

Unit

5

AP Chemistry

Kinetics

Rates · Rate laws · Half-life · Collisions · Energy profiles · Mechanisms · Catalysis

Unit 1

7–9%
Atomic
structure

Unit 2

7–9%
Compound
structure

Unit 3

18–22%
Substances
and
mixtures

Unit 4

7–9%
Chemical
reactions

Unit 5

7–9%
Kinetics

Unit 6

7–9%
Thermo-
chemistry

Unit 7

7–9%
Equilibrium

Unit 8

11–15%
Acids and
bases

Unit 9

7–9%
Thermo-
dynamics,
electro-
chemistry

Unit 5 is 7–9% of the multiple-choice section. In the free-response section it shows up in both long and short questions: finding a rate law and k from a table of trials, the order from a graph, or whether a proposed mechanism fits the rate law.

5.1

Reaction rates

5.2

Introduction to rate
law

5.3

Concentration
changes over time

5.4

Elementary
reactions

5.5

Collision model

5.6

Reaction energy
profile

5.7

Reaction
mechanisms

5.8

Mechanism and
rate law

5.9

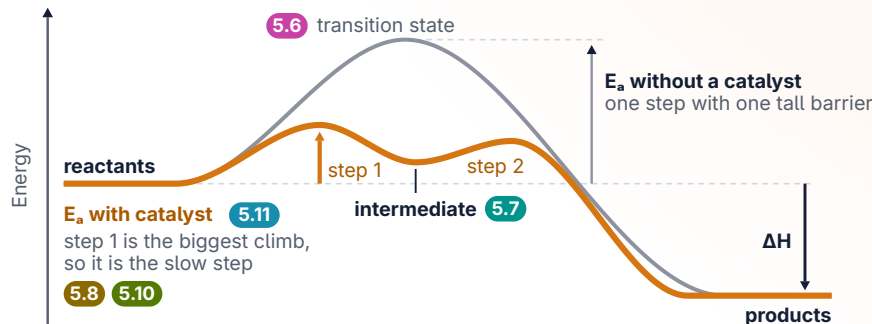
Pre-equilibrium
approximation

5.10

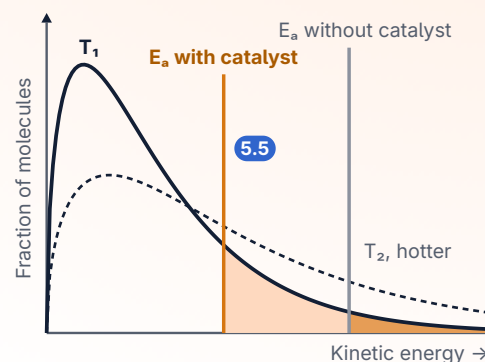
Multistep reaction
energy profile

5.11

Catalysis



Reaction progress: how far the atoms have rearranged (not time)



— without a catalyst — with a catalyst ■ molecules that can react only with a catalyst ■ molecules that can react with or without one
 E_a is the activation energy. Heating leaves E_a where it is but flattens the curve and stretches it right, so more molecules pass it.

⊙ What the exam asks most

- The order of a reaction, from data.** Compare two trials where only one concentration changes. Doubling $[X]$ leaves the rate the same (zero order in X), doubles it (first order) or quadruples it (second order). With concentration–time data, plot $[A]$, $\ln[A]$ and $1/[A]$ against time; the straight one gives the order. (5.2) (5.3)
- The rate constant k , with its units.** Put one trial's numbers into the rate law and solve for k , or take k from the slope of the straight-line plot. Leaving off k 's units can cost a point on its own. (5.2) (5.3)
- One substance's rate from another's.** Use only the coefficients: in $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$, O_2 appears at half the rate NO_2 disappears. (5.1)

- Why a change speeds a reaction up.** More concentrated reactants or smaller pieces of a solid give more collisions per second. A higher temperature gives a larger fraction of collisions with at least the activation energy. (5.1) (5.5)
- Whether a mechanism fits the data.** The steps must add up to the overall equation. Write the slow step's rate law, replace any intermediate, and check it against the measured one. A catalyst is used in one step and made again later; an intermediate is made, then used. (5.7) (5.8) (5.9)
- Energies on an energy profile.** Measure each activation energy from the energy where its own step starts, not from the bottom of the graph. A catalyst lowers the peaks but never changes ΔH . (5.6) (5.10) (5.11)

📖 Formulas and facts to know

Given on the equation sheet:

Zero order $[A]_t - [A]_0 = -kt$
 First order $\ln[A]_t - \ln[A]_0 = -kt$
 Second order $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
 Half-life, first order $t_{1/2} = \frac{0.693}{k}$

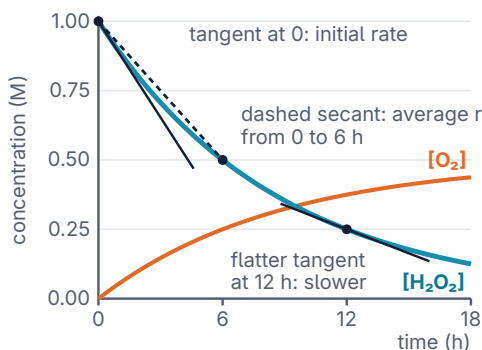
Not given, so know them by heart:

- rate = $k[A]^m[B]^n$, where the orders m and n come from experiments. You can be sure they equal the coefficients only for a single elementary step.
- The straight-line plot gives the order: $[A]$ for zero, $\ln[A]$ for first, $1/[A]$ for second order.
- Units of k : M s^{-1} , s^{-1} , $\text{M}^{-1} \text{s}^{-1}$ for zero, first and second order.

Not on the exam: Arrhenius-equation calculations (k from temperature and E_a). Know the trend: a higher temperature or a lower E_a gives a larger k .

5.1 Reaction rates

A reaction rate is how fast a concentration changes, in M s^{-1} (moles per liter per second). On a graph of concentration against time it is the slope, with the minus sign dropped for a reactant so that a rate is always positive.



Hydrogen peroxide decomposing, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$, with sample numbers.

Rates of different substances in one reaction

A reactant's concentration falls, so its rate is $-\Delta[\text{A}]/\Delta t$; a product's rises, so its rate is $+\Delta[\text{P}]/\Delta t$. For $a\text{A} \rightarrow b\text{B}$, divide each rate by its coefficient and they come out equal:

$$-\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t}$$

Worked example

$[\text{H}_2\text{O}_2]$ falls from 1.000 M to 0.500 M in 6.00 h, then to 0.250 M by 12.00 h. Find the average rate in each 6-hour interval.

- 0 to 6 h: $(1.000 - 0.500) \text{ M} \div 6.00 \text{ h} = 0.0833 \text{ M h}^{-1}$
- 6 to 12 h: $(0.500 - 0.250) \text{ M} \div 6.00 \text{ h} = 0.0417 \text{ M h}^{-1}$

The rate halved when the concentration halved, a first hint that the reaction is first order.

To follow a reaction, measure something that changes with concentration: the absorbance of a colored substance (proportional to its concentration), the volume or pressure of a gas made, the mass lost as a gas escapes, or the time until a color change. If the same amount reacts each time, half the time means twice the rate.

Worked example

In $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$, NO_2 disappears at $6.52 \times 10^{-7} \text{ M s}^{-1}$. How fast does O_2 appear?

$$1 \quad 6.52 \times 10^{-7} \text{ M s}^{-1} \times \frac{1 \text{ mol O}_2}{2 \text{ mol NO}_2}$$

O_2 appears at $3.26 \times 10^{-7} \text{ M s}^{-1}$. NO has the same coefficient as NO_2 , so it appears at $6.52 \times 10^{-7} \text{ M s}^{-1}$.

Exam trap

Giving every substance the same rate, or flipping the ratio. Two NO_2 are used up for each O_2 made, so O_2 forms at half the rate: $6.52 \times 10^{-7} \times \frac{1}{2} = 3.26 \times 10^{-7} \text{ M s}^{-1}$, not 1.30×10^{-6} . Only the coefficients go into this conversion, never the rate law.

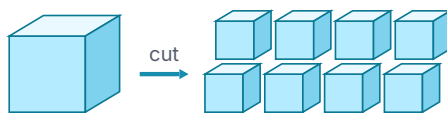
Testing one factor at a time

Compare trials that differ only in the factor you're testing. Here equal masses of the same fine marble (CaCO_3) powder react with excess HCl at one temperature:

[HCl]	Time to finish
1.0 M	67 s
3.0 M	22 s

If a question claims the reaction is zero order in HCl , answer:

I disagree. With the same powder, raising $[\text{HCl}]$ from 1.0 M to 3.0 M cut the time from 67 s to 22 s. If it were zero order in HCl , the time would not change.



one 2 cm cube
24 cm² of surface

eight 1 cm cubes
48 cm² of surface

Smaller pieces expose more particles, so the acid hits the solid more often each second.

Exam trap

- Saying smaller pieces make more product. Grinding a lump into powder doesn't change how much CaCO_3 there is, so it makes the same amount of CO_2 , only sooner.
- Stopping at "more surface area". Finish the explanation with collisions: more surface area means more collisions per second between the acid and the solid, so the rate increases. An answer that stops at surface area misses that point.

5.2 Introduction to rate law

In rate = $k[\text{A}]^m[\text{B}]^n$, the exponents m and n are the **orders**, found only by experiment; their sum is the overall order. Multiply a concentration by a factor and the rate changes by that factor raised to the order: triple a second-order reactant and the rate goes up $3^2 = 9$ times.

Worked example

Vitamin C (HAsc) reacts with triiodide, I_3^- . Find the rate law and k .

Trial	[HAsc] (M)	$[\text{I}_3^-]$ (M)	Rate ($\times 10^{-4} \text{ M s}^{-1}$)
1	0.450	1.200	2.457
2	0.450	0.600	1.229
3	0.900	1.200	4.914

- Trials 1 and 3: $[\text{I}_3^-]$ is the same, [HAsc] doubles and the rate doubles, so first order in HAsc.
- Trials 1 and 2: [HAsc] is the same, $[\text{I}_3^-]$ halves and the rate halves, so first order in I_3^- .
- Trial 1: $k = 2.457 \times 10^{-4} \text{ M s}^{-1} \div [(0.450 \text{ M})(1.200 \text{ M})]$

$$\text{rate} = k[\text{HAsc}][\text{I}_3^-]$$

$$k = 4.55 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

Units of k

$k = \text{rate} \div \text{concentrations}$, so divide the units too: for rate = $k[\text{HAsc}][\text{I}_3^-]$, $(\text{M s}^{-1}) \div (\text{M} \times \text{M}) = \text{M}^{-1} \text{ s}^{-1}$.

Exam trap

- Taking orders from the coefficients. For $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, experiments give rate = $k[\text{NO}]^2[\text{H}_2]$: H_2 has a coefficient of 2 but is first order.
- Dropping k 's units or its power of ten. Without the $\times 10^{-4}$, k comes out 10,000 times too big, and a missing unit can cost a point by itself.
- Thinking a new concentration gives a new k . Concentrations change the rate, not k : all three trials above give the same k . A change in temperature or a catalyst is what changes k .

Quick check

Rate = $k[\text{A}]^2[\text{B}]$. You triple $[\text{A}]$ and halve $[\text{B}]$. What happens to the rate?

Answer: $3^2 \times \frac{1}{2} = 4.5$ times as fast.

5.3 Concentration changes over time

The plot that comes out as a straight line tells you the order

Order	[A] against time	ln[A] against time	1/[A] against time	On the equation sheet	k and half-life
Zero rate = k	 slope = -k straight	 straight	 straight	$[A]_t - [A]_0 = -kt$	k is in $M s^{-1}$. Each half-life is shorter than the last.
First rate = k[A]	 straight	 slope = -k straight	 straight	$\ln[A]_t - \ln[A]_0 = -kt$	k is in s^{-1} . The half-life never changes: $t_{1/2} = 0.693/k$.
Second rate = k[A] ²	 straight	 straight	 slope = +k straight	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$	k is in $M^{-1} s^{-1}$. Each half-life is longer than the last.

Each row is one reaction starting at 0.100 M, with a point every 20 s; the dashed line joins the first and last points to show how much a plot bends. The first- and second-order reactions both reach 0.0500 M at 20 s, so two data points alone can't tell you the order.

How to justify an order from a graph

The plot of $1/[NO_2]$ against time is **linear**, so the reaction is second order in NO_2 .

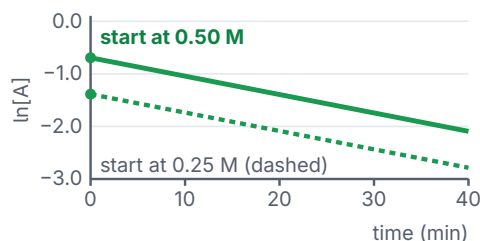
Name what is plotted: "the graph on the right is linear" doesn't earn the point.

Worked example

Read from the solid line in the graph below: $\ln[A]$ is about -0.80 at 3 min and -1.00 at 9 min, and $[A]$ halves from 0.50 M to 0.25 M in about 20 min. Find k both ways.

- slope = $(-1.00 - (-0.80)) \div (9 - 3)$ min = -0.033 min^{-1} , so $k = 0.033 \text{ min}^{-1}$
- $k = 0.693 \div t_{1/2} = 0.693 \div 20 \text{ min} = 0.035 \text{ min}^{-1}$

$k = 0.033$ or 0.035 min^{-1} . Both are fine, since graph readings are never exact.



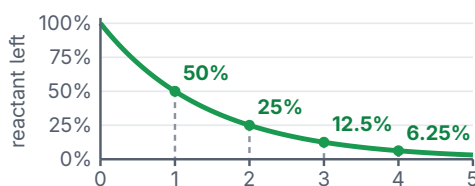
Starting at half the concentration at the same temperature, the $\ln[A]$ line starts 0.693 ($\ln 2$) lower but keeps the same slope, since k is unchanged.

Exam trap

- **Taking the slope as k for every order.** For the $[A]$ and $\ln[A]$ plots the slope is $-k$, so a slope of -0.033 min^{-1} means $k = 0.033 \text{ min}^{-1}$; only the $1/[A]$ plot has slope $+k$. k is never negative, and its time unit matches the time axis.

Half-life

The half-life is the time for half of a reactant to be used up. Only in a first-order reaction does it stay the same, whatever the concentration.



After n half-lives, $(\frac{1}{2})^n$ of the reactant remains.

Worked example

N_2O_5 decomposes: 0.16, 0.08, 0.04 and 0.02 M at 0, 1.67, 3.34 and 5.01 h. Find the order and k.

- The concentration halves every 1.67 h. A half-life that stays the same means first order.
- $k = \frac{0.693}{1.67 \text{ h}} = 0.415 \text{ h}^{-1}$

First order, $k = 0.415 \text{ h}^{-1}$

Exam trap

- **Thinking two half-lives finish the reaction.** The second half-life uses up half of what is left, not the rest of it, so after two half-lives a quarter remains.
- **Calling a reaction first order when its half-life changes.** If each half-life is shorter than the one before, the reaction is zero order; if each is longer, it is second order.
- **Using log instead of ln.** The first-order equation uses the natural log. The natural log of 0.0300 is -3.507, but log 0.0300 is -1.523, so the wrong key gives the wrong time.

Finding the order and k from concentration-time data

- Find the plot that is a straight line. What is on its y-axis tells you the order.
- Get k from its slope: $k = -\text{slope}$ for $[A]$ and $\ln[A]$, $k = +\text{slope}$ for $1/[A]$.
- Use that order's equation from the equation sheet to find $[A]$ at a given time, or the time to reach a given $[A]$.

Worked example

Second order: $1/[A]$ climbs from 10.0 M^{-1} at 0 s to 40.0 M^{-1} at 60 s. Find k and $[A]$ at 80 s.

- $k = \frac{40.0 - 10.0}{60 \text{ s}} = 0.500 \text{ M}^{-1} \text{ s}^{-1}$
- $1/[A] = 10.0 + (0.500)(80) = 50.0 \text{ M}^{-1}$
- Take the reciprocal: $[A] = 1/50.0$

$[A] = 0.0200 \text{ M}$ at 80 s

Worked example

First order, $k = 0.0347 \text{ s}^{-1}$, $[A]_0 = 0.100 \text{ M}$. When is $[A] = 0.0300 \text{ M}$?

- $\ln 0.0300 - \ln 0.100 = -(0.0347 \text{ s}^{-1}) t$
- $-1.204 = -(0.0347 \text{ s}^{-1}) t$

$t = 34.7 \text{ s}$

Natural logs on the calculator

TI-84 Plus CE. Press $\ln$, type 0.0300, then enter : -3.507. To get a concentration back from $\ln[A]$, press 2^{nd} $\ln$ (e^x): $e^{(-3.507)} = 0.0300$.

TI-Nspire CX. Type $\ln(0.0300)$ with the letter keys and press enter . The e^x key undoes $\ln$.

Desmos. Type $\ln(0.0300)$; $e^x(\dots)$ undoes it. Desmos's log is base 10.

5.4 Elementary reactions

An elementary step happens in one event, exactly as written: one particle rearranges, two collide, or, rarely, three collide. So its rate law comes straight from its equation, and the **coefficients become the exponents**.

Elementary step	Particles	Rate law
$A \rightarrow \text{products}$	1, unimolecular	$k[A]$
$A + B \rightarrow \text{products}$	2, bimolecular	$k[A][B]$
$2A \rightarrow \text{products}$	2, bimolecular	$k[A]^2$
$2A + B \rightarrow \text{products}$	3, termolecular (rare)	$k[A]^2[B]$

This works because the rate depends on how often particles collide. Double $[A]$ in $A + B \rightarrow \text{products}$ and each B meets twice as many A's, so the rate doubles. In $2A \rightarrow \text{products}$ there are twice as many A's, each meeting twice as many others, so the rate goes up $2 \times 2 = 4$ times.

Worked example

The elementary step $A + BC \rightarrow AB + C$ has $k = 4.00 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. Find the rate when $[A] = 1.00 \times 10^{-3} \text{ M}$ and $[BC] = 2.00 \times 10^{-3} \text{ M}$.

- The step is elementary, with one A and one BC, so rate = $k[A][BC]$.
- $(4.00 \times 10^2)(1.00 \times 10^{-3})(2.00 \times 10^{-3})$, and the units are $\text{M}^{-1} \text{ s}^{-1} \times \text{M} \times \text{M} = \text{M s}^{-1}$

$$\text{rate} = 8.00 \times 10^{-4} \text{ M s}^{-1}$$

Exam trap

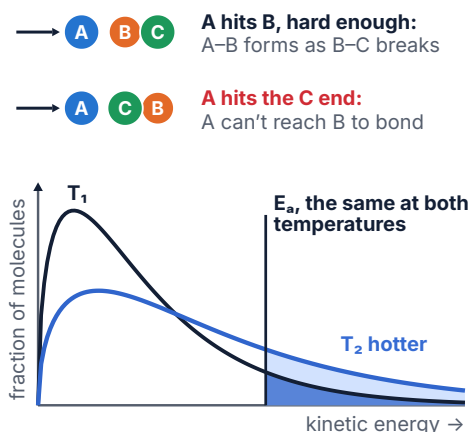
- Writing a rate law from an overall equation.** Coefficients become exponents only in a step the question calls elementary. For $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, experiments give rate = $k[\text{NO}]^2[\text{H}_2]$, not $k[\text{NO}]^2[\text{H}_2]^2$.

Molecularity and order

Molecularity is the number of particles that meet in one elementary step; order is measured for the whole reaction. The two are sure to be equal only when the whole reaction is a single elementary step.

5.5 Collision model

Most collisions don't lead to a reaction. A collision makes products only if it has **at least the activation energy (E_a)** and **an orientation that lets the bonds rearrange**.



The shaded area right of E_a is the fraction of molecules with enough energy to react: the dark area at T_1 , dark plus light at T_2 . Both curves enclose the same area: the number of molecules is the same.

Explaining why heating speeds a reaction up

At the higher temperature, a **greater fraction of collisions have energy equal to or greater than E_a** , so more collisions per second are successful and the rate increases.

Hotter molecules also collide a little more often, but that effect is small.

Explaining why most collisions fail

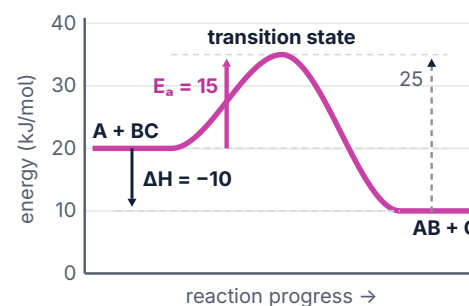
In the elementary step $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$, most collisions have **less than the activation energy** or the **wrong orientation**: the N of NO_2 must hit an F of F_2 for the N-F bond to form.

Exam trap

- Stopping at "the molecules move faster".** Finish the explanation: faster molecules have more energy, so more collisions reach E_a and succeed.
- Saying that heating lowers E_a .** The barrier stays the same height; heating gives more molecules enough energy to get over it.
- Reading the taller T_1 peak as more reaction.** The peak is just the most common energy; what counts is the area right of E_a , which is larger at T_2 .

5.6 Reaction energy profile

An energy profile shows how the energy changes as one step turns reactants into products: they climb to the **transition state**, where bonds are partly broken and partly formed, then fall.



The reverse reaction climbs from the products, so its E_a (the dashed arrow) is $35 - 10 = 25 \text{ kJ/mol}$.

Know by heart

- Forward $E_a = \text{peak} - \text{reactants}$
- Reverse $E_a = \text{peak} - \text{products}$
- $\Delta H = \text{products} - \text{reactants}$
- So reverse $E_a = \text{forward } E_a - \Delta H$

With everything else the same, k grows as the temperature rises and shrinks as E_a grows.

Worked example

Reactants sit at 40 kJ/mol, the peak at 100 and the products at 10. Find E_a , ΔH and the reverse E_a .

- $E_a = 100 - 40 = 60 \text{ kJ/mol}$
- $\Delta H = 10 - 40 = -30 \text{ kJ/mol}$, so the reaction is exothermic
- Reverse $E_a = 100 - 10 = 90 \text{ kJ/mol}$

$$E_a = 60 \text{ kJ/mol}, \Delta H = -30 \text{ kJ/mol}, \text{reverse } E_a = 90 \text{ kJ/mol}$$

Exam trap

- Measuring E_a from zero.** E_a is the climb from the reactants to the peak. Above, that is $100 - 40 = 60 \text{ kJ/mol}$, not 100.
- Thinking an exothermic reaction must be fast.** ΔH only compares start and finish; speed depends on the barrier. A hydrogen-oxygen mix sits unreacted at room temperature until a spark gets it over the barrier.
- Reading the horizontal axis as time.** It shows how far the rearrangement has gone, so a wide hump is not a slow step: only the height of the climb matters.

5.7 Reaction mechanisms

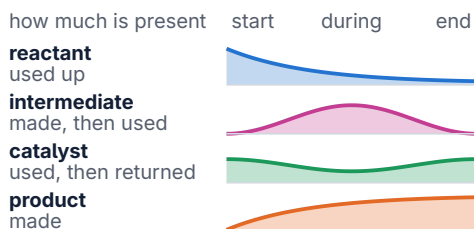
A mechanism is the list of elementary steps a reaction actually goes through. Add the steps and cancel anything that appears on both sides: you must get the overall equation back.

Worked example

Show that these steps add up to $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$.

- $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ slow
- $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ fast
- Add them. NO_3 and one NO_2 appear on both sides, so they cancel.

The steps add up to $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$. NO_3 is an intermediate.



Intermediates and catalysts both cancel out of the overall equation, so the order of the steps tells them apart.

Worked example

In "elephant toothpaste", iodide speeds up $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. Name the catalyst and the intermediate.

- $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$
- $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^-$

I^- is the catalyst: used in step 1, made again in step 2. IO^- is the intermediate: made in step 1, used in step 2.

Exam trap

- Calling anything on both sides a catalyst. Count how many go in and how many come out. In the $\text{NO}_2 + \text{CO}$ mechanism, two NO_2 go in and only one comes out, so NO_2 is used up: it is a reactant.
- Saying that a detected intermediate or a matching rate law proves a mechanism. Both only support it. Take $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ (Topic 5.9, at right). A different route, $\text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3$ (fast) then $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$ (slow), gives the same rate law. Rate data can rule a mechanism out but never prove it.

5.8 Mechanism and rate law

A reaction can go no faster than its slowest step. When the **first step is the slow one**, its rate law, written from its coefficients, is the rate law of the whole reaction.

Below about 225 °C, $\text{NO}_2 + \text{CO}$ reacts by the mechanism at left. Its slow first step is $\text{NO}_2 + \text{NO}_2$, so **rate = $k[\text{NO}_2]^2$** . CO reacts only in the fast second step, so it isn't in the rate law: the reaction is zero order in CO.

original mix		rate $\times 1$
$[\text{CO}] \times 2$		rate $\times 1$
$[\text{NO}_2] \times 2$		rate $\times 4$

Bar length is the rate. Doubling $[\text{CO}]$ changes nothing; doubling $[\text{NO}_2]$ makes the reaction 4 times as fast, as **rate = $k[\text{NO}_2]^2$** predicts.

Checking a mechanism

- Check that the steps add up to the overall equation.
- Write the slow step's rate law from its coefficients.
- If that rate law contains an intermediate, replace it (Topic 5.9).
- Compare the result with the measured rate law.

If they match, the mechanism is **consistent** with the data. Never say it is proved: another mechanism might fit just as well.

Writing that a mechanism is consistent

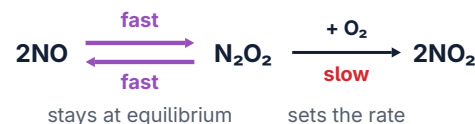
The slow first step, $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$, has rate = $k[\text{NO}_2]^2$, which matches the experimental rate law, so the mechanism is consistent with the data.

Exam trap

- Writing rate = $k[\text{NO}_2][\text{CO}]$ from the overall equation. The overall equation says what reacts, not how fast. The rate law comes from the slow step, which has two NO_2 and no CO.
- Writing the rate law from a fast step. The slowest step holds the whole reaction back, so it sets the rate law. Fast step 2 here would give rate = $k[\text{NO}_3][\text{CO}]$, which contains an intermediate and doesn't match the data.

5.9 Pre-equilibrium approximation

When a **fast, reversible step comes first**, the slow step still sets the rate, but its rate law contains an intermediate. The fast equilibrium gives you an expression to replace it with.



The measured rate law for $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is **rate = $k[\text{NO}]^2[\text{O}_2]$** . In this mechanism two NO molecules join as N_2O_2 and split again quickly; now and then an O_2 hits an N_2O_2 and reacts.

Replacing the intermediate

Step 1 has rate constants k_1 forward and k_{-1} in reverse; the slow step's is k_2 .

- Slow step:** rate = $k_2[\text{N}_2\text{O}_2][\text{O}_2]$
- N_2O_2 is an intermediate, so it can't stay in the final rate law.
- Fast equilibrium:** forward rate = reverse rate, so $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$ and $[\text{N}_2\text{O}_2] = (k_1/k_{-1})[\text{NO}]^2$
- Substitute:** rate = $(k_2k_1/k_{-1})[\text{NO}]^2[\text{O}_2] = k[\text{NO}]^2[\text{O}_2]$, with $k = k_2k_1/k_{-1}$

The same steps work for any mechanism like this. With $\text{A} + \text{B} \rightleftharpoons \text{X}$ fast and $\text{X} + \text{B} \rightarrow \text{P}$ slow (X is the intermediate, P the product), rate = $k_2[\text{X}][\text{B}]$ and $[\text{X}] = K[\text{A}][\text{B}]$ ($K = k_1/k_{-1}$), so **rate = $k[\text{A}][\text{B}]^2$** .

Stating the assumption

Because step 1 is a **fast equilibrium**, its forward and reverse rates are equal, so $[\text{N}_2\text{O}_2] = (k_1/k_{-1})[\text{NO}]^2$. Substituting into the slow step gives rate = $k[\text{NO}]^2[\text{O}_2]$, **consistent with the data**.

Exam trap

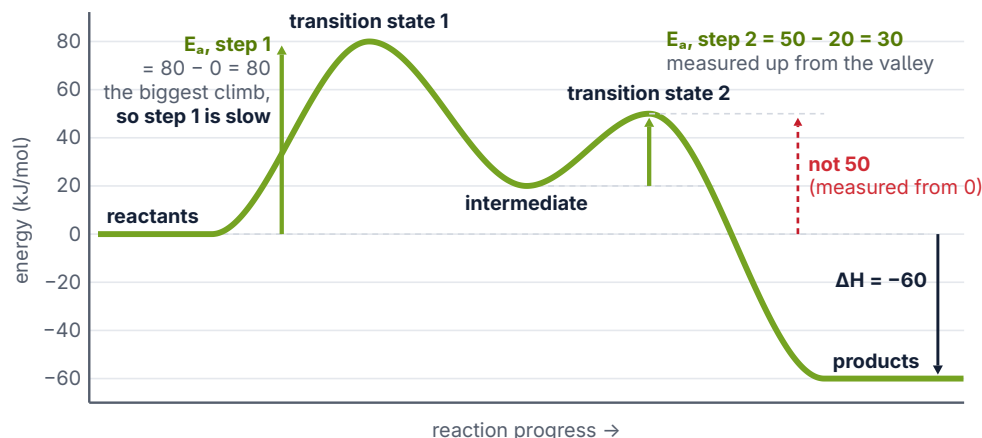
- Leaving an intermediate in the final rate law. You can't choose an intermediate's concentration in an experiment, so the final law can contain only reactants (or sometimes a product or a catalyst). Replace $[\text{N}_2\text{O}_2]$ using the fast equilibrium.

Quick check

For $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$: $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$ (fast), then $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$ (slow). Find the rate law.

Answer: rate = $k_2[\text{NOBr}_2][\text{NO}]$ and $[\text{NOBr}_2] = K[\text{NO}][\text{Br}_2]$, so **rate = $k[\text{NO}]^2[\text{Br}_2]$** .

5.10 Multistep reaction energy profile



⚠ Exam trap

- Reading step 2's E_a from zero. Each climb starts where its own step starts. Above, step 2 starts in the valley at 20 kJ/mol and peaks at 50, so its E_a is 30 kJ/mol, not 50.

⚡ A real two-step reaction: $\text{NO}_2 + \text{CO}$

Below about 225 °C, this reaction takes the two steps in Topic 5.7. Step 1, $2\text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$, is uphill and slow, so the valley for the intermediate NO_3 sits **above** the starting energy. Step 2 has only a small climb, and the reaction ends far below where it began.

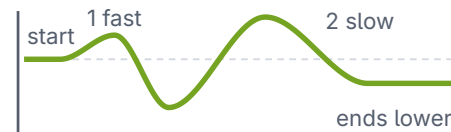
📖 Sketching a profile from a mechanism

- Draw **one hump** for each step, with a valley for each intermediate between them.
- An **endothermic step** ends higher than it starts.
- Give the **slow step** the **biggest climb**, measured from where that step starts.
- If the reaction is **exothermic overall**, end the products below the reactants.

🔍 Quick check

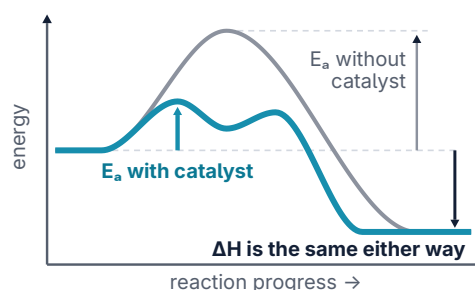
Sketch the profile of a two-step reaction: step 1 is fast and exothermic, step 2 is slow and endothermic, and the reaction is exothermic overall.

Answer:

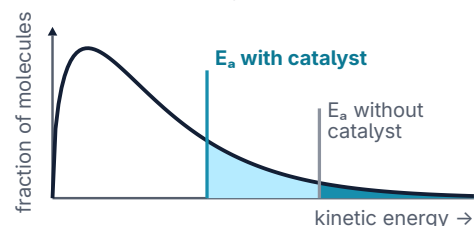


5.11 Catalysis

A catalyst gives the reaction a **new route** with a lower activation energy, or one that holds the reactants in a better orientation. One step uses the catalyst and a later step makes it again, so it never appears in the overall equation.



The thin gray line is the reaction without a catalyst; the bold line is the catalyzed route.



The molecules' energies don't change. With the lower E_a , far more of them have enough energy to react (light plus dark, not just dark), so more collisions succeed each second.

How catalysts work

⚡ On a metal surface

In a car's catalytic converter, CO and O_2 stick to platinum, O_2 splits into O atoms, and a bound CO meets a bound O to make CO_2 . A star (*) is an empty site on the metal, and CO^* is a CO stuck to one:

Times it happens Step

twice	$\text{CO} + * \rightarrow \text{CO}^*$
once	$\text{O}_2 + 2* \rightarrow 2\text{O}^*$
twice	$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2*$
sum	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$

The sites are used and freed again, so the surface is the catalyst; CO^* and O^* are intermediates.

⚡ In an enzyme

An enzyme holds its reactant in a pocket, turned the right way. Carbonic anhydrase II holds CO_2 next to an OH^- bound to zinc. The OH^- adds to the CO_2 to make HCO_3^- , up to about a million times a second per enzyme. The enzyme- CO_2 complex is a new intermediate.

⚠ Exam trap

Drawing the catalyzed products at a lower energy. A catalyst only changes the path, so if ΔH is -60 kJ/mol without a catalyst, it is -60 kJ/mol with one.

A catalyst changes It never changes

the mechanism and E_a in both directions	ΔH , set by the start and finish energies
k and the rate, forward and reverse	K, the equilibrium constant
how fast equilibrium is reached	the amounts at equilibrium (the yield)

🔗 Showing a substance is a catalyst

In acid catalysis, H_3O^+ gives a proton to a reactant and takes it back later. Here it speeds up the reaction of methyl glycolate ($\text{C}_3\text{H}_6\text{O}_3$), an ester, with water to make glycolic acid ($\text{HC}_2\text{H}_3\text{O}_3$) and methanol:
 Step 1: $\text{C}_3\text{H}_6\text{O}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{C}_2\text{H}_5\text{O}_3^+ + \text{CH}_3\text{OH}$
 Step 2: $\text{C}_2\text{H}_5\text{O}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_3 + \text{H}_3\text{O}^+$
 If a question claims H_3O^+ is a catalyst, answer:

I agree. H_3O^+ is consumed in step 1 and regenerated in step 2.

⚠ Exam trap

- Answering with a definition.** "A catalyst speeds up the reaction" is true but doesn't show that H_3O^+ is one. Point to the steps that use it and make it again.
- Calling H_3O^+ a spectator ion** because it isn't in the overall equation. A spectator ion never reacts, and H_3O^+ reacts in step 1.

What earns points on the free-response questions

When the question asks	What earns the point	What loses it
How a graph shows the order	Name what is plotted: "The plot of $1/[A]$ against time is linear, so the reaction is second order." For first order the straight plot is $\ln[A]$; for zero order, $[A]$.	"The graph on the right is linear."
k from a graph or a half-life	k is the slope with its minus sign removed for the $[A]$ and $\ln[A]$ plots, and the slope itself for $1/[A]$. For first order, $k = 0.693/t_{1/2}$ also works. k's time unit matches the time axis.	A negative k, or log in place of ln.
Drawing the line for a new starting concentration (first order)	At the same temperature k is the same, so draw a line parallel to the first, starting from the new $\ln[A]_0$.	Changing the slope.
Agree or disagree: "zero order in X"	If changing only $[X]$ changed the rate (or the time to finish), write "I disagree", name the two trials and give their numbers.	An answer with no numbers from the table.
The effect of temperature	At the higher temperature, a greater fraction of collisions have energy equal to or greater than E_a , so more collisions per second succeed.	"The particles move faster," with no link to E_a .
The effect of particle size	Smaller pieces have more surface area, so there are more collisions per second and the rate increases. The amount of product doesn't change.	Surface area with no mention of collisions.
Whether a substance is a catalyst	It is consumed in one step and regenerated in a later step. Name the steps.	A textbook definition, or "spectator ion".
An energy profile, then the same reaction with a catalyst	Draw one hump per step and give the slow step the biggest climb. Measure each E_a from the start of its own step. With a catalyst, draw lower humps but keep the same start and finish.	Drawing the catalyzed products at a different energy, or measuring E_a from zero.

A full question, worked point by point

A student measures the initial rate at which N_2 forms in $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$, at one temperature.

Trial	$[NO] (M)$	$[H_2] (M)$	Rate of N_2 formation ($M \min^{-1}$)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	3.0×10^{-5}
4	0.0020	0.0060	1.2×10^{-4}

A proposed mechanism: step 1, $2NO \rightleftharpoons N_2O_2$ (fast); step 2, $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow); step 3, $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast).

The question	An answer that earns the point	Why it works
Order in H_2 , with a reason	In trials 1 and 2, $[NO]$ is held constant while $[H_2]$ doubles and the rate doubles, so it is first order in H_2 .	It names the trials, what stayed the same, and both changes.
Order in NO	In trials 3 and 4, $[H_2]$ is held constant while $[NO]$ doubles and the rate goes up 4 times, so it is second order in NO.	It names the trials and what stayed the same, and $4 = 2^2$ gives order 2.
Rate law and k, with units	rate = $k[NO]^2[H_2]$; from trial 1, $k = 1.8 \times 10^{-4} \div [(0.0060)^2(0.0010)] = 5.0 \times 10^3 M^{-2} \min^{-1}$	The units: $(M \min^{-1}) \div (M^2 \times M) = M^{-2} \min^{-1}$. Every trial gives the same k.
How fast H_2 is used up in trial 1	$2 \times 1.8 \times 10^{-4} = 3.6 \times 10^{-4} M \min^{-1}$	Two H_2 are used for each N_2 made.
Is the mechanism consistent with the rate law?	The steps add up to the overall equation. The slow step gives rate = $k_2[N_2O_2][H_2]$, and the fast equilibrium gives $[N_2O_2] = K[NO]^2$, so rate = $k[NO]^2[H_2]$. That matches, so the mechanism is consistent with the rate law.	It shows the substitution and says "consistent", not "proved".
The intermediates	N_2O_2 and N_2O	N_2O_2 is made in step 1 and used in step 2; N_2O is made in step 2 and used in step 3.

Links to other units

Unit 6 The ΔH on an energy profile is the enthalpy change of the reaction.

Unit 7 At equilibrium, the forward and reverse rates are equal. A catalyst speeds up both by the same factor, so K doesn't change.

Unit 9 A reaction can be thermodynamically favorable ($\Delta G < 0$) and still too slow to notice if its E_a is large. Diamond turning into graphite is favorable, but at room temperature it is far too slow to see.

Enter powers of ten

TI-84 Plus CE. Type 1.8, then $\boxed{2nd} \boxed{,} \boxed{(EE)}$, then $\boxed{(-)} \boxed{4}$. The screen shows $1.8E-4$. Use $\boxed{(-)}$ for a negative sign, never the subtraction key.

TI-Nspire CX. Type 1.8 $\boxed{\times} \boxed{10} \boxed{^{\wedge}} \boxed{(-)} \boxed{4}$. Use $\boxed{(-)}$ for a negative sign, never the subtraction key.

Desmos. Type 1.8×10^{-4} .

Small things that cost points

- "Calculate" means showing the numbers you put in, the units and sensible significant figures, not just the final number.
- Write "consistent with" for a mechanism, never "proves".