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Topic 5.7: Introduction to Reaction Mechanisms

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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A Mechanism Is a Sequence of Elementary Steps

The overall equation of a reaction shows only the net change: which species are consumed and which are produced. It says nothing about the route between the two.

A reaction mechanism is the sequence of elementary steps by which the reaction actually happens. Each step is one molecular event (Topic 5.4), and the steps occur one after another.

The steps are chained: the products of one step are the reactants of the next.

A mechanism cannot be read off the overall equation: it is a proposed pathway built from evidence, and two different mechanisms can share one overall equation.

Adding the Steps: Recovering the Overall Equation

Write the steps one below another and add them, all left sides together and all right sides together. Any species appearing on both sides cancels, exactly as in algebra.

What survives the cancellation is the overall equation: only the net reactants and the net products.

Sometimes a step must first be multiplied through by a whole number, so the amount of a species produced in one step matches the amount consumed in another and the cancellation comes out exact.

No intermediate and no catalyst ever appears in the result: whatever cancelled was never a net reactant or a net product.

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Intermediates: Produced First, Consumed Later

An intermediate is a species formed in one step of a mechanism and consumed in a later step, existing only while the reaction runs.

Because it is made and then used up inside the sequence, it cancels when the steps are added and never appears in the overall equation.

Its concentration follows a fixed pattern: it starts at zero, rises while the step that makes it runs ahead, then falls as the consuming step catches up, returning to zero by the end.

On an energy profile, an intermediate sits in a valley between two peaks, at a local energy minimum (Topic 5.6). It is a real species, so it can sometimes be detected during the reaction.

Catalysts: Consumed First, Regenerated Later

A catalyst takes part in the mechanism but is not used up overall: it is consumed in an early step and regenerated in a later step.

It cancels on addition just as an intermediate does, so it never appears in the overall equation either.

The order of its appearances is the reverse of an intermediate's: used first, remade later. That order, not the species, decides which label applies.

Its amount is unchanged by the reaction: all present at the start, it dips while tied up inside the sequence and is fully restored by the end.

Transition States Belong to Steps

Every elementary step passes through exactly one transition state, its energy maximum. A two-step mechanism therefore has two transition states, a three-step mechanism three.

On the energy profile, each step contributes one peak, and between two peaks sits one valley, holding the intermediate formed by the first step and consumed by the second.

A transition state is not a species: it is a fleeting arrangement of atoms at a peak, so it cannot be isolated or detected as a substance, and never appears in any step's equation.

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Judging a Proposed Mechanism

A proposed mechanism must pass two tests. First, its steps must add up to the overall equation, every intermediate and catalyst cancelling.

Second, it must agree with the experimental evidence, above all the measured rate law. The overall rate is governed by the slowest step, so the rate law reflects that step and can never be read from the coefficients of the overall equation.

Each step must also be plausible as a single event: steps of one or two particles are routine, three-particle steps are extremely rare, and four particles arriving together is treated as impossible.

Passing every test supports a mechanism but never proves it, because another sequence might fit the same evidence. Failing any one test rejects it outright.

Worked Examples

Example 1: Adding two steps. Step 1: NO + Br_2 → $NOBr_2$. Step 2: $NOBr_2$ + NO → 2NOBr. Adding gives 2NO + Br_2 + $NOBr_2$ on the left and $NOBr_2$ + 2NOBr on the right; $NOBr_2$ cancels, leaving the overall equation 2NO + Br_2 → 2NOBr. $NOBr_2$ is formed in step 1 and consumed in step 2, so it is the intermediate.

Example 2: One mechanism holding both special species. Hydrogen peroxide decomposes as $2H_2O_2 \rightarrow 2H_2O + O_2$, catalysed by iodide ions. Step 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$. Step 2: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$. Adding the steps cancels both IO^- and I^-. IO^- is made in step 1 and used in step 2: an intermediate, whose concentration rises from zero to a maximum of about 0.006 mol/L partway through, then falls back to zero. I^- is used in step 1 and remade in step 2: the catalyst, present at 0.100 mol/L at the start and still 0.100 mol/L at the end.

Example 3: When a step must run twice. Step 1: $X_2 \rightarrow 2X$. Step 2: $X + Y_2 \rightarrow XY_2$. Step 1 produces two X particles, but step 2 consumes one X per run, so step 2 must run twice for every one run of step 1. Doubling step 2 gives $2X + 2Y_2 \rightarrow 2XY_2$, and adding now cancels both X particles: the overall equation is $X_2 + 2Y_2 \rightarrow 2XY_2$, and X is the intermediate.

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Example 4: The species that comes back. Step 1: XY + Z → XZ + Y. Step 2: XZ + W → XZW. Step 3: Y + XZ_2 → XZ + YZ. XZ is produced in step 1 and consumed in step 2, which looks like an intermediate, but step 3 produces it again. In the sum, XZ is produced twice and consumed once, so one XZ survives on the right: the overall equation is XY + Z + W + XZ_2 → XZ + XZW + YZ, and XZ is a net product. Only Y is made once and used once, fully cancelled, so Y alone is the intermediate.

Traps That Cost Marks in Topic 5.7

Used first means catalyst, made first means intermediate. The two labels differ only in the order of appearance. Check where the species first appears: as a reactant, it is heading for catalyst; as a product, for intermediate.

A species in a step is not automatically an intermediate. If it is produced again in a later step after being consumed, part of it survives the cancellation and it is a net product, as XZ was in Example 4. Only a full cancellation makes an intermediate.

Reading the rate law from the overall equation. Writing rate = $k[O_3]^2$ for $2O_3 \rightarrow 3O_2$, from the coefficient 2, repeats the Topic 5.2 error. The overall equation is a sum of steps; the rate law comes from the slow step.

Counting a transition state as a species. Transition states belong to steps, one per step, and sit on peaks. Intermediates are species and sit in valleys. The two are never interchangeable.

A mechanism that sums correctly is proved. Summing correctly is necessary but not sufficient: the mechanism must also match the experimental rate law, and even then it is supported, not proved.

Leaving the intermediate in the overall equation. If a species was produced and later consumed, it cancels. An overall equation that still contains it has been added up wrongly.

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Key Relationships to Remember

- Mechanism: a sequence of elementary steps whose sum is the overall equation
- Adding steps: add all left sides and right sides, then cancel species appearing on both sides; a step may need multiplying first
- Intermediate: produced in one step, consumed in a later step; cancels, so absent from the overall equation; concentration rises, then falls to zero; sits in a valley on the energy profile
- Catalyst: consumed in an early step, regenerated in a later step; cancels, so absent from the overall equation; total amount unchanged at the end
- Transition state: one per elementary step; a peak on the energy profile; an arrangement of atoms, never a species in an equation
- Valid mechanism: steps sum to the overall equation AND agreement with experimental evidence such as the rate law; passing both supports but never proves it
- The overall rate law reflects the slowest step, never the coefficients of the overall equation

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