KSQUARE CAREER INSTITUTE

CHEMICAL KINETICS

Class 12 Chemistry • Rate, Order, Zero & First Order, Half-life • NEET / JEE Notes

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Topics Covered

1. Rate of reaction — average & instantaneous; rate in terms of stoichiometry
2. Rate law, order of reaction, unit of rate constant
3. Elementary & complex reactions; rate-determining step; mechanism questions
4. Zero-order & first-order reactions — integrated rate equations, half-life, completion time
5. PYQs (AIPMT 2009, NEET 2017, NEET 2018) & practice
6. Added: molecularity, pseudo first order, collision theory, Arrhenius equation, catalyst

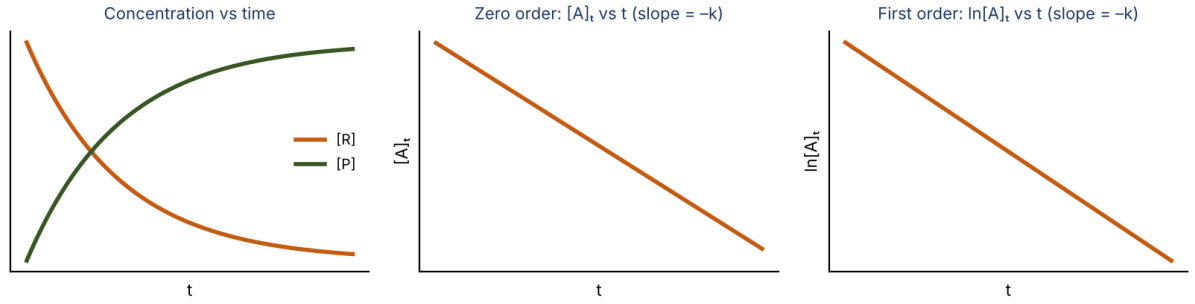
NEET Point / PYQ Alert

Chemical kinetics usually gives **2–3 questions** in NEET.

Thermodynamics deals with energy changes (feasibility); **chemical kinetics** deals with the **speed / rate** of a reaction.

RATE OF REACTION

- For R → P, the rate of reaction **can never be negative**.
- In terms of **concentration**: rate = change in concentration of reactant or product per unit time = **ΔC/Δt** (mol L^{-1} s^{-1}).
- In terms of **pressure** (only for gases): rate = **ΔP/Δt** (atm s^{-1}).



- [R] decreases with time (reactant consumed); [P] increases (product formed); both curves flatten as the reaction slows down.

Type	Reactant	Product
Average rate (interval $t_1 \rightarrow t_2$)	$-(C_2 - C_1)/(t_2 - t_1)$ $(C_1 > C_2)$	$+(C_2 - C_1)/(t_2 - t_1)$ $(C_2 > C_1)$
Instantaneous rate (slope of tangent at t)	$-d[R]/dt$	$+d[P]/dt$

Rate of Reaction is Defined for 1 mol

Example: $2SO_2 + O_2 \rightarrow 2SO_3$

$$\text{Rate} = -\tfrac{1}{2}\,d[SO_2]/dt = -\,d[O_2]/dt = +\tfrac{1}{2}\,d[SO_3]/dt$$

Shortcut

Reactants → **minus** sign; products → **plus** sign.

Divide by the stoichiometric coefficient ("SC se divide hoga").

Rate of Disappearance & Appearance

- Disappearance → reactant; appearance → product. Here we do **not** divide by the stoichiometric coefficient.
- $N_2 + 3H_2 \rightarrow 2NH_3$: rate of disappearance of $N_2 = -d[N_2]/dt$; of $H_2 = -d[H_2]/dt$; rate of appearance of $NH_3 = +d[NH_3]/dt$.

Practice

Q1. For $aA + bB \rightarrow$ products, $-d[A]/dt$ is equal to

(1) $-d[B]/dt$
(2) $-(b/d)\,d[B]/dt$
(3) $-(a/b)\,d[B]/dt$
(4) $-(b/a)\,d[B]/dt$

Answer: (3) — $-(1/a)d[A]/dt = -(1/b)d[B]/dt$.

Q2. In $2X + Y \rightarrow X_2Y$, X disappears at

(1) half the rate of disappearance of Y
(2) the same rate as disappearance of Y
(3) the same rate as appearance of X_2Y
(4) twice the rate of appearance of X_2Y

Answer: (4) — $-\tfrac{1}{2}\,d[X]/dt = +d[X_2Y]/dt$.

Q3. For $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of change of $[H_2]$ is -0.3×10^{-4} M s^{-1}. The rate of change of $[NH_3]$ is

(1) -0.2×10^{4}
(2) 0.2×10^{-4}
(3) 0.1×10^{-4}
(4) 0.3×10^{-4}

Answer: (2) — $d[NH_3]/dt = (2/3) \times 0.3 \times 10^{-4}$.

Q4. Rate of formation of SO_3 in $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 g min^{-1}. The rate of disappearance of O_2 is

(1) 50 g min^{-1}
(2) 40 g min^{-1}
(3) 200 g min^{-1}
(4) 20 g min^{-1}

Answer: (4) — Convert to moles: 100/80 = 1.25 mol SO_3 ⇒ O_2 = 0.625 mol × 32 = 20 g min^{-1}.

RATE LAW & ORDER OF REACTION

Rate law

Rate is proportional to the product of molar concentrations of reactants, each raised to a power **found experimentally**.

aA + bB → cC + dD: **Rate = $k[A]^x[B]^y$** (k = rate constant; x, y are **not** from coefficients a, b).

Symbol	Meaning
x	Order w.r.t. A
y	Order w.r.t. B
x + y	**Overall order**

- Order is an **experimental** quantity; it can be **zero, positive, negative or fractional** (½, 3/2 …).
- Contrast: **molecularity** (theoretical) is always a whole number — 1, 2 or 3.

Unit of Rate Constant

General formula

$$k \equiv (\text{mol L}^{-1})^{1-n}\,\text{s}^{-1} \quad (n = \text{order})$$

Order	Substitution	Unit of k
Zero	$(\text{mol L}^{-1})^1\,\text{s}^{-1}$	**$\text{mol L}^{-1}\,\text{s}^{-1}$**
First	$(\text{mol L}^{-1})^0\,\text{s}^{-1}$	**s^{-1}** (min^{-1}, h^{-1})
Second	$(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$	**$\text{mol}^{-1}\,\text{L}\,\text{s}^{-1}$**

ELEMENTARY & COMPLEX REACTIONS

Elementary Reaction

- Completes in a **single step**; **no reaction intermediate**.
- **Order = stoichiometric coefficients**: 2A + 3B → product ⇒ rate = $k[A]^2[B]^3$, order = 5.

NEET Point / PYQ Alert

A zero-order reaction can never be elementary — rate = $k[A]^0$ would need a stoichiometric coefficient of 0, i.e. A would not take part at all.

Complex Reaction

- Completed in **multiple steps**; **reaction intermediates** are present (formed in a step but absent from the final equation — "vo hai jo final rxn me nahi hota").
- E.g. A → C (fast) → D (**slow**) → B (fast): C, D are intermediates.

Rate-determining step (RDS)

The overall rate is controlled by the **slowest step** — the narrowest bottleneck sets the overall rate.

The rate expression (order) must be **free from reaction intermediates**.

Q5. $A_2 + B_2 \rightarrow 2AB$ follows: $A_2 \rightleftharpoons A + A$ (fast); $A + B_2 \rightarrow AB + B$ (slow); $A + B \rightarrow AB$ (fast). The order of the overall reaction is

(1) 2
(2) 1
(3) 1.5
(4) 0

Answer: (3) — Slow step: rate = $k[A][B_2]$; A is an intermediate. $K_{eq} = [A]^2/[A_2] \Rightarrow [A] = (K_{eq}[A_2])^{1/2} \Rightarrow$ rate = $k'[A_2]^{1/2}[B_2] \Rightarrow$ order = 3/2.

Example 2: $A_2 + \frac{1}{2}B_2 \rightarrow A + AB$ (slow); $A + \frac{1}{2}B_2 \rightarrow AB$ (fast). Slow step has no intermediate $\Rightarrow$ rate = $k[A_2]^1[B_2]^{1/2} \Rightarrow$ order = **1.5**.

ZERO-ORDER REACTION (N = 0) — VVIMP

- A → products; **rate = $k[A]^0 = k$** — the rate does **not depend on concentration**.

Integrated rate equation

$$-d[A]/dt = k \Rightarrow \int d[A]\ (A_0 \rightarrow A_t) = -k \int dt\ (0 \rightarrow t)$$

$$A_t = A_0 - kt \quad (y = c + mx;\ \text{intercept } A_0,\ \text{slope } -k)$$

$$t_{½} = A_0/2k\ ;\ \ t_{100\%} = A_0/k = 2 \times t_{½}$$

Symbol	% completed	% left	A_t
$t_{50\%}$	50%	50%	0.5 A_o
$t_{60\%}$	60%	40%	0.4 A_o
$t_{75\%}$	75%	25%	0.25 A_o

- Examples (Added): decomposition of NH_3 on hot Pt surface; decomposition of HI on gold surface; photochemical $H_2 + Cl_2$.

FIRST-ORDER REACTION (N = 1)

Integrated rate equation

$$-d[A]/dt = k[A] \Rightarrow \int d[A]/[A] = -k \int dt$$

$$\ln(A_t/A_0) = -kt\ ;\ \ A_t = A_0\, e^{-kt}$$

$$k = (1/t)\ln(A_0/A_t) = (2.303/t)\log(A_0/A_t) \quad (\ln x = 2.303 \log x)$$

$$t_{½} = \ln 2/k = 0.693/k \quad (\text{independent of initial concentration})$$

First order — never completed	Zero order
$A_t = A_0e^{-kt}$	$A_t = A_o - kt$
$k = (2.303/t)\log(A_o/A_t)$	$t½ = A_o/2k$
$t½ = 0.693/k$	$t_{100\%} = A_o/k$
Never reaches $A_t = 0$ — **no $t_{100\%}$**	Completes in finite time

- Examples (Added): radioactive decay; decomposition of N_2O_5, H_2O_2; hydrogenation of ethene.

▸ Half-life and Order

Order	t½	Dependence on A_o
Zero	$A_o/2k$	$t½ \propto A_o^1$
First	ln 2/k	$t½ \propto A_o^o$ (independent)
Second	$1/(kA_o)$	$t½ \propto A_o^{-1}$

General

$$t½ \propto (A_0)^{1-n}$$

After n half-lives: $A_t = A_0/2^n$ $(100 \rightarrow 50 \rightarrow 25 \rightarrow 12.5)$

PYQS & PRACTICE

Q6. Half-life of a first-order reaction is 1386 s. The specific rate constant is **[AIPMT 2009]**

(1) $5.0 \times 10^{-3}\ s^{-1}$
(2) $0.5 \times 10^{-2}\ s^{-1}$
(3) $0.5 \times 10^{-3}\ s^{-1}$
(4) $5.0 \times 10^{-2}\ s^{-1}$

Answer: (3) — $k = 0.693/1386 = 5 \times 10^{-4}\ s^{-1}$.

Q7. A first-order reaction has $k = 10^{-2}\ s^{-1}$. Time for 20 g of reactant to reduce to 5 g is **[NEET 2017]**

(1) 238.6 s
(2) 138.6 s
(3) 346.5 s
(4) 693.0 s

Answer: (2) — $t = (1/k)\ln 4 = 100 \times 2 \times 0.693 = 138.6$ s (two half-lives).

Q8. When the initial concentration is doubled, the half-life of a zero-order reaction **[NEET 2018]**

(1) is halved
(2) remains unchanged
(3) is tripled
(4) is doubled

Answer: (4) — $t½ \propto A_o$.

Q9. k for a zero-order reaction is 2×10^{-2} mol $L^{-1}\ s^{-1}$. If the concentration after 25 s is 0.5 M, the initial concentration was

(1) 0.5 M
(2) 1.25 M
(3) 12.5 M
(4) 1.0 M

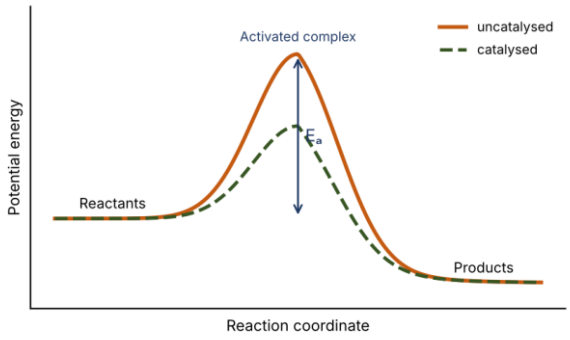
Answer: (4) — $A_o = A_t + kt = 0.5 + 0.5$.

MOLECULARITY & PSEUDO FIRST ORDER (ADDITIONAL TOPIC)

Order	Molecularity
Experimental	Theoretical
Can be 0, fractional or negative	Always a whole number (1, 2, 3); never zero
For overall (complex) reaction	Only for elementary steps
Determined from rate law	Number of species colliding simultaneously

- **Pseudo first-order**: one reactant in large excess, so its concentration is effectively constant — e.g. **acid hydrolysis of ethyl acetate** and **inversion of cane sugar** (water in excess): molecularity 2, order 1.

TEMPERATURE, ARRHENIUS EQUATION & CATALYST (ADDITIONAL TOPIC)



- For most reactions, rate (and k) **nearly doubles for every 10 °C rise** (temperature coefficient = $k_{t+10}/k_t \approx 2–3$).

Arrhenius equation

$$k = A\, e^{-E_a/RT} \quad (A = \text{frequency factor}, E_a = \text{activation energy})$$

$$\ln k = \ln A - E_a/RT \quad (\text{plot of } \ln k \text{ vs } 1/T\text{: slope} = -E_a/R)$$

$$\log (k_2/k_1) = [E_a / 2.303R] \times [(T_2 - T_1)/(T_1T_2)]$$

- **Collision theory:** rate = $Z_{AB} \times e^{-E_a/RT} \times P$ (P = steric/orientation factor). Only collisions with sufficient energy (≥ threshold) and **proper orientation** are effective.
- **Catalyst** provides an alternative path with **lower activation energy**; it does **not change ΔH, ΔG or K_{eq}** — it only helps reach equilibrium faster and is unchanged at the end.

QUICK REVISION

- Rate = $-(1/a)d[A]/dt = +(1/c)d[C]/dt$; never negative; unit mol L^{-1} s^{-1} (or atm s^{-1}).

- Rate = $k[A]^x[B]^y$; order experimental (0, +, –, fraction); k unit = $(\text{mol } L^{-1})^{1-n}\ s^{-1}$.
- Elementary: order = coefficients; zero-order can never be elementary; complex: RDS = slowest step; rate law free of intermediates.
- Zero order: $A_t = A_o - kt$; $t½ = A_o/2k$; $t_{100\%} = A_o/k$.
- First order: $k = (2.303/t)\log(A_o/A_t)$; $t½ = 0.693/k$; $A_t = A_o/2^n$ after n half-lives.
- $t½ \propto A_o^{1-n}$; Arrhenius $k = Ae^{-E_a/RT}$; catalyst lowers E_a.

2–3 questions every year — master the formulas!

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