

Chapter 3 · Chemical Kinetics

CBSE Class 12 Chemistry (043) · Physical · Unit 3 = 7 marks · Ultimate Revision Sheet

60-SECOND RECALL

Rate law	Rate = $k[A]^x[B]^y$ — powers come from experiment , not the equation
Order	$x + y$ · can be 0, fractional or negative
Molecularity	Always a whole number, 1 2 or 3 , never zero
Zero order	$[A] = [A]_0 - kt$ · $t_{1/2} = [A]_0/2k$ · k unit $\text{mol L}^{-1} \text{s}^{-1}$
First order	$k = (2.303/t) \log([A]_0/[A])$ · $t_{1/2} = 0.693/k$ · k unit s^{-1}
Arrhenius	$k = Ae^{-E_a/RT}$ · $\log(k_2/k_1) = (E_a/2.303R)(1/T_1 - 1/T_2)$
Catalyst	Lowers E_a · does NOT change ΔH or K

1. Rate of Reaction

FORMULAS

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

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

The **minus sign** makes the rate positive for a disappearing reactant. Always **divide by the stoichiometric coefficient**.

FACTORS AFFECTING RATE

Concentration · **temperature** (roughly doubles the rate for each 10 K) · **catalyst** · **surface area** · **nature of reactants** · **radiation** for photochemical reactions.

2. Order and Molecularity

THE DISTINCTION — asked almost every year

Basis	ORDER	MOLECULARITY
Meaning	Sum of the powers in the experimentally determined rate law	Number of species colliding in an elementary step
Determined by	Experiment	The balanced elementary equation
Possible values	0, fractional, even negative	Whole numbers only , 1, 2 or 3
Applies to	Elementary and complex reactions	Elementary steps only

For a multi-step reaction, the **order is decided by the slowest (rate-determining) step**.

3. Integrated Rate Equations

ZERO ORDER

$$[A] = [A]_0 - kt \quad k = ([A]_0 - [A])/t \quad t_{1/2} = [A]_0/2k$$

Plot $[A]$ against $t \rightarrow$ a straight line of slope $-k$. Rate is independent of concentration.

Examples: decomposition of HI on a gold surface; NH_3 on a hot platinum surface (surface-catalysed reactions).

FIRST ORDER

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

$$t_{1/2} = 0.693/k \text{ — independent of initial concentration}$$

Plot $\log[A]$ against $t \rightarrow$ a straight line of slope $-k/2.303$.

Examples: all radioactive decay; decomposition of N_2O_5 ; hydrogenation of ethene.

TRAP Only the first-order half-life is independent of the starting concentration. For zero order $t_{1/2} \propto [A]_0$.

Units of k give away the order: zero order $\text{mol L}^{-1} \text{s}^{-1}$, first order s^{-1} , second order $\text{L mol}^{-1} \text{s}^{-1}$. General form: $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$.

A **pseudo first order** reaction is second order in principle but behaves as first order because one reactant is in **large excess** — e.g. hydrolysis of an ester or of cane sugar in water.

4. Temperature Dependence and Collision Theory

ARRHENIUS EQUATION

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

$$\log k = \log A - E_a/2.303RT \rightarrow \text{plot } \log k \text{ vs } 1/T, \text{ slope } -E_a/2.303R$$

$$\log(k_2/k_1) = (E_a/2.303R)(1/T_1 - 1/T_2)$$

COLLISION THEORY A reaction occurs only when molecules collide with (1) **sufficient energy** — at least the activation energy — and (2) **the proper orientation**.

$$\text{Rate} = P Z_{AB} e^{-E_a/RT} \quad Z = \text{collision frequency}, P = \text{steric (probability) factor}$$

Why temperature matters so much: a modest rise in T greatly increases the **fraction of molecules with energy above E_a** — this is what doubles the rate, not the small rise in collision frequency.

CATALYST A catalyst provides an **alternative path with lower activation energy**. It therefore speeds up the forward **and** the backward reaction equally.

It does **NOT** change ΔH , the **equilibrium constant**, or the position of equilibrium — only the **time taken to reach it**.

WORKED EXAMPLE A first-order reaction is 50% complete in 30 minutes. Find k and the time for 75% completion.

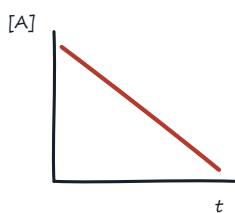
$$k = 0.693/t_{1/2} = 0.693/30 = 0.0231 \text{ min}^{-1}$$

$$\text{For 75\%: } [A]_0/[A] = 100/25 = 4$$

$$t = (2.303/k) \log 4 = (2.303/0.0231) \times 0.602 = 60 \text{ minutes}$$

Shortcut: 75% complete = two half-lives = $2 \times 30 = 60 \text{ min}$ ✓

(a) The plot that gives a STRAIGHT line tells you the order



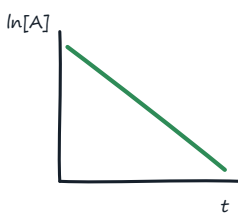
ZERO order

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

$$\text{slope} = -k$$

$$t_{1/2} = [A]_0/2k$$

$t_{1/2}$ **DEPENDS** on conc.



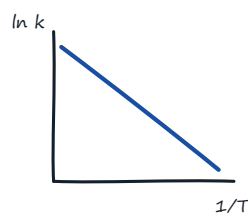
FIRST order

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

$$\text{slope} = -k/2.303 \text{ (log plot)}$$

$$t_{1/2} = 0.693/k$$

$t_{1/2}$ is **INDEPENDENT** of conc.



ARRHENIUS

$$k = Ae^{-E_a/RT}$$

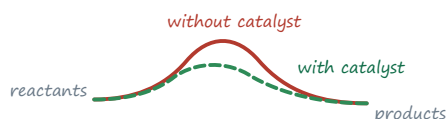
$$\text{slope} = -E_a/R$$

$$\text{intercept} = \ln A$$

Steeper line $\rightarrow$ larger E_a

(b) A catalyst lowers E_a **ONLY**

It cannot change ΔH , and it cannot change K — it speeds up both directions equally.



A fitted straight line is the proof of order — if the examiner gives you data, plot the one that comes out straight. **Only first-order $t_{1/2}$ is concentration-independent**, which is why radioactive decay is first order.

5. Question Triggers which formula the wording wants

If the question says...	Use
"half-life does not depend on concentration"	First order
"rate is independent of concentration"	Zero order
"k has units s^{-1} "	First order
"one reactant is in large excess"	Pseudo first order
"rate constant at two temperatures"	Arrhenius, $\log(k_2/k_1)$
"catalyst added — effect on ΔH / K "	No change ; only E_a falls
"slope of $\log k$ vs $1/T$ "	$-E_a/2.303R$
"why does rate roughly double per 10 K"	More molecules exceed E_a

MOST-ASKED BOARD QUESTIONS

- [3M]** Derive the **integrated rate equation** for a first-order reaction and show $t_{1/2} = 0.693/k$.
- [3M]** Numerical using the Arrhenius equation to find E_a from k at two temperatures.
- [2M]** Distinguish between **order** and **molecularity**.
- [2M]** Explain **pseudo first order** with an example.
- [2M]** Determine the order and rate law from a table of initial rates.

6. [1M] How does a catalyst affect ΔH ? $\rightarrow$ Not at all

THE HABIT THAT SCORES — When a numerical gives you the **units of k**, read the order straight off them before doing anything else. It tells you which integrated equation to use and takes two seconds.