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Topic 6.2: Energy Diagrams

Worksheet · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the parts of the diagram and the two readings taken from it. Section B practises the skills: reading full diagrams, reverse barriers, catalysed pathways, two-peak diagrams, sketching from data, and comparing two reactions. Section C is exam style: judging claims, reconstructing a diagram from two values, and a full two-step analysis.

Reference facts. All values are in kJ/mol and every ΔH is reported from the system's point of view. ΔH = product level − reactant level. E_a(forward) = peak − reactants. E_a(reverse) = peak − products = E_a(forward) − ΔH. A catalyst lowers the peak only: the reactant and product levels, and therefore ΔH, do not move.

Three habits protect every answer. Subtract levels, never read a value straight off the axis from zero. Measure every barrier from the level that step starts from. And check reverse barriers with the identity E_a(reverse) = E_a(forward) − ΔH before you finish.

Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) State what the vertical axis of an energy diagram shows, with its units. (b) State what the horizontal axis shows, and state what it does not show. (c) State the three levels or points whose energies carry every value on a one-step diagram. (d) State where reactants and products sit on the diagram, left or right.

A2. (a) Write the formula for ΔH in terms of the reactant and product levels. (b) Write the formula for E_a(forward) in terms of the reactant level and the peak. (c) Write the formula for E_a(reverse), and the identity connecting E_a(reverse), E_a(forward) and ΔH. (d) State what the peak represents, and the name of the atomic arrangement at the peak. (e) State two properties of that arrangement.

A3. For each description, state whether the reaction is exothermic or endothermic, and state the sign of ΔH from the system's point of view. (a) Products sit 60 kJ/mol below the reactants. (b) Products sit 25 kJ/mol above the reactants. (c) The curve finishes at exactly the level it started. (d) The system absorbs heat from the surroundings as it reacts. (e) The surroundings warm up as the reaction runs.

A4. (a) State what a catalyst does to the peak of an energy diagram. (b) State what a catalyst does to the reactant level, the product level and ΔH. (c) State what happens to E_a(forward) and E_a(reverse) when a catalyst lowers the peak by 30 kJ/mol. (d) State whether heating the reaction or doubling a concentration redraws the diagram, and explain your answer in one sentence each.

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A5. (a) A diagram shows two peaks. State how many elementary steps the reaction has, and what the valley between the peaks holds. (b) State how the activation energy of the second step is measured. (c) State which step is the rate-determining step. (d) A student says the tallest peak on a two-peak diagram is always the rate-determining step. State whether this is always true, and explain in one sentence.

Section B: Core Practice

B1. Profile P: reactants at 80 kJ/mol, peak at 210 kJ/mol, products at 20 kJ/mol. (a) Calculate E_a(forward), showing the subtraction. (b) Calculate ΔH, showing the subtraction, and classify the reaction. (c) State how much heat is transferred per mole, and in which direction. (d) Calculate E_a(reverse) directly from the levels. (e) Check your part (d) value with the identity.

B2. Profile Q: reactants at 20 kJ/mol, peak at 140 kJ/mol, products at 95 kJ/mol. (a) Calculate E_a(forward). (b) Calculate ΔH and classify the reaction. (c) Apply the built-in endothermic check: state what E_a must exceed, and confirm it does. (d) Calculate E_a(reverse) by both routes. (e) State which direction, forward or reverse, is exothermic, and which crosses the smaller barrier.

B3. An uncatalysed reaction has reactants at 60 kJ/mol, a peak at 190 kJ/mol and products at 10 kJ/mol. A catalyst draws a new peak at 140 kJ/mol. (a) Calculate the uncatalysed E_a(forward) and ΔH. (b) Calculate the catalysed E_a(forward). (c) Calculate E_a(reverse) on both pathways. (d) State by how much each barrier fell, and relate that number to the peak. (e) State the catalysed ΔH, and explain why it has that value.

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B4. Profile R, a two-step reaction: reactants at 30 kJ/mol, first peak at 110 kJ/mol, valley at 90 kJ/mol, second peak at 150 kJ/mol, products at 50 kJ/mol. (a) State how many transition states and how many intermediates the diagram shows. (b) Calculate the activation energy of each step, stating the level each is measured from. (c) Identify the rate-determining step, and explain why the taller second peak does not decide the answer. (d) Calculate the ΔH of each step. (e) Calculate the overall ΔH directly from the endpoints, and check it against the sum of the step values.

B5. Sketch data: a reaction has E_a(forward) = 90 kJ/mol and ΔH = +40 kJ/mol, with reactants at 50 kJ/mol. (a) Calculate the energy of the peak. (b) Calculate the energy of the products. (c) Describe the sketch in words: the order of the three levels from lowest to highest. (d) Classify the reaction. (e) Calculate E_a(reverse), and confirm the endothermic check from part (c) of B2 holds.

B6. Two reactions start from reactants at 100 kJ/mol. Reaction A: peak at 150 kJ/mol, products at 0 kJ/mol. Reaction B: peak at 180 kJ/mol, products at 80 kJ/mol. (a) Calculate E_a and ΔH for each reaction. (b) State which reaction is faster, and what decides it. (c) State which reaction releases more heat per mole, and what decides it. (d) Calculate E_a(reverse) for each reaction. (e) State what these four values together show about the link between rate and enthalpy change.

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Section C: Exam Style

C1. Judge each claim, supporting each verdict with the rule it depends on. (a) "The activation energy is the height of the peak above zero." (b) "Adding a catalyst makes a reaction more exothermic, because the pathway is lower." (c) "The species at the peak can be collected, because it sits at a definite energy." (d) "A reaction with a very negative ΔH must be fast." (e) "On a two-peak diagram, the valley species is a transition state."

C2. A reaction is known only from two values: E_a(reverse) = 140 kJ/mol and ΔH(forward) = −50 kJ/mol, with reactants at 70 kJ/mol. (a) Calculate E_a(forward), showing which rearrangement of the identity you use. (b) Calculate the energy of the peak. (c) Calculate the energy of the products. (d) Classify the forward reaction, and state the classification and ΔH of the reverse reaction. (e) Verify all three original values from your reconstructed levels.

C3. A two-step mechanism is proposed for an endothermic reaction, with this profile: reactants at 40 kJ/mol, first peak at 130 kJ/mol, valley at 70 kJ/mol, second peak at 170 kJ/mol, products at 90 kJ/mol. (a) State the number of steps, transition states and intermediates the profile shows, and state what a mechanism must have to match it. (b) Calculate the activation energy of each step. (c) Calculate the ΔH of each step, then the overall ΔH, and check the sum. (d) Identify the rate-determining step, with your reason. (e) Calculate the reverse barrier of step 2 directly from the levels, and check it with the identity for that step. (f) A catalyst lowers the second peak to 140 kJ/mol. State the new step 2 barrier, state whether the rate-determining step changes, and state the overall ΔH on the catalysed route.

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Answer Key

A1. (a) Potential energy, in kJ/mol. (b) Reaction progress, the reaction coordinate: how far the rearrangement from reactants to products has advanced. It does not show time. (c) The reactant level, the peak, and the product level. (d) Reactants on the left, products on the right.

A2. (a) ΔH = product level − reactant level. (b) E_a(forward) = peak − reactant level. (c) E_a(reverse) = peak − product level, and E_a(reverse) = E_a(forward) − ΔH. (d) The peak is the transition state; the arrangement there is the activated complex, with old bonds partly broken and new bonds partly formed. (e) Any two: it is the energy maximum of the pathway; it exists only for the instant of the rearrangement; it cannot be isolated or stored; it is the least stable arrangement on the route.

A3. (a) Exothermic, ΔH negative: products below reactants means the system lost enthalpy. (b) Endothermic, ΔH positive. (c) Neither in net terms: ΔH = 0, because the levels are equal. (d) Endothermic, ΔH positive: heat flowing into the system raises its enthalpy. (e) Exothermic, ΔH negative: the surroundings can only warm if the system released heat to them.

A4. (a) It provides an alternative pathway with a lower peak. (b) Nothing: the reactant level, product level and ΔH are all unchanged. (c) Both fall by exactly 30 kJ/mol, because both climbs end at a peak that is 30 kJ/mol lower while their starting levels stay fixed. (d) Neither redraws it. Heating changes how many particles can cross the unchanged barrier, not the barrier; concentration changes how often particles meet, not any energy level.

A5. (a) Two elementary steps; the valley holds an intermediate, a real species formed in step 1 and consumed in step 2. (b) From the valley level up to the second peak. (c) The step with the largest activation energy, measured from its own starting level. (d) Not always: a later peak can stand higher on the axis yet have the smaller barrier, because its barrier is measured from its valley, not from the reactant level.

B1. (a) E_a(forward) = 210 − 80 = 130 kJ/mol. (b) ΔH = 20 − 80 = −60 kJ/mol. Negative, so exothermic. (c) 60 kJ per mole is released by the system to the surroundings. (d) E_a(reverse) = 210 − 20 = 190 kJ/mol. (e) Identity: E_a(forward) − ΔH = 130 − (−60) = 190 kJ/mol. The two routes agree.

B2. (a) E_a(forward) = 140 − 20 = 120 kJ/mol. (b) ΔH = 95 − 20 = +75 kJ/mol. Positive, so endothermic. (c) E_a must exceed ΔH: 120 is greater than 75, so the check holds. (d) Directly: 140 − 95 = 45 kJ/mol. By the identity: 120 − 75 = 45 kJ/mol. (e) The reverse direction is exothermic, because it runs from 95 down to 20 kJ/mol, and it crosses the smaller barrier, 45 kJ/mol against 120 kJ/mol.

B3. (a) E_a(forward) = 190 − 60 = 130 kJ/mol. ΔH = 10 − 60 = −50 kJ/mol. (b) Catalysed E_a(forward) = 140 − 60 = 80 kJ/mol. (c) Uncatalysed E_a(reverse) = 190 − 10 = 180 kJ/mol. Catalysed E_a(reverse) = 140 − 10 = 130 kJ/mol. (d) Each barrier fell by 50 kJ/mol, which is exactly the peak drop, 190 − 140 = 50 kJ/mol. (e) ΔH is still −50 kJ/mol: the catalyst moved only the peak, and ΔH is read from the endpoints, which stayed at 60 and 10 kJ/mol.

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B4. (a) Two transition states (the two peaks) and one intermediate (in the valley). (b) Step 1: 110 − 30 = 80 kJ/mol, measured from the reactant level. Step 2: 150 − 90 = 60 kJ/mol, measured from the valley. (c) Step 1: its barrier, 80 kJ/mol, is larger than step 2's 60 kJ/mol. The second peak stands higher on the axis, but a barrier is a climb, not an altitude, and step 2 climbs only from its valley at 90 kJ/mol. (d) Step 1 ΔH = 90 − 30 = +60 kJ/mol. Step 2 ΔH = 50 − 90 = −40 kJ/mol. (e) Overall ΔH = 50 − 30 = +20 kJ/mol. Sum of steps: +60 + (−40) = +20 kJ/mol. They agree, and the overall reaction is endothermic.

B5. (a) Peak = reactants + E_a = 50 + 90 = 140 kJ/mol. (b) Products = reactants + ΔH = 50 + 40 = 90 kJ/mol. (c) Lowest: reactants at 50, then products at 90, then the peak at 140 kJ/mol. (d) Endothermic: ΔH is positive and the products finish above the reactants. (e) E_a(reverse) = 140 − 90 = 50 kJ/mol. Check: E_a(forward) − ΔH = 90 − 40 = 50 kJ/mol, and E_a(forward) = 90 exceeds ΔH = 40, as an endothermic diagram requires.

B6. (a) Reaction A: E_a = 150 − 100 = 50 kJ/mol; ΔH = 0 − 100 = −100 kJ/mol. Reaction B: E_a = 180 − 100 = 80 kJ/mol; ΔH = 80 − 100 = −20 kJ/mol. (b) Reaction A is faster: its barrier is lower, 50 against 80 kJ/mol, so more of its particles can cross per second. (c) Reaction A releases more heat: its ΔH is more negative, 100 against 20 kJ per mole. (d) A: E_a(reverse) = 150 − 0 = 150 kJ/mol. B: E_a(reverse) = 180 − 80 = 100 kJ/mol. (e) Here the faster reaction also releases more heat, but that is coincidence, not a rule: rate is decided by E_a alone and heat by ΔH alone, and either can be large while the other is small.

C1. (a) False. E_a is the climb from the reactant level to the peak, not the peak's height above zero: reactants at 50 with a peak at 120 give E_a = 70, not 120 kJ/mol. (b) False. A catalyst lowers only the peak; the endpoints are unchanged, so ΔH is identical and the reaction is exactly as exothermic as before. It is faster, not more exothermic. (c) False. The peak species is the activated complex, which exists only at the energy maximum for an instant and cannot be isolated or collected. (d) False. ΔH measures the endpoint gap and says nothing about the barrier: a very exothermic reaction can sit behind a tall peak and run slowly until it is lit or catalysed. (e) False. The valley holds an intermediate, a real species at a local minimum. Transition states are the peaks.

C2. (a) From E_a(reverse) = E_a(forward) − ΔH, rearranged: E_a(forward) = E_a(reverse) + ΔH = 140 + (−50) = 90 kJ/mol. (b) Peak = reactants + E_a(forward) = 70 + 90 = 160 kJ/mol. (c) Products = reactants + ΔH = 70 + (−50) = 20 kJ/mol. (d) Forward: exothermic, ΔH = −50 kJ/mol, because the products sit below the reactants. Reverse: endothermic, ΔH = +50 kJ/mol. (e) From the levels: E_a(forward) = 160 − 70 = 90 kJ/mol; ΔH = 20 − 70 = −50 kJ/mol; E_a(reverse) = 160 − 20 = 140 kJ/mol. All three match the values given.

C3. (a) Two steps, two transition states (the peaks) and one intermediate (in the valley). A matching mechanism must have exactly two elementary steps and exactly one intermediate; any other count cannot produce this profile. (b) Step 1: 130 − 40 = 90 kJ/mol, from the reactant level. Step 2: 170 − 70 = 100 kJ/mol, from the valley. (c) Step 1 ΔH = 70 − 40 = +30 kJ/mol. Step 2 ΔH = 90 − 70 = +20 kJ/

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mol. Overall ΔH = 90 − 40 = +50 kJ/mol. Check: +30 + 20 = +50 kJ/mol. (d) Step 2: its barrier, 100 kJ/mol, is larger than step 1's 90 kJ/mol, so it is crossed most slowly and limits the overall rate. (e) Directly: E_a(reverse, step 2) = 170 − 90 = 80 kJ/mol. By the identity for step 2: 100 − 20 = 80 kJ/mol. (f) New step 2 barrier = 140 − 70 = 70 kJ/mol. Step 1, at 90 kJ/mol, now has the largest barrier, so the rate-determining step changes to step 1. The overall ΔH is unchanged at +50 kJ/mol, because the catalyst moved a peak, not an endpoint.

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