Totally Epic AP Chem Review: Collision Theory and Reaction Mechanisms

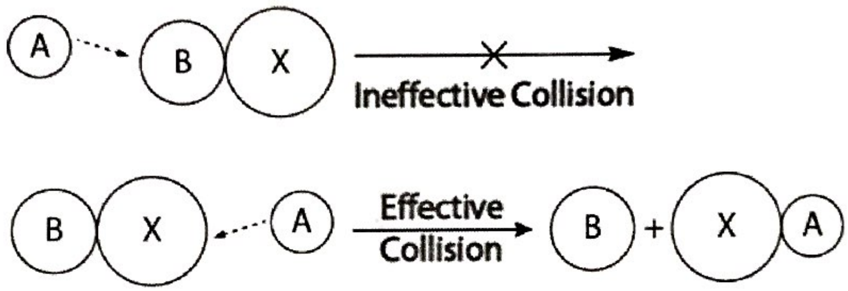
Collision Theory: A Model that Explains Reaction Rates

For a given reaction to occur, molecules that collide must meet two conditions before an effective collision will occur (and the reaction takes place):

1. **Correct** orientation
2. **Sufficient** energy (i.e. activation energy)

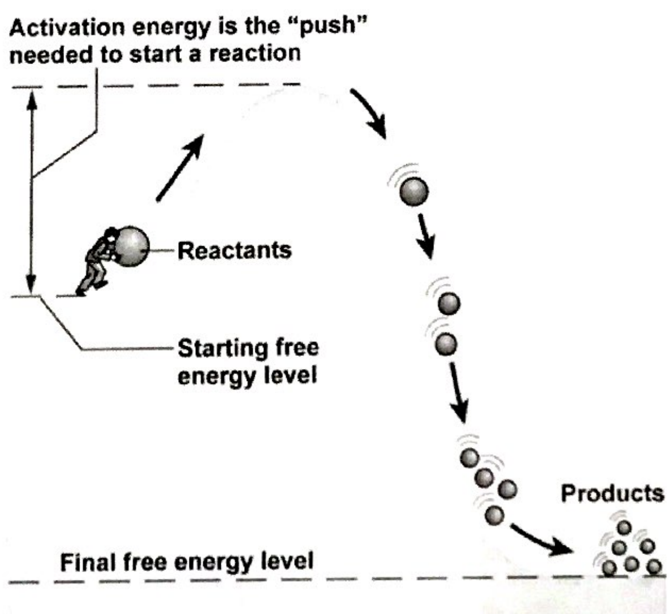
For example:

$$A + BX \longrightarrow B + AX$$



Activation energy (Ea): energy barrier (or hump) that must be overcome for reactants to convert into products.

IMPORTANT: The higher the activation energy, the slower the reaction rate!!!!!



Activated complex (or **transition state**): the high energy transient state that is the collision product of the reactants, with some bonds partially broken and some bonds partially formed. The activated complex can either revert to reactants or proceed to products.

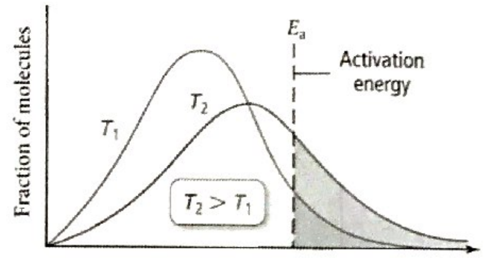
Effect of Temperature on Effective Collisions

As temperature increases, by definition the average Kinetic energy of the particles also increases.

- Heat 'em up = Speed 'em up!
- More speed = more collisions with greater energy
- Thus, more chances of an effective collision.

Note: As temperature ↑ (from $T_1 \rightarrow T_2$) the fraction of molecules of particles energetic enough to achieve E_a ↑, thus more particles react and the reaction rate ↑.

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



Two very important concepts:

1. Only changing activation energy or temperature can change the rate constant!
2. Sooooo important:

↑ Temperature does NOT decrease activation energy!!!!!!

(only a catalyst can decrease activation energy: ~~more on that shortly~~!)

Reaction Mechanisms: Elementary, my dear Watson!

Collision theory assumes that most reactions occur in a series of steps where one or more reactant particles collide, known as the reaction mechanism.

Elementary steps: each single step in the mechanism → must add up to overall balanced equation for mechanism!

Molecularity: # of molecules participating in an elementary step

To be correct, the reaction mechanism:

1. Must be determined by experiment.
2. Must agree with overall stoichiometry.
3. Must agree with the experimentally determined rate law.

Rate Laws for Elementary Steps

- Each elementary step in the mechanism has its own activation energy and its own rate law.
- Although the rate law and orders for an overall reaction MUST be determined experimentally, the rate laws and orders of an elementary step can be derived from the stoichiometry of that specific elementary step.

Example

Overall reaction

$2NO_2(g) + F_2(g) \rightleftharpoons 2NO_2F(g)$ $\quad rate = k_0[NO_2]^{\text{from exp.data}}[F_2]^{\text{from exp.data}}$

Reaction Mechanism

Step 1: $NO_2(g) + F_2(g) \rightleftharpoons NO_2F(g) + F(g)$ $\quad rate = k_1[NO_2]^1[F_2]^1$ from step 1 coefficients

Step 2: $NO_2(g) + F(g) \rightleftharpoons NO_2F(g)$ $\quad rate = k_2[NO_2]^1[F]^1$ from step 2 coefficients

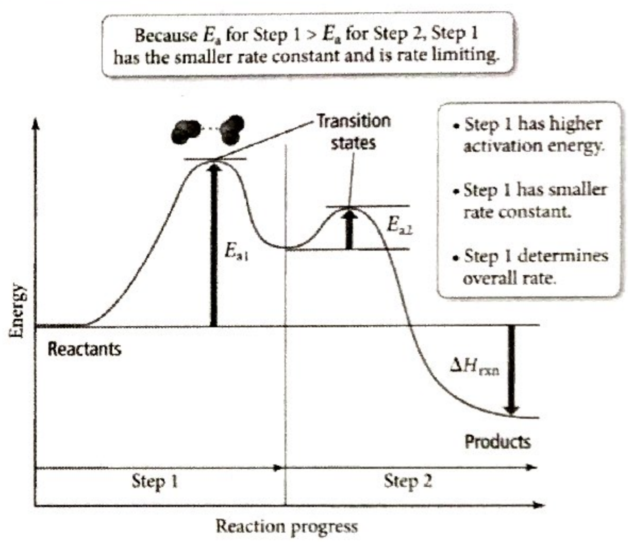
TABLE 13.3 Rate Laws for Elementary Steps

Elementary Step	Molecularity	Rate Law
A ⟶ products	1	Rate = k[A]
A + A ⟶ products	2	Rate = $k[A]^2$
A + B ⟶ products	2	Rate = k[A][B]
A + A + A ⟶ products	3 (rare)	Rate = $k[A]^3$
A + A + B ⟶ products	3 (rare)	Rate = $k[A]^2[B]$
A + B + C ⟶ products	3 (rare)	Rate = k[A][B][C]

Reaction Mechanisms and Rate Expressions:

- The rate determining step (RDS) is always the **slowest** step (with the highest activation energy)
- **Rate of overall reaction** = combined rates of all elementary steps up to and including slowest step in mechanism.

Energy Diagram for a Two-Step Mechanism



To validate a reaction mechanism, two conditions must be met:

1. Elementary steps must Sum to overall reaction.
2. Rate law predicted by the mechanism (the combined rates of all elementary steps up to and including slowest step (RDS) in the mechanism) must be consistent with the experimentally observed rate law.

To get credit for free response: you MUST relate the Coefficients from the balanced RDS (Slow step) to the exponents of the rate law to justify the mechanism! ★ order w/ respect to that reactant

Example: Consider the following two step mechanism:

Reaction Mechanism

Step 1:	$2A \rightarrow A_2$	slow
Step 2:	$A_2 + B \rightarrow A_2B$	fast

a. Determine the overall reaction. $2A + B \rightarrow A_2B$

b. Predict the rate law for the overall reaction. Justify your answer. rate = $k[A]^2$

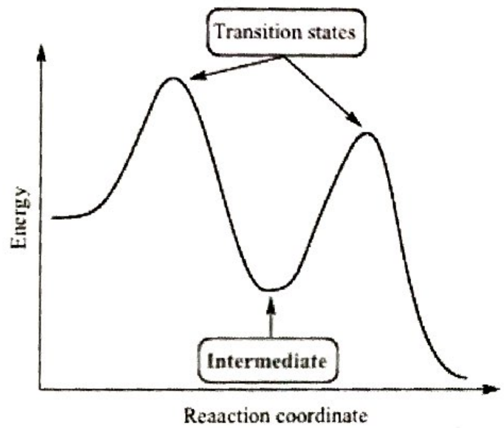
The first step of the mechanism is the slow step, so the rate law can be determined by the stoichiometry of that step: since A has a coefficient of 2 in the slow step, the rxn must be 2nd order w/ respect to A (and 0th order with respect to B, since B isn't part of the slow step).

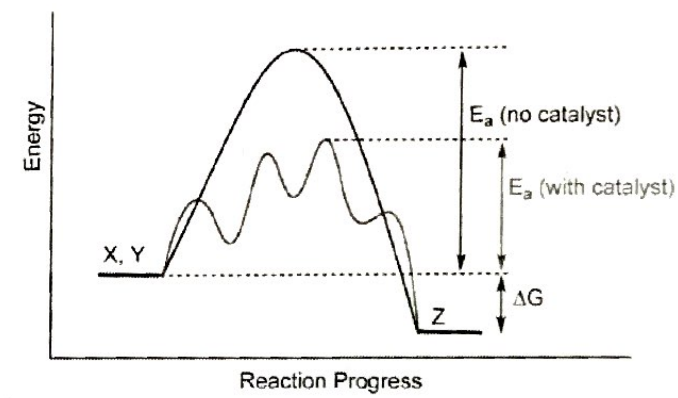
Catalysts vs. Intermediates

Intermediate: formed in an early step and consumed in a later step.

Catalyst: something that increases the rate of a reaction without being consumed in the reaction.

- Provides a surface or better orientation (an alternate pathway) for reaction, increasing # of effective collisions
- Usually replaces 1 high activation energy step with 2 or more lower activation energy steps (you need to draw a new energy diagram for catalyzed reaction)
- Is consumed in an early mechanism step and then produced in a later step.
- Does not change thermodynamics, only kinetics! (can speed up a reaction, but ΔH is the same)





Catalysts vs. Intermediates: two species that can appear in a reaction mechanism, but NOT in the overall reaction!

→ Both are species crossed off when summing a reaction mechanism into overall reaction

- If a species forms as a product in ~~one~~ an earlier step and is used up as a reactant in a later step (and cancels out), it's an **intermediate**.
- If a species ~~starts~~ is used as a reactant ✓ in an earlier step and is re-formed as a product in a later step (and cancels out), it's a **catalyst**.

$$H_2O_{2\,(aq)} + I^-_{(aq)} \rightarrow H_2O_{(l)} + IO^-_{(aq)} \qquad \textit{slow}$$
$$H_2O_{2\,(aq)} + IO^-_{(aq)} \rightarrow H_2O_{(l)} + O_{2\,(g)} + I^-_{(aq)} \qquad \textit{fast}$$

Example: Does this reaction mechanism have an intermediate and/or catalyst? Identify and explain your classification.

IO^- is an intermediate: produced in early step, consumed in later step

I^- is a catalyst: consumed in early step, produced in later step