Topic 5.8: Reaction Mechanism and Rate Law

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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The Rate-Determining Step

The steps of a mechanism (Topic 5.7) do not all run at the same speed.

The slowest step is the bottleneck: nothing later in the sequence can happen faster than this step supplies it.

That slowest step is the rate-determining step. It alone sets the overall rate, and the overall rate law is built from it.

On an energy profile it carries the highest activation energy barrier, measured from the level just before its peak (Topic 5.6).

Steps after it are fast follow-ups. They cannot change the overall rate, so their reactants never appear in the overall rate law.

When the Slow Step Comes First

An elementary step's rate law is written from its own reactants, the order in each equal to its coefficient in the step (Topic 5.4).

If the slow step comes first, nothing before it can interfere: the overall rate law is simply its own law.

Every species in it is a starting reactant with a measurable concentration, so the law is complete as it stands, with the slow step's own constant.

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Why an Intermediate Cannot Appear in a Rate Law

A finished rate law may contain only species whose concentrations are known and measurable: the reactants placed in the vessel, and any catalyst added at the start.

An intermediate fails that test. It is made and consumed inside the mechanism, its concentration rises and falls during the run, and it cannot be measured directly or set in advance.

A rate law still containing an intermediate is therefore unfinished: correct for one step, not yet the overall law.

A catalyst is different: added at the start in a known amount, it may legitimately appear in an overall rate law when it is a reactant of the slow step.

A Fast Equilibrium Before the Slow Step

Often the slow step is not first: a fast reversible step runs before it and settles into a fast equilibrium while the slow step creeps behind it. This is a pre-equilibrium.

The slow step's law then contains an intermediate made by the fast step, and the intermediate is replaced using the equilibrium, in four moves.

Write the rate law of the slow step from its own reactants. Write the equilibrium constant expression of the fast step and rearrange it for the intermediate's concentration. Substitute. Then fold the equilibrium constant and the slow step's constant into a single overall k, leaving a finished law with only measurable species in it.

Its orders can differ from the slow step's own: an order can double when the equilibrium builds the intermediate from two particles, or become a fraction when it splits one particle into two.

When There Is No Fast Equilibrium

The substitution works only because the fast step is an equilibrium, holding the intermediate at a concentration fixed by the reactants.

If the step before the slow step is fast but effectively one-way, no equilibrium expression exists to substitute, and a law containing an intermediate cannot be simplified here. It needs the steady-state approximation of Topic 5.9.

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Judging a Mechanism Against Experiment

A proposed mechanism must pass two tests. First, its steps must add up to the overall equation (Topic 5.7).

Second, the rate law it predicts must match the experimental rate law: the same species, to the same powers.

If the predicted law disagrees, the mechanism is rejected, however neatly its steps sum.

If it agrees, the mechanism is consistent with the data: supported, not proved, since another mechanism may predict the same law and kinetics alone cannot choose between two that both fit.

Worked Examples

Example 1: Slow step first. The reaction $NO_2 + CO \rightarrow NO + CO_2$ is proposed to run in two steps. Step 1: $2NO_2 \rightarrow NO_3 + NO$ (slow). Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast). The slow step is first, so the overall rate law is its own law: rate = $k[NO_2]^2$. NO_3 is an intermediate, and CO, reacting only after the bottleneck, appears nowhere in the law. With k = 0.60 L mol^{-1} s^{-1} and $[NO_2]$ = 0.10 mol/L, the rate is $0.60 \times (0.10)^2 = 6.0 \times 10^{-3}$ mol L^{-1} s^{-1}.

Example 2: A fast equilibrium first. The oxidation $2NO + O_2 \rightarrow 2NO_2$ is proposed to run as: Step 1: $2NO \rightleftharpoons N_2O_2$ (fast equilibrium, constant K). Step 2: $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow, constant k_2). The slow step's law, rate = $k_2[N_2O_2][O_2]$, contains the intermediate N_2O_2. From step 1, $K = [N_2O_2]/[NO]^2$, so $[N_2O_2] = K[NO]^2$. Substituting gives rate = $k_2K[NO]^2[O_2] = k[NO]^2[O_2]$, with one constant $k = k_2K$. With K = 2.0 L/mol and $k_2 = 1.5 \times 10^3$ L mol^{-1} s^{-1}, $k = 3.0 \times 10^3$ L^2 mol^{-2} s^{-1}. Check: at [NO] = 0.020 mol/L, $[N_2O_2] = 8.0 \times 10^{-4}$ mol/L, and with $[O_2]$ = 0.010 mol/L both laws give a rate of 0.012 mol L^{-1} s^{-1}.

Example 3: Two mechanisms, one experimental law. For $H_2 + 2ICl \rightarrow I_2 + 2HCl$, experiment gives rate = $k[H_2][ICl]$. Mechanism I: Step 1: $H_2 + ICl \rightarrow HI + HCl$ (slow). Step 2: $HI + ICl \rightarrow I_2 + HCl$ (fast). Its slow step predicts rate = $k[H_2][ICl]$: a match, so Mechanism I is consistent. Mechanism II: Step 1: $2ICl \rightarrow I_2 + Cl_2$ (slow). Step 2: $H_2 + Cl_2 \rightarrow 2HCl$ (fast). Its steps sum to the same overall equation, but its slow step predicts rate = $k[ICl]^2$, which disagrees with experiment, so Mechanism II is rejected.

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Example 4: Slow step in the middle. The reaction $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ has experimental rate law rate = $k[NO]^2[H_2]$. Proposed mechanism: Step 1: $2NO \rightleftharpoons N_2O_2$ (fast equilibrium, K). Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow, k_2). Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast). Step 2 gives rate = $k_2[N_2O_2][H_2]$, and step 1 gives $[N_2O_2] = K[NO]^2$, so the predicted law is rate = $k[NO]^2[H_2]$, exactly the experimental law: consistent. The power of H_2 is 1, not 2, because only the H_2 reacting in the slow step affects the rate; the second H_2 reacts afterwards, in fast step 3. Check: with K = 0.50 L/mol, $k_2 = 2.0 \times 10^2$ L mol^{-1} s^{-1}, [NO] = 0.030 and $[H_2]$ = 0.020 mol/L, both laws give 1.8×10^{-3} mol L^{-1} s^{-1}.

Traps That Cost Marks in Topic 5.8

Reading the law from the overall equation. Overall coefficients are not orders. The equation $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ does not imply rate = $k[NO]^2[H_2]^2$: its measured law is rate = $k[NO]^2[H_2]$.

Handing in a law with an intermediate in it. rate = $k_2[N_2O_2][O_2]$ is the law of one step, not of the reaction. Until the intermediate is replaced by measurable reactants, the answer is unfinished.

Assuming the first step is rate-determining. The slow step can sit anywhere. Trust the (slow) label, or the highest barrier on the profile, not the position.

Letting later steps into the law. A reactant appearing only after the slow step, like CO in Example 1, has no effect on the overall rate and no place in the law.

Leaving two constants in the finished law. The finished law has one constant, k. The fast step's equilibrium constant is folded into it, $k = k_2K$, and does not survive as a separate factor.

Claiming a matching law proves the mechanism. A match makes a mechanism consistent with the data, nothing more: another mechanism may predict the same law.

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Key Relationships to Remember

- Rate-determining step: the slowest step of a mechanism, with the highest activation energy barrier; it alone sets the overall rate
- Slow step first: the overall rate law is the slow step's own law, orders equal to its coefficients
- A finished rate law contains only measurable species: reactants, and a catalyst added at the start; an intermediate must always be eliminated
- Pre-equilibrium: express the intermediate through the fast step's equilibrium constant, substitute into the slow step's law, and fold the constants into one k
- Orders can differ from the slow step's orders: they can rise, or become fractional, according to how the equilibrium forms the intermediate
- Judging a mechanism: the steps must sum to the overall equation AND the predicted rate law must match the experimental law; a match supports but never proves
- Steps after the rate-determining step have no effect on the rate law at all

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Topic 5.8 Worksheet

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