ANSWER KEY.

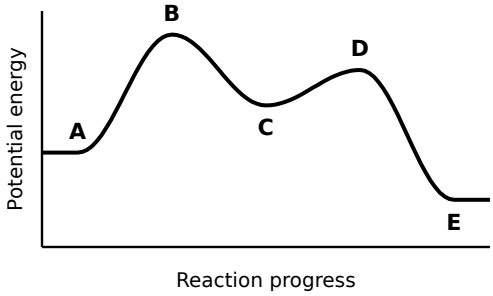
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5.10 Multistep Reaction Energy Profile

AP Chemistry | ANSWER KEY

Measure each E_a from the bottom of that step, not from the start of the graph. Justify each answer.

1. Use the energy profile below.



(a) How many elementary steps are in this mechanism?
(b) Which letter shows an intermediate? Which letters show transition states?
(c) Which step is rate-determining? Justify your answer.
(d) Is the overall reaction exothermic or endothermic? Is step 1 exothermic or endothermic?

(a) 2 steps (two hills). (b) Intermediate: C (valley). Transition states: B and D (peaks).

(c) Step 1. Its E_a (A up to B) is much larger than step 2's (C up to D).

(d) Overall exothermic (E is lower than A). Step 1 is endothermic (C is higher than A).

2. A three-step mechanism has the energies in the table.

Point on the profile	Energy (kJ/mol)
Reactants	50
Transition state 1	110
Intermediate 1	20
Transition state 2	100
Intermediate 2	30
Transition state 3	60
Products	0

(a) Find E_a for each step.
(b) Which step is rate-determining?
(c) Find the overall ΔH. Is the reaction exothermic or endothermic?
(d) Which step is endothermic? Explain.
(e) How many intermediates are in this mechanism?

(a) E_{a1} = 110 − 50 = 60 kJ/mol; E_{a2} = 100 − 20 = 80 kJ/mol; E_{a3} = 60 − 30 = 30 kJ/mol

(b) Step 2 (largest E_a, 80 kJ/mol). (c) ΔH = 0 − 50 = −50 kJ/mol, exothermic.

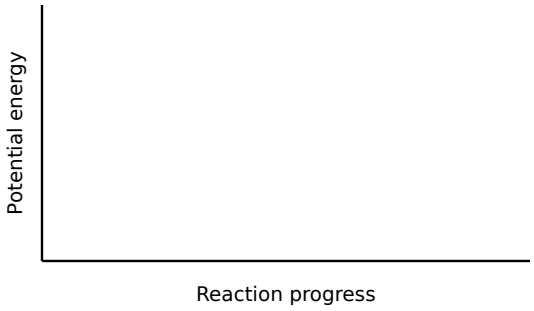
(d) Step 2: it goes from 20 up to 30 kJ/mol (ΔH = +10 kJ/mol). Steps 1 and 3 go down. (e) 2

3. In a two-step mechanism, scientists can sometimes detect the species made in step 1, but they can never isolate the species at the top of either hill. Use the idea of an energy profile to explain this difference.

The species made in step 1 is an intermediate. It sits in a dip (valley) in energy, so it is a little bit stable and can last long enough to be detected. The species at a peak is a transition state, at the highest energy point of a step, so it cannot be isolated at all.

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4. A two-step reaction has a **fast, exothermic** first step and a **slow, endothermic** second step. The overall reaction is **endothermic**. Sketch its energy profile on the axes. Label the reactants, intermediate, products, E_{a2}, and ΔH.



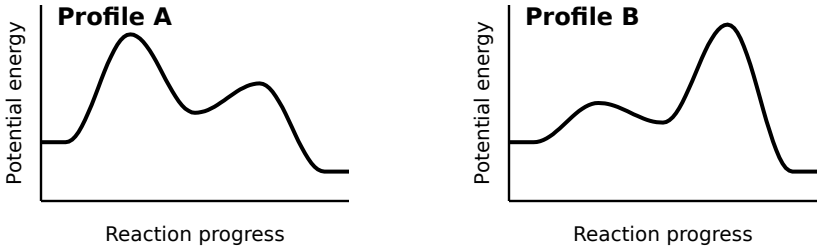
Reactants in the middle on the left. Step 1: small hill, then a valley (intermediate) *lower* than the reactants. Step 2: tall hill from the valley (E_{a2} arrow from the valley to the peak), ending at products *higher* than the reactants. ΔH arrow points up from reactants to products.

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5. A proposed mechanism for the reaction of NO_2 with CO is shown.

Step 1 (slow): $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$



(a) Write the overall reaction.

(b) Identify the intermediate.

(c) Which profile, A or B, matches this mechanism? Justify your answer.

(d) Where on the matching profile is the intermediate found?

(a) $NO_2 + CO \rightarrow NO + CO_2$ (one NO_2 and the NO_3 cancel).

(b) NO_3 (made in step 1, used in step 2).

(c) Profile A. Step 1 is slow, so it needs the larger E_a; in A the first hill is much bigger than the climb from the valley to the second peak. B has a slow second step.

(d) In the valley between the two hills.

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6. A student looks at the data in problem 2 and says, "Step 1 is the rate-determining step because transition state 1 is the highest point on the whole profile." Do you agree? Explain.

Disagree. Each E_a must be measured from the bottom of its own step, not from the start of the graph. Step 2 starts from the low intermediate (20 kJ/mol), so its climb (80 kJ/mol) is larger than step 1's (60 kJ/mol). Step 2 is the slow step.

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