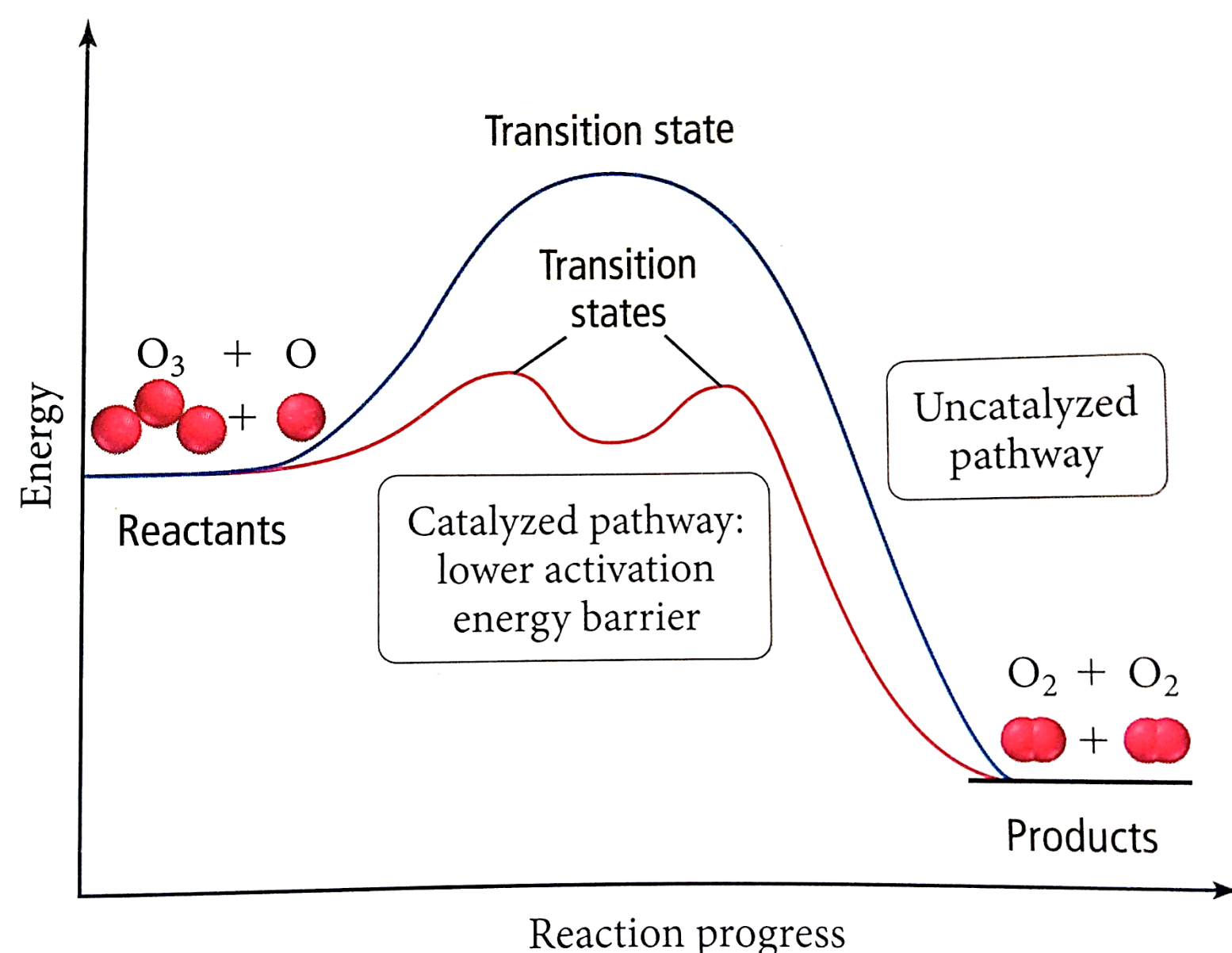


Destruction of ozone layer in upper atmosphere

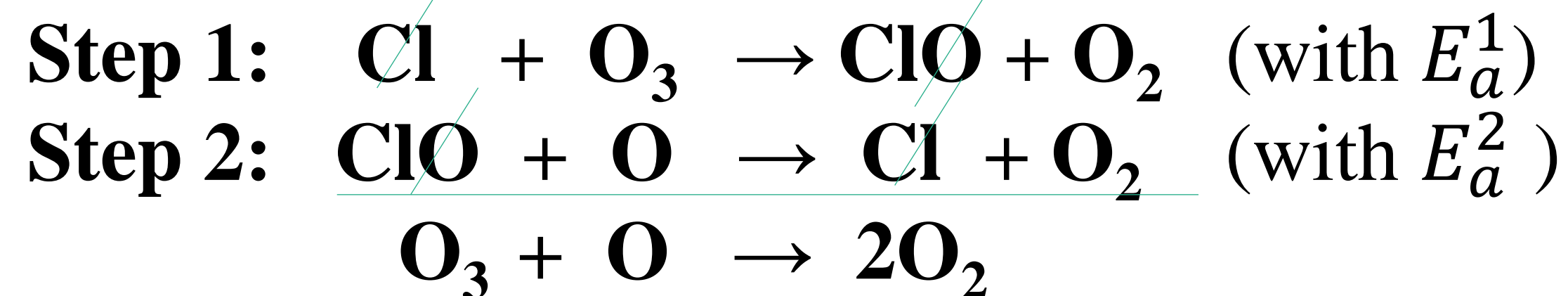


Energy diagram for catalyzed and uncatalyzed pathways for ozone decomposition

- Consider first the non-catalytic reaction

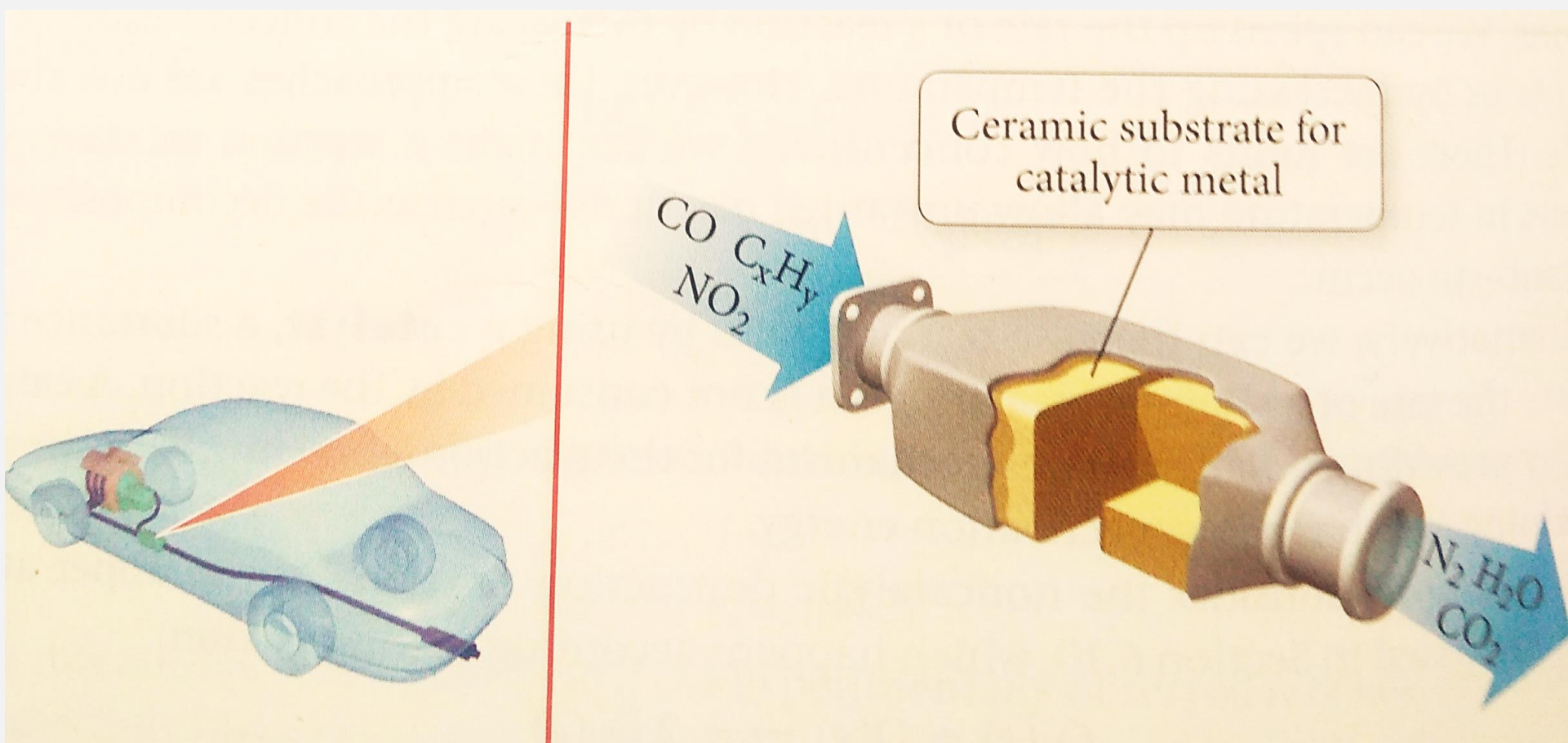


- E_a for this reaction is pretty high, therefore the ozone layer does not rapidly decompose into O₂
- The presence of Cl atoms, created from photodissociation of chlorofluorocarbons (created by humans), in the upper layer avails the above reaction another pathway which is very fast and leads to destruction of O₃
- The first step is called the catalytic destruction of ozone



- Note that Cl is not consumed in the overall reaction. Catalyst!
- The activation energy for the rate-limiting step is much smaller than E_a for uncatalyzed reaction

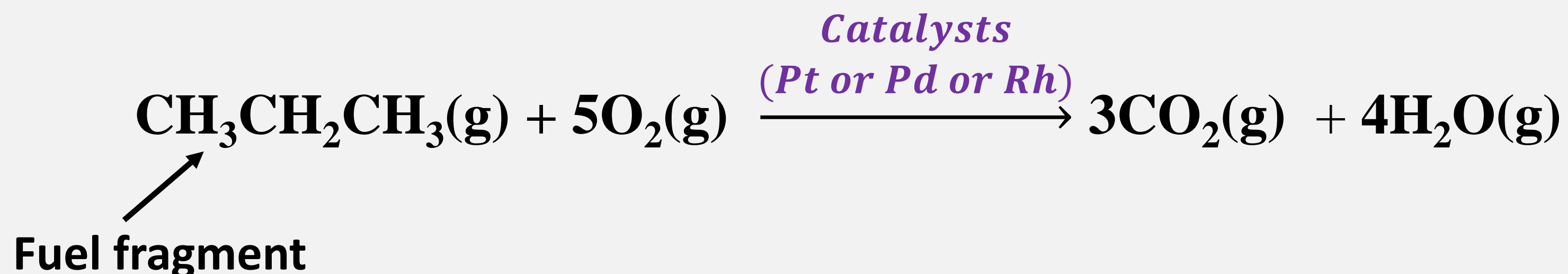
Catalytic convertor in exhaust system of vehicles



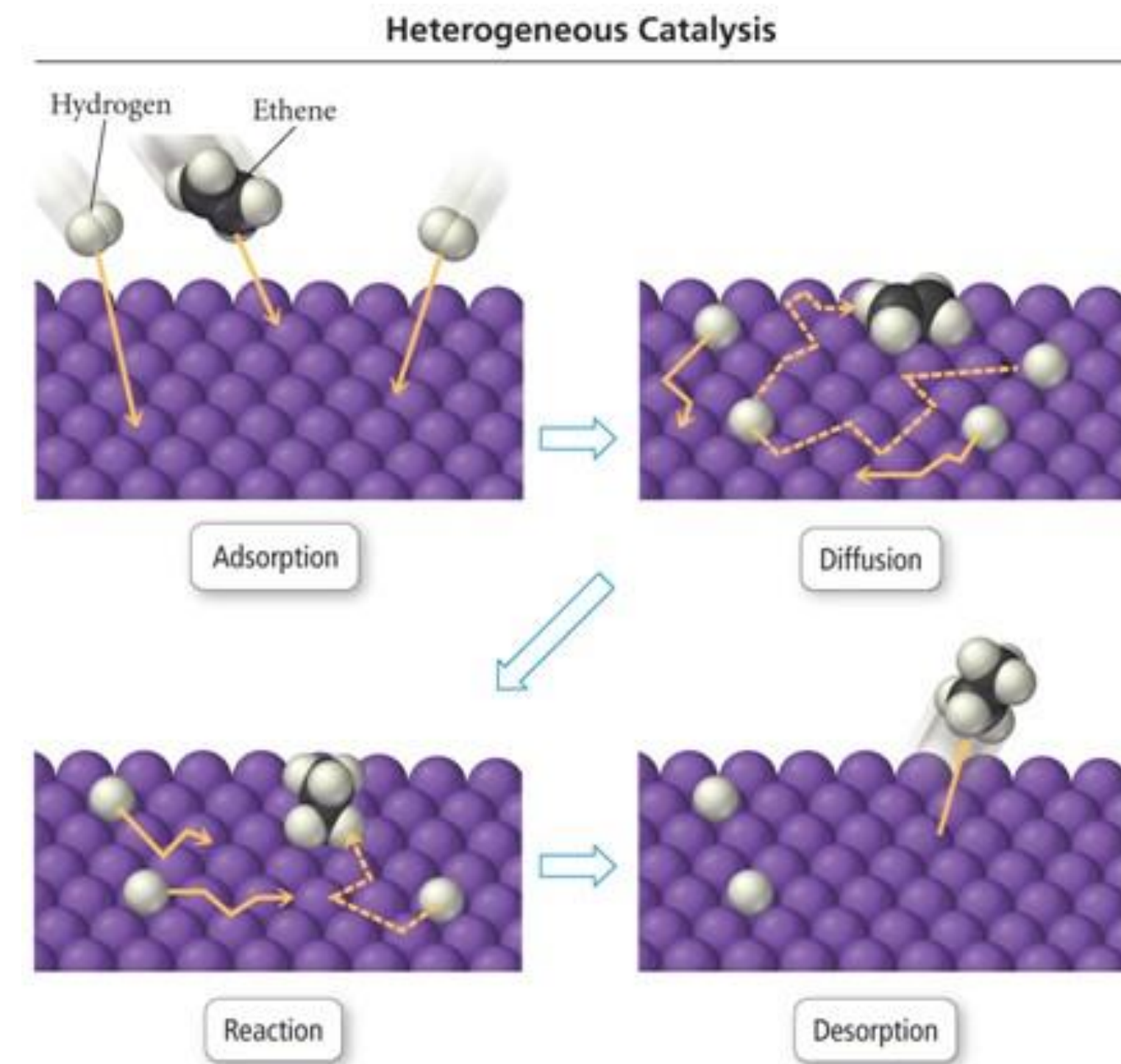
- Catalytic convertor contains solid catalysts (Pt, Pd and Rh) dispersed on high-surface-area ceramic structure
- These catalysts convert exhaust pollutants such as nitrogen monoxide and carbon monoxide into less harmful substances:



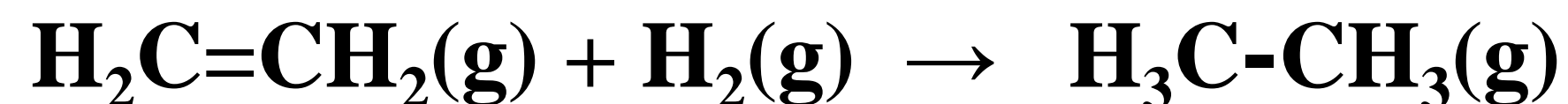
- The catalytic convertor also promotes the complete combustion of any fuel fragment present in the exhaust:



Hydrogenation of double bonds within alkenes using heterogeneous catalysis

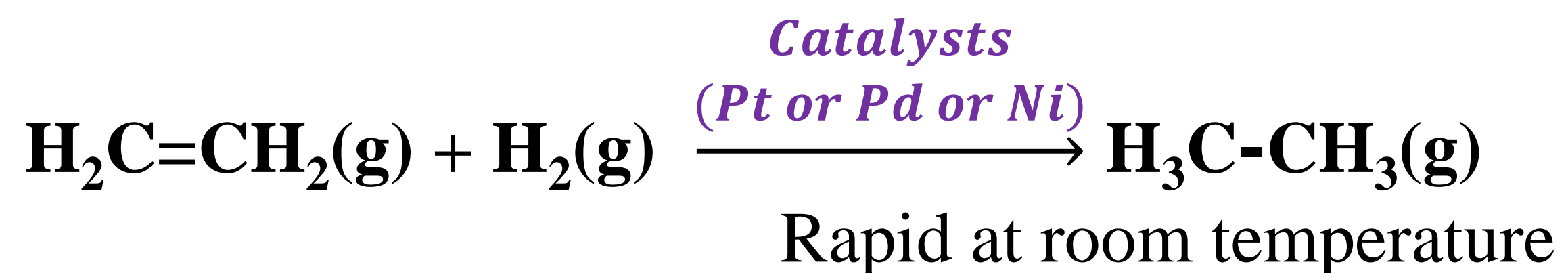


- Consider the reaction between ethene and hydrogen



Slow at room temperature

- In the presence of finely divided **Pt or Pd or Ni**, the reaction is fast



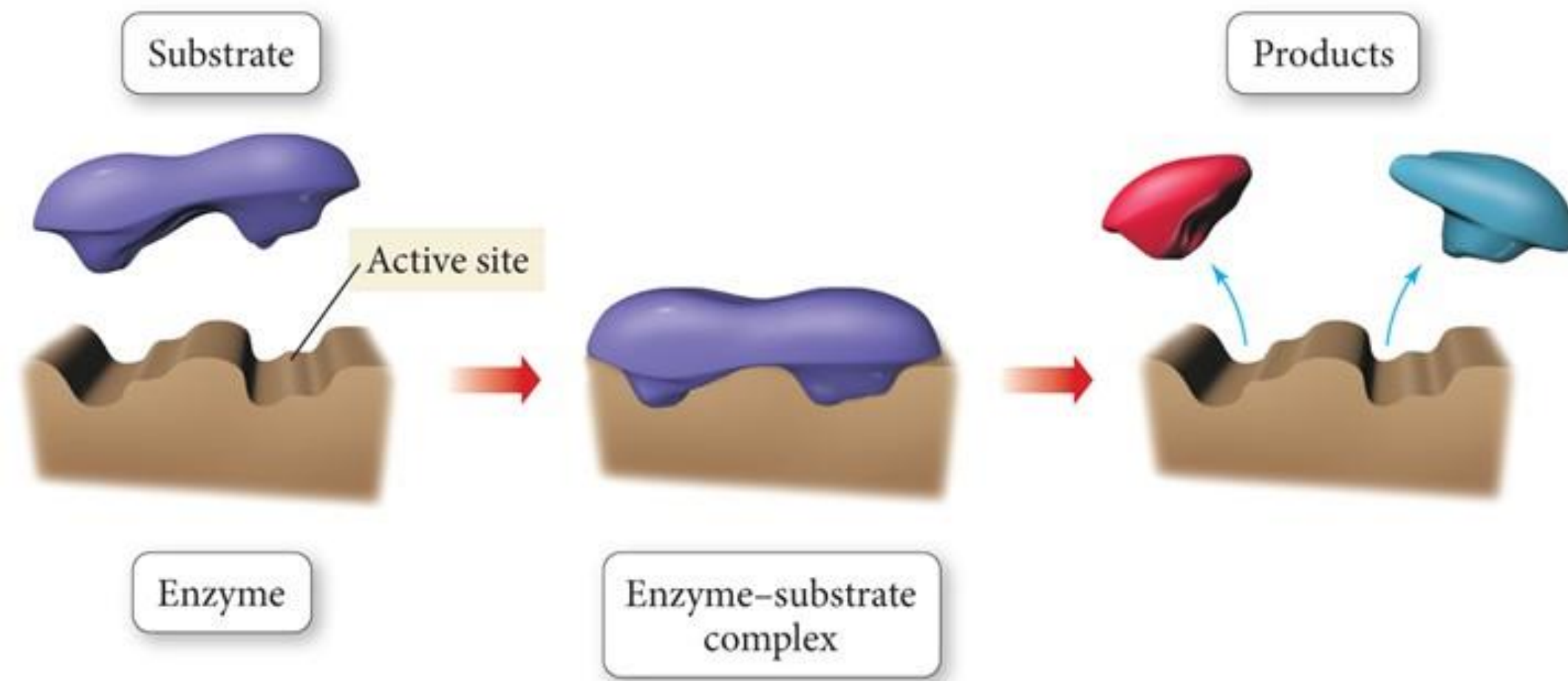
Catalysis occurs by 4 step process

- Adsorption:** the reactant are adsorbed on to the metal surface
- Diffusion:** the reactant diffuse in the metal surface until they approach each other
- Reaction:** the reactants react to form the products
- Desorption:** the products desorb from the surface into the gas phase

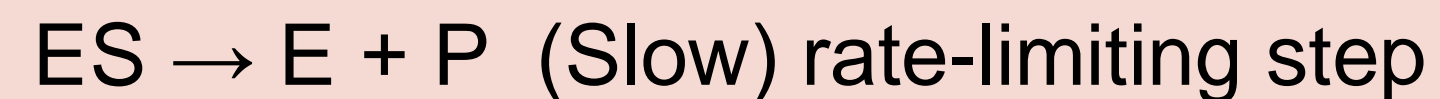
- The large E_a of the hydrogenation reaction (primarily due to the H-H bond in H_2) is greatly lowered when the reactants adsorb onto the surface

Enzymes: Biological Catalysts

Enzyme-Substrate Binding



Enzyme-Substrate Binding



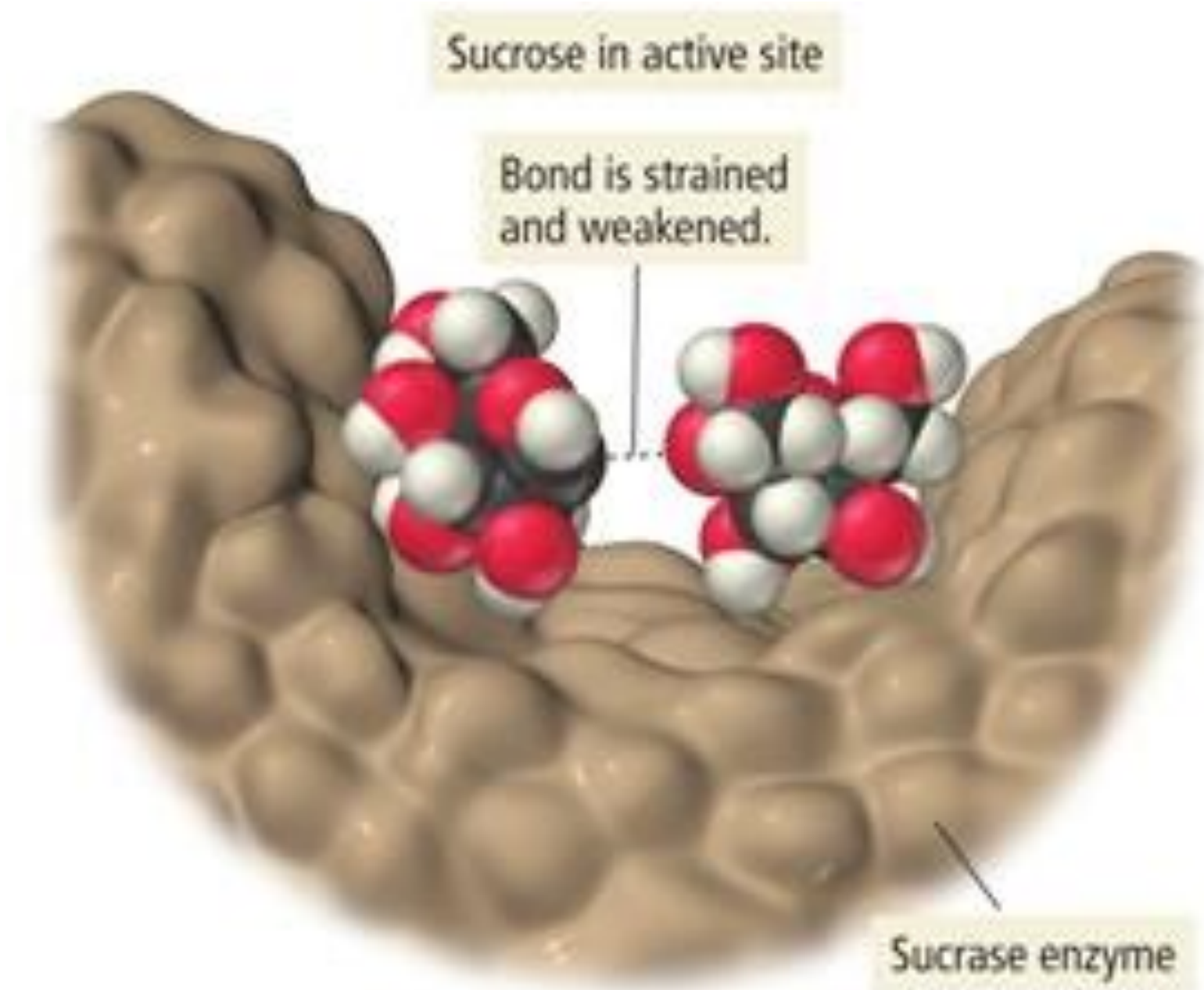
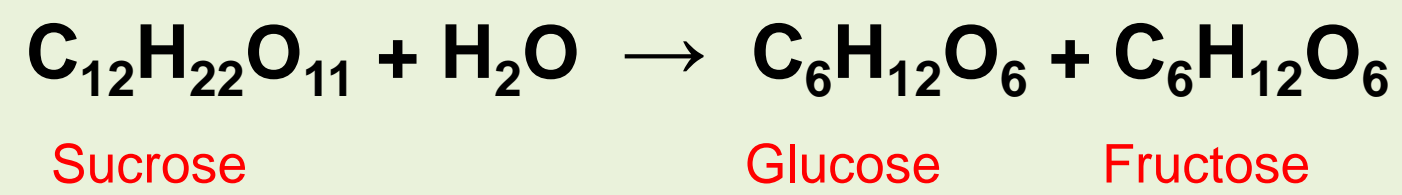
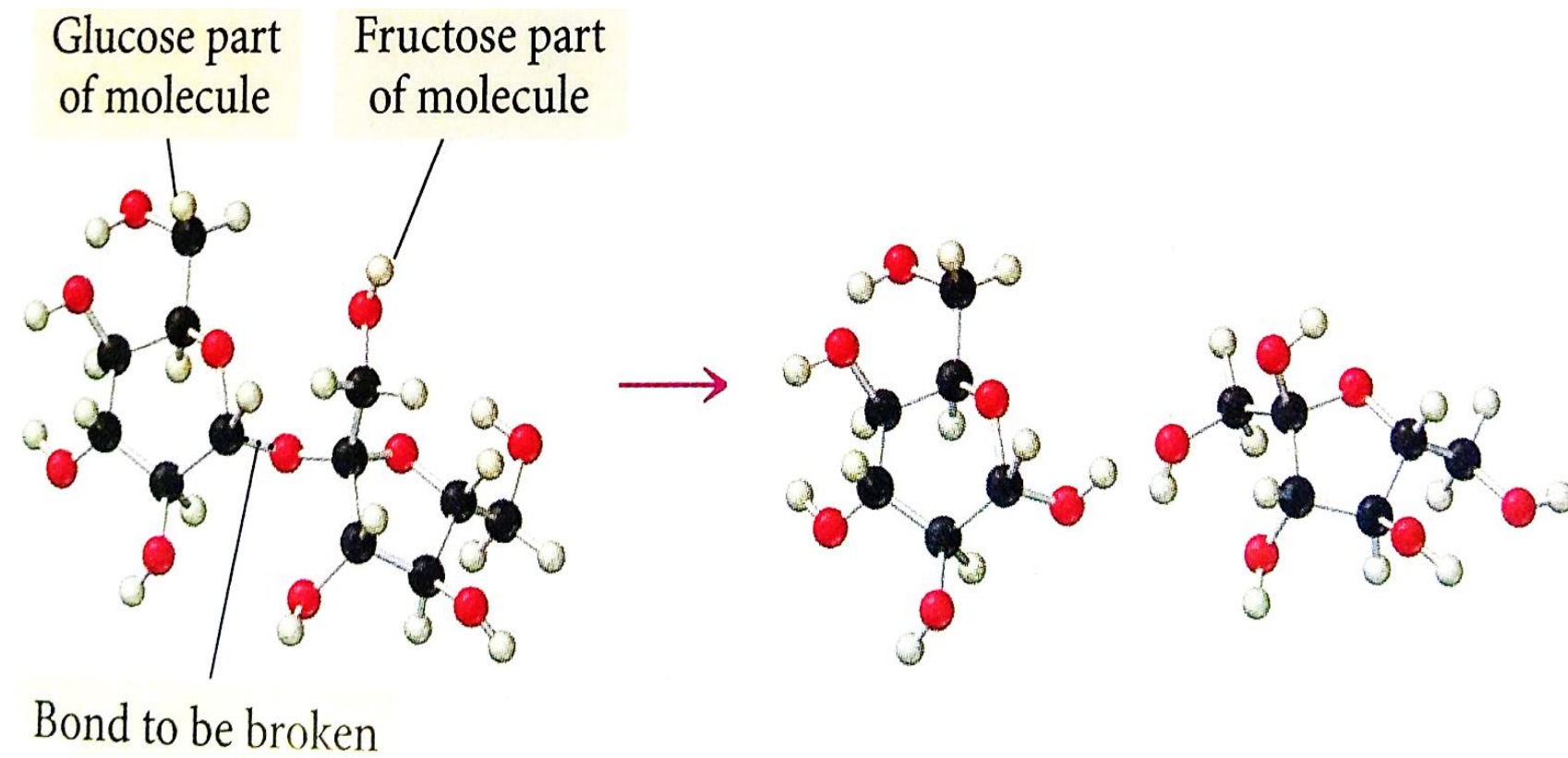
- Chemical catalysis is prevalent in living organism

- In a living organism, thousands of chemical reactions that must occur for the organism to survive may be too slow at normal temperature. These reactions occur in the presence of enzymes (which are basically proteins which acts as catalyst).

- An enzyme increases the rates of biological reactions
- Active site in an enzyme is an specific area where substrate/reactant molecule binds via hydrogen bonding, dispersion interactions or covalent bonding.

Enzymes: Biological Catalysts

- **Example:** Sucrase enzyme catalyzes breaking up of sucrose (table sugar) into glucose and fructose within the body during digestion
- Note at body temperature, the sucrose does not break into glucose or fructose because the activation energy is high (very slow)

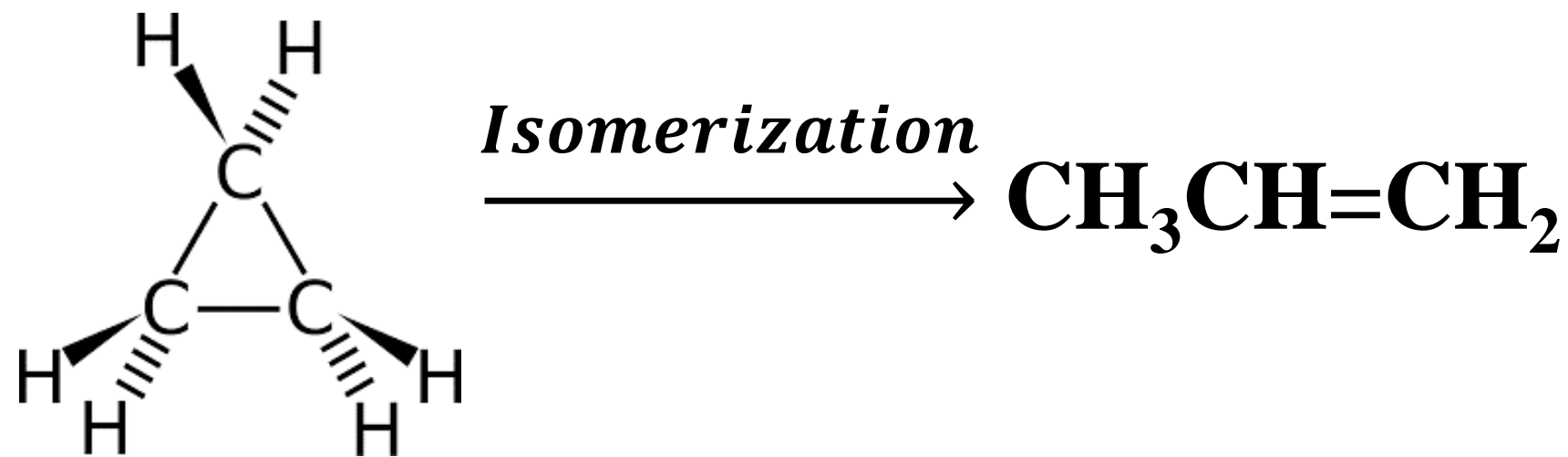


An enzyme-catalyzed reaction

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Unimolecular Reaction Mechanism

A number of gas-phase reactions follow first-order kinetics, as in the isomerization of cyclopropane into propene



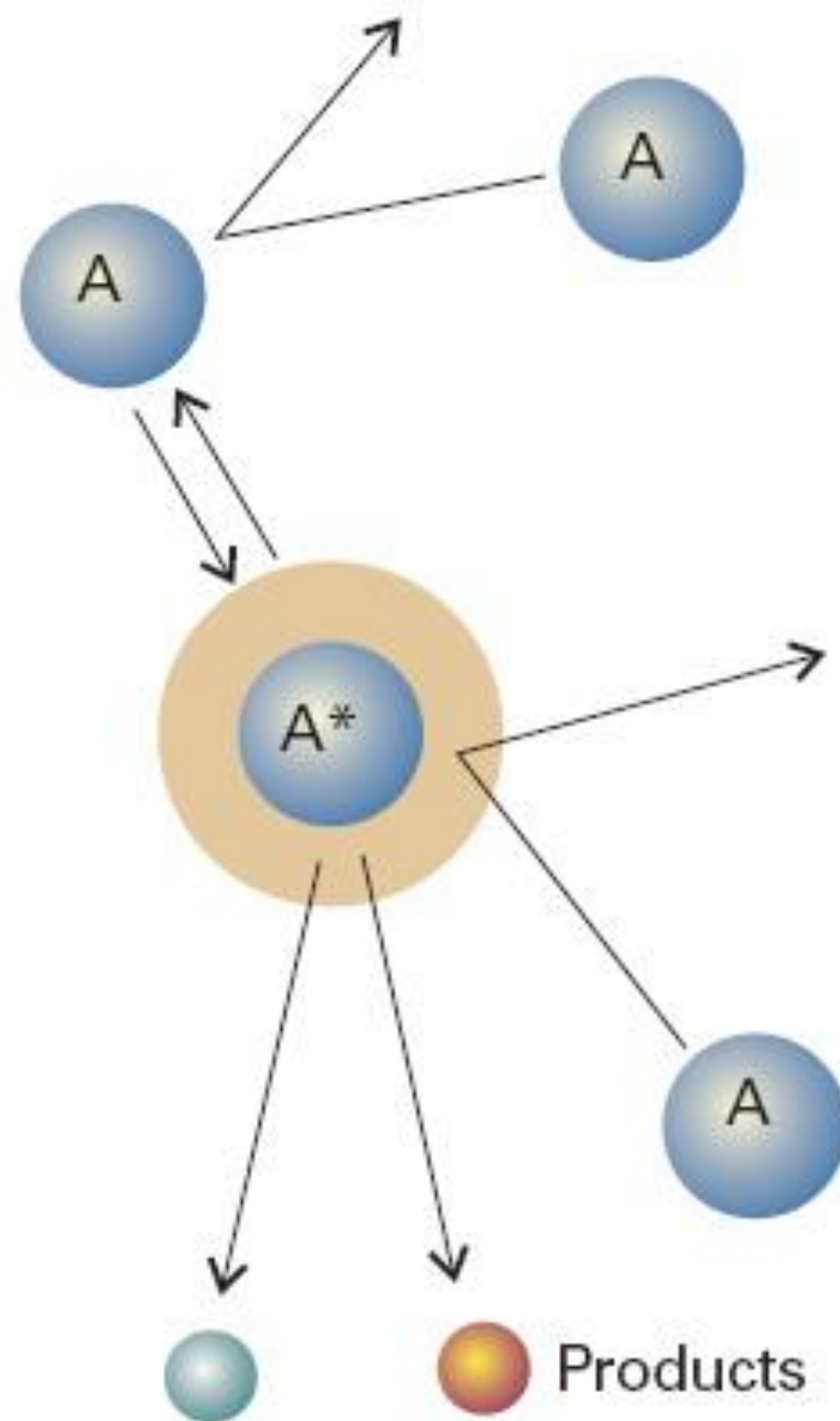
$$\text{Rate} = k[\text{cyclo-CH}_3\text{CH}=\text{CH}_2]$$

- To interpretate the first-order rate laws it is assumed that a molecule acquires enough energy to react as a result of its collisions with other molecules.

- However, collisions are simple **bimolecular** events, so how can they result in a first-order rate law?

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

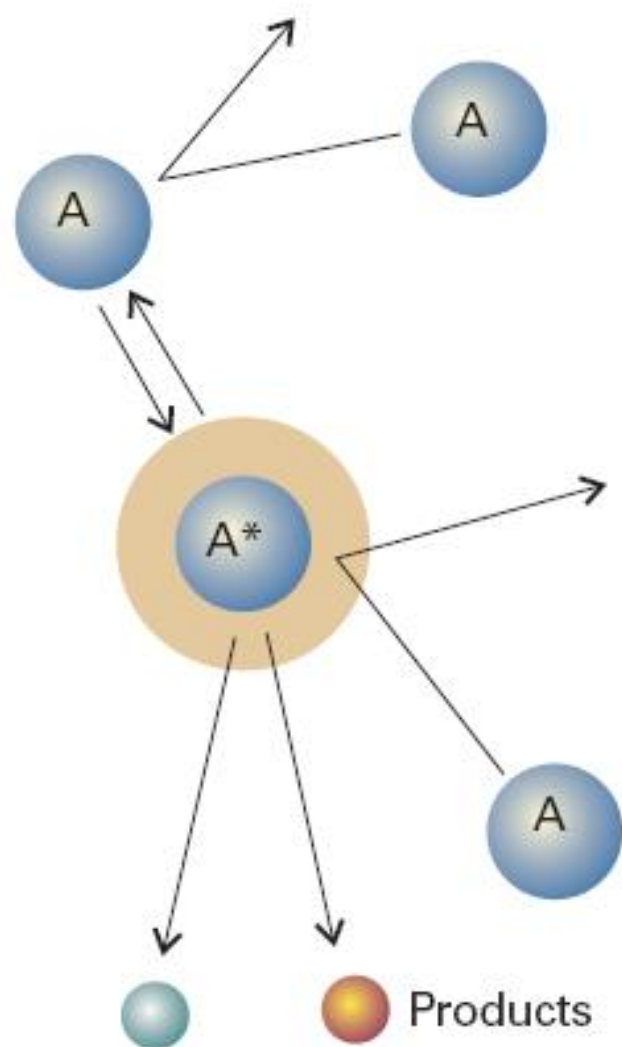
Unimolecular Reaction Mechanism: The Lindemann–Hinshelwood mechanism



A representation of the Lindemann–Hinshelwood mechanism of unimolecular reactions. The species **A** is **excited** by collision with **A**, and the **excited A** molecule (**A***) may **either be deactivated** by a collision with **A** or go on to decay by a **unimolecular process** to form products.

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

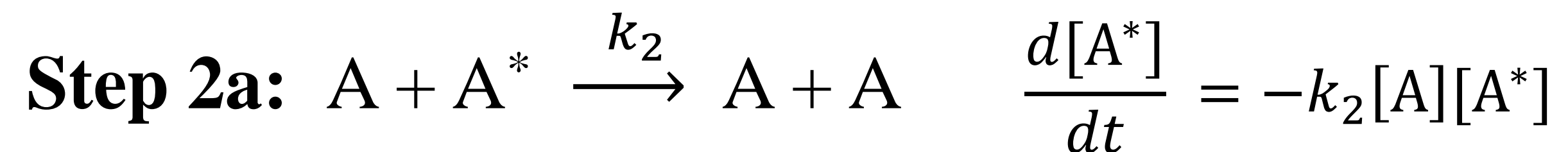
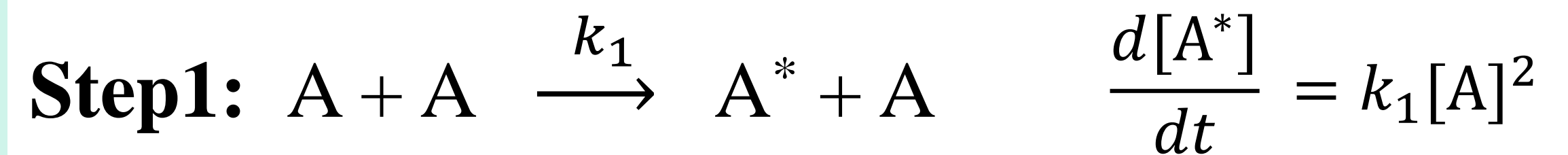
Unimolecular Reaction Mechanism: The Lindemann–Hinshelwood mechanism



In LH mechanism, it is supposed that a reactant molecule A becomes energetically excited by collision with another A molecule (**activation of A**)

The energized molecule (A*) might lose its excess energy by collision with another molecule (**deactivation of A***)

Alternatively, the excited molecule might shake itself apart and form products P. That is, it might undergo the **unimolecular** decay

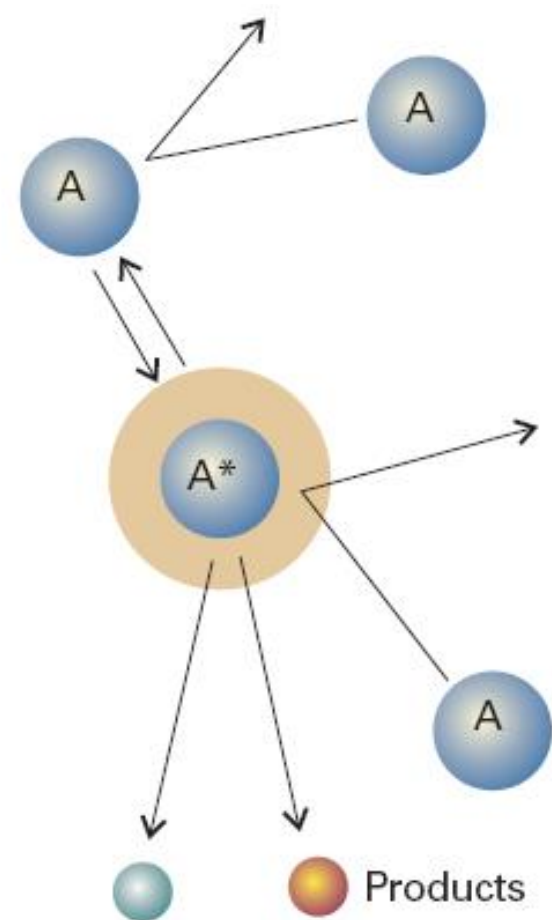


- **Argument:** If step 2b is slow enough to be the rate determining step, the overall reaction will have first-order kinetics.

- **Demonstration:** Write the net rate of formation and apply steady-state approximation

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Unimolecular Reaction Mechanism: The Lindemann–Hinshelwood mechanism



Net rate of formation of $[A^*]$

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_3[A^*]$$

Apply Steady-state approximation

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_3[A^*] \approx 0$$

Solving for $[A^*]$

$$[A^*] = \frac{k_1[A]^2}{k_3 + k_2[A]}$$

Rate of formation of P

$$\frac{d[P]}{dt} = k_3[A^*] = \frac{k_1 k_3 [A]^2}{k_3 + k_2[A]}$$

Argument: if step 2a dominates over step 2b (high pressure limit i.e. ≥ 1 atm)

Result: Neglect k_3 in the denominator

Rate of formation of P

• **Rate law is still not first-order**

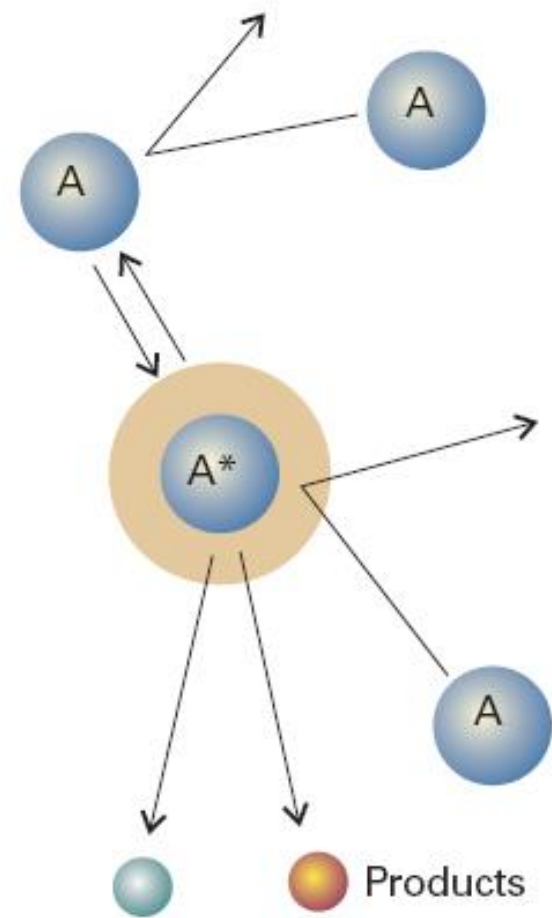
$$k_2[A][A^*] \gg k_3[A^*] \Rightarrow k_2[A] \gg k_3$$

$$\frac{d[P]}{dt} = k[A] \quad \text{where} \quad k = \frac{k_1 k_3}{k_2}$$

First-order rate law which we anticipated!

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Unimolecular Reaction Mechanism: The Lindemann–Hinshelwood mechanism



Argument: What if [A] is reduced (low-pressure limit i.e. ≤ 0.5 atm) ? i.e when $k_2[A] \ll k_3$

Rate of formation of P

$$\frac{d[P]}{dt} = \frac{k_1 k_3 [A]^2}{k_3 + k_2 [A]} = k_1 [A]^2$$

Rate law becomes second-order

Physical interpretation for the change of order: At low pressure (small [A]), the rate-determining step is bimolecular formation of A (i.e. Step 1)

Full rate law:

$$\frac{d[P]}{dt} = k[A] \quad \text{where} \quad \frac{1}{k} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1 [A]}$$

\Rightarrow When we plot $1/k$ vs $1/[A]$, we should expect a straight line.

Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions

Unimolecular Reaction Mechanism: The Activation Energy of Composite Reaction

Consider the high-pressure limit of Lindemann–Hinshelwood mechanism

If each of the rate constants follows Arrhenius law of temperature dependence, then

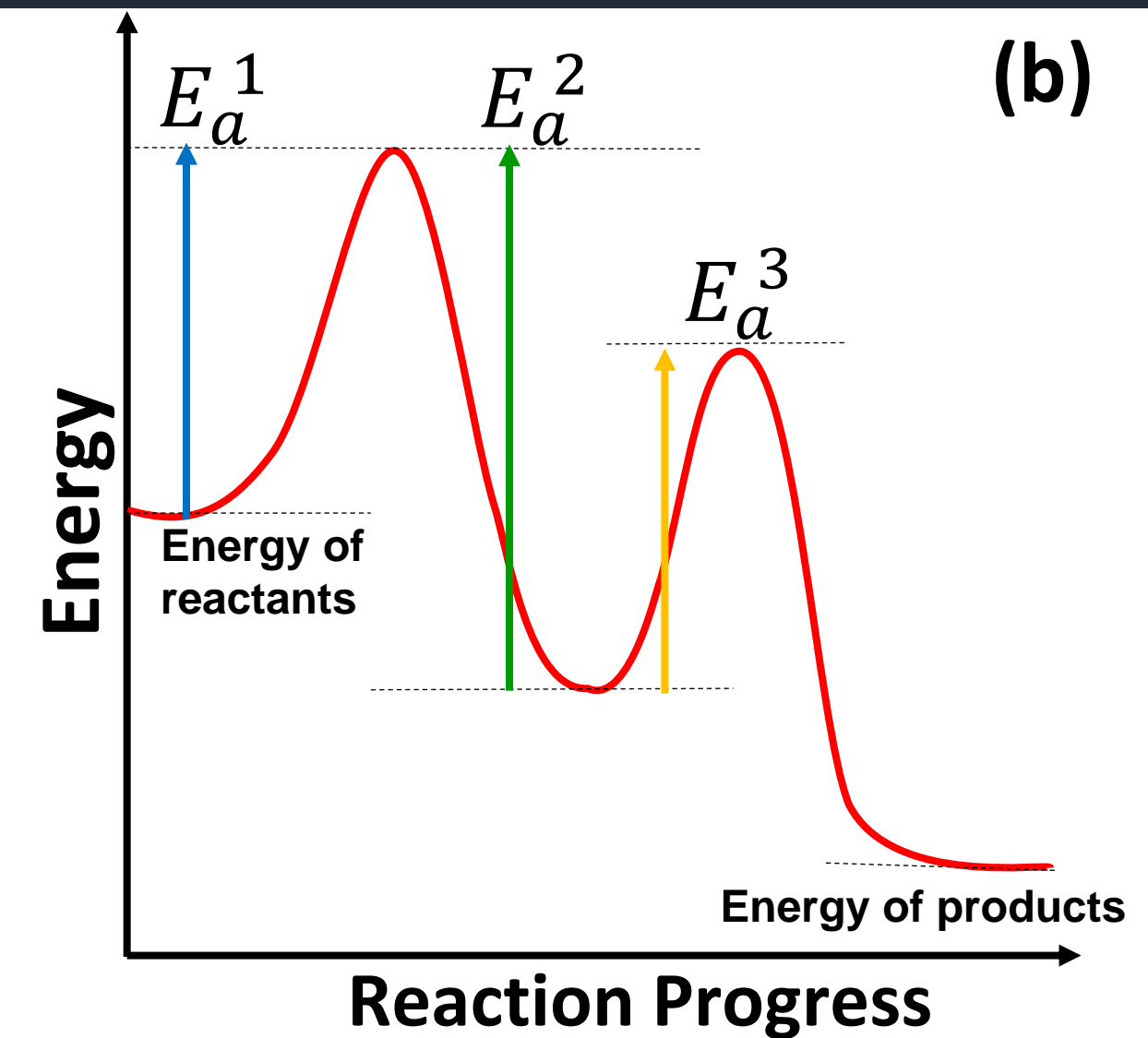
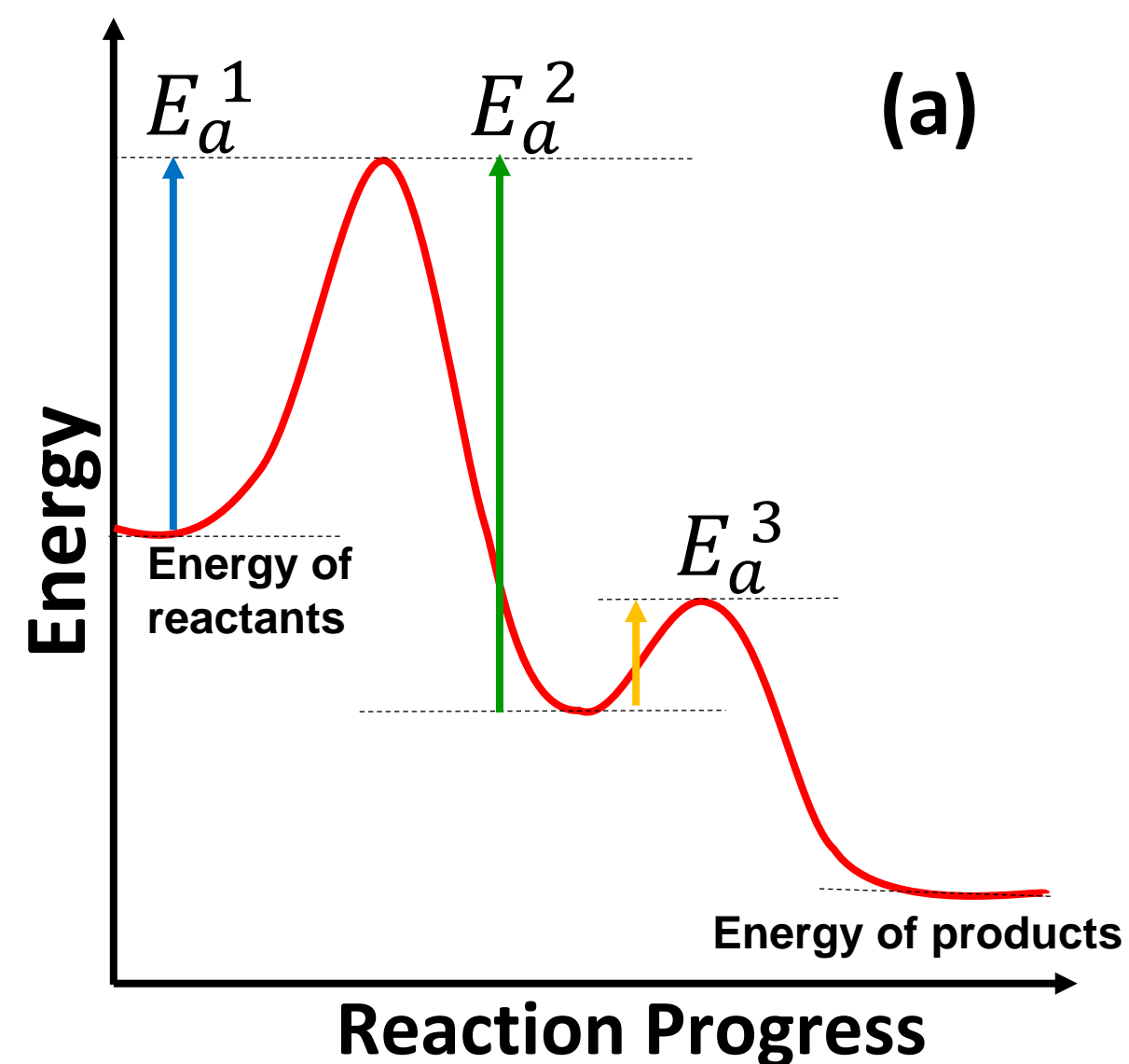
$$k = \frac{k_1 k_3}{k_2} = \frac{A_1 e^{-E_a^1/RT} A_3 e^{-E_a^3/RT}}{A_2 e^{-E_a^2/RT}} = \frac{A_1 A_3}{A_2} e^{-[E_a^1 + E_a^3 - E_a^2]/RT}$$

⇒ The composite rate constant k also follows **Arrhenius law** with activation energy

$$E_a = E_a^1 + E_a^3 - E_a^2$$

(a) When $E_a^1 + E_a^3 < E_a^2$, E_a is negative and rate decreases with increasing the temperature

(reverse reaction is so sensitive to temperature and its rate increases with increasing temperature. i.e. deactivation of A^* becomes faster with increasing the temperature)

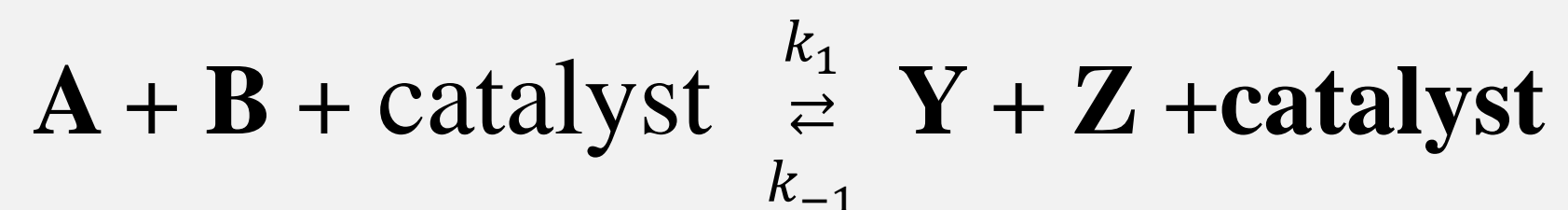


(b) When $E_a^1 + E_a^3 > E_a^2$, E_a is positive and rate increases with increasing the temperature

Doubt-clearing Slide

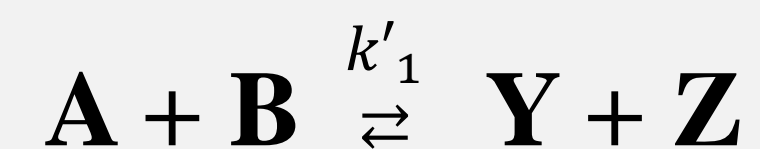
- Can we simply put the [catalyst]=0 for reaction without the catalyst?

With Catalyst



- **Rate from left to right:** $v_1 = k_1[\text{A}][\text{B}][\text{catalyst}]$
- **Rate from right to left:** $v_{-1} = k_{-1}[\text{Y}][\text{Z}][\text{catalyst}]$

Without Catalyst



- **Rate from left to right:** $v_1 = k'_1[\text{A}][\text{B}]$
- **Rate from right to left:** $v_{-1} = k'_{-1}[\text{Y}][\text{Z}]$

- **Can $p > 1$?** Reactions between individual atoms usually have orientation factor p close to 1. But a few reactions have p value greater than 1. Example: For $\text{Br}_2(\text{g}) + \text{K}(\text{g}) \rightarrow \text{KBr}(\text{g}) + \text{Br}(\text{g})$, $p = 4.8$. This means in such reactions, there are more reactions than just collision. The reactants do not need to even collide to react! Some other mechanism (e.g. electron transfer) may be possible.

- **When can we apply steady state approximation?** When the intermediate is unstable (can be metastable w.r.t. reactant or product). In usual cases, the intermediates are highly unstable (e.g. carbocation or radical, intermediates formed in $\text{S}_{\text{N}}2$ reactions) and quickly react to form the product.