [(T_2 - T_1)/(T_1 T_2)]$$

$$\log(3.2 \times 10^{-2}/1.6 \times 10^{-2}) = (E_a/(2.303 \times 8.314)) \times [(310 - 300)/(300 \times 310)]$$

$$\log(2) = (E_a/19.147) \times (10/93000)$$

$$0.301 = E_a \times 5.226 \times 10^{-6} / 19.147$$

$$0.301 = E_a \times 2.73 \times 10^{-7}$$

$$E_a = 0.301 / 2.73 \times 10^{-7} = \mathbf{1.103 \times 10^6 \text{ J/mol} \approx 55.3 \text{ kJ/mol}}$$

Example 4: Determining Order from Data

Q: For the reaction $2A + B \rightarrow C$, the following data is given:

Exp	[A]	[B]	Rate
1	0.1	0.1	2×10^{-3}
2	0.2	0.1	4×10^{-3}
3	0.1	0.2	2×10^{-3}

Find the order and rate law.

Solution:

Comparing Exp 1 & 2: [A] doubles, [B] same $\rightarrow$ rate doubles $\rightarrow$ order w.r.t. A = 1

Comparing Exp 1 & 3: [B] doubles, [A] same $\rightarrow$ rate unchanged $\rightarrow$ order w.r.t. B = 0

Rate law: **Rate** = $k[A]^1[B]^0 = k[A] \rightarrow$ Overall order = 1

Important Questions for Board Exams

1 Mark Questions

1. Define the order of a reaction.
2. What is the unit of rate constant for a first order reaction?
3. Write the half-life expression for a zero order reaction.
4. What is activation energy?
5. Give an example of a pseudo first order reaction.

2 Mark Questions

1. Distinguish between order and molecularity.
2. A first order reaction has $k = 2 \times 10^{-3} \text{ s}^{-1}$. Find the half-life.
3. What is the effect of a catalyst on activation energy? Draw energy profile diagram.
4. Explain why the rate of reaction increases with temperature.

3 Mark Questions

1. Derive the integrated rate equation for a first order reaction.
2. For a first order reaction, show that $t_{1/2} = 0.693/k$.
3. State Arrhenius equation. How can E_a be determined graphically?
4. The rate constant doubles when temperature increases from 300 K to 310 K. Calculate E_a .

5 Mark Questions

1. What is meant by order and molecularity? Derive the integrated rate equation for first order reaction. Also derive the expression for half-life.
2. Explain collision theory of chemical kinetics. What are the conditions for effective collisions? Write the Arrhenius equation and explain the significance of each term.

Quick Revision Points

- Rate = change in concentration per unit time; always positive

- Order: experimental; Molecularity: theoretical (elementary step only)
- Zero order: $[A] = [A]_0 - kt$, $t_{1/2} = [A]_0/2k$
- First order: $k = (2.303/t) \log([A]_0/[A])$, $t_{1/2} = 0.693/k$ (independent of $[A]_0$)
- Pseudo first order: 2nd order reaction with one reactant in large excess
- Arrhenius: $k = Ae^{(-E_a/RT)}$; plot $\log k$ vs $1/T \rightarrow$ straight line
- For two temperatures: $\log(k_2/k_1) = (E_a/2.303R)[(T_2 - T_1)/(T_1 T_2)]$
- Catalyst lowers E_a but doesn't change ΔH or equilibrium
- 10°C rise $\approx$ doubles the rate (temperature coefficient ≈ 2)
- All radioactive decays follow first order kinetics

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