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Topic 5.6: Reaction Energy Profile

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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The Reaction Coordinate Diagram

A reaction energy profile plots potential energy on the vertical axis, in kJ/mol, against reaction progress on the horizontal axis, the reaction coordinate. The horizontal axis is not time: it tracks how far the rearrangement of atoms has advanced.

The curve begins on a flat level at the energy of the reactants, climbs to a peak, then falls to a flat level at the energy of the products. Every value you need is a difference between two of these three numbers: the two levels and the peak.

The Peak: Transition State and Activated Complex

The highest point of the curve is the transition state. The atomic arrangement at that instant, old bonds partly broken and new bonds partly formed, is the activated complex.

The transition state is an energy maximum, not a substance. It cannot be isolated and exists only for the instant of the rearrangement before the atoms fall back to reactants or forward to products. It is the least stable arrangement on the pathway.

Reading Activation Energy and ΔH

Activation energy. E_a is the climb from the reactant level to the peak: E_a = peak energy minus reactant energy. It is never measured from zero, and never from the product level.

A large E_a means only a small fraction of collisions can cross, so the reaction is slow; a small E_a means the opposite.

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Enthalpy change. ΔH is products minus reactants: the difference between the two flat levels, taken with its sign. The peak plays no part in it. If the products sit lower, ΔH is negative and the reaction is exothermic; if the products sit higher, ΔH is positive and the reaction is endothermic.

Because ΔH depends only on the start and end levels, no feature of the pathway can change it: not the peak height, not the number of steps, not any catalyst.

Exothermic and Endothermic Profiles

An exothermic profile, such as methane combustion, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, ends below where it started. The drop from reactants to products is the energy released to the surroundings.

The size of the drop says nothing about the height of the climb: combustion releases a great deal of energy yet still needs a spark, because the climb must be made before any of the drop can happen.

An endothermic profile, such as the decomposition $CaCO_3 \rightarrow CaO + CO_2$, ends above where it started, because the products hold more energy than the reactants. The curve falls from the peak only partway.

A built-in check follows: for an endothermic reaction E_a is always larger than ΔH, because the peak must stand above the product level as well as above the reactants. If your numbers break this rule, one was misread.

Reading the Profile Backwards: The Reverse Reaction

The same profile read from right to left is the reverse reaction. The products become the starting level, the peak stays at the same energy, and the reverse activation energy is the climb from the product level to that same peak: E_a(reverse) = peak minus products.

The three values obey one identity: $E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H$. Given any two of the three numbers, the third follows at once.

So the reverse of an exothermic reaction is endothermic, with the larger activation energy, because its climb starts from the lower level yet must reach the same peak. Its ΔH is equal in size and opposite in sign to the forward ΔH.

Two Peaks: Intermediates and Steps

Some profiles show two peaks with a valley between them. Each peak is the transition state of one elementary step, so two peaks mean a two-step mechanism.

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The valley is a local energy minimum, and it holds an intermediate: a real species formed in the first step and consumed in the second. An intermediate is more stable than the transition states beside it and can sometimes be detected.

Each step has its own activation energy, measured from the level that step starts from: the reactant level for step 1, the valley for step 2. The step with the tallest barrier is crossed most slowly, so it limits the overall rate: it is the rate-determining step.

Catalysts and Temperature on the Diagram

A catalyst provides an alternative pathway, drawn as a second curve over the same endpoints with a lower peak. The reactant and product levels do not move, so ΔH is unchanged.

Both activation energies fall, because both climbs now end at the lower peak, so the catalyst speeds up both directions. The catalysed route may pass through a different transition state, and even a different number of steps; only the start, the end and ΔH are shared.

Temperature changes none of the labelled energies: the levels, the peak and ΔH are fixed by the reaction and its pathway. Heating instead changes how many particles can cross the unchanged barrier, which is why the rate rises while the diagram stays identical.

Worked Examples

Example 1: An exothermic profile. Reactants 120, peak 200, products 40 kJ/mol. E_a(forward) = 200 − 120 = 80 kJ/mol. ΔH = 40 − 120 = −80 kJ/mol: exothermic. E_a(reverse) = 200 − 40 = 160 kJ/mol. Check with the identity: 80 − (−80) = 160 kJ/mol. The reverse reaction is endothermic and faces twice the barrier.

Example 2: An endothermic profile. Reactants 30, peak 110, products 90 kJ/mol. E_a(forward) = 110 − 30 = 80 kJ/mol. ΔH = 90 − 30 = +60 kJ/mol, so the reaction is endothermic, and E_a exceeds ΔH as it must. E_a(reverse) = 110 − 90 = 20 kJ/mol. Check: 80 − 60 = 20 kJ/mol. The reverse reaction is exothermic and runs over a small barrier.

Example 3: Adding a catalyst. On the Example 1 profile, a catalyst draws a new peak at 160 kJ/mol. The catalysed E_a(forward) = 160 − 120 = 40 kJ/mol, half the original barrier. The catalysed E_a(reverse) = 160 − 40 = 120 kJ/mol. ΔH is still 40 − 120 = −80 kJ/mol: the endpoints never moved.

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Example 4: A two-peak profile. Reactants 50, first peak 120, valley 80, second peak 190, products 30 kJ/mol. The step 1 barrier = 120 − 50 = 70 kJ/mol. The step 2 barrier = 190 − 80 = 110 kJ/mol, measured from the valley, not from the reactants. Step 2 has the tallest barrier, so it is rate-determining. The intermediate sits at 80 kJ/mol, and overall ΔH = 30 − 50 = −20 kJ/mol, exothermic.

Traps That Cost Marks in Topic 5.6

E_a is the height of the peak. It is the climb from the reactant level: a peak at 200 kJ/mol with reactants at 120 kJ/mol gives E_a = 80 kJ/mol, not 200 kJ/mol.

ΔH depends on the peak. ΔH uses the two flat levels only. A taller or shorter peak, and any number of steps in between, leave ΔH unchanged.

A catalyst makes ΔH more negative. It never does. A catalyst lowers the peak only; reactants and products keep their energies, so ΔH is identical on both pathways.

An intermediate is a kind of transition state. Peaks are transition states; valleys are intermediates. The transition state cannot be isolated; an intermediate is a real species resting at a local minimum.

The reverse reaction has the same E_a as the forward reaction. The reverse barrier is measured from the product level to the same peak, so it differs from the forward barrier by exactly ΔH.

Heating redraws the diagram. Temperature moves no level and no peak. It changes the fraction of particles able to cross the barrier, not the barrier itself.

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Key Relationships to Remember

- E_a(forward) = peak energy − reactant energy
- ΔH = product energy − reactant energy: negative for exothermic, positive for endothermic, and independent of the pathway
- E_a(reverse) = peak energy − product energy = E_a(forward) − ΔH
- Peak = transition state, or activated complex: an energy maximum that cannot be isolated
- Valley between two peaks = intermediate: a real species at a local energy minimum, formed in one step and consumed in the next
- Two peaks = two elementary steps; the step with the tallest barrier, measured from its own starting level, is rate-determining
- Catalyst: a lower peak over unchanged endpoints, so both activation energies fall and ΔH stays the same
- Temperature changes no labelled energy on the profile; it changes how many particles cross the barrier

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Topic 5.6 Quiz: Reaction Energy Profile

Topic 5.6 Worksheet

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