

Mechanisms, catalysts and activation energy

AP Chemistry · Lesson

Quick answer: A reaction mechanism is a sequence of elementary steps whose sum is the overall equation. The slowest step sets the rate law. A catalyst opens an alternative mechanism with lower activation energy and is restored, whereas an intermediate is made and then used up. Energy profiles show peaks (transition states), valleys (intermediates), E_a and ΔH .

Level: AP Chemistry · **Curriculum:** AP Chem Unit 5

What is a reaction mechanism?

Most reactions do not happen in one collision. A mechanism is the sequence of simple steps by which reactants become products. Each step is called an elementary step, and for an elementary step, and only for it, the rate law can be written straight from the coefficients.

Definition

An **elementary step** is a single molecular event. Its **molecularity** is the number of particles that collide in it: unimolecular (1), bimolecular (2), termolecular (3, rare). An **intermediate** is formed in one step and used up in a later one, so it is absent from the overall equation.

Elementary step	Molecularity	Rate law
$A \rightarrow \text{products}$	Unimolecular	$\text{rate} = k[A]$
$A + B \rightarrow \text{products}$	Bimolecular	$\text{rate} = k[A][B]$
$2 A \rightarrow \text{products}$	Bimolecular	$\text{rate} = k[A]^2$

How does the slow step set the rate law?

In a chain of steps, the slowest one is the rate-determining step, like the narrowest door in a corridor. The rate of the overall reaction equals the rate of that step. A proposed mechanism is acceptable only if its steps add up to the overall equation and its predicted rate law matches experiment.

Worked example 1

Kofi in Accra studies $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ and finds $\text{rate} = k[\text{NO}_2]^2$. A proposed mechanism is: step 1 (slow) $2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; step 2 (fast) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$. Add the steps: $2 \text{NO}_2 + \text{NO}_3 + \text{CO} \rightarrow \text{NO}_3 + \text{NO} + \text{NO}_2 + \text{CO}_2$. Cancel NO_3 (intermediate) and one NO_2 : $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ ✓.

The slow step is bimolecular in NO_2 , so $\text{rate} = k_1[\text{NO}_2]^2$ — **it matches the experiment**. CO does not appear because it reacts after the slow step.

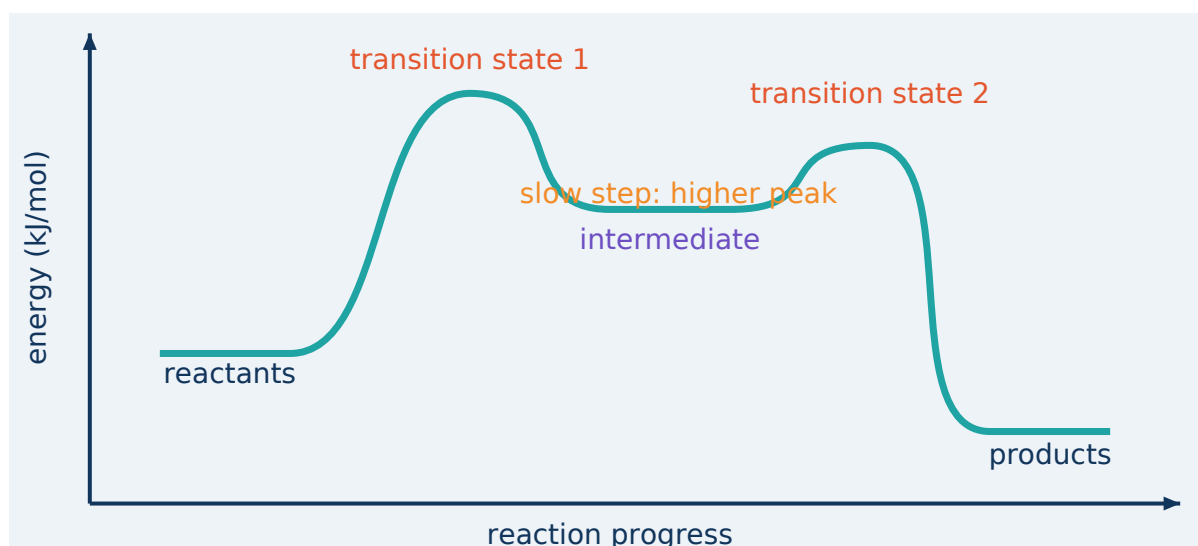
If the slow step contains an intermediate, replace it using a fast step that comes before it. When the first step is fast and reversible, it reaches equilibrium, so $= K \times$.

Worked example 2

For $2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$, step 1 is a fast equilibrium: $2 \text{ NO} \rightleftharpoons \text{N}_2\text{O}_2$ (equilibrium constant K).

Step 2 is slow: $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2 \text{ NO}_2$ (k_2).

Rate $= k_2[\text{N}_2\text{O}_2][\text{O}_2]$. Since $[\text{N}_2\text{O}_2] = K[\text{NO}]^2$, rate $= k_2K[\text{NO}]^2[\text{O}_2] = k[\text{NO}]^2[\text{O}_2]$, with $k = k_2K$. The rate law is third order overall.



A two-step mechanism has two peaks and one valley; the higher peak belongs to the rate-determining step.

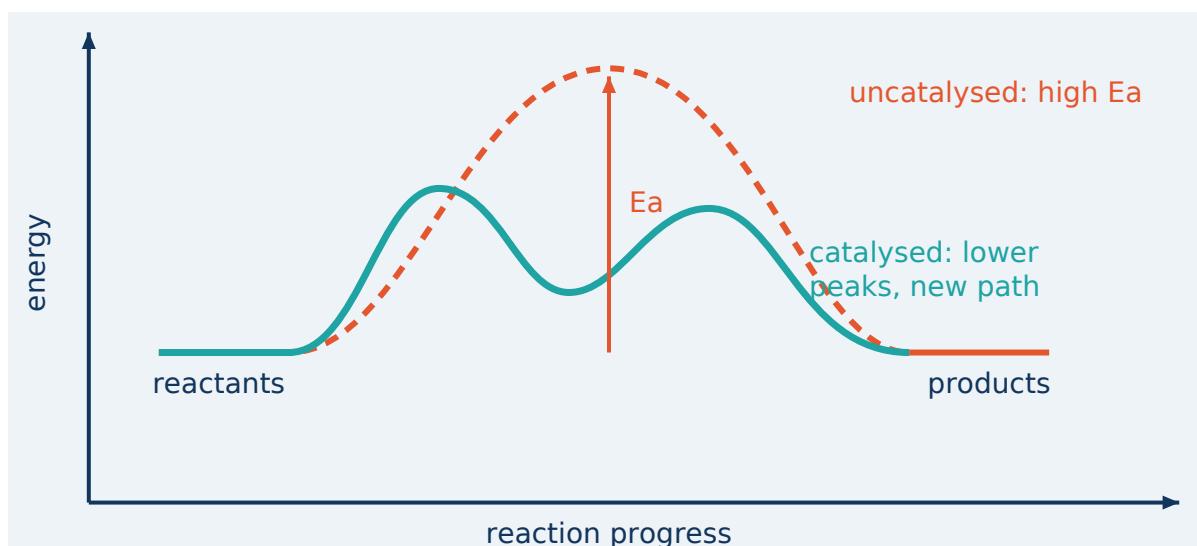
What does an energy profile show?

An energy profile plots potential energy against progress of the reaction. Each peak is a transition state, each valley an intermediate. The activation energy E_a is the climb from the reactants to a peak. The overall enthalpy change ΔH is the difference between products and reactants. The step with the highest peak above its starting level is normally the slow one.

How does a catalyst speed up a reaction?

A catalyst provides a different mechanism with a lower activation energy and is restored at the end. It speeds up the forward and reverse reactions equally, so it does not change ΔH or the equilibrium position.

Feature	Catalyst	Intermediate
First appears	Reactant side (consumed early)	Product side of an early step
Fate	Restored in a later step	Used up in a later step
In the overall equation?	No (cancels)	No (cancels)
Effect	Lowers E_a	None by itself



A catalyst gives a different route with lower peaks. The reactants, products and ΔH stay the same.

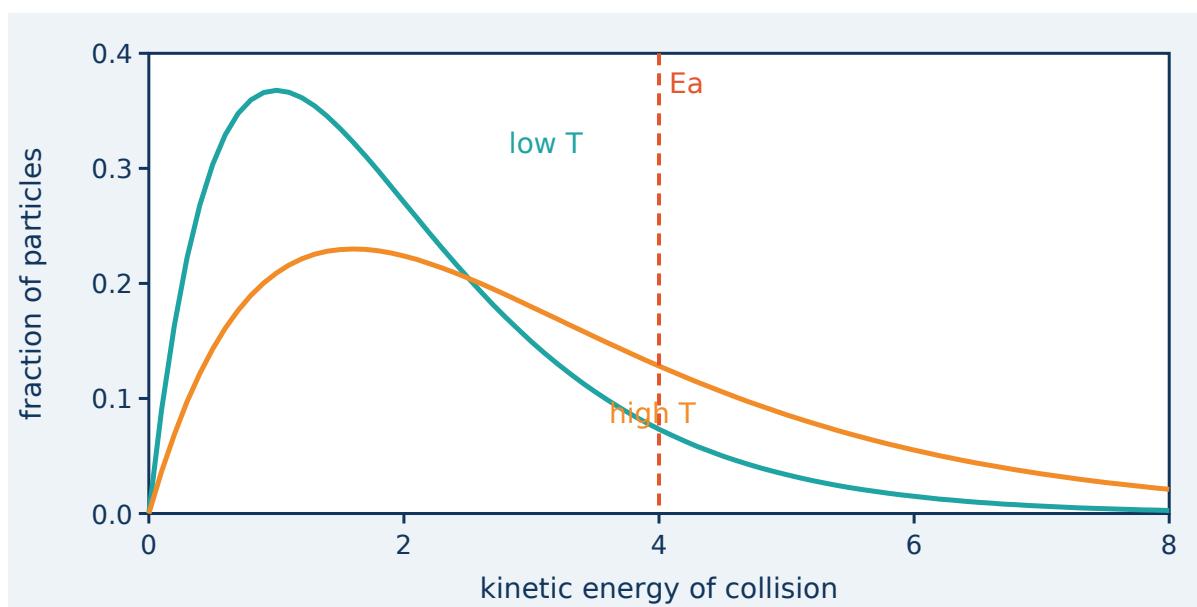
Common mistake

A catalyst does not make a reaction “more favourable” and does not shift the equilibrium. It does not lower the energy of the products. Also remember that a catalyst is consumed in one step and re-formed in another, while an intermediate is formed and then consumed; both cancel in the overall equation, so you need the mechanism to tell them apart.

How are rate constant, temperature and activation energy linked?

Arrhenius equation

$k = Ae^{-E_a/RT}$, so $\ln k = \ln A - E_a/(RT)$. For two temperatures: $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$. E_a in J/mol, $R = 8.314$ J/(mol K), T in kelvin, A = frequency factor.



At the higher temperature more collisions have energy of at least E_a , so k is larger.

Worked example 3

Emma in Leeds measures $k = 1.0 \times 10^{-3} \text{ s}^{-1}$ at 300 K and $4.0 \times 10^{-3} \text{ s}^{-1}$ at 320 K. Find E_a .
 $\ln 4.0 = 1.386$; $1/300 - 1/320 = 2.083 \times 10^{-4} \text{ K}^{-1}$.

$$E_a = 8.314 \times 1.386 / (2.083 \times 10^{-4}) = 5.53 \times 10^4 \text{ J/mol} = \mathbf{55 \text{ kJ/mol}}.$$

A catalyst that lowered E_a by 15 kJ/mol at 300 K would raise k by $e^{15000/(8.314 \times 300)} = e^{6.01} \approx \mathbf{4 \times 10^2}$, if A is unchanged.

Lina's tip

To tell a catalyst from an intermediate, add the steps and cross out what appears on both sides. A species that is on the left of the first step it enters and returns on the right later is the catalyst; a species born first and spent later is the intermediate.

Key points to remember

- Elementary step rate law = coefficients as exponents; overall reactions need experiments.
- The slowest step is rate-determining; the mechanism must add up to the overall equation.
- Catalyst: lowers E_a , restored, unchanged ΔH and equilibrium; intermediate: formed then consumed.
- Arrhenius: $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$, with $R = 8.314 \text{ J/(mol K)}$.
- Raising temperature increases the fraction of collisions with energy $\geq E_a$.

Mechanisms, catalysts and activation energy: frequently asked questions

How do you know which step is rate-determining?

It is the slowest step, usually the one with the largest activation energy. The experimental rate law helps: the slow step must produce the same concentration terms.

Can an intermediate appear in the rate law?

Not in the final rate law, because intermediates cannot be measured easily. Replace them using an earlier fast equilibrium so that only reactants and catalysts remain.

Does a catalyst change the equilibrium constant?

No. It lowers the activation energy in both directions by the same amount, so equilibrium is reached sooner but at the same position.

What is the difference between a transition state and an intermediate?

A transition state is the peak of the profile and cannot be isolated. An intermediate sits in a valley between two peaks and may live long enough to be detected.

Why does a small rise in temperature increase the rate so much?

The fraction of collisions with energy at least E_a grows exponentially with temperature. For

many reactions, 10 °C raises the rate by roughly two or three times.