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Topic 6.2: Energy Diagrams

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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What an Energy Diagram Shows

An energy diagram plots potential energy on the vertical axis, in kJ/mol, against reaction progress on the horizontal axis, also called the reaction coordinate. That axis is not time: it tracks the rearrangement itself as reactants turn into products.

The curve starts on a flat level at the reactants' energy, climbs to a peak, then falls to a flat level at the products' energy. Three numbers carry everything the diagram can tell you: the reactant level, the peak, and the product level. Every value is a difference between two of them, in kJ per mole of reaction as written.

Reading ΔH From the Two Levels

Enthalpy change is read from the two flat levels only, always from the system's point of view.

$\Delta H = H(\text{products}) - H(\text{reactants})$

Products below reactants give a negative difference: the system lost enthalpy, heat flowed to the surroundings, exothermic. Products above reactants give a positive difference: the system gained enthalpy, heat flowed in, endothermic.

The vertical gap between the levels is ΔH itself, taken with its sign. The peak plays no part in ΔH: the gap stays the same, because ΔH is fixed by the reactants and products, never by the pathway between them.

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The Peak, the Barrier and the Rate

The peak is the transition state: the highest-energy arrangement along the pathway, where old bonds are partly broken and new bonds are partly formed. The arrangement itself, the activated complex, exists only at that maximum: it is not a substance, cannot be isolated or stored, and is the least stable arrangement on the route.

Activation energy, E_a, is the climb from the reactant level up to the peak.

E_a = peak energy − reactant energy

It is never measured from zero, and never from the product level.

A tall barrier means few particles can cross, so the reaction is slow; a low barrier means many can cross, so it is fast. E_a and ΔH are independent: one measures the hill, the other where products finish relative to reactants. A reaction can have a small barrier and a huge ΔH, or the reverse.

Exothermic and Endothermic Shapes Compared

An exothermic diagram finishes downhill.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Methane combustion ends far below where it starts, and the size of the drop is the heat released. The drop says nothing about the climb: combustion still needs a spark, because the climb must be made before any of the drop can be collected.

An endothermic diagram finishes uphill.

$CaCO_3 \rightarrow CaO + CO_2$

The decomposition ends above where it starts, because the products hold more enthalpy than the reactants, and the curve falls from the peak only partway.

The peak always stands above both flat levels. A check follows for endothermic reactions: E_a must exceed ΔH, because the peak stands above the product level too.

Reading the Diagram Backwards

The same diagram read from right to left is the reverse reaction. The product level becomes the starting level, the peak stays at exactly the same energy, and only the climbs change. The reverse activation energy is the climb from the product level to that same peak.

E_a(reverse) = peak energy − product energy

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The three values obey one identity.

E_a(reverse) = E_a(forward) − ΔH

So any two give the third at once. The reverse ΔH is equal in size and opposite in sign, so the reverse of an exothermic reaction is endothermic and faces the larger barrier: its climb starts lower yet must reach the same peak.

Catalysts and Two Peaks on the Same Diagram

A catalyst provides an alternative pathway with a lower peak, drawn as a second curve between the same reactant and product levels. Because the endpoints do not move, ΔH is identical on both pathways, and both activation energies fall by the size of the peak drop, so the catalyst speeds up both directions together. Only a catalyst redraws the diagram this way: heating and changing concentration change no level and no peak.

A diagram with two peaks shows a two-step mechanism. Each peak is one step's transition state, and the valley between them is a local minimum holding an intermediate, a real species formed in the first step and consumed in the second.

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 largest barrier, measured that way, is the slowest, the rate-determining step. The tallest peak is not automatically that step, because a later barrier is measured from its valley. Step ΔH values add up exactly to the overall ΔH.

Worked Examples

> **Example 1: The standard reading. Reactants at 50 kJ/mol, peak at 120 kJ/mol, products at 30 kJ/mol. E_a(forward) = 120 − 50 = 70 kJ/mol. ΔH = 30 − 50 = −20 kJ/mol, from the system's point of view: exothermic, and the surroundings gain 20 kJ per mole. E_a(reverse) = 120 − 30 = 90 kJ/mol. Check: 70 − (−20) = 90 kJ/mol.**

> **Example 2: An endothermic diagram. Reactants at 40 kJ/mol, peak at 150 kJ/mol, products at 110 kJ/mol. E_a(forward) = 150 − 40 = 110 kJ/mol. ΔH = 110 − 40 = +70 kJ/mol: endothermic, and E_a exceeds ΔH as it must. E_a(reverse) = 150 − 110 = 40 kJ/mol. Check: 110 − 70 = 40 kJ/mol.**

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Example 3: Adding a catalyst to Example 1. The catalyst draws a new peak at 90 kJ/mol over the same endpoints. Catalysed E_a(forward) = 90 − 50 = 40 kJ/mol, and E_a(reverse) = 90 − 30 = 60 kJ/mol: both barriers have fallen by exactly the 30 kJ/mol peak drop. ΔH is still −20 kJ/mol: the catalyst changed the route, not the endpoints.

Example 4: A two-peak diagram. Reactants at 60 kJ/mol, first peak at 140 kJ/mol, valley at 90 kJ/mol, second peak at 180 kJ/mol, products at 40 kJ/mol. Step 1 barrier = 140 − 60 = 80 kJ/mol, step 1 ΔH = 90 − 60 = +30 kJ/mol. Step 2 barrier = 180 − 90 = 90 kJ/mol, measured from the valley, step 2 ΔH = 40 − 90 = −50 kJ/mol. Step 2 has the largest barrier, so it is rate-determining. Overall ΔH = 40 − 60 = −20 kJ/mol, and the step values check: +30 + (−50) = −20 kJ/mol.

Traps That Cost Marks in Topic 6.2

"E_a is the height of the peak." E_a is the climb from the reactant level. A peak at 120 kJ/mol with reactants at 50 kJ/mol gives E_a = 70 kJ/mol, not 120 kJ/mol.

"The peak is the intermediate." Peaks are transition states; intermediates sit in valleys between peaks. The activated complex at a peak cannot be isolated; an intermediate is a real species resting at a local minimum.

"A catalyst makes ΔH smaller, and a lower E_a means a more exothermic reaction." A catalyst moves only the peak, so both pathways have exactly the same ΔH. Barrier and enthalpy gap are independent: a lower E_a means a faster reaction, and says nothing about heat released.

"The horizontal axis is time, and heating lowers the peak." The axis is reaction progress, and temperature moves no level and no peak: it increases the fraction of particles able to cross the unchanged barrier, so the rate rises while the diagram stays identical.

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Key Relationships to Remember

- Vertical axis: potential energy in kJ/mol; horizontal axis: reaction progress (the reaction coordinate), not time
- ΔH = product level − reactant level, from the system's point of view: negative and exothermic when products sit lower, positive and endothermic when higher
- E_a(forward) = peak − reactants; E_a(reverse) = peak − products = E_a(forward) − ΔH
- Peak = transition state, or activated complex: partial bonds, maximum energy, cannot be isolated
- ΔH depends only on the endpoint levels, never on the peak, the number of steps, or any catalyst
- Catalyst: a lower peak over unchanged endpoints, so both activation energies fall and ΔH stays the same
- Two peaks = two elementary steps; the valley holds an intermediate; each barrier is measured from the level before its peak, and step ΔH values sum to the overall ΔH

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