Topic 9.4: Thermodynamic and Kinetic Control

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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Two Questions, Two Different Answers

Thermodynamics decides where a reaction can go. The sign of ΔG states whether a process is favorable and which side equilibrium favors.

Kinetics decides how fast it gets there. Rate is governed by the activation energy, Ea: the height of the barrier a step must climb.

The two are independent. A reaction can be favorable and fast, favorable and immeasurably slow, or unfavorable and therefore unable to proceed as written. No value of ΔG predicts a rate.

Activation Energy and the Transition State

Every step climbs a barrier. Before bonds can rearrange, the reacting species must reach the top of an energy hill. Ea is measured from the step's starting level up to the peak.

The peak is a transition state. A transition state is the highest energy arrangement along a step, neither reactant nor product. It cannot be isolated.

Barrier height sets the pace. At a given temperature, only collisions carrying at least Ea can react. A higher barrier lets a smaller fraction through, so the step is slower.

Reading a Reaction Coordinate Diagram

The axes are fixed. The vertical axis is potential energy; the horizontal axis is reaction progress.

Count the peaks to count the steps. Each peak is one transition state and one elementary step.

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Valleys are intermediates. A valley between two peaks is a local energy minimum: a real species, formed in one step and consumed in the next, with a finite lifetime.

The rate determining step has the highest barrier. Its Ea is measured from the level immediately before its peak.

The level difference gives ΔH. Products below reactants means ΔH is negative and the reaction is exothermic; products above means ΔH is positive. Barriers set rates, level differences set the energy change.

Kinetic Control: The Fastest Product Wins

Two products compete through two barriers. Each product is reached by its own pathway with its own activation energy.

At low temperature and short times, the lower barrier wins. Few molecules cross the higher barrier, and the reaction stops before products can rearrange. The fastest-forming product dominates.

The kinetic product need not be the stable one. It wins on speed alone.

Thermodynamic Control: The Most Stable Product Wins

Given time and energy, products interconvert. At high temperature, molecules cross barriers in both directions repeatedly, so products revert and re-form until the mixture settles at its lowest free energy.

The product lowest in energy dominates. The most stable product, with the most negative ΔG, is the thermodynamic product.

The same reaction can switch winner. Cold and brief, the kinetic product dominates; hot and long, the thermodynamic product.

Favorable but Immeasurably Slow

Diamond to graphite. The conversion below has a negative ΔG, because graphite is more stable. Yet the rate is effectively zero: rearranging the bonded diamond network demands an extremely high activation energy, so diamonds persist for millions of years.

$C(s, \text{diamond}) \rightarrow C(s, \text{graphite})$

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Gasoline in air. The combustion below is strongly favorable, but at room temperature its barrier is too high to cross. A spark starts it, and the heat released then sustains it.

$2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(l)$

Other favorable reactions wait too. The mixture for the reaction below sits unchanged until ignited, and rusting creeps over months: both favorable, both barrier limited.

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$

An unfavorable reaction cannot be rescued by speed. With ΔG positive, the process does not proceed as written however long it is left.

What a Catalyst Can and Cannot Do

A catalyst lowers Ea. It provides an alternative pathway with a lower activation energy, so equilibrium is reached sooner.

It speeds both directions equally. Forward and reverse barriers fall together, so the equilibrium position does not move.

It cannot change ΔG, ΔH, ΔS or K. Reactant and product energies are untouched; only the path between them changes.

It can change which product forms fastest. Where two products compete, a catalyst that lowers one pathway's barrier more than the other's changes the relative rates, so under kinetic control it can change which product dominates.

Temperature's Double Role

Raising the temperature speeds every step. More molecules clear each barrier, reactions run faster, and products interconvert.

Temperature does not lower Ea. Barrier heights belong to the pathway. Heat gives molecules more energy to cross them; it does not shrink them.

Raising the temperature can also flip ΔG. Where ΔS is nonzero, the Gibbs equation below changes sign at the crossover temperature of Topic 9.3. Heat does two separate jobs: it unlocks barriers kinetically, and for some reactions it changes which direction is favorable.

$\Delta G = \Delta H - T\Delta S$

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Worked Examples

Example 1: Two products, two barriers. A reactant can form product P (E_a = 50 kJ mol^{-1}, ΔG = −20 kJ mol^{-1}) or product Q (E_a = 90 kJ mol^{-1}, ΔG = −80 kJ mol^{-1}). Cold and brief, P dominates: its barrier is 40 kJ mol^{-1} lower, so it forms far faster. Q sits 60 kJ mol^{-1} lower in energy, so with time and heat it dominates instead. The reverse barriers explain why Q then stays: climbing back from P costs 70 kJ mol^{-1}, from Q 170 kJ mol^{-1}.

Example 2: Reading a two step diagram. A mechanism has 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}. Step 1 has E_a = 75 kJ mol^{-1}. Step 2 has E_a = 110 − 20 = 90 kJ mol^{-1}, the higher barrier, so step 2 is rate determining. Products lie 40 kJ mol^{-1} below reactants, so ΔH = −40 kJ mol^{-1}: exothermic, with two transition states and one intermediate.

Example 3: Two products, new numbers. A reactant can form X (E_a = 60 kJ mol^{-1}, ΔG = −10 kJ mol^{-1}) or Y (E_a = 95 kJ mol^{-1}, ΔG = −55 kJ mol^{-1}). The barriers differ by 95 − 60 = 35 kJ mol^{-1}. Cold and brief, X dominates: its barrier is lower, so it forms far faster. Hot and long, Y dominates: it is 45 kJ mol^{-1} more stable.

Example 4: Reading a three step diagram. Reactants sit at 0 kJ mol^{-1}, peaks at +80, +55 and +95 kJ mol^{-1}, valleys at +30 and +10 kJ mol^{-1}, and products at −25 kJ mol^{-1}. The step barriers are 80 − 0 = 80, 55 − 30 = 25 and 95 − 10 = 85 kJ mol^{-1}. Step 3 has the highest barrier, so it is rate determining. ΔH = −25 kJ mol^{-1}, so the reaction is exothermic.

Traps That Cost Marks in Topic 9.4

Reading "favorable" as "fast". A negative ΔG licenses a reaction; it never times it.

Calling a valley a transition state. Valleys hold intermediates, real species with finite lifetimes. Transition states are peaks: momentary and impossible to isolate.

Measuring a step's E_a from zero. Each barrier is measured from the level immediately before its peak.

Claiming a catalyst shifts equilibrium. A catalyst changes how soon equilibrium arrives, never where it lies.

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Saying heat lowers activation energy. Temperature leaves every barrier unchanged.

Picking the stable product under kinetic control. Cold, short conditions are decided by barrier heights alone.

Key Relationships to Remember

- ΔG decides thermodynamic favorability; Ea decides rate; neither can be inferred from the other
- Kinetic control: the product reached by the lowest Ea pathway dominates, favored by low temperature and short time
- Thermodynamic control: the most stable product, with the lowest free energy, dominates, favored by high temperature and long time
- Reaction coordinate diagrams plot potential energy against reaction progress; each peak is a transition state and one elementary step
- A valley between peaks is an intermediate, a real species with a finite lifetime; a transition state has no measurable lifetime
- The rate determining step is the step with the highest activation energy barrier
- Products below reactants mean $\Delta H < 0$ (exothermic); products above mean $\Delta H > 0$ (endothermic)
- A catalyst lowers Ea for both directions equally: equilibrium position, ΔG and K are unchanged, and an unfavorable reaction stays unfavorable
- Raising the temperature speeds all steps and allows reversibility, but lowers no barrier

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