JEE MAIN · PAPER 1 · CHEMISTRY

08 Chemical Kinetics

Formula & concept sheet

How fast reactions go and why: rate and rate law, order and molecularity, integrated rate equations and half-lives for zero, first and second order, the Arrhenius equation and collision theory, catalysis, and reaction mechanisms. Each idea is explained first, then the formulas, shortcuts and traps.

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READ ALONGSIDE NCERT XII · Chemical Kinetics

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 08

Chemical Kinetics

NCERT XII · Chemical Kinetics

Covers: rate of reaction, rate law, order and molecularity · integrated rate laws, half-life · pseudo-first-order · Arrhenius equation, activation energy · collision theory · effect of catalyst · elementary steps and rate-determining step · steady-state treatment.

1 Rate of reaction, rate law, order and molecularity

- Thermodynamics says whether a reaction can go; **kinetics** says how fast. The **rate** is the change of concentration per unit time. The **average** rate uses a time interval; the **instantaneous** rate is the slope of the concentration-time curve at one moment.
- For $aA + bB \rightarrow cC + dD$ the rate of **reaction** is the same whichever species is followed once each is divided by its coefficient; a species is used up (negative sign) or formed (positive).
- The **rate law** relates the rate to concentrations raised to experimental powers. It cannot be read from the balanced equation (except for an elementary step).

RATE OF REACTION

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

units mol L^{-1} s^{-1} (or atm s^{-1} for gases)

RATE LAW

$$r = k\,[A]^x[B]^y, \quad \text{order} = x + y$$

x, y found by experiment; k is the rate constant (depends on T and catalyst, not on concentrations)

UNITS OF k BY ORDER

ORDER n	UNIT OF k	GENERAL
zero	mol L^{-1} s^{-1}	$(\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$
first	s^{-1}	
second	L mol^{-1} s^{-1}	
third	L^2 mol^{-2} s^{-1}	

ORDER

- Experimental; can be zero, fractional or even negative.
- Defined for the **overall** reaction, including complex, multistep ones.
- Sum of the powers in the rate law; the order for each reactant is its own power.

MOLECULARITY

- Theoretical; the number of species colliding in one **elementary** step: $1, 2$ or (rarely) 3, never 0 or fractional.
- Meaningless for a complex reaction as a whole.
- For an elementary step the order **equals** the molecularity.

ORDER FROM INITIAL-RATE DATA

1. Choose two experiments where only one concentration changes.
2. Take the ratio of the rates: $\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^x$, solve for x (doubling the concentration doubles the rate: $x = 1$; quadruples it: $x = 2$; no change: $x = 0$).
3. Repeat for each reactant, add the powers, then use any run to find k.

TRAP

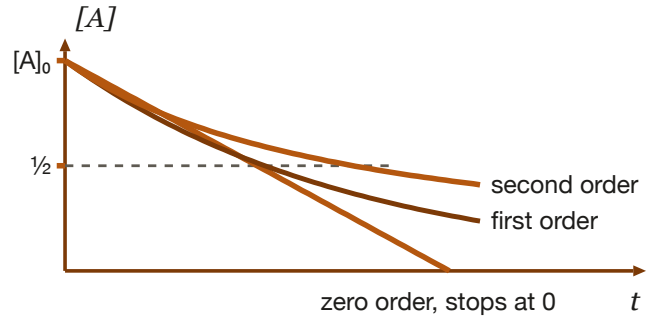
Rate of disappearance of a species is not the rate of reaction unless its coefficient is 1: for $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$, $-\frac{d[N_2O_5]}{dt} = 2r$. Do not read the order from the stoichiometry: $H_2 + I_2 \longrightarrow 2\,HI$-type equations can be of any order.

QUICK CHECK

Doubling $[A]$ doubles the rate, and doubling $[B]$ quadruples it. Rate law and the effect of doubling both?

Answer: $r = k[A][B]^2$, order 3; doubling both gives $2 \times 4 = 8$ times the rate.

2 Integrated rate laws and half-life

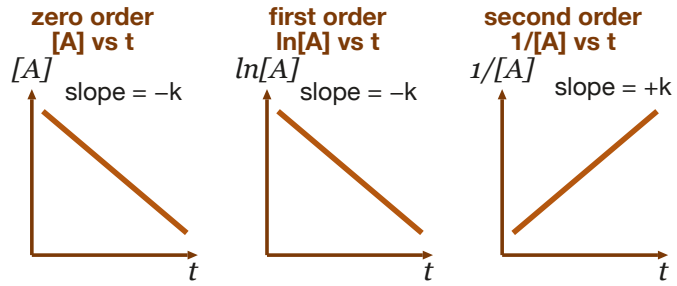


only the zero-order curve reaches zero in finite time

- **Zero order**: the rate does not depend on concentration (a catalyst surface saturated with reactant: NH_3 on hot platinum at high pressure, HI on gold). The concentration falls linearly and reaches zero at a finite time.
- **First order**: rate $\propto [A]$. Concentration decays exponentially and never quite reaches zero; the fraction reacting per unit time is constant (radioactive decay, N_2O_5 and H_2O_2 decomposition).
- **Second order**: rate $\propto [A]^2$; the tail is longer than first order.

INTEGRATED RATE EQUATIONS AND HALF-LIVES

	ZERO ORDER	FIRST ORDER	SECOND ORDER ($2\,A$ OR EQUAL)
integrated	$[A] = [A]_0 - kt$	$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$; $[A] = [A]_0 e^{-kt}$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
half-life $t_{1/2}$	$\frac{[A]_0}{2k}$	$\frac{0.693}{k}$ (independent of $[A]_0$)	$\frac{1}{k[A]_0}$
straight-line plot	$[A]$ against t; slope $-k$	$\ln[A]$ (or $\log[A]$) against t; slope $-k$ ($-k/2.303$)	$1/[A]$ against t; slope $+k$
$t_{1/2}$ against $[A]_0$	direct proportion	horizontal line (constant)	inverse
general	$t_{1/2} \propto [A]_0^{1-n}$		



the straight-line plot identifies the order

TELLING THE ORDER FROM A PLOT

- ✓ Straight line for $[A]$ against t: zero order; for $\ln[A]$ against t: first order; for $1/[A]$ against t: second order.
- ✓ The slope gives k (for the $\log$ plot the slope is $-k/2.303$).
- ✓ Successive half-lives tell the same story: equal for first order, each half as long as the one before for zero order, each twice as long for second order.

AFTER n HALF-LIVES (FIRST ORDER)

$$[A] = \frac{[A]_0}{2^n}, \quad n = \frac{t}{t_{1/2}}$$

fraction left $= \left(\frac{1}{2}\right)^{t/t_{1/2}}$

FRACTIONAL LIVES (FIRST ORDER)

$t_{75\%} = 2t_{1/2},\ t_{87.5\%} = 3t_{1/2}$

$t_{90\%} = \dfrac{2.303}{k} = 3.32\, t_{1/2}$; $t_{99\%} = 2t_{90\%} = 6.64\, t_{1/2}$; $t_{99.9\%} \approx 10\, t_{1/2}$

ZERO ORDER COMPLETION

$$t_{complete} = \frac{[A]_0}{k}$$

exactly twice the half-life, $2t_{1/2}$

GAS PHASE, $\mathrm{A(g)} \longrightarrow \mathrm{B(g)} + \mathrm{C(g)}$

$$k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$

p_i initial pressure of A, p_t total at time t; $p_A = 2p_i - p_t$

ANY MEASURED PROPERTY

$$k = \frac{2.303}{t} \log \frac{X_\infty - X_0}{X_\infty - X_t}$$

volume of titrant, optical rotation, absorbance: $X_\infty - X_t \propto [A]$ left

SPECIAL CASES

- **Pseudo-first order**: one reactant is in large excess, so its concentration is nearly constant and the rate looks first order: acid hydrolysis of ethyl acetate (water in excess), inversion of cane sugar.
- **Parallel reactions** $\mathrm{A} \longrightarrow \mathrm{B}$ (k_1), $\mathrm{A} \longrightarrow \mathrm{C}$ (k_2), both first order: $k_{eff} = k_1 + k_2$ and $[B]/[C] = k_1/k_2$.
- **Radioactive decay** is first order: $t = \dfrac{2.303}{k} \log \dfrac{N_0}{N}$; wood with $^{14}\mathrm{C}$ at $1/8$ of the atmosphere is 3 half-lives old $= 17190$ y ($t_{1/2} = 5730$ y).

TRAP

Zero-order $t_{1/2}$ depends on $[A]_0$: never use $0.693/k$ for it. For a first-order reaction the half-life is the same for every starting amount, which also means it does not depend on the volume. Use the $\log$ values given in the question, with 2.303.

QUICK CHECK

A first-order reaction is 50% complete in 120 min. Time for 90%?

Answer: $t_{90\%} = 120 \times \dfrac{\log 10}{\log 2} = 120 \times 3.322 \approx 399$ min.

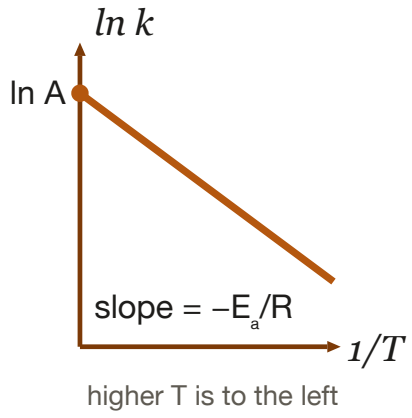
QUICK CHECK

$t_{1/2} = 6.93$ min for a first-order reaction. Time for 99% ?

Answer: $k = 0.1$ min^{-1}; $t = \dfrac{2.303}{0.1} \log 100 = 46$ min.

3 Temperature dependence, collision theory and catalysis

- A reaction needs reactant molecules to **collide** with energy at least the **activation energy** E_a and with the right orientation. The fraction of molecules with energy $\geq E_a$ is $e^{-E_a/RT}$; a 10 K rise roughly doubles to triples this (the rate), mostly because that tail of the distribution grows, not because collisions are much more frequent.
- A **catalyst** gives an alternative path with a lower E_a; it speeds the forward and backward reactions equally and so changes neither ΔH, ΔG nor K.



higher T is to the left

steeper slope means larger E_a

ARRHENIUS EQUATION

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

A frequency (pre-exponential) factor; $R = 8.314$ J K^{-1} mol^{-1}, T in K, E_a in J mol^{-1}; slope of $\ln k$ against $1/T$ is $-E_a/R$, intercept $\ln A$

TWO TEMPERATURES

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a}{2.303R}\,\frac{T_2 - T_1}{T_1 T_2}$$

; E_a larger gives a stronger temperature effect

FROM $k = Ae^{-B/T}$

$E_a = B\,R$

B in kelvin; $B = 28000$ K gives $E_a = 233$ kJ mol^{-1}

WITH CATALYST

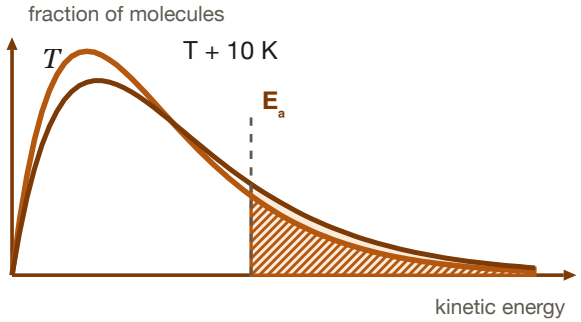
$$\frac{k_{cat}}{k} = e^{(E_a - E_a')/RT}$$

same A; lowering E_a by 20 kJ at 300 K raises k about 3000-fold

ENERGY PROFILE

$E_a(\text{fwd}) - E_a(\text{rev}) = \Delta H$

the catalysed path has a lower barrier in both directions



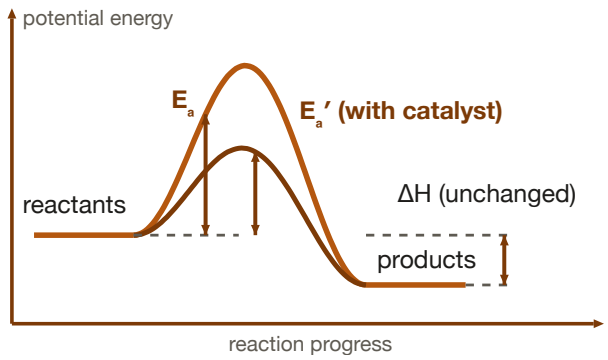
a 10 K rise lifts the fraction above E_a by about 2 to 3 times for typical E_a (the widening here is exaggerated)

READING THE DISTRIBUTION

- The area under each curve is 1 (all molecules). The shaded part to the right of E_a is the fraction able to react.
- At $T + 10$ K the curve flattens and shifts right: the peak falls but the tail beyond E_a grows markedly.
- The most probable energy changes only a little, so the rate rises because of the **tail**.
- A catalyst moves the E_a line to the left instead of changing the curves.

COLLISION THEORY IN BRIEF

IDEA	STATEMENT
rate	$r = P\,Z_{AB}\,e^{-E_a/RT}$: steric factor P (< 1) $\times$ collision frequency $Z_{AB}\times$ fraction with $E \geq E_a$
threshold energy	reactants must climb to the activated complex: $E_{threshold} = E_a +$ average energy of reactants
temperature coefficient	$k_{T+10}/k_T \approx 2$ to 3 (rule of thumb from NCERT, not a law)
effective collision	enough energy and correct orientation; most collisions are ineffective



a catalyst lowers E_a for both directions; ΔH and K are unchanged

WHAT A CATALYST DOES

- Opens a path with a lower activation energy: $E_a' < E_a$ for the forward and the reverse reaction alike.
- Leaves ΔH, ΔG, K and the equilibrium composition unchanged; it only brings equilibrium sooner.
- Is not used up, and does not start a reaction that is thermodynamically impossible.

WHY IT WORKS

The $e^{-E_a/RT}$ term decides almost everything: a 10 K rise at 300 K with $E_a = 50$ kJ mol^{-1} raises the fraction above E_a by 1.9 times. The smaller the E_a, the less sensitive the rate to temperature.

QUICK CHECK

k doubles when T rises from 300 K to 310 K. Find E_a.

Answer: $E_a = \dfrac{2.303R\log 2 \times 300 \times 310}{10} = 53.6$ kJ mol^{-1}.

4 Reaction mechanism

Most reactions are a sequence of **elementary steps**. The overall rate is controlled by the **slowest** step, the rate-determining step (RDS): the rate law is written from the molecularity of that step, with any fast pre-equilibrium intermediate replaced by the reactants that make it. An **intermediate** is formed in one step and used in the next; it never appears in the overall equation.

STEADY STATE

$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}: \quad \dfrac{d[B]}{dt} = 0 \Rightarrow [B] = \dfrac{k_1}{k_2}[A]$

the intermediate B is used up as fast as it forms

RATE FROM THE RDS

$r = k[\text{species in RDS}]$

write the RDS, then eliminate any intermediate with the preceding fast equilibrium: e.g. $2\,\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{NO_2}$ third order overall

WHAT A MECHANISM MUST SATISFY

- The elementary steps add up to the overall equation.
- The rate law from the RDS agrees with the experimental rate law.
- Unimolecular and bimolecular steps are common; termolecular steps are rare (three-body collisions are improbable).

TRAP

A rate law of a given order does not prove a mechanism, it only fits it. Order 0 for a reactant means it is not involved up to and including the RDS; molecularity of 0 or a fractional value is impossible.

5 Worked examples

ORDER FROM DATA

Rate (mol L^{-1} s^{-1}) for $[A] = 0.1, 0.2, 0.1$ and $[B] = 0.1, 0.1, 0.2$: $2 \times 10^{-3}, 4 \times 10^{-3}, 8 \times 10^{-3}$. Rate law, k?

A doubles: rate $\times 2$, order 1; B doubles: rate $\times 4$, order 2. $r = k[A][B]^2$; $k = \dfrac{2 \times 10^{-3}}{0.1 \times 0.01} = 2$ L^2 mol^{-2} s^{-1}

FIRST-ORDER k

A first-order reaction is 25% complete in 30 min. k and $t_{1/2}$?

$k = \dfrac{2.303}{30}\log\dfrac{100}{75} = 9.6 \times 10^{-3}$ min^{-1}; $t_{1/2} = \dfrac{0.693}{k} = 72$ min

ZERO ORDER

A zero-order reaction has $[A]_0 = 0.5$ M and $k = 0.01$ M min^{-1}. $t_{1/2}$ and the time to completion?

$t_{1/2} = \dfrac{0.5}{2 \times 0.01} = 25$ min; complete in $\dfrac{0.5}{0.01} = 50$ min

SECOND ORDER

$k = 0.01$ L mol^{-1} s^{-1}, $[A]_0 = 0.5$ M. $t_{1/2}$?

$\dfrac{1}{k[A]_0} = \dfrac{1}{0.01 \times 0.5} = 200$ s

GAS-PHASE PRESSURE

$\mathrm{A(g)} \longrightarrow \mathrm{B(g)} + \mathrm{C(g)}$: $p_i = 0.5$ atm and $p_t = 0.8$ atm at 10 min. k?

$p_A = 2(0.5) - 0.8 = 0.2$; $k = \dfrac{2.303}{10}\log\dfrac{0.5}{0.2} = 0.0916$ min^{-1}

ACTIVATION ENERGY

$k = (5.5 \times 10^{11}\ \mathrm{s^{-1}})e^{-28000\,\mathrm{K}/T}$. E_a?

$E_a = 28000 \times 8.314 = 2.33 \times 10^5$ J mol^{-1} $= 233$ kJ mol^{-1}

CARBON DATING

Wood has $^{14}C/^{12}C$ equal to $1/8$ of the atmospheric ratio; $t_{1/2} = 5730$ y. Age?

$\frac{1}{8} = \left(\frac{1}{2}\right)^3 : 3 \times 5730 = 17190$ y

FRACTION LEFT

^{82}Br has $t_{1/2} = 36$ h. Fraction left after 24 h?

$2^{-24/36} = 2^{-2/3} = 0.63$

ORDER FROM HALF-LIVES

The half-life is 100 s at 0.1 M and 50 s at 0.2 M. Order and k?

$t_{1/2} \propto 1/[A]_0$: second order; $k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{100 \times 0.1} = 0.1$ L mol^{-1} s^{-1}

EQUAL RATE CONSTANTS

$k_1 = 10^{10}e^{-20000/T}$ and $k_2 = 10^{12}e^{-24000/T}$. At what T are they equal?

$\ln \frac{A_1}{A_2} = \frac{B_1 - B_2}{T} : T = \frac{-4000}{\ln 0.01} = 869$ K

CATALYST

A catalyst lowers E_a from 100 to 80 kJ mol^{-1} at 300 K. Factor in k (same A)?

$e^{20000/(8.314 \times 300)} = e^{8.02} \approx 3.0 \times 10^3$

PARALLEL REACTIONS

$A \longrightarrow B$ ($k_1 = 3 \times 10^{-3}$ s^{-1}) and $A \longrightarrow C$ ($k_2 = 1 \times 10^{-3}$ s^{-1}). Overall k, half-life, $[B]/[C]$?

$k = 4 \times 10^{-3}$ s^{-1}; $t_{1/2} = \frac{0.693}{0.004} = 173$ s; $[B]/[C] = 3$

6 Last-minute checklist

BEFORE YOU ANSWER

Order from experiment, not the equation. Which order do the units of k or the half-life behaviour point to? Temperature in kelvin? Which log values does the question give?

- $r = k[A]^x[B]^y$; units of k: $(\text{mol L}^{-1})^{1-n}\text{s}^{-1}$; rate of reaction = rate of change divided by the coefficient.
- Zero: $[A]_0 - [A] = kt$, $t_{1/2} = [A]_0/2k$. First: $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$, $t_{1/2} = 0.693/k$. Second: $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$, $t_{1/2} = \frac{1}{k[A]_0}$.
- $t_{1/2}$ constant: first order; $\propto [A]_0$: zero; $\propto 1/[A]_0$: second. First order: $t_{75\%} = 2t_{1/2}$, $t_{90\%} = 3.32t_{1/2}$, $t_{99\%} = 6.64t_{1/2}$.
- Gas $A \longrightarrow B + C$: $k = \frac{2.303}{t}\log\frac{p_i}{2p_i - p_t}$; parallel first order: $k_{eff} = k_1 + k_2$; pseudo-first order when one reactant is in excess.
- $k = Ae^{-E_a/RT}$; $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\frac{T_2 - T_1}{T_1T_2}$; $E_a = BR$ from $e^{-B/T}$; $E_a(\text{fwd}) - E_a(\text{rev}) = \Delta H$.
- Catalyst lowers E_a (both ways), not ΔH, K or the equilibrium; the RDS fixes the rate law; molecularity is $1, 2, 3$ only.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**