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Topic 9.4: Thermodynamic and Kinetic Control

Worksheet · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the ideas: the two kinds of control, the anatomy of a reaction coordinate diagram, why favorable reactions can sit still, and what a catalyst cannot do. Section B practices the working skills: picking the winning product under each regime, reading barriers off a diagram, and tracking what a catalyst does to one. Section C is exam style: a three step diagram, a competing products problem, and three claims to judge.

Reference facts: every value you need is printed inside the question that uses it. All diagram energies are in kJ mol^{-1}, relative to the reactants at 0 unless stated otherwise. Two fixtures recur across the sheet: the competing pair P (E_a = 50 kJ mol^{-1}, $\Delta G = -20$ kJ mol^{-1}) and Q (E_a = 90 kJ mol^{-1}, $\Delta G = -80$ kJ mol^{-1}), formed from one reactant; and a two step diagram with reactants at 0, peaks at +75 and +110, an intermediate at +20, and products at -40 kJ mol^{-1}.

One working habit ties the sheet together: ask first whether the issue is thermodynamic (the sign of ΔG, which product is lowest in energy) or kinetic (barrier heights, which step or product is fastest).

The answer key gives full working for every part. Attempt every question before looking at it.

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Section A: Recall and Concepts

A1. (a) Define kinetic control and thermodynamic control. (b) For a reaction that can form two products, state which product dominates under each. (c) State the temperature and reaction time conditions that favor each.

A2. (a) State what is plotted on each axis of a reaction coordinate diagram. (b) State what a peak represents, and what a valley between two peaks represents. (c) A diagram shows three peaks. State how many elementary steps and how many intermediates it has. (d) State one difference between an intermediate and a transition state, in terms of lifetime.

A3. (a) The conversion C(s, diamond) → C(s, graphite) has a negative ΔG, yet diamonds persist for millions of years. Explain this in terms of activation energy. (b) Gasoline does not ignite in air at room temperature, although its combustion is strongly favorable. Explain why a spark is needed. (c) A student claims: "A negative ΔG guarantees a fast reaction." Judge the claim.

A4. (a) State what a catalyst changes about a reaction, and list three things it cannot change. (b) Explain why a catalyst speeds the reverse reaction as much as the forward reaction. (c) A reaction has ΔG > 0. A student adds a catalyst and waits. State, with a reason, whether it will proceed as written.

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A5. Judge each claim, giving a reason. (a) "Raising the temperature lowers the activation energy." (b) "The rate determining step is the step ending in the lowest valley." (c) "Under thermodynamic control, the fastest product dominates." (d) "An intermediate could in principle be isolated, but a transition state could not."

Section B: Core Practice

B1. A reactant can form product P (Ea = 50 kJ mol^{-1}, ΔG = −20 kJ mol^{-1}) or product Q (Ea = 90 kJ mol^{-1}, ΔG = −80 kJ mol^{-1}). (a) State which product dominates at low temperature with a short reaction time, and explain why in terms of the barriers. (b) State which product dominates after a long time at high temperature, and explain why. (c) Calculate the activation energy for the reverse reaction of each product, back to the reactant. (d) Use (c) to explain why, once Q has formed, it does not convert back and then into P.

B2. A two step mechanism has this diagram: reactants at 0 kJ mol^{-1}, a first peak at +75 kJ mol^{-1}, an intermediate at +20 kJ mol^{-1}, a second peak at +110 kJ mol^{-1}, and products at −40 kJ mol^{-1}. (a) Calculate the activation energy of step 1. (b) Calculate the activation energy of step 2. (c) Identify the rate determining step, with a reason. (d) State the value and sign of ΔH for the overall reaction, and whether it is exothermic or endothermic. (e) State how many transition states and how many intermediates the diagram shows.

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B3. Two competing pathways from one reactant have activation energies of 60 kJ mol^{-1} and 95 kJ mol^{-1}. The 60 kJ mol^{-1} pathway leads to product X ($\Delta G = -10$ kJ mol^{-1}); the 95 kJ mol^{-1} pathway leads to product Y ($\Delta G = -55$ kJ mol^{-1}). (a) Calculate the difference between the two activation energies. (b) State which product dominates at low temperature with a short reaction time, and name the kind of control. (c) State which product dominates at high temperature after a long time, and name the kind of control. (d) Explain why (c) does not contradict (b).

B4. A catalyst is added to the two step reaction of B2. It provides a new pathway for step 2 only, lowering the second peak from +110 kJ mol^{-1} to +70 kJ mol^{-1}; all other levels are unchanged. (a) Calculate the activation energy of step 2 on the catalyzed pathway. (b) Identify the rate determining step of the catalyzed reaction, with a reason. (c) State the value of ΔH for the catalyzed reaction, and explain your answer. (d) State what happens to the position of equilibrium, and explain why the catalyst cannot change it.

B5. Products M and N compete from one reactant. Product M: Ea = 80 kJ mol^{-1}, $\Delta G = -30$ kJ mol^{-1}. Product N: Ea = 55 kJ mol^{-1}, $\Delta G = -60$ kJ mol^{-1}. (a) State which product dominates under kinetic control, with a reason. (b) State which product is the thermodynamic product, with a reason. (c) A catalyst lowers the barrier to M by 40 kJ mol^{-1} and leaves the barrier to N unchanged. Calculate the new barrier to M, and state which product now dominates under kinetic control. (d) State whether this catalyst changes which product is the thermodynamic product, and explain why.

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B6. (a) A mixture of hydrogen and oxygen, for the reaction 2 $H_2(g)$ + $O_2(g)$ → 2 $H_2O(l)$, stands unchanged for years, then reacts explosively when a spark is introduced. Explain both observations using ΔG and Ea. (b) A favorable reaction with ΔS < 0 is heated strongly. State the two separate effects of the heating: one kinetic, one thermodynamic. (c) A different reaction has ΔH > 0 and ΔS < 0, so its ΔG is positive at every temperature. A student argues that heating it for long enough, with a catalyst, must eventually make it run. Judge the argument.

Section C: Exam Style

C1. A three step mechanism has this diagram: reactants at 0 kJ mol^{-1}; peaks at +80, +55 and +95 kJ mol^{-1}; valleys at +30 and +10 kJ mol^{-1} between them; products at −25 kJ mol^{-1}. (a) State the number of elementary steps, transition states and intermediates. (b) Calculate the activation energy of each step. (c) Identify the rate determining step, with a reason. (d) State the value of ΔH and whether the reaction is exothermic or endothermic. (e) A catalyst lowers the third peak to +60 kJ mol^{-1}, leaving everything else unchanged. Calculate the new activation energy of step 3, identify the new rate determining step, and state whether the overall reaction becomes faster or slower.

C2. A reactant can form product R (Ea = 45 kJ mol^{-1}, ΔG = −15 kJ mol^{-1}) or product S (Ea = 85 kJ mol^{-1}, ΔG = −65 kJ mol^{-1}). (a) The reaction is run cold and analyzed after five minutes. State which product dominates, and explain why. (b) The reaction is instead heated and left for several hours. State which product dominates, and explain why. (c) Calculate the reverse barrier for each product, and use the values to explain why S, once formed, accumulates rather than converting into R. (d) A catalyst lowers the barrier to S by 50 kJ mol^{-1} and does not affect the barrier to R. The reaction is run cold for five minutes. State which product now dominates, and state two things the catalyst has not changed.

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C3. Judge each claim, explaining your reasoning. (a) "The ΔG for converting diamond to graphite is negative, so a diamond will visibly turn into graphite within a few years." (b) "Adding a catalyst to an unfavorable reaction will eventually make it proceed, because the catalyst keeps lowering the barrier." (c) "At higher temperature the thermodynamic product dominates because temperature lowers the activation energy on the pathway to the stable product."

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Answer Key

A1. (a) Kinetic control: the mixture is decided by relative rates, so the product reached through the lowest activation energy dominates. Thermodynamic control: the mixture is decided by stability, so the lowest free energy product dominates, once the products can interconvert. (b) Kinetic: the fastest-forming product. Thermodynamic: the most stable product, with the most negative ΔG. (c) Kinetic control: low temperature, short time. Thermodynamic control: high temperature, long time, allowing crossings in both directions until the mixture equilibrates.

A2. (a) Potential energy on the vertical axis, reaction progress on the horizontal axis. (b) A peak is a transition state, the highest energy arrangement along one elementary step. A valley is an intermediate, a real species in a local energy minimum between two steps. (c) Three elementary steps, one for each peak, and two intermediates, one in each valley. (d) An intermediate has a finite lifetime as a real species. A transition state has no measurable lifetime: it is a momentary arrangement passed through.

A3. (a) The negative ΔG makes the conversion favorable, but favorable is not fast. Rearranging diamond's rigid bond network carries an extremely high activation energy, which almost no atoms acquire at ordinary temperatures, so the rate is effectively zero. (b) Combustion's activation energy is too high for room temperature collisions to cross. The spark gets the first molecules over the barrier; the heat released then sustains the reaction. (c) False. ΔG reports favorability only. Rate is set by the activation energy, which ΔG does not contain: diamond and gasoline both have negative ΔG values and both sit still.

A4. (a) A catalyst changes the rate: it provides an alternative pathway with a lower activation energy, for both directions alike. It cannot change ΔG, the position of equilibrium (or K), or reactant and product energies, so ΔH and ΔS are unchanged too. (b) The catalyzed pathway lowers the peak while leaving both ends fixed, so the climb from the product side falls by the same amount as from the reactant side: both directions speed up equally. (c) No. A positive ΔG means the reaction as written is unfavorable, with equilibrium on the reactant side. Lowering a barrier cannot change which side is favored; only the reverse proceeds.

A5. (a) False. Temperature changes no barrier height; it increases the molecules' energy, so a larger fraction can cross the unchanged barrier. (b) False. The rate determining step is the step with the highest activation energy barrier, measured from the level just before its peak. Valleys mark intermediates, not slow steps. (c) False. Under thermodynamic control the most stable product dominates; the fastest product dominates under kinetic control. (d) True. An intermediate is a real species in a valley with a finite lifetime, so it can in principle be isolated. A transition state is a momentary peak arrangement with no lifetime, so it never can.

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B1. (a) P dominates. Its barrier is 40 kJ mol^{-1} lower than Q's (50 against 90), so it forms far faster; in the cold few molecules cross the higher barrier at all, and the short time allows no rearrangement. (b) Q dominates. Q is more stable, 60 kJ mol^{-1} lower in free energy (ΔG = −80 against −20 kJ mol^{-1}); given heat and time the products interconvert and the mixture settles into Q. (c) Reverse barriers, from each product's level to its peak: P: 50 − (−20) = 70 kJ mol^{-1}. Q: 90 − (−80) = 170 kJ mol^{-1}. (d) Q must climb 170 kJ mol^{-1} to turn back, far more than P's 70 kJ mol^{-1}. Even where P can revert and re-form, Q effectively cannot, so Q accumulates.

B2. (a) Step 1 starts at the reactants, 0, and peaks at +75, so Ea = 75 − 0 = 75 kJ mol^{-1}. (b) Step 2 starts at the intermediate, +20, and peaks at +110, so Ea = 110 − 20 = 90 kJ mol^{-1}. The barrier is not 110: it is measured from the valley, not from zero. (c) Step 2 is rate determining: it has the higher barrier, 90 against 75 kJ mol^{-1}. (d) ΔH = −40 − 0 = −40 kJ mol^{-1}. Products lie below reactants, so the reaction is exothermic. (e) Two transition states, one at each peak, and one intermediate.

B3. (a) 95 − 60 = 35 kJ mol^{-1}. (b) Product X dominates: reached over the lower barrier, 60 kJ mol^{-1}, it forms much faster when crossings are rare and time is short. Kinetic control. (c) Product Y dominates: with ΔG = −55 kJ mol^{-1} it is more stable, and heat plus time let the system equilibrate into it. Thermodynamic control. (d) No contradiction: the answers describe different regimes of one system. Which product dominates depends on whether conditions let the products interconvert: cold and brief, only speed matters; hot and long, only stability.

B4. (a) The catalyzed step 2 runs from the intermediate at +20 to the new peak at +70, so Ea = 70 − 20 = 50 kJ mol^{-1}. (b) Step 1 is now rate determining: its unchanged barrier of 75 kJ mol^{-1} now exceeds step 2's 50 kJ mol^{-1}. (c) ΔH is still −40 kJ mol^{-1}: the catalyst moved a peak, not the reactants or products, and ΔH depends only on those two levels. (d) Unchanged. Barriers fell but neither end's energy moved, so the balance point set by ΔG stays put; the mixture just reaches it sooner.

B5. (a) N dominates under kinetic control: its barrier, 55 kJ mol^{-1}, is lower than M's 80 kJ mol^{-1}, so N forms faster. (b) N is also the thermodynamic product: its ΔG of −60 kJ mol^{-1} is more negative than M's −30 kJ mol^{-1}. (c) The new barrier to M is 80 − 40 = 40 kJ mol^{-1}, now below N's unchanged 55 kJ mol^{-1}. M forms fastest, so M dominates under kinetic control. (d) No. Stability is fixed by the products' ΔG values, and the catalyst changed only a barrier. N remains the thermodynamic product; rates changed, energies did not.

B6. (a) The reaction has a negative ΔG, so it is favorable, but its activation energy is high: at room temperature essentially no collisions can cross the barrier, so the mixture stands unchanged, kinetically blocked. The spark lets the first molecules cross, and the heat released raises the temperature until crossings become general and the reaction runs explosively. (b) Kinetic effect: the reaction runs faster, as more molecules cross its barrier. Thermodynamic effect: with ΔS < 0, the term −TΔS is positive and grows with T, so ΔG becomes less negative; past the crossover temperature the reaction is not favorable at all. (c) The argument fails. A catalyst cannot change ΔG, and neither can time. With ΔG positive at every temperature there is no favorable direction to

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accelerate: heating and catalysis speed up only what thermodynamics permits. The reverse reaction is the favorable one.

C1. (a) Three elementary steps (three peaks), three transition states (one at each peak) and two intermediates (one in each valley). (b) Step 1: Ea = 80 − 0 = 80 kJ mol^{-1}. Step 2: Ea = 55 − 30 = 25 kJ mol^{-1}. Step 3: Ea = 95 − 10 = 85 kJ mol^{-1}. Each is measured from the level just before its peak. (c) Step 3 is rate determining: its barrier, 85 kJ mol^{-1}, is the highest of the three. (d) ΔH = −25 − 0 = −25 kJ mol^{-1}; products lie below reactants, so the reaction is exothermic. (e) The new step 3 barrier is 60 − 10 = 50 kJ mol^{-1}. Step 1, still 80 kJ mol^{-1}, is now the highest barrier and becomes rate determining. The reaction becomes faster: the bottleneck barrier has fallen from 85 to 80 kJ mol^{-1}.

C2. (a) R dominates. Its barrier is 45 kJ mol^{-1} against 85 kJ mol^{-1} for S, so in the cold almost all crossings lead to R, and five minutes allows no rearrangement: kinetic control. (b) S dominates. S is more stable by 50 kJ mol^{-1} (ΔG = −65 against −15 kJ mol^{-1}); hours of heating let the products interconvert until the mixture settles into S: thermodynamic control. (c) Reverse barriers: R: 45 − (−15) = 60 kJ mol^{-1}. S: 85 − (−65) = 150 kJ mol^{-1}. R leaks back and re-forms readily; S, facing two and a half times the climb, is trapped and accumulates. (d) The barrier to S falls to 85 − 50 = 35 kJ mol^{-1}, below R's 45 kJ mol^{-1}, so S now forms fastest and dominates even in the cold, short run. Unchanged: the products' ΔG values and the position of equilibrium.

C3. (a) The claim confuses favorability with speed. The negative ΔG means graphite is more stable, but rearranging the diamond lattice carries an extremely high activation energy, so the rate at room temperature is effectively zero. "Favorable" says where equilibrium lies, not how soon it is reached. (b) Wrong twice. A catalyst lowers a barrier once, to its alternative pathway's height; it does not keep lowering it. And no reduction could help anyway: with ΔG > 0, equilibrium lies on the reactant side, and a catalyst changes neither ΔG nor that position. (c) Right outcome, wrong mechanism. Temperature lowers no activation energy; barriers belong to the pathways. Heat raises the molecules' energy, making crossings of both barriers frequent, so the products interconvert and settle into the most stable one.

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