

Unit 5: Kinetics

Unit 5 asks how fast reactions happen and why. It covers measuring reaction rates, writing rate laws from experimental data, tracking how concentrations change over time, the collision model that explains temperature and concentration effects, step-by-step reaction mechanisms, and how catalysts speed things up.

AP Chemistry

Kinetics

About 13 minutes to read

How to use this guide

Read it in order the first time because the topics build on each other. Measuring rates motivates the rate law, the rate law leads to the integrated forms that track concentration over time, the collision model explains why those rates behave the way they do, mechanisms break the overall reaction into steps, and catalysis shows how the steps can change. Exam questions often hand you a data table or a mechanism and ask you to derive the rate law.

After the first read, use the trap boxes and the tables to review the distinctions that exam questions test most often. Finish with the practice questions, then complete the recall check on the last page out loud and note any items you cannot explain yet.

What this unit is worth. Kinetics is about 7 to 9 percent of the AP Chemistry exam. It also carries more weight than that number suggests, because the rate ideas here return in Unit 7 when equilibrium is treated as two opposing rates, and reaction mechanisms show up again in acid-base chemistry. If rate laws feel shaky now, equilibrium will feel shaky later.

5.1 Reaction Rates

The **reaction rate** is the amount of reactant converted to product per unit time. In practice you measure it as a change in concentration divided by a change in time, with units like M/s. For the reaction $A \rightarrow B$, the rate can be written as $-\Delta[A]/\Delta t$ or $\Delta[B]/\Delta t$. The negative sign on the reactant keeps the rate positive, since $[A]$ decreases as the reaction runs.

You measure rates by tracking any property that changes as the reaction proceeds. If a gas is produced, you can track pressure or volume. If a colored species is consumed, you can track light absorbance. If H^+ is involved, you can track pH. The method depends on the reaction, but the idea is the same: watch a concentration change over time and divide.

Several **factors affect reaction rate**. Higher **concentration** means more particles per volume and more frequent collisions. Higher **temperature** means particles move faster and collide with more energy. Greater **surface area** matters for solids, since only the exposed surface can react, which is why powdered zinc reacts with acid far faster than a solid chunk. A **catalyst** speeds the reaction without being consumed. These four show up constantly, so learn them as a set.

Trap. Rate is not the same as extent. A reaction can be fast but produce little product, or slow but go nearly to completion. Thermodynamics (Unit 9) decides how far a reaction goes. Kinetics decides how fast it gets there. A question about speed is never answered with ΔH or K .

5.2 Introduction to Rate Law

The **rate law** is an expression relating the reaction rate to reactant concentrations, each raised to a power: $\text{rate} = k[A]^m[B]^n$. The **reaction order** is the exponent on each reactant, and the **overall order** is the sum of the individual orders. For $\text{rate} = k[\text{NO}]^2[\text{O}_2]$, the reaction is second order in NO, first order in O_2 , and third order overall.

The **rate constant k** is the proportionality constant in the rate law. It depends on temperature: warm the reaction and k grows. Its units reflect the overall order, because the rate always comes out in M/s. For a first-order rate law, k has units s^{-1} . For second order, $M^{-1}s^{-1}$. For third order, $M^{-2}s^{-1}$. If you can write the rate law, you can work out the units of k , and exam questions test exactly that.

Trap. Reaction orders come from experiment, never from the balanced equation. For $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, you cannot look at the coefficients and write $\text{rate} = k[\text{NO}]^2[\text{O}_2]$. It happens to be correct for this reaction, but that is a coincidence you are not allowed to assume. Orders are measured, not read off the equation.

5.2b The Method of Initial Rates

The **method of initial rates** determines reaction orders experimentally. You run several trials with different starting concentrations, measure the initial rate of each, and compare. Using initial rates avoids the complication that concentrations change as the reaction proceeds.

Consider the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ with this data:

TRIAL	[NO] (M)	[O ₂] (M)	INITIAL RATE (M/S)
1	0.010	0.010	2.5
2	0.020	0.010	10
3	0.010	0.020	5.0

Compare trials 1 and 2: [NO] doubles while [O₂] is held constant, and the rate goes from 2.5 to 10, a factor of 4. Since $2^2 = 4$, the reaction is second order in NO. Compare trials 1 and 3: [O₂] doubles while [NO] is held constant, and the rate doubles, so the reaction is first order in O₂. The rate law is $\text{rate} = k[\text{NO}]^2[\text{O}_2]$.

To find k, plug one trial into the rate law: $2.5 = k(0.010)^2(0.010)$, so $k = 2.5 / 1.0 \times 10^{-6} = 2.5 \times 10^6 \text{ M}^{-2}\text{s}^{-1}$. The units check out: $\text{M}^{-2}\text{s}^{-1} \times \text{M}^3 = \text{M/s}$. Any trial gives the same k, so use whichever has the simplest numbers.

Trap. When comparing trials, hold everything else constant. If two concentrations change between trials, you cannot tell which one caused the rate change. Pick the pair of trials where only one reactant's concentration differs, and ignore the rest of the table for that comparison.

5.3 Concentration Changes Over Time

The **integrated rate laws** give concentration as a function of time. Each order has its own form, and each form tells you which plot gives a straight line. That straight-line test is how you identify the order from concentration-versus-time data.

ORDER	INTEGRATED RATE LAW	STRAIGHT-LINE PLOT	HALF-LIFE
Zeroth	$[A]_t = [A]_0 - kt$	$[A]$ vs t	$[A]_0 / 2k$
First	$\ln[A]_t = \ln[A]_0 - kt$	$\ln[A]$ vs t	$0.693 / k$
Second	$1/[A]_t = 1/[A]_0 + kt$	$1/[A]$ vs t	$1 / (k[A]_0)$

The **half-life ($t_{1/2}$)** is the time for half of a reactant to be consumed. Only for first-order reactions is it constant: $t_{1/2} = 0.693/k$, independent of starting concentration. For zeroth and second order, the half-life depends on $[A]_0$, so each successive half-life takes a different amount of time.

Radioactive decay follows first-order kinetics, which is why carbon-14 dating works. With a half-life of 5,730 years, a sample with half the expected ^{14}C is about 5,730 years old, and one with a quarter is about 11,460 years old. The constant half-life is what makes the clock readable.

A worked example: for the second-order decomposition $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ with $k = 0.54 \text{ M}^{-1}\text{s}^{-1}$ and $[\text{NO}_2]_0 = 0.50 \text{ M}$, find $[\text{NO}_2]$ after 10 s. Using $1/[A]_t = 1/[A]_0 + kt$: $1/[A]_t = 1/0.50 + (0.54)(10) = 2.0 + 5.4 = 7.4$, so $[A]_t = 1/7.4 = 0.14 \text{ M}$.

Trap. A constant half-life is a first-order signature, not a general rule. If a question gives you two half-lives for the same reaction and they are equal, that tells you the reaction is first order. If they differ, it is not. Do not apply $t_{1/2} = 0.693/k$ to a second-order reaction.

5.4 Elementary Reactions

An **elementary reaction** is a single step in a reaction mechanism. For an elementary step, and only for an elementary step, the rate law can be written directly from the stoichiometry of the colliding particles. A unimolecular step $A \rightarrow \text{products}$ has rate $= k[A]$. A bimolecular step $A + B \rightarrow \text{products}$ has rate $= k[A][B]$. The **molecularity** is just the count of reactant particles in that step: one, two, or three.

Termolecular collisions, three particles colliding at once, are rare. Getting three particles to arrive at the same place at the same time with the right energy and orientation is improbable, so elementary steps involving three particles are uncommon. When a mechanism needs three particles to react, it almost always does so in two bimolecular steps instead.

Trap. Molecularity and reaction order are different ideas that use similar words. Molecularity counts particles in one elementary step and is always a whole number from the step's stoichiometry. Reaction order is an experimental exponent in the overall rate law and can be zero, fractional, or negative. Do not use one where the question asks for the other.

5.5 Collision Model

The **collision model** says reactants must collide to react, and a collision succeeds only if the particles have enough energy and the correct orientation. Most collisions fail. Two molecules can hit each other with plenty of energy but bounce apart if the wrong atoms make contact, because bonds cannot form from that geometry.

The **Maxwell-Boltzmann distribution** shows the spread of particle energies at a given temperature. Only the fraction of molecules with energy above the activation energy can react. Raising the temperature shifts the whole distribution toward higher energies, so a much larger fraction clears the barrier. That is the main reason warming a reaction speeds it up: not just more collisions, but far more *effective* collisions.

Trap. Temperature increases the rate mostly by increasing the fraction of molecules with enough energy, not just by making collisions more frequent. If a question asks why a 10 K rise can double a rate, the answer is the Maxwell-Boltzmann shift, because the fraction above the barrier grows exponentially with temperature.

5.6 Reaction Energy Profile

A **reaction energy profile** plots potential energy against the reaction coordinate. Read it left to right: it starts at the energy of the reactants, climbs to a peak, then falls to the energy of the products. The peak is the **transition state**, the highest-energy arrangement along the path, partway between reactants and products. It is not a stable species and cannot be isolated.

The **activation energy (E_a)** is the height of the climb: the energy of the transition state minus the energy of the reactants. The difference between products and reactants is ΔH , the enthalpy change. In an exothermic reaction the products sit lower than the reactants (ΔH negative). In an endothermic reaction the products sit higher (ΔH positive). The activation energy is always positive and always measured from the reactants upward.

The **Arrhenius equation** links the rate constant to temperature and activation energy: $k = Ae^{-E_a/RT}$. The CED asks only for conceptual understanding, which comes down to two statements. A higher temperature makes k larger, because more molecules clear the barrier. A higher activation energy makes k smaller, because fewer molecules clear it. You will not be asked to calculate with this equation.

Trap. Activation energy is measured from the reactants, not from the products and not from zero. On an energy diagram, find the reactant level first, then measure up to the peak. Also, ΔH tells you nothing about the rate: a strongly exothermic reaction can be extremely slow if its barrier is high, as with the combustion of paper sitting on your desk.

5.7 Reaction Mechanism

A **reaction mechanism** is the series of elementary steps by which a reaction occurs. The steps must add up to the overall balanced equation, and the mechanism must predict the experimentally observed rate law. A mechanism is a proposal, and the rate law is the test it has to pass.

A **reaction intermediate** is a species produced in one elementary step and consumed in a later one. It exists only while the reaction is running, so it never appears in the overall balanced equation. Do not confuse it with a catalyst: an intermediate is made and then used up, while a catalyst is used and then regenerated.

A **catalyst** in a mechanism appears in the elementary steps but is regenerated, so it is not consumed overall. Because it participates and is restored, it speeds the reaction by providing a lower-energy pathway. Like an intermediate, it cancels out of the overall equation, which is why you cannot spot a catalyst or an intermediate from the balanced equation alone.

Trap. Intermediates and catalysts both vanish from the overall equation, but for opposite reasons. An intermediate is produced first and consumed later. A catalyst is consumed first and regenerated later. If a species appears as a reactant in an early step and a product in a later step, it is a catalyst. If it appears as a product first and a reactant later, it is an intermediate.

5.8 The Rate-Limiting Step

The **rate-limiting (slow) step** is the slowest elementary step in a mechanism, and it controls the overall rate. Think of it as the narrowest part of a funnel: pouring faster upstream does not change how fast liquid comes out the bottom.

When the slow step is the first step, its molecularity gives the overall rate law directly. For the mechanism $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ (slow) followed by $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ (fast), the rate law is $\text{rate} = k[\text{NO}_2]^2$, straight from the slow step. When the slow step is not first, you need the pre-equilibrium approximation from topic 5.9 to eliminate any intermediate from the rate expression, because rate laws may not contain intermediates.

Trap. The slow step determines the rate law only when it is the first step. If a fast step comes first, the slow step's reactants may include an intermediate, and you must substitute it out using the pre-equilibrium approximation. Writing the slow step's rate law with an intermediate still in it is the most common error on mechanism questions.

5.9 Pre-Equilibrium Approximation

The **pre-equilibrium approximation** handles mechanisms where a fast step comes before the slow step. Treat the fast step as being at equilibrium, write its equilibrium expression, and use it to replace the intermediate in the slow step's rate law.

Work through the classic example. The reaction $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$ proceeds by: Step 1: $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$ (fast); Step 2: $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$ (slow). The slow step gives rate = $k_2[\text{NOBr}_2][\text{NO}]$, but NOBr_2 is an intermediate and cannot stay. From the fast pre-equilibrium, $K = [\text{NOBr}_2] / ([\text{NO}][\text{Br}_2])$, so $[\text{NOBr}_2] = K[\text{NO}][\text{Br}_2]$. Substituting gives rate = $k_2K[\text{NO}]^2[\text{Br}_2]$, which is written as rate = $k[\text{NO}]^2[\text{Br}_2]$ with $k = k_2K$. Notice the result matches the experimental rate law, which is how the mechanism earns its keep.

Trap. Intermediates may never appear in the final rate law. If your derived rate law still contains a species that is produced in one step and consumed in another, you have not finished the problem. Go back to the fast pre-equilibrium step and substitute it out.

5.10 Multistep Reaction Energy Profile

A **multistep reaction energy profile** combines the energetics of each elementary step into one diagram. Each peak is a transition state for one step, each valley between peaks is a reaction intermediate, and the highest peak corresponds to the rate-limiting step. The overall ΔH is still just products minus reactants, the same as if you ignored the steps entirely.

Read the diagram the way the exam asks you to. Count the peaks to count the steps. Find the tallest peak to find the slow step. Valleys are intermediates, not transition states: a valley is a local minimum where a species briefly exists, while a peak is a maximum that no species occupies for long.

Trap. The rate-limiting step is the tallest barrier measured from its own preceding valley, not simply the highest point on the diagram. In most textbook diagrams these coincide, but the barrier for each step is measured from the valley right before it. If a question asks which step is slowest, compare barrier heights, not peak elevations.

5.11 Catalysis

A **catalyst** increases reaction rate by providing an alternative pathway with a lower activation energy. It is not consumed in the overall reaction. On an energy profile, a catalyzed pathway has a lower peak but starts and ends at the same reactant and product energies, so ΔH is unchanged and the equilibrium position is unchanged. A catalyst makes the reaction faster, not more favorable.

Enzymes are biological catalysts. They bind reactants and position them precisely so the activation energy drops. **Acid-base catalysis** works through proton transfer that creates new reaction intermediates, as in the acid-catalyzed hydrolysis of esters. **Surface catalysis** happens when reactants bind to a solid surface that facilitates the reaction: the catalytic converter in a car uses platinum, palladium, and rhodium surfaces to convert CO, unburned hydrocarbons, and nitrogen oxides into CO₂, H₂O, and N₂.

Trap. A catalyst changes the rate, not the thermodynamics. It does not change ΔH , it does not change the equilibrium constant, and it does not change how much product forms. It only changes how fast equilibrium is reached. Any answer choice claiming a catalyst shifts equilibrium is wrong.

Confusions That Cost Points

PAIR	HOW TO KEEP THEM STRAIGHT
Reaction order vs stoichiometric coefficient	Orders come from experimental data. Coefficients come from the balanced equation. They match only by coincidence.
Rate constant k vs reaction rate	The rate changes as concentrations change. k changes only with temperature (and the catalyst). Warming the reaction raises k ; adding reactant raises the rate.
First-order vs other half-lives	Only first order has a constant half-life, $t_{1/2} = 0.693/k$. For other orders the half-life depends on concentration.
Molecularity vs reaction order	Molecularity counts particles in one elementary step. Order is an experimental exponent in the overall rate law. They are equal only for an elementary reaction.
Intermediate vs catalyst	An intermediate is produced first, then consumed. A catalyst is consumed first, then regenerated. Neither appears in the overall equation.
Transition state vs intermediate	The transition state is an energy maximum that cannot be isolated. An intermediate is an energy minimum (a valley) that exists briefly between steps.
Lower E_a vs more negative ΔH	A catalyst lowers the barrier (faster rate) without touching ΔH . Exothermicity says nothing about speed.

Practice Questions

Original questions written for this guide in the style of the AP exam. Answers and explanations are on the next page, so complete the questions before checking them.

1. For the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, three trials give these initial rates: trial 1, $[\text{NO}] = 0.010 \text{ M}$ and $[\text{O}_2] = 0.010 \text{ M}$, rate = 2.5 M/s ; trial 2, $[\text{NO}] = 0.020 \text{ M}$ and $[\text{O}_2] = 0.010 \text{ M}$, rate = 10 M/s ; trial 3, $[\text{NO}] = 0.010 \text{ M}$ and $[\text{O}_2] = 0.020 \text{ M}$, rate = 5.0 M/s . What is the rate law?

- A. rate = $k[\text{NO}][\text{O}_2]$
- B. rate = $k[\text{NO}]^2[\text{O}_2]$
- C. rate = $k[\text{NO}][\text{O}_2]^2$
- D. rate = $k[\text{NO}]^2[\text{O}_2]^2$

2. A first-order reaction has $k = 0.0462 \text{ s}^{-1}$. What is its half-life?

- A. 15 s
- B. 30 s
- C. 0.693 s
- D. 21.6 s

3. Which plot gives a straight line for a second-order reaction?

- A. $[\text{A}]$ vs t
- B. $\ln[\text{A}]$ vs t
- C. $1/[\text{A}]$ vs t
- D. Rate vs $[\text{A}]$

4. The Maxwell-Boltzmann distribution explains why reaction rate rises with temperature mainly because:

- A. collisions become more frequent
- B. a larger fraction of molecules have energy above E_a
- C. the activation energy decreases
- D. the orientation requirement is relaxed

5. A proposed mechanism: Step 1, $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$ (fast); Step 2, $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$ (slow). What is the overall rate law?
- A. $\text{rate} = k[\text{NO}][\text{Br}_2]$
 - B. $\text{rate} = k[\text{NO}]^2[\text{Br}_2]$
 - C. $\text{rate} = k[\text{NOBr}_2][\text{NO}]$
 - D. $\text{rate} = k[\text{NOBr}_2]$
6. A catalyst increases reaction rate by:
- A. increasing the temperature of the system
 - B. shifting the equilibrium toward products
 - C. providing an alternative pathway with lower activation energy
 - D. increasing the energy of the reactants
7. Which statement about the transition state is true?
- A. It is a stable intermediate that can be isolated
 - B. It is the highest-energy arrangement along the reaction coordinate
 - C. It has the same energy as the products
 - D. It exists only in catalyzed reactions
8. For the second-order reaction $\text{A} \rightarrow \text{products}$, $[\text{A}]$ drops from 0.80 M to 0.20 M in 40 s. What is k ?
- A. $0.015 \text{ M}^{-1}\text{s}^{-1}$
 - B. $0.094 \text{ M}^{-1}\text{s}^{-1}$
 - C. 0.017 s^{-1}
 - D. $0.25 \text{ M}^{-1}\text{s}^{-1}$

Answer Key

- 1. B.** Trials 1 and 2: $[\text{NO}]$ doubles with $[\text{O}_2]$ constant, and the rate quadruples ($2.5 \rightarrow 10$), so the order in NO is 2. Trials 1 and 3: $[\text{O}_2]$ doubles with $[\text{NO}]$ constant, and the rate doubles, so the order in O_2 is 1. A and C swap or drop the exponents. D doubles the O_2 order without evidence.
- 2. A.** For first order, $t_{1/2} = 0.693/k = 0.693 / 0.0462 = 15 \text{ s}$. B doubles the answer, a common slip from misreading the half-life expression. C reports the numerator alone without dividing by k . D inverts the division ($k/0.693$ instead of $0.693/k$).
- 3. C.** The second-order integrated rate law is $1/[\text{A}]_t = 1/[\text{A}]_0 + kt$, so $1/[\text{A}]$ vs t is linear. A is the zeroth-order plot. B is the first-order plot. D is linear only for first order, and the question asks about second order.
- 4. B.** Warming shifts the Maxwell-Boltzmann distribution so that a much larger fraction of molecules exceed E_a ; that fraction grows steeply with temperature. A is a real but minor effect. C is wrong because E_a is a fixed barrier for the pathway. D is wrong because orientation requirements do not change with temperature.
- 5. B.** The slow step gives $\text{rate} = k_2[\text{NOBr}_2][\text{NO}]$, but NOBr_2 is an intermediate and must be eliminated. The fast pre-equilibrium gives $[\text{NOBr}_2] = K[\text{NO}][\text{Br}_2]$, so the rate law is $\text{rate} = k[\text{NO}]^2[\text{Br}_2]$. A uses only the first step. C leaves the intermediate in the rate law, which is never allowed. D drops a reactant from the slow step.
- 6. C.** A catalyst provides a lower-energy alternative pathway; it is not consumed. A confuses the catalyst with heating. B is the classic error: catalysts never shift equilibrium or change ΔH . D describes raising reactant energy, which is what temperature does, not what a catalyst does.
- 7. B.** The transition state is the maximum on the energy profile, partway between reactants and products. A confuses it with an intermediate, which sits in a valley and exists briefly. C would make the activation energy zero. D is wrong because every reaction path has a transition state, catalyzed or not.
- 8. B.** For second order, $1/[\text{A}]_t - 1/[\text{A}]_0 = kt$: $1/0.20 - 1/0.80 = 5.0 - 1.25 = 3.75 = k(40 \text{ s})$, so $k = 0.094 \text{ M}^{-1}\text{s}^{-1}$. A comes from using the first-order half-life expression by mistake. C has the wrong units for a second-order constant. D divides concentration by time without the reciprocal form.

One-Page Recall Check

- Define reaction rate and give its units.
- Name the four factors that affect reaction rate.
- Write a general rate law and explain what each symbol means.
- Explain why reaction orders come from experiment, not the balanced equation.
- Use the method of initial rates to find orders from a data table.
- Determine the units of k for a second-order rate law.
- Write all three integrated rate laws and name the straight-line plot for each.
- State the first-order half-life expression and explain why it is constant only for first order.
- Explain why radioactive decay follows first-order kinetics.
- Define elementary reaction and molecularity, and explain why termolecular steps are rare.
- State the two requirements for a successful collision in the collision model.
- Explain how the Maxwell-Boltzmann distribution accounts for the temperature effect on rate.
- Sketch a reaction energy profile and label reactants, products, transition state, E_a , and ΔH .
- State the two conceptual claims of the Arrhenius equation.
- Distinguish a reaction intermediate from a catalyst.
- Explain when the slow step gives the rate law directly and when you need the pre-equilibrium approximation.
- Work the $\text{NO} + \text{Br}_2$ mechanism to its overall rate law.
- Explain how a catalyst changes an energy profile and what it leaves unchanged.
- Name three catalytic mechanisms and give an example of each.

Study this unit in Rycal. Drill the Kinetics flashcards, then test yourself with AP-style questions at rycal.web.app/apchem. If you have a test date, add it in the Test Planner. You can also start your next review with a Brain Dump, then check what you missed against this guide.

Key terms for this unit

Reaction rate, Factors affecting reaction rate, Rate law, Reaction order, Rate constant (k), Method of initial rates, First-order integrated rate law, Second-order integrated rate law, Zeroth-order integrated rate law, Half-life ($t_{1/2}$), Radioactive decay, Elementary reaction, Termolecular collisions, Collision model, Maxwell-Boltzmann distribution, Reaction energy profile, Transition state, Activation energy (E_a), Arrhenius equation (concept), Reaction mechanism, Reaction intermediate, Catalyst (mechanism role), Rate-limiting (slow) step, Molecularity, Pre-equilibrium approximation, Multistep reaction energy profile, Catalyst (function), Enzymes, Acid-base catalysis, Surface catalysis.

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