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Topic 5.10: Multistep Reaction Energy Profile

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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A Profile With More Than One Peak

Topic 5.6 covered a reaction in a single step: one climb, one peak, one fall. Most reactions take several elementary steps (Topic 5.7), and the profile climbs and falls once for each step.

Count the peaks to count the steps: each peak is the transition state of one elementary step. Between neighbouring peaks the curve dips into a valley, and each valley holds an intermediate, formed in one step and consumed in a later step.

A mechanism with n steps shows n peaks and n − 1 valleys, so n − 1 intermediates.

Every Step Has Its Own Barrier

Each step has its own activation energy, measured from the level that step starts from: E_a(step) = the step's peak minus the level before it.

Step 1 starts at the reactant level, step 2 at the first valley, step 3 at the second valley. A later barrier is never measured from the reactant level or from zero: it starts in neither place.

The absolute height of a peak is not its barrier. A peak can be the highest point on the diagram yet carry a small barrier, if the valley before it sits high. Only the climb counts. Each step also has its own ΔH: end level minus start level, with its sign.

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The Rate-Determining Step

The steps run one after another, so the slowest step limits the whole sequence: later steps cannot outrun the step that feeds them. The slowest step is the one with the largest activation energy, every barrier measured from its own starting level, and it is the rate-determining step.

It can be any step in the sequence: decide only after measuring every barrier from its own valley, never by which peak stands tallest.

Overall ΔH and the Step ΔH Values

Overall ΔH is read exactly as in Topic 5.6: products minus reactants, endpoints only. No peak or valley plays any part in it.

The step ΔH values add up to the overall ΔH: each step's rise or fall is part of the journey, so the signed steps must sum to the signed whole. Use it as a check on profile arithmetic.

Classification comes from the endpoints alone. Products below reactants means exothermic, whatever the peaks do; products above means endothermic; products level with reactants means ΔH = 0 overall. Two mechanisms for the same reaction still give the same overall ΔH: they share the same endpoints.

Matching a Profile to a Proposed Mechanism

A mechanism and a profile must agree, and the first test is counting: the mechanism's steps must equal the profile's peaks. A two-step proposal cannot describe a three-peak profile: it is missing a step.

The second test is the intermediates: the valleys must match the mechanism's intermediates in number. Take ozone decomposition: step 1, $O_3 \rightarrow O_2 + O$; step 2, $O + O_3 \rightarrow 2O_2$. The steps sum to $2O_3 \rightarrow 3O_2$, with O as the one intermediate, so its profile must show exactly two peaks and one valley.

Matching counts makes a mechanism consistent, not proven: the experimental rate law (Topic 5.8) is the evidence that supports or rejects it.

Catalysed Multistep Profiles

A catalyst provides an alternative pathway: a new curve over the same endpoints, with the reactant and product levels unmoved and overall ΔH unchanged.

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The catalysed peaks are lower, and the pathway may have a different number of steps and different intermediates; only the endpoints and ΔH are shared. The catalysed route is faster because its tallest barrier is lower than the uncatalysed rate-determining barrier.

Worked Examples

Example 1: A three-step profile. Reactants 40, first peak 130, first valley 90, second peak 210, second valley 150, third peak 190, products 20 kJ/mol. Three peaks mean three steps; the two valleys hold two intermediates, at 90 and 150 kJ/mol. Step barriers: 130 − 40 = 90, 210 − 90 = 120, and 190 − 150 = 40 kJ/mol. Step 2 has the largest barrier, so it is rate-determining. The third peak stands below the second, yet its barrier is the smallest. Step ΔH values: +50, +60 and −130 kJ/mol, summing to −20 kJ/mol, which matches overall ΔH = 20 − 40 = −20 kJ/mol: exothermic overall.

Example 2: The highest peak is not the bottleneck. Reactants 100, first peak 230, valley 170, second peak 250, products 60 kJ/mol. The step 1 barrier is 230 − 100 = 130 kJ/mol. The step 2 barrier, measured from the valley, is 250 − 170 = 80 kJ/mol. The second peak is the highest point on the diagram, but step 1, with the taller climb, is rate-determining. Step ΔH values are +70 and −110 kJ/mol, summing to the overall ΔH of −40 kJ/mol.

Example 3: Matching a mechanism to its profile. A proposed mechanism runs: step 1, $X_2 \rightarrow 2X$; step 2, $X + Y_2 \rightarrow XY + Y$; step 3, $X + Y \rightarrow XY$. Adding the steps and cancelling species on both sides gives the overall equation $X_2 + Y_2 \rightarrow 2XY$. The intermediates are X, formed in step 1 and consumed in steps 2 and 3, and Y, formed in step 2 and consumed in step 3. The profile reads: reactants 60, first peak 150, first valley 100, second peak 210, second valley 130, third peak 170, products 40 kJ/mol: three peaks, two valleys, as required. The barriers are 90, 110 and 40 kJ/mol, so step 2 is rate-determining. The step ΔH values are +40, +30 and −90 kJ/mol, summing to the overall ΔH of −20 kJ/mol: exothermic overall.

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Example 4: A catalysed two-step reaction. Uncatalysed: reactants 80, first peak 200, valley 140, second peak 240, products 50 kJ/mol. The barriers are 120 and 100 kJ/mol, so step 1 is rate-determining, and overall ΔH = 50 − 80 = −30 kJ/mol. With a catalyst: reactants 80, first peak 150, first valley 110, second peak 170, second valley 120, third peak 160, products 50 kJ/mol. The catalysed route has three steps, not two, with barriers of 70, 60 and 40 kJ/mol. Its step ΔH values, +30, +10 and −70 kJ/mol, still sum to −30 kJ/mol: the endpoints never moved. The largest barrier has fallen from 120 to 70 kJ/mol.

Traps That Cost Marks in Topic 5.10

Measuring every barrier from the reactants. Only step 1 starts there. Each later step starts at its own valley, and its barrier is the climb from that valley.

Calling the tallest peak the rate-determining step. Peak height is an absolute energy; a barrier is a climb. A step under the highest peak can carry a smaller barrier than one under a lower peak.

Adding the activation energies to get ΔH. The sum of the step barriers has no physical meaning. ΔH comes from the endpoints only; it is the step ΔH values that sum to it.

Reading a valley as a product or a transition state. A valley species is an intermediate: formed in one step, consumed in a later one, absent from the overall equation. Peaks hold transition states.

Counting the steps from the overall equation. The balanced equation shows only the net change. A simple equation can hide a three-step mechanism; count peaks, not molecules.

Assuming step 1 is always rate-determining. Any step can carry the largest barrier. Measure all of them from their own starting levels before deciding.

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Key Relationships to Remember

- Number of peaks = number of elementary steps; number of valleys = steps − 1 = number of intermediates
- Top of each peak = the transition state of that step; each valley = an intermediate, formed in one step and consumed in a later step
- E_a(step) = the step's peak − the level before it: reactants for step 1, the preceding valley for later steps
- Rate-determining step = the step with the largest barrier from its own starting level; it can be any step
- ΔH(step) = the level after the step − the level before it; the step ΔH values sum exactly to the overall ΔH
- Overall ΔH = products − reactants: endpoints only, identical for every mechanism of the same reaction
- E_a(reverse) for one step = E_a(forward) for that step − ΔH for that step
- Catalysed profile: same endpoints and ΔH, lower peaks, possibly a different step count, largest barrier below the uncatalysed rate-determining barrier

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