Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry

Chapter 3: Chemical Kinetics

NCERT 2026-27 / New NCERT, Class 12th Chemistry (Part 1)

What this chapter is about

Thermodynamics tells us *whether* a reaction will occur; chemical kinetics tells us *how fast* and through *what mechanism*. This chapter develops the language of rates (average rate, instantaneous rate, rate law, order, molecularity, half-life) and the two big results that govern temperature dependence: the Arrhenius equation and collision theory. You will use these ideas constantly in physical chemistry numericals (board, JEE, NEET) and again in biochemistry to describe enzyme kinetics.

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Quick Tip

NCERT Class 12 Chemistry Chapter 3 typically carries 5–7 marks on the CBSE board and is one of the most prolific numerical-question sources for JEE Main and NEET. Master the integrated rate equations and the Arrhenius two-temperature form first; those two yield the majority of testable problems.

Also see for this chapter

Step-by-step worked answers: NCERT Solutions for Class 12 Chemistry Chapter 3 Chemical Kinetics.
One-page revision: Chemical Kinetics Formula Sheet.
Tougher problems: NCERT Exemplar Solutions for Chemical Kinetics.

1 Rate of a Chemical Reaction

The rate of a reaction is the change in concentration of a reactant or product per unit time. Reactions span an enormous range of speeds: precipitation of AgCl from $AgNO_3$ and NaCl is virtually instantaneous, rusting of iron takes years, and the conversion of diamond to graphite is so slow that it never becomes observable in a human lifetime, which is why "diamond is forever" is a kinetic statement, not a thermodynamic one.

1.1 Average and Instantaneous Rate

Consider the hypothetical reaction R $\longrightarrow$ P. Let $[R]_1$ and $[R]_2$ be the concentrations at times t_1 and t_2. Define $\Delta t = t_2 - t_1$, $\Delta[R] = [R]_2 - [R]_1$, $\Delta[P] = [P]_2 - [P]_1$.

Average Rate of Reaction

Rate of disappearance of R:

$$r_{\text{av}} = -\frac{\Delta[R]}{\Delta t}$$

Rate of appearance of P:

$$r_{\text{av}} = +\frac{\Delta[P]}{\Delta t}$$

The minus sign for the reactant keeps the rate positive. Units: mol L^{-1} s^{-1} (or atm s^{-1} for gas-phase reactions in terms of partial pressure).

The average rate gives the mean speed over the interval $[t_1, t_2]$ but tells us nothing about how the rate changes instant to instant. As $\Delta t \to 0$, the average rate becomes the **instantaneous rate**:

$$r_{\text{inst}} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}$$

Graphically, r_{inst} at time t is the slope of the tangent to the concentration–time curve at that point.

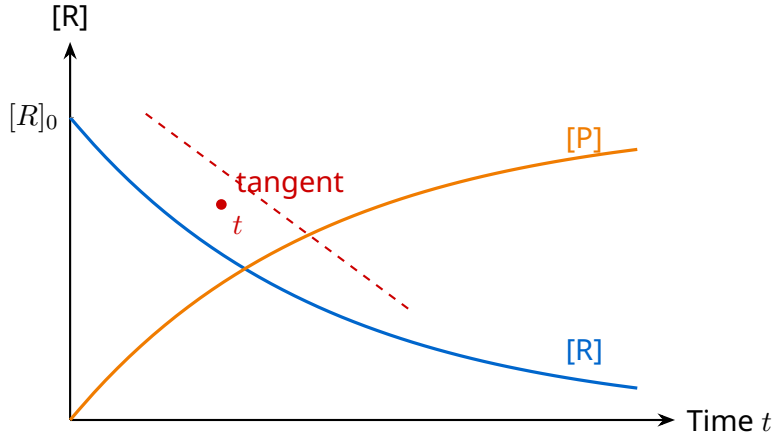

Fig. 1: Concentration of reactant $[R]$ falls (blue) while product $[P]$ rises (orange) with time. The instantaneous rate at time t equals the slope of the tangent (red dashed) at that point.

1.2 Rate in Terms of Stoichiometric Coefficients

For a reaction with stoichiometric coefficients other than 1, the rate of consumption of a reactant is not the same as the rate of appearance of a product. To get a *unique* rate for the reaction, divide each term by its stoichiometric coefficient.

For the general reaction

$$aA + bB \longrightarrow cC + dD$$

Unique Rate of Reaction

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

Example. For $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$:

$$\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

So the rate of appearance of NO_2 is *four times* the rate of disappearance of N_2O_5 divided by 2, i.e. twice the unique rate.

Common Mistake

Students routinely forget the stoichiometric divisor. Writing "Rate $= -d[N_2O_5]/dt = d[O_2]/dt$" is wrong; the correct relation is $-\frac{1}{2}d[N_2O_5]/dt = d[O_2]/dt$. Always check: if the rate is defined uniquely, every species must give the same number.

Real-World Application

Why does food spoil faster outside the fridge? Spoilage is a network of microbial enzyme reactions, and almost all of them speed up sharply with temperature. The same kinetic law that governs lab beakers governs your kitchen: chilling roughly halves the rate constant for every 10°C drop, so 4°C storage buys you days where room temperature buys hours.

2 Factors Influencing the Rate

The four big knobs that control reaction rate are: **concentration** of reactants, **temperature**, **catalyst**, and (for gases) **pressure**. Surface area, solvent, and light play roles for specific reaction types.

2.1 Dependence of Rate on Concentration: Rate Law

For the general reaction $aA + bB \rightarrow cC + dD$, experiment shows

$$\text{Rate} \propto [A]^x[B]^y \quad \text{i.e.} \quad \text{Rate} = k[A]^x[B]^y$$

This expression is the **rate law** or **rate equation**; k is the **rate constant**. Importantly, the exponents x and y are *determined experimentally*; they may or may not equal the stoichiometric coefficients a and b.

Rate Law (Differential Form)

$$-\frac{d[R]}{dt} = k\,[A]^x[B]^y$$

x = order with respect to A, y = order with respect to B,
Overall order $n = x + y$.

Example. For $2\,NO + O_2 \longrightarrow 2\,NO_2$, experimental data show that doubling $[NO]$ quadruples the rate while doubling $[O_2]$ only doubles it. So

$$\text{Rate} = k\,[NO]^2[O_2]$$

Here the exponents happen to equal the stoichiometric coefficients, but that is a coincidence. For

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl, \quad \text{Rate} = k\,[CHCl_3][Cl_2]^{1/2}$$

the half-integer order tells you a non-trivial mechanism is at play.

Rate law is empirical

You cannot read off the rate law from the balanced equation. It must be determined by experiment, usually by the method of initial rates, where one reactant concentration is varied while the others are held constant.

2.2 Order of a Reaction

The **order** of a reaction with respect to a reactant is the power to which that reactant's concentration is raised in the experimentally determined rate law. The **overall order** is the sum of these powers.

- Order can be 0, 1, 2, 3, a fraction (e.g. $1/2$, $3/2$), or even negative.
- A **zero-order** reaction has rate independent of reactant concentration.
- For Rate $= k\,[A]^{1/2}[B]^{3/2}$, overall order $= 1/2 + 3/2 = 2$.
- For Rate $= k\,[A]^{3/2}[B]^{-1}$, overall order $= 3/2 - 1 = 1/2$.

2.3 Units of the Rate Constant

Since rate has units of mol L^{-1} s^{-1} and

$$k = \frac{\text{Rate}}{[A]^n} = \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{(\text{mol L}^{-1})^n}$$

the units of k depend on the overall order n.

Order n	Units of k	Example reaction
0	mol L^{-1} s^{-1}	$2\,NH_3 \longrightarrow N_2 + 3\,H_2$ on Pt
1	s^{-1}	N_2O_5 decomposition
2	L mol^{-1} s^{-1}	$2\,HI \longrightarrow H_2 + I_2$
3	L^2 mol^{-2} s^{-1}	$2\,NO + O_2 \longrightarrow 2\,NO_2$
n	L^{n-1} mol^{1-n} s^{-1}	general n

Table 1: Units of k depend on overall order. Inverting this lets you read off the order from k's units.

Quick Tip

You can read the reaction order off the units of k alone. If k is in s^{-1}, it is first order; if it is in L mol^{-1} s^{-1}, it is second order. This shortcut routinely saves time on JEE/NEET MCQs.

2.4 Molecularity of a Reaction

Molecularity is the number of reacting species (atoms, ions, molecules) that must collide simultaneously in an *elementary* step to bring about a reaction.

- **Unimolecular** (1): e.g. $NH_4NO_2 \longrightarrow N_2 + 2\,H_2O$ in the rate-determining step.
- **Bimolecular** (2): e.g. $2\,HI \longrightarrow H_2 + I_2$.
- **Trimolecular / termolecular** (3): e.g. $2\,NO + O_2 \longrightarrow 2\,NO_2$. Three-body collisions are statistically rare, so molecularity 3 is uncommon and slow.
- Molecularity ≥ 4 is never observed in practice; such "reactions" are always composite.

Complex reaction example. The reaction

$$KClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \longrightarrow KCl + 3\,Fe_2(SO_4)_3 + 3\,H_2O$$

appears to need ten species in one step, but it is actually a second-order reaction. The reaction proceeds in several elementary steps; the slowest step (the **rate-determining step**) sets the overall order. Picture a relay race: the team's speed is the speed of its slowest runner.

Order vs Molecularity: the key distinction

Order is empirical and applies to overall reactions (elementary or complex). It can be zero, fractional, or negative.
Molecularity is theoretical and applies only to elementary reactions. It is a positive integer (1, 2, rarely 3).
For an elementary step, order = molecularity. For a complex reaction, "molecularity" of the overall reaction is meaningless, but the molecularity of the rate-determining step equals the overall order.

Memory Aid

"O.M.I.": **O**rder is e**M**pirical, **I**nteger or fraction; **M**olecularity is **M**echanistic, **M**ust be a positive integer.

Common Mistake

Do not claim a reaction has "molecularity = 0" or "molecularity = 2.5". Molecularity comes from counting colliding species in one step; both zero and fractions are physically impossible. Only *order* can be zero or fractional.

2.5 Pseudo First Order Reactions

When a higher-order reaction is run with one reactant in such large excess that its concentration barely changes, the rate appears to depend only on the other reactant. The reaction then behaves as first order; we call it a **pseudo first order reaction**.

Acid hydrolysis of ethyl acetate (catalysed by H^+):

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

The reaction is genuinely second order, but with water present in 1000-fold excess, $[H_2O]$ is effectively constant. The rate law reduces to

$$\text{Rate} = k'[CH_3COOC_2H_5], \qquad k' = k[H_2O]$$

where k' is the **pseudo rate constant**.

Inversion of cane sugar is another classical example (catalysed by H^+):

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

(glucose + fructose). Again pseudo first order in sucrose.

Real-World Application

Many enzyme reactions in living cells run under pseudo-first-order conditions because water (or another co-reactant) is always abundant in the cellular

medium. Pharmacokinetics of most drugs (the rate at which a dose clears from the bloodstream) is modelled as first-order decay for the same reason.

3 Integrated Rate Equations

The differential rate law $-d[R]/dt = k[R]^n$ relates rate to instantaneous concentration. To compare with experiment we need a relation between concentration and *time directly*, so we integrate. NCERT derives the integrated forms only for zero and first order.

3.1 Zero Order Reactions

Rate is independent of $[R]$:

$$-\frac{d[R]}{dt} = k[R]^0 = k$$

Separate and integrate:

$$d[R] = -k\,dt \;\Rightarrow\; [R] = -kt + I$$

At $t = 0$, $[R] = [R]_0$, so $I = [R]_0$.

Zero Order Integrated Rate Law

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

$$k = \frac{[R]_0 - [R]}{t}$$

A plot of $[R]$ vs t is a *straight line* with slope $= -k$ and intercept $= [R]_0$. Units of k: mol L^{-1} s^{-1}.

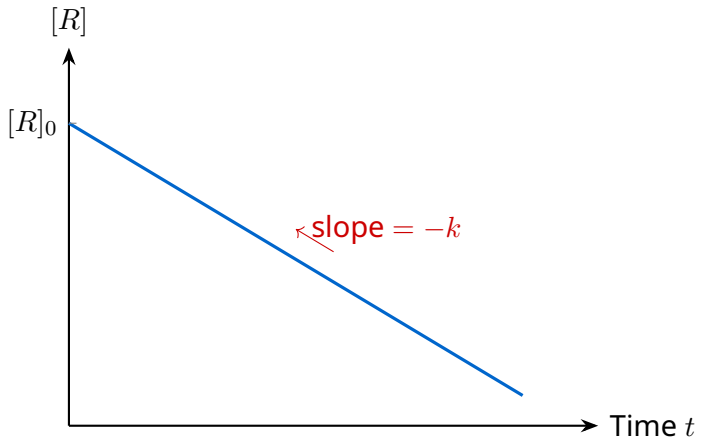

Fig. 2: Zero-order reaction. $[R]$ falls linearly with time. The rate constant equals the negative of the slope.

Examples. Zero-order kinetics is unusual but appears for reactions on catalyst surfaces when the surface is saturated. The decomposition of ammonia on hot platinum is a textbook case:

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g) \qquad \text{(Pt catalyst, 1130 K)}$$

At high NH_3 pressure every Pt site is occupied; adding more NH_3 cannot speed the reaction up, so the rate is constant. Thermal decomposition of HI on gold surfaces is similar.

3.2 First Order Reactions

Rate is directly proportional to $[R]$:

$$-\frac{d[R]}{dt} = k[R]$$

Separate and integrate:

$$\int \frac{d[R]}{[R]} = -\int k\,dt \;\Rightarrow\; \ln[R] = -kt + I$$

At $t = 0$, $\ln[R]_0 = I$, so

$$\ln[R] = -kt + \ln[R]_0$$

First Order Integrated Rate Law

$$\ln\left(\frac{[R]_0}{[R]}\right) = kt$$

$$k = \frac{1}{t}\ln\left(\frac{[R]_0}{[R]}\right) = \frac{2.303}{t}\log\left(\frac{[R]_0}{[R]}\right)$$

Exponential form: $[R] = [R]_0\,e^{-kt}$. Units of k: s^{-1}.

Two equivalent linear-plot forms:

- Plot $\ln[R]$ vs t: straight line, slope $= -k$, intercept $= \ln[R]_0$.
- Plot $\log([R]_0/[R])$ vs t: straight line through origin, slope $= k/2.303$.

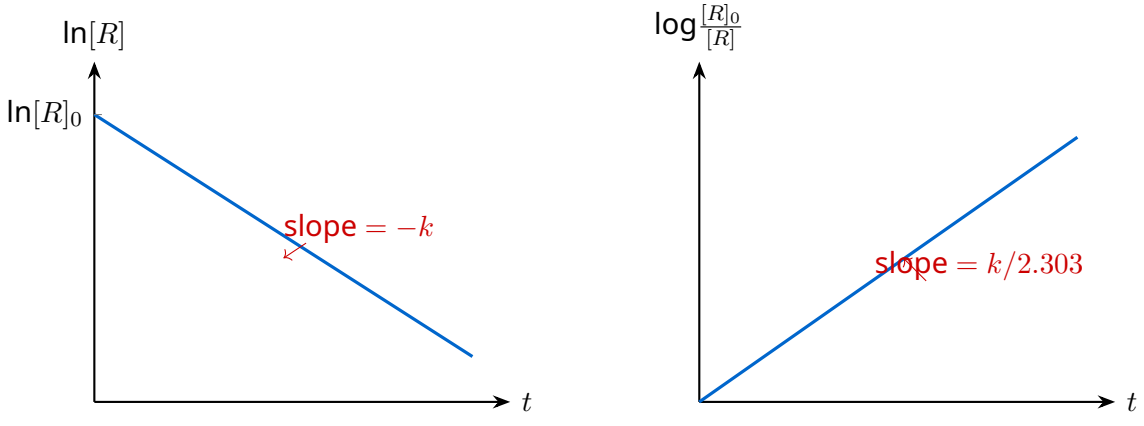

Fig. 3: Two linear forms of the first-order rate law. Left: $\ln[R]$ *vs* t*. Right:* $\log([R]_0/[R])$ *vs* t*.*

Examples of first-order reactions.

- Hydrogenation of ethene: $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$, Rate $= k[C_2H_4]$.
- Decomposition of N_2O_5 and N_2O.
- All natural and artificial radioactive decays:

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}, \quad \text{Rate} = k[\text{Ra}]$$

3.3 Gas-Phase First Order: Pressure Form

For a first-order gas-phase reaction $A(g) \longrightarrow B(g) + C(g)$ run in a closed vessel, partial pressures replace concentrations. Let p_i = initial pressure of A and p_t = total pressure at time t. If A's pressure has dropped by x, then B and C are each present at pressure x:

$$p_t = (p_i - x) + x + x = p_i + x \;\Rightarrow\; x = p_t - p_i$$

So $p_A = p_i - x = 2p_i - p_t$, and

First Order Gas-Phase (Pressure Form)

$$k = \frac{2.303}{t}\log\left(\frac{p_i}{p_A}\right) = \frac{2.303}{t}\log\left(\frac{p_i}{2p_i - p_t}\right)$$

This form is what you use for board-question data given as "initial pressure" and "total pressure at time t".

3.4 Half-Life of a Reaction

The **half-life** $t_{1/2}$ is the time taken for $[R]$ to fall to $[R]_0/2$.

Zero order. Setting $[R] = [R]_0/2$ in $k = ([R]_0 - [R])/t$:

$$k = \frac{[R]_0 - [R]_0/2}{t_{1/2}} = \frac{[R]_0}{2t_{1/2}} \;\Rightarrow\; \boxed{t_{1/2} = \frac{[R]_0}{2k}}$$

First order. Setting $[R] = [R]_0/2$ in $k = (2.303/t)\log([R]_0/[R])$:

$$k = \frac{2.303}{t_{1/2}}\log 2 = \frac{2.303 \times 0.301}{t_{1/2}} \;\Rightarrow\; \boxed{t_{1/2} = \frac{0.693}{k}}$$

Half-Lives

Zero order: $t_{1/2} = \dfrac{[R]_0}{2k}$ (depends on $[R]_0$)

First order: $t_{1/2} = \dfrac{0.693}{k} = \dfrac{\ln 2}{k}$ (independent of $[R]_0$)

The signature of a first-order reaction

For a first-order reaction the half-life is a *constant*; it does not depend on the starting concentration. Plot $[R]$ vs t; each successive half-period takes the same time. Radioactive decay is the canonical example: ^{14}C halves every 5730 years no matter how much you start with.

Quick Tip

For a first-order reaction, time for 99.9% completion $= 10\,t_{1/2}$, time for 99% completion $\approx 6.64\,t_{1/2}$, time for 90% completion $\approx 3.32\,t_{1/2}$. Memorising these multipliers makes board numericals trivial.

Order	Differential rate law	Integrated rate law	Linear plot	Half-life
0	$-d[R]/dt = k$	$[R] = [R]_0 - kt$	$[R]$ vs t	$[R]_0/2k$
1	$-d[R]/dt = k[R]$	$\ln[R] = \ln[R]_0 - kt$	$\ln[R]$ vs t	$0.693/k$

Table 2: Summary of integrated rate laws for zero and first order.

3.5 [JEE/NEET Extension] Second-Order Reactions

Although not in the NCERT main text, JEE/NEET routinely tests second-order behaviour. For $-d[R]/dt = k[R]^2$:

$$\frac{1}{[R]} - \frac{1}{[R]_0} = kt, \qquad t_{1/2} = \frac{1}{k[R]_0}$$

A plot of $1/[R]$ vs t is linear with slope $= k$. Half-life is *inversely* proportional to $[R]_0$; doubling the starting concentration halves the half-life.

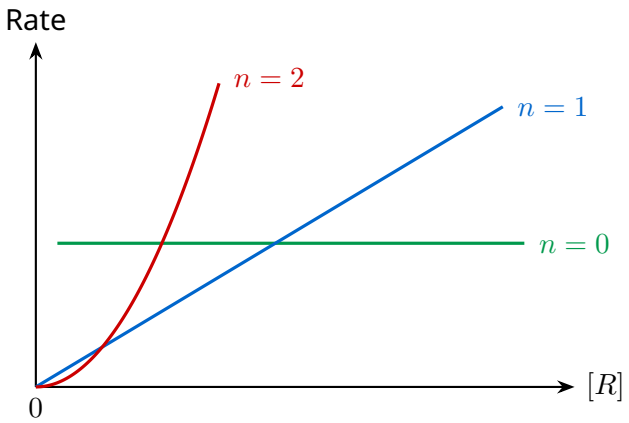

Fig. 8: Reaction rate vs reactant concentration for three orders. Zero order (green) is flat, first order (blue) is linear through the origin, and second order (red) is parabolic. The shape of this plot, together with the units of k, fixes the order uniquely.

Memory Aid

Half-life dependence on $[R]_0$: "**Z**ero **P**roportional, **F**irst **I**ndependent, **S**econd **I**nverse." Zero order $t_{1/2} \propto [R]_0$; first order $t_{1/2}$ doesn't care; second order $t_{1/2} \propto 1/[R]_0$.

4 Arrhenius Equation

Almost every reaction rate increases sharply with temperature. As a rule of thumb, the rate constant nearly doubles for each 10 K rise. This is captured quantitatively by the Arrhenius equation, originally proposed by van't Hoff and given a physical interpretation by Svante Arrhenius.

Arrhenius Equation

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

k = rate constant at temperature T
A = Arrhenius factor / frequency factor / pre-exponential factor (specific to the reaction)
E_a = activation energy (J mol^{-1})
R = 8.314 J K^{-1} mol^{-1}
T = temperature (K)

4.1 Activation Energy and the Energy Profile

Reactants do not transform directly into products; they pass through a high-energy intermediate called the **activated complex** (transition state). The energy needed to climb from the reactant level to the activated complex is the **activation energy** E_a.

For $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$, an H_2 molecule and an I_2 molecule must collide hard enough to form a four-centred activated complex which then breaks down into two HI molecules.

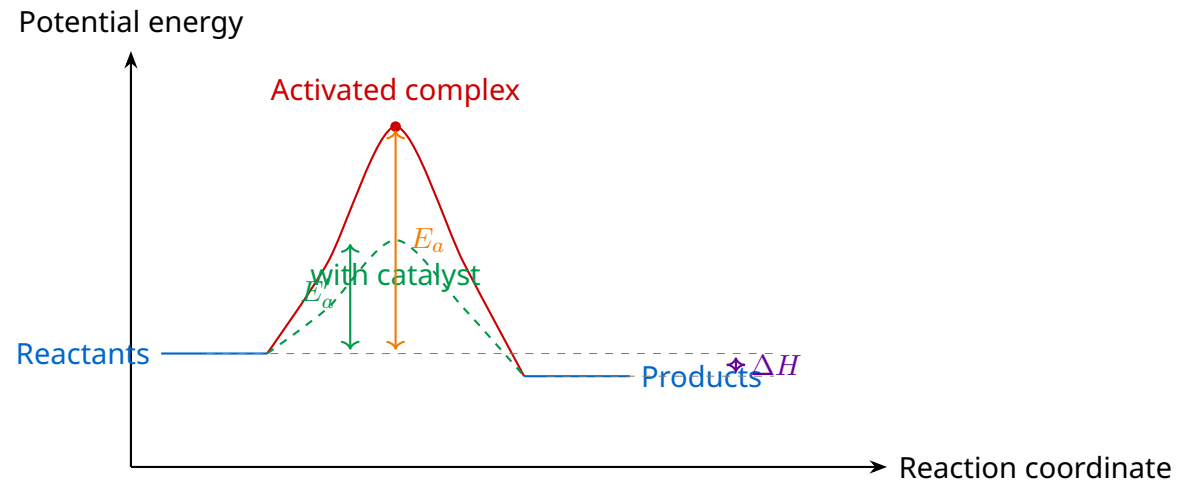

Fig. 4: Potential energy along the reaction coordinate. The energy barrier E_a (orange) separates reactants from products. A catalyst (green dashed) lowers the barrier to E_a' without changing ΔH between reactants and products.

4.2 Maxwell–Boltzmann Distribution and the Effect of Temperature

Not all molecules have the same kinetic energy. At a given temperature, the fraction of molecules with energy E is described by the **Maxwell–Boltzmann distribution**. The peak of the curve is the most probable kinetic energy; only the fraction with energy $\geq E_a$ (the area under the tail) can react.

Raising the temperature shifts the peak right and broadens the curve. The area under the tail beyond E_a *roughly doubles* for every 10 K rise, and this is exactly why the rate constant roughly doubles.

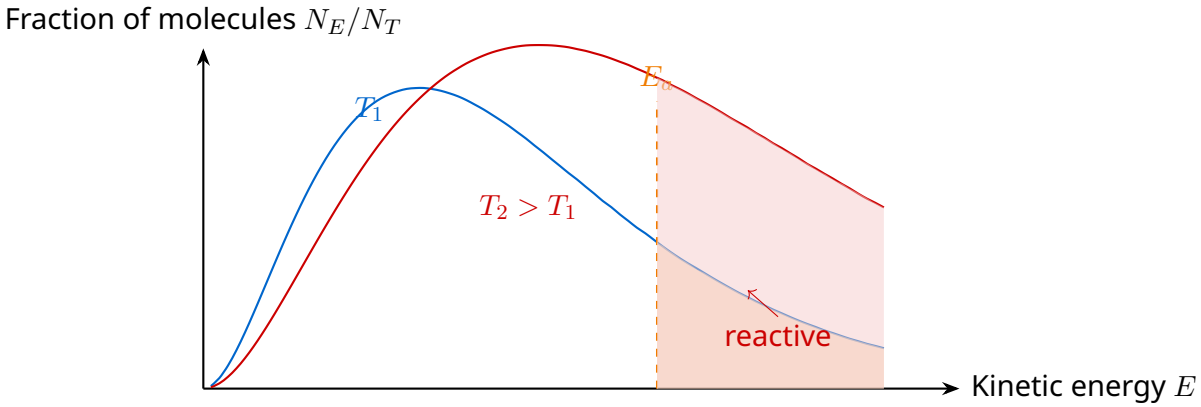

Fig. 5: Maxwell–Boltzmann energy distributions at two temperatures. The shaded area beyond E_a shows the fraction of molecules with energy sufficient to react. Heating from T_1 to T_2 flattens and shifts the curve; the reactive fraction grows roughly twofold per 10 K.

4.3 Linear (Arrhenius) Plot

Taking natural log of $k = A\,e^{-E_a/RT}$:

$$\ln k = \ln A - \frac{E_a}{RT}$$

A plot of $\ln k$ vs $1/T$ is a straight line. Slope $= -E_a/R$, intercept (at $1/T = 0$) $= \ln A$.

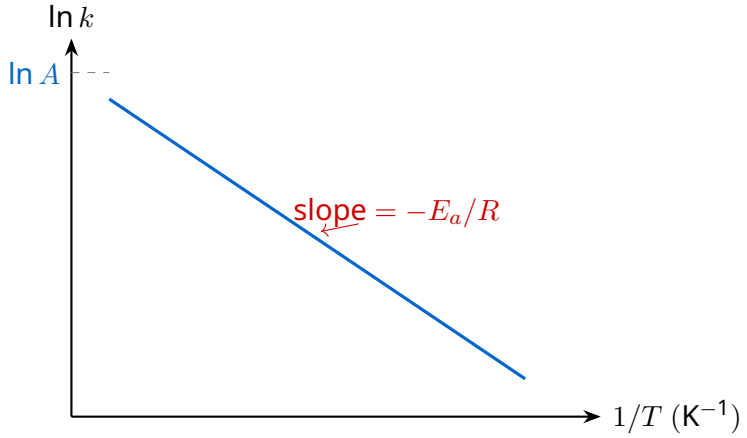

Fig. 6: Arrhenius plot. From the slope ($-E_a/R$) and intercept ($\ln A$) one extracts the activation energy and the pre-exponential factor.

4.4 Two-Temperature Form of the Arrhenius Equation

Combining the Arrhenius equation at two temperatures T_1 and T_2:

Arrhenius Equation (Two-Temperature)

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

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

This is the workhorse formula for board, JEE and NEET numericals: given k_1 at T_1 and k_2 at T_2, solve for E_a; or given E_a and k_1, predict k_2.

Worked example. $k_1 = 0.02$ s^{-1} at 500 K and $k_2 = 0.07$ s^{-1} at 700 K. Find E_a and A.

$$\log\left(\frac{0.07}{0.02}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{700 - 500}{500 \times 700}\right)$$

$$0.544 = \frac{E_a \times 5.714 \times 10^{-4}}{19.15}$$

$$E_a = \frac{0.544 \times 19.15}{5.714 \times 10^{-4}} \approx 18230.8 \text{ J mol}^{-1} \approx 18.2 \text{ kJ mol}^{-1}$$

Then $A = k\,e^{E_a/RT} = 0.02 \times e^{18230.8/(8.314 \times 500)} \approx 1.61$.

Common Mistake

A common error in two-temperature Arrhenius problems is using E_a in kJ but R in J K^{-1} mol^{-1} (or vice versa). Always convert to consistent units before substituting; E_a in J and $R = 8.314$ J K^{-1} mol^{-1} is safest.

Memory Aid

The two-temperature Arrhenius is the only formula you really need to memorise here: "**log of k-ratio = E_a over 2.303R, times (T_2 minus T_1) over T_1T_2.**" Every board variant flows from this single equation.

4.5 Effect of a Catalyst

A **catalyst** is a substance that increases the rate of a reaction without itself being permanently consumed. (A substance that slows a reaction is called an **inhibitor**, not a catalyst.) For example, MnO_2 catalyses the decomposition of potassium chlorate:

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2 \qquad (MnO_2 \text{ catalyst})$$

MnO_2 provides an alternative pathway with a lower activation energy (see the green dashed curve in Fig. 4). From the Arrhenius equation, a smaller E_a means a much larger k.

What a catalyst does *not* do

A catalyst:

- lowers E_a by providing an alternative pathway (intermediate-complex theory);
- speeds up both forward *and* backward reactions equally;
- helps equilibrium be reached *faster* but does **not** change the equilibrium constant K;
- does **not** change ΔG of the reaction; spontaneous reactions stay spontaneous and non-spontaneous reactions are not made spontaneous.

Real-World Application

Industrial chemistry runs on catalysts. The Haber process uses iron with promoters to fix N_2 into NH_3 at conditions far milder than the uncatalysed reaction would allow; the catalytic converter in your car uses Pt/Rh/Pd to oxidise CO and unburnt hydrocarbons and reduce NO_x at exhaust temperatures. Enzymes in your body lower activation energies by factors of 10^{10} or more; with-

out them, you would not metabolise glucose fast enough to live.

5 Collision Theory of Chemical Reactions

Arrhenius's equation works empirically, but *why* does it have that form? Collision theory (Max Trautz and William Lewis, 1916–18) gives a microscopic explanation rooted in the kinetic theory of gases.

5.1 Collision Frequency and Effective Collisions

Treat reactant molecules as hard spheres. The number of collisions per unit volume per unit time between A and B is the **collision frequency** Z_{AB}. For a bimolecular elementary reaction A + B $\longrightarrow$ Products, collision theory gives

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

Comparing with the Arrhenius equation $k = A\, e^{-E_a/RT}$, we see $A \approx Z_{AB}$: the pre-exponential factor is, to a good approximation, the collision frequency.

Not every collision leads to product. A collision is **effective** only if (i) the colliding molecules have kinetic energy $\geq$ threshold energy and (ii) they collide in the correct *orientation*.

Threshold and Activation Energy

$$\text{Threshold energy} = E_a + \text{energy already possessed by the molecules}$$

The fraction of molecules with energy $\geq E_a$ is $e^{-E_a/RT}$, which is exactly the exponential factor in the Arrhenius equation.

5.2 Steric Factor

For collisions involving non-trivial molecules, orientation matters. CH_3Br + OH^- only gives CH_3OH + Br^- when the hydroxide approaches the carbon from the side opposite the bromine; head-on collisions on the bromine face simply bounce. To capture this, collision theory introduces the **steric (probability) factor** P:

Collision Theory with Steric Factor

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

$P \leq 1$ is the fraction of collisions with the correct geometry. For simple atoms, $P \approx 1$. For large organic molecules, P can be as small as 10^{-5}.

Fig. 7: Effective collisions require correct orientation. Left: OH^- approaching the Br side simply rebounds. Right: back-side attack on the carbon leads to product. The steric factor P captures the orientation probability.

5.3 Limitations of Collision Theory

Collision theory works well for atoms and simple molecules but deviates for complex molecules. The hard-sphere model ignores molecular structure entirely, which is the reason for introducing the empirical P. Modern theories (e.g. transition-state theory, you'll meet these in higher chemistry) treat the activated complex with full quantum-mechanical detail.

Quick Tip

For board/NEET, three things to remember about collision theory: (i) Rate $= PZ_{AB}e^{-E_a/RT}$, (ii) two requirements for an effective collision are sufficient energy and correct orientation, (iii) A in the Arrhenius equation is roughly Z_{AB}.

6 Summary, Key Numericals and Quick Reference

6.1 One-Page Formula Sheet

All-in-one Chemical Kinetics formulae

Rate (general): $\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = +\frac{1}{c}\frac{d[C]}{dt}$

Rate law: $\text{Rate} = k[A]^x[B]^y$; overall order $n = x + y$

Zero order: $[R] = [R]_0 - kt$; $k = \frac{[R]_0 - [R]}{t}$; $t_{1/2} = \frac{[R]_0}{2k}$

First order: $[R] = [R]_0 e^{-kt}$; $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$; $t_{1/2} = \frac{0.693}{k}$

First order (gas, pressure): $k = \frac{2.303}{t}\log\frac{p_i}{2p_i - p_t}$

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

Arrhenius (two-T): $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\cdot\frac{T_2 - T_1}{T_1 T_2}$

Collision theory: $\text{Rate} = PZ_{AB}\,e^{-E_a/RT}$

Second order (JEE/NEET): $\frac{1}{[R]} - \frac{1}{[R]_0} = kt$; $t_{1/2} = \frac{1}{k[R]_0}$

6.2 Key Constants and Values

Quantity	Value
Gas constant R	$8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$
$2.303\,R$	$19.15\ \text{J K}^{-1}\ \text{mol}^{-1}$
$\ln 2$	0.693
$\log 2$	0.301
Rule of thumb	Rate doubles per 10 K rise
E_a from log Arrhenius	$E_a = 2.303R \cdot T_1T_2/(T_2 - T_1) \cdot \log(k_2/k_1)$

6.3 First-Order Completion Times

% completion	kt	t in terms of $t_{1/2}$
50%	0.693	$1.00\,t_{1/2}$
75%	1.386	$2.00\,t_{1/2}$
90%	2.303	$3.32\,t_{1/2}$
99%	4.606	$6.64\,t_{1/2}$
99.9%	6.909	$9.97\,t_{1/2} \approx 10\,t_{1/2}$

Table 3: Useful first-order completion multipliers.

6.4 Order vs Molecularity: Comparison Table

Property	Order	Molecularity
Definition	Sum of powers of concentrations in rate law	No. of species colliding in elementary step
Origin	Experimental	Theoretical (mechanism)
Possible values	$0, 1, 2, 3, \frac{1}{2}, \frac{3}{2}, -1, \ldots$	$1, 2$, rarely 3
Applies to	Elementary and complex reactions	Only elementary steps
Can be zero?	Yes	No
Can be fractional?	Yes	No

Table 4: Order versus molecularity: the single most-tested conceptual distinction in this chapter.

Quick Tip

Last-minute checklist for the exam:

- Rate law is **experimental**; never quote stoichiometry as order.
- Zero-order $t_{1/2}$ depends on $[R]_0$; first-order $t_{1/2}$ does not.
- For first-order, $t_{99.9\%} = 10\,t_{1/2}$.
- Catalyst lowers E_a, does not change ΔG or K_{eq}.
- Use $R = 8.314$ J K^{-1} mol^{-1} with E_a in J; or $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} with E_a in kJ.
- Effective collision needs both sufficient energy *and* correct orientation.

6.5 Worked Examples for Revision

Example 1: Average rate from concentration data. For $C_4H_9Cl + H_2O \longrightarrow C_4H_9OH + HCl$, $[C_4H_9Cl]$ falls from 0.100 mol L^{-1} at $t = 0$ to 0.0905 mol L^{-1} at $t = 50$ s. Find the average rate.

$$r_{\text{av}} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{0.0905 - 0.100}{50} = \frac{0.0095}{50}$$

$$r_{\text{av}} = 1.9 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Example 2: Identifying order from units. $k_1 = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}; $k_2 = 3 \times 10^{-4}$ s^{-1}. Identify orders.

- k_1 has units L mol^{-1} s^{-1} $\Rightarrow$ second order.
- k_2 has units s^{-1} $\Rightarrow$ first order.

Example 3: First-order rate constant from concentrations. For $N_2O_5 \longrightarrow$ products at 318 K, $[N_2O_5]_0 = 1.24 \times 10^{-2}$ mol L^{-1} falls to 0.20×10^{-2} mol L^{-1} in 60 min. Find k.

$$k = \frac{2.303}{t} \log\left(\frac{[R]_0}{[R]}\right) = \frac{2.303}{60} \log\left(\frac{1.24}{0.20}\right)$$

$$k = \frac{2.303}{60} \log(6.2) = \frac{2.303 \times 0.7924}{60} \approx 0.0304 \text{ min}^{-1}$$

Example 4: Half-life from k. A first-order reaction has $k = 5.5 \times 10^{-14}$ s^{-1}. Find $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}} \approx 1.26 \times 10^{13} \text{ s}$$

Example 5: Two-temperature Arrhenius. At 600 K, $k = 1.60 \times 10^{-5}$ s^{-1} for $C_2H_5I \longrightarrow C_2H_4 + HI$, and $E_a = 209$ kJ mol^{-1}. Find k at 700 K.

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

$$= \frac{209000}{2.303 \times 8.314} \cdot \frac{100}{600 \times 700}$$

$$= \frac{209000}{19.15} \cdot \frac{100}{420000} = 10913 \times 2.381 \times 10^{-4}$$

$$\log(k_2/k_1) = 2.599$$

$$\log k_2 = \log(1.60 \times 10^{-5}) + 2.599 = -4.796 + 2.599 = -2.197$$

$$k_2 = 10^{-2.197} \approx 6.36 \times 10^{-3}\ \text{s}^{-1}$$

Example 6: Age of an artefact (first-order radioactive decay). ^{14}C has $t_{1/2} = 5730$ years. An archaeological wood sample retains 80% of the original ^{14}C. Estimate its age.

$$k = \frac{0.693}{5730} = 1.209 \times 10^{-4}\ \text{yr}^{-1}$$

$$t = \frac{2.303}{k}\log\left(\frac{100}{80}\right) = \frac{2.303}{1.209 \times 10^{-4}}\log 1.25$$

$$= 19046 \times 0.09691 \approx 1846\ \text{years}$$

Example 7: Time for 99.9% completion (first order). Show $t_{99.9\%} = 10\,t_{1/2}$.

For 99.9% completion, $[R] = 0.001\,[R]_0$, so $[R]_0/[R] = 1000$.

$$t_{99.9\%} = \frac{2.303}{k}\log 1000 = \frac{2.303 \times 3}{k} = \frac{6.909}{k}$$

$$\frac{t_{99.9\%}}{t_{1/2}} = \frac{6.909/k}{0.693/k} = \frac{6.909}{0.693} = 9.97 \approx 10$$

6.6 Big-Picture Takeaway

Three numbers that describe a reaction

Chemical kinetics is the bridge between thermodynamics (which only tells you whether a reaction can happen) and the molecular picture (which tells you why). Three numbers (order, rate constant, activation energy) characterise a reaction almost completely.

- **Order** tells you how the rate scales with concentration.
- **Rate constant** k tells you the absolute speed at a given temperature.
- **Activation energy** E_a tells you the temperature sensitivity.

Master these three and you can predict the behaviour of any reaction in this chapter, and answer almost every numerical the boards, JEE, or NEET will throw at you.

Real-World Application

Why is chemical kinetics indispensable in the modern world? Pharmacokinetic dosing schedules ensure your antibiotic concentration stays above the minimum effective level (first-order elimination); food shelf-life is set by Arrhenius extrapolation from accelerated-ageing tests; catalytic converters in vehicles, the Haber process for ammonia, the contact process for H_2SO_4, and fluid catalytic cracking in oil refineries are all designed by chemical engineers using exactly the equations in this chapter. The half-life concept under-

pins radiometric dating (^{14}C for archaeology, $^{238}U/Pb$ for rocks) and nuclear-medicine dosing.

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