FREE NOTES · NCERT + JEE/NEET LEVEL

Chemical Kinetics

Rate of reaction, factors affecting it, rate law, order and molecularity, integrated rate equations for zero and first order, half-life, pseudo first order, Arrhenius equation, activation energy and collision theory.

01 Rate of reaction
02 Factors affecting rate
03 Rate law & order
04 Molecularity
05 Zero order reactions
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01 Rate of reaction

Rate = change in concentration per unit time. Unit: mol L^{-1} s^{-1}.

$$\text{Average rate} = -\Delta[R]/\Delta t = +\Delta[P]/\Delta t$$

$$\text{Instantaneous rate} = -d[R]/dt \text{ (slope of the tangent to the [R]–t curve)}$$

$$\text{For } aA + bB \rightarrow cC + dD:\ \text{rate} = -(1/a)d[A]/dt = -(1/b)d[B]/dt = (1/c)d[C]/dt = (1/d)d[D]/dt$$

Example: $2N_2O_5 \rightarrow 4NO_2 + O_2$ ⇒ rate = -½ $d[N_2O_5]/dt$ = ¼ $d[NO_2]/dt$ = $d[O_2]/dt$.

02 Factors affecting rate

- **Concentration:** more reactant ⇒ more collisions ⇒ faster (except zero order).
- **Temperature:** about every 10°C rise roughly doubles the rate (temperature coefficient ≈ 2–3).
- **Catalyst:** gives a new path with lower E_a. It does not change ΔH, ΔG or the equilibrium constant, only how fast equilibrium is reached.
- **Surface area:** powder reacts faster than a lump.
- **Nature of reactants** and **radiation** (photochemical reactions).

03 Rate law & order

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

x and y are found **by experiment**, not from the balanced equation. Order = x + y. Order can be 0, a fraction, or even negative. k = rate constant (depends only on temperature).

Order	Unit of k	Example
0	mol L^{-1} s^{-1}	$2NH_3 \rightarrow N_2 + 3H_2$ on hot Pt; 2HI on gold
1	s^{-1}	Radioactive decay, N_2O_5 decomposition
2	L mol^{-1} s^{-1}	$2NO_2 \rightarrow 2NO + O_2$
n	$(\text{mol } L^{-1})^{1-n}$ s^{-1}	General

INITIAL RATE METHOD

Keep [B] fixed, double [A]. If rate doubles ⇒ order 1 in A; ×4 ⇒ order 2; no change ⇒ order 0.

04 Molecularity

Order	Molecularity
Experimental	Theoretical: number of species colliding in one **elementary step**
Can be 0 or fractional	Always a whole number 1, 2 or 3 (never 0)
For the overall reaction	Only for an elementary step

In a complex reaction the **slowest step decides the rate** (rate-determining step). Order of the overall reaction = molecularity of the slowest step (when no fast pre-equilibrium).

PSEUDO FIRST ORDER

One reactant is in huge excess, so its concentration barely changes. Hydrolysis of ethyl acetate in water: $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$, rate = k′[ester]. Inversion of cane sugar is another example.

05 Zero order reactions

$\text{Rate} = k[R]^0 = k$

$$[R] = [R]_0 - kt$$

$t_{1/2} = [R]_0/2k$ (depends on starting concentration)

Graph of [R] vs t is a straight line with slope -k. Happens when the surface of a catalyst is fully covered (saturated).

06 First order reactions & half-life

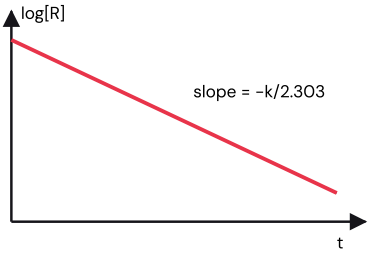
$$k = (2.303/t)\log([R]_0/[R])$$

$[R] = [R]_0\, e^{-kt}$

$\mathbf{t_{1/2} = 0.693/k}$ (independent of concentration)

$t_{99.9\%} \approx 10\ t_{1/2}$, after n half-lives $[R] = [R]_0/2^n$

Gas phase A(g) → B(g) + C(g): $k = (2.303/t)\log[p_o/(2p_o - p_t)]$.



First order: log[R] vs t is a straight line

QUICK CHECK

Same half-life again and again ⇒ first order. All radioactive decay is first order.

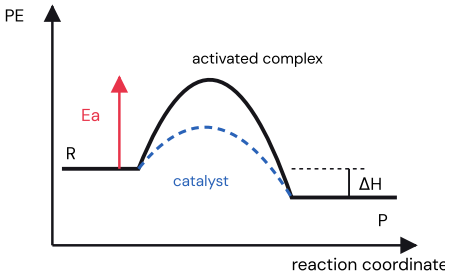
07 Arrhenius equation & activation energy

$$k = A\, e^{-E_a/RT}$$

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

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

A = frequency (pre-exponential) factor. Plot of ln k vs 1/T is a straight line with slope $-E_a/R$. $e^{-Ea/RT}$ = fraction of molecules with energy ≥ E_a.



Energy profile: a catalyst lowers Ea, ΔH stays the same

Activation energy: the minimum extra energy reactants need to form the **activated complex**. Higher E_a ⇒ slower reaction. Raising T increases the fraction of molecules above E_a (Maxwell-Boltzmann curve shifts right and flattens).

08 Collision theory

Molecules must **collide**. A collision is effective only if (1) energy ≥ threshold energy and (2) the **orientation is proper**.

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

Z_{AB} = collision frequency, P = probability (steric) factor for orientation. Threshold energy = E_a + average energy of reactants.

09 JEE Extra + Tricks

JEE LEVEL

- Half-life: zero order $t_{½} = [A]_o/2k$ ($\propto [A]_o$); first order $t_{½} = 0.693/k$ (independent); second order $1/(k[A]_o)$.
- First order: time for 75% = 2 $t_{½}$, 87.5% = 3 $t_{½}$, 99.9% ≈ 10 $t_{½}$.
- Units of k: $(\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$ ⇒ zero order mol L^{-1} s^{-1}, first s^{-1}, second L mol^{-1} s^{-1}.
- Arrhenius: $k = Ae^{-Ea/RT}$; $\log(k_2/k_1) = (Ea/2.303R)(1/T_1 - 1/T_2)$. Rule of thumb: rate doubles per 10 °C rise.
- Pseudo-first order: hydrolysis of ester in excess water, inversion of cane sugar.
- Catalyst lowers Ea of both forward and backward reactions equally; does not change ΔH or K.

10 Solved numericals

Q1. A first order reaction has $k = 1.15 \times 10^{-3}\ s^{-1}$. Find $t_{½}$.

$t_{½} = 0.693/1.15 \times 10^{-3} =$ **≈ 602.6 s**.

Q2. A first order reaction is 75% complete in 32 min. When will it be 50% complete?

75% = 2 half-lives ⇒ $t_{½}$ = **16 min**.

Q3. Rate constant doubles from 300 K to 310 K. Find E_a. (R = 8.314)

$\log 2 = E_a/(2.303 \times 8.314) \times 10/(300 \times 310) \Rightarrow 0.301 = E_a \times 10/(19.147 \times 93000) \Rightarrow E_a \approx$ **53.6 kJ/mol**.

Q4. For A + B → P, doubling [A] doubles the rate; doubling [B] makes it 4 times. Rate law?

Rate = $k[A][B]^2$, overall order **3**.

11 Mistakes, formula sheet & practice

- Taking order from the coefficients of the balanced equation.
- Saying molecularity can be zero or fractional.
- Thinking a catalyst changes ΔH or the equilibrium constant.
- Using natural log with 2.303 (either ln, or 2.303 × log, not both).

Zero order	$[R] = [R]_0 - kt$; $t_{1/2} = [R]_0/2k$
First order	$k = (2.303/t)\log([R]_0/[R])$; $t_{1/2} = 0.693/k$
Arrhenius	$k = Ae^{-Ea/RT}$
Two temperatures	$\log(k_2/k_1) = Ea(T_2-T_1)/(2.303RT_1T_2)$
Units of k	$(\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$

1. Unit of k is L mol^{-1} s^{-1}. Order?
2. Why does rate fall with time?
3. $t_{1/2}$ of a zero order reaction when $[R]_0$ is doubled?
4. Define rate-determining step.

ANSWERS

1) Second · 2) Reactant concentration decreases · 3) Doubles · 4) The slowest step of a mechanism, which controls the overall rate

12 Quick revision: 5 minutes before the exam

BASICS

- Rate = -(1/a) d[A]/dt.
- Order: experimental, can be 0/fraction.
- Molecularity: 1, 2, 3 only.

EQUATIONS

- Zero: $[R] = [R]_0 - kt$.
- First: $t_{1/2} = 0.693/k$.
- $k = Ae^{-Ea/RT}$.

GRAPHS

- Zero: [R] vs t straight.
- First: log[R] vs t straight.
- ln k vs 1/T: slope -Ea/R.

CATALYST

- Lowers Ea only.
- ΔH, ΔG, K unchanged.
- Effective collision = energy + orientation.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.