The Arrhenius Equation (Svante Arrhenius, 1889)

- **The rates of chemical reactions are highly sensitive to temperature**

- Lizards become lethargic when their body temperature drops
- For example, typically a 10 Kelvin increase in temperature increases the rate of a typical biological reaction by two or three times

- How do we explain this highly sensitive temperature dependence?

Temperature dependence of a reaction rate is contained in the rate constant, k

The Arrhenius Equation (Svante Arrhenius, 1889)

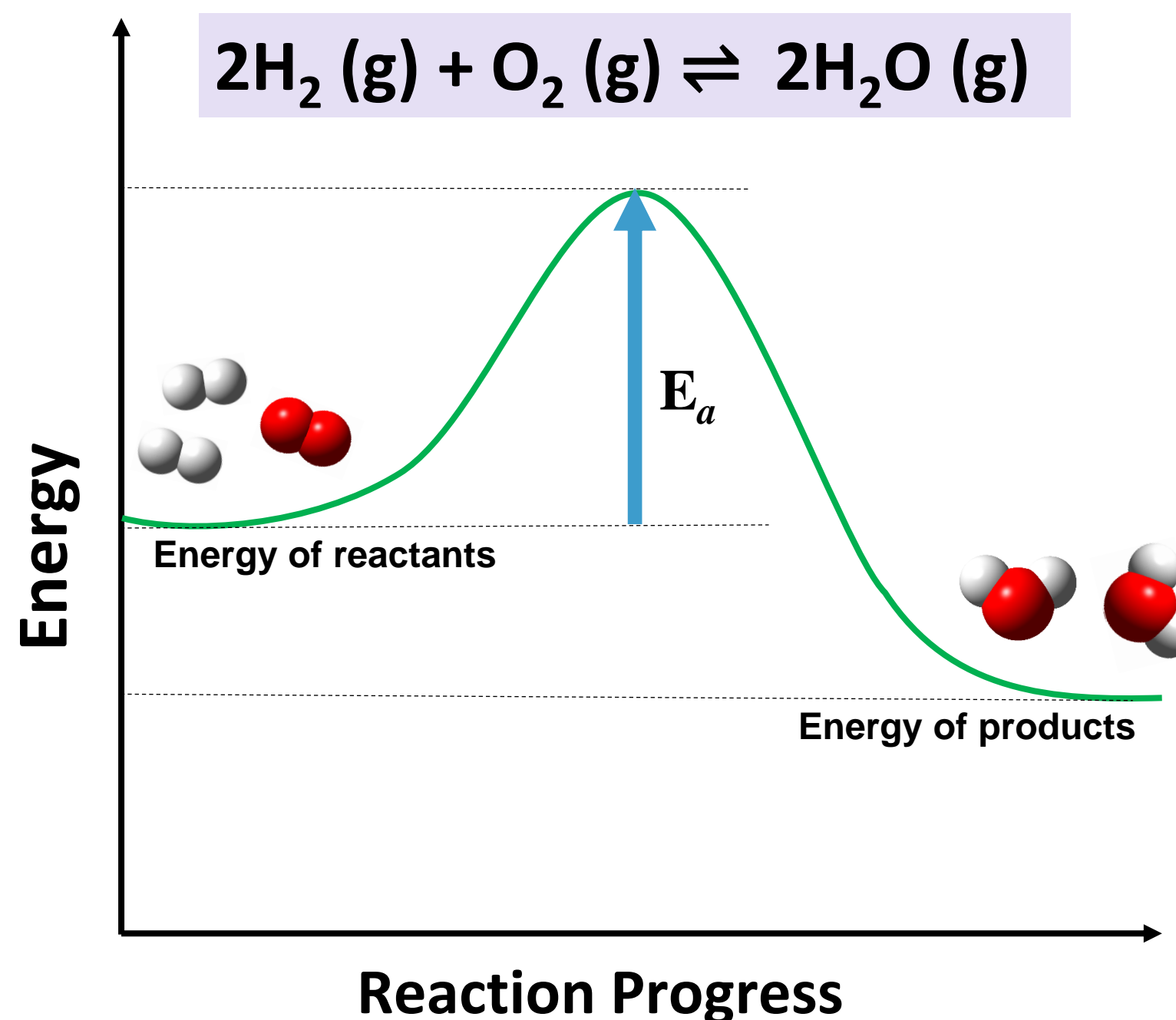**Activation energy**

$$k = Ae^{-E_a/RT}$$

Pre-exponential factor or Frequency factor

Exponential factor

Activation energy (E_a): An energy barrier that must be surmounted by the reactants to transform into the products
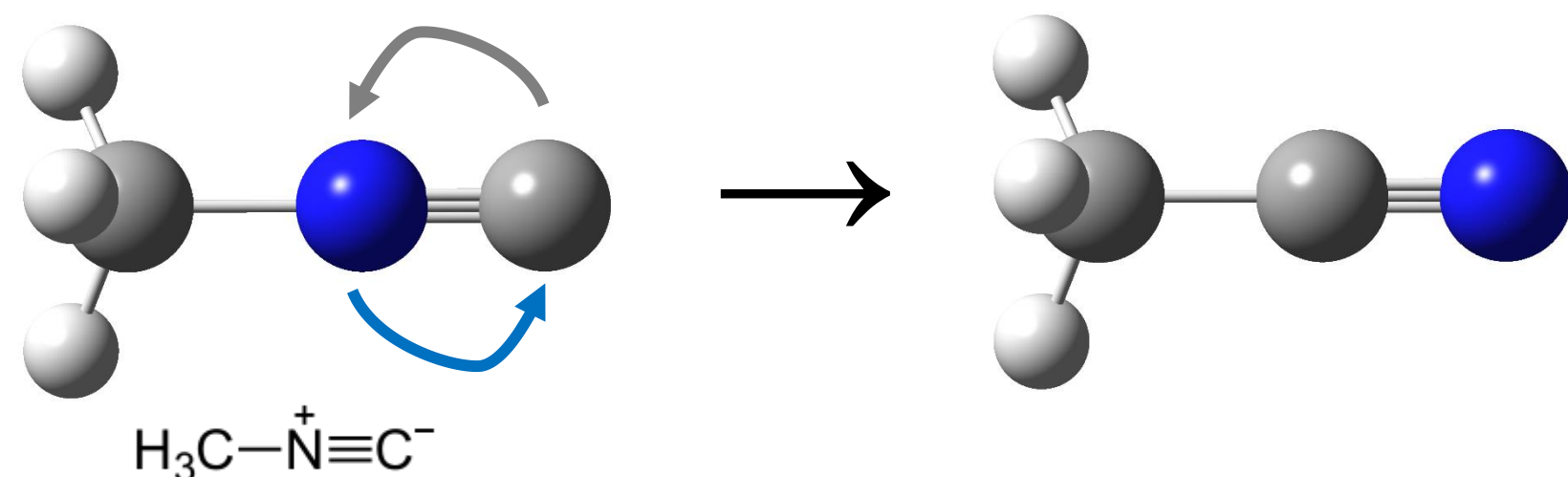
Frequency factor (A) : Number of times the reactants approach the activation barrier per unit time

- **T should be in Kelvin (K)**
- **R=8.314 J mol^{-1} K^{-1}**

2H$_2$ (g) + O$_2$ (g) $\rightleftharpoons$ 2H$_2$O (g)

Energy

E_a

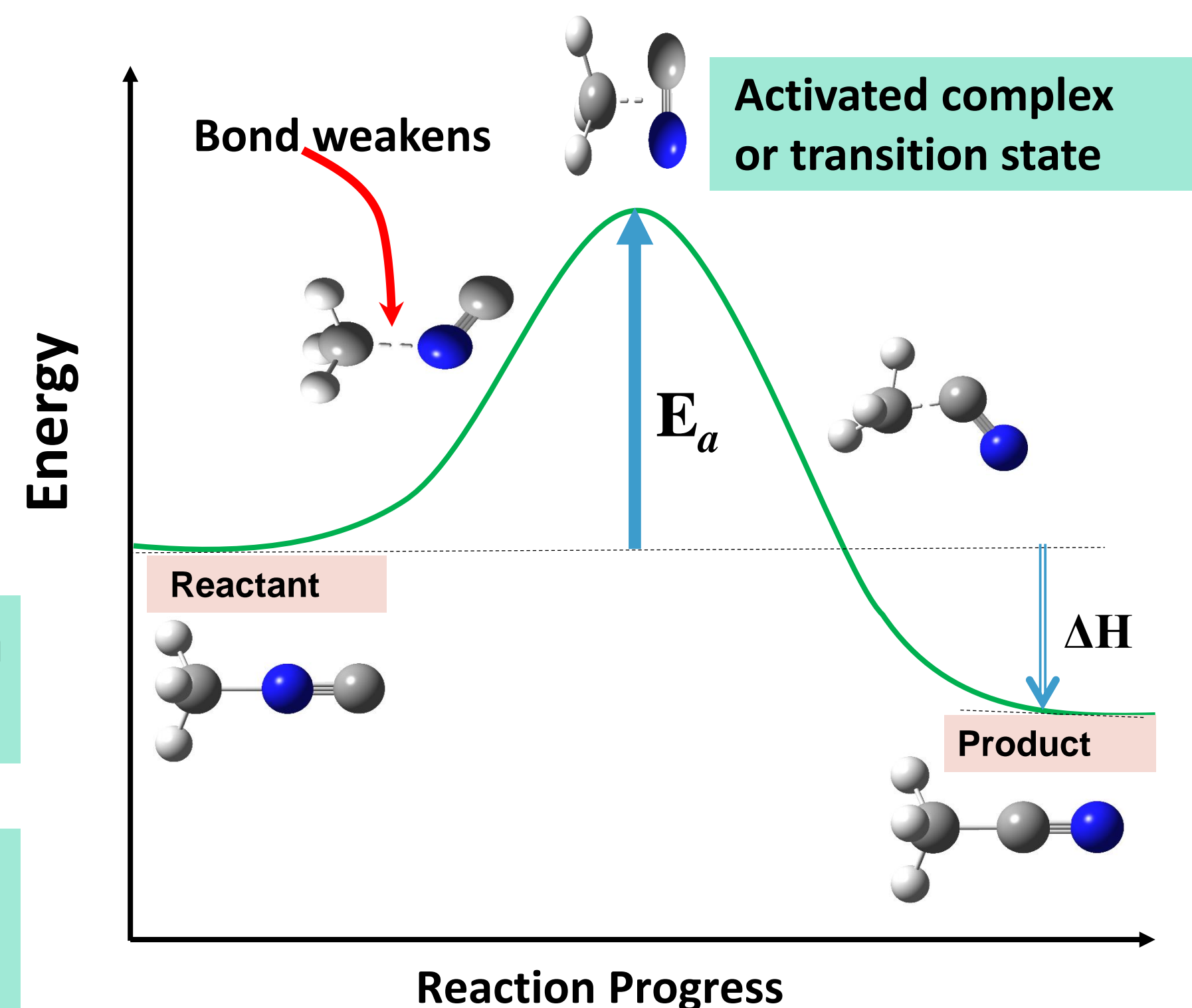Energy of reactants

Energy of products

Reaction Progress

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The Activation Energy (E_a)

Consider the following reaction in which methyl isonitrile (CH_3NC) rearranges to form acetonitrile (CH_3CN)

$H_3C\!-\!\overset{+}{N}\!\equiv\!C^-$

To reach from the reactant to product, the molecule must go through a high energy state called as **activated complex** or **transition state**

Even though $\Delta H < 0$ (exothermic, energetically downhill), it must go uphill to reach the activated complex because energy is required to initially weaken the H_3C-N bond and allow the NC group to begin to rotate

Bond weakens

Activated complex or transition state

E_a

Reactant

ΔH

Product

Energy

Reaction Progress

Higher is the activation energy, the slower the reaction rate

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The Frequency Factor (A)

$$k = Ae^{-E_a/RT}$$
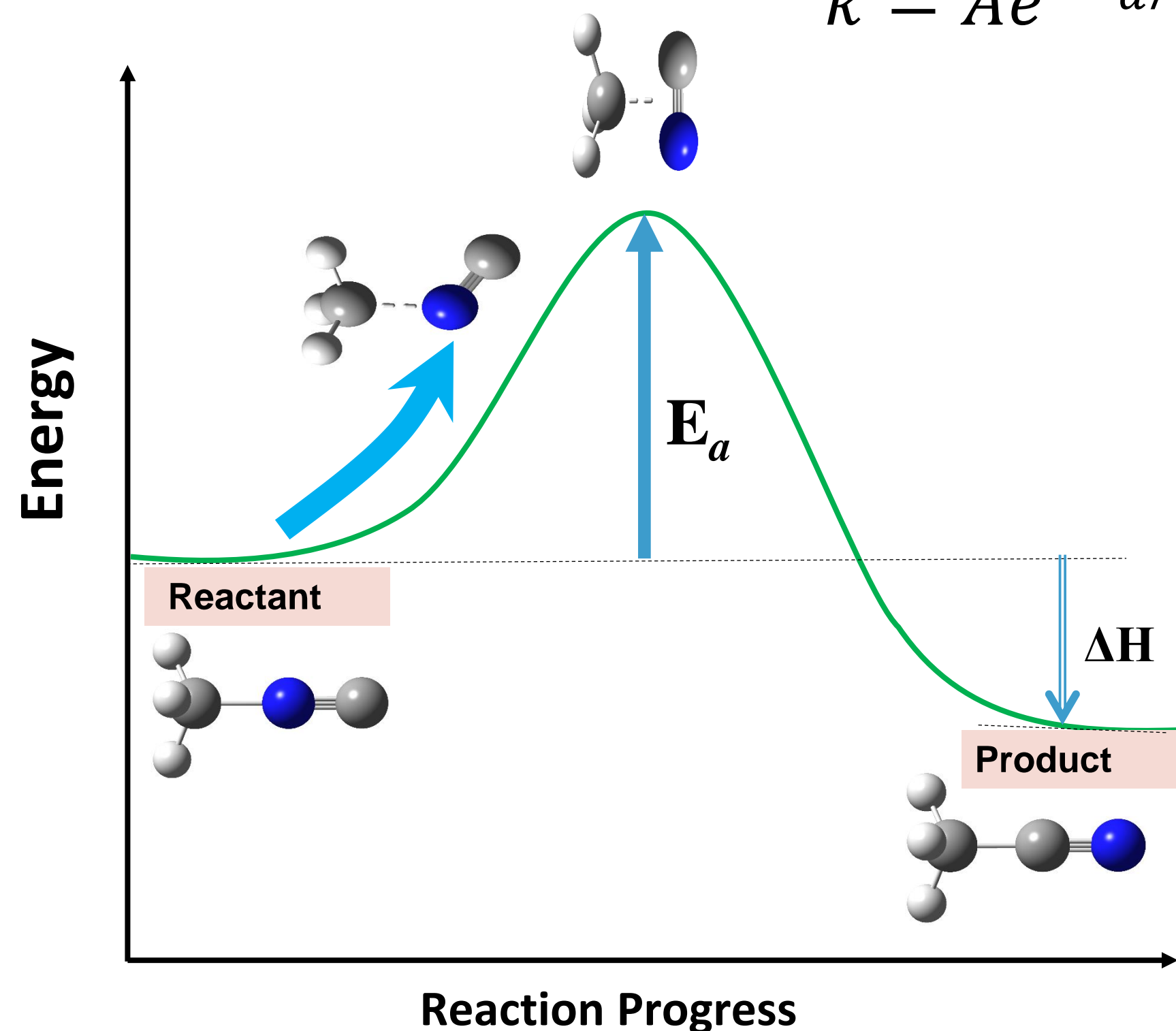
E_a

ΔH

Reactant

Product

Energy

Reaction Progress

Frequency factor (A) : Number of times the reactants approach the activation barrier per unit time   **[Recall]**

- In this example, any time the NC group begins to rotate it approaches the activation barrier

- For this reaction, "A" represents the rate at which the NC part of the molecule wags (vibrates side-by-side)
- With each wag, the reactant approaches the activation barrier

- However, approaching the barrier does not mean surmounting it.
- Only some approaches pass and most fail to make it over the activation barrier because of lack of enough energy.

The Frequency Factor (A closer look through collision model)

$$A(g) + B(g) \rightarrow product$$
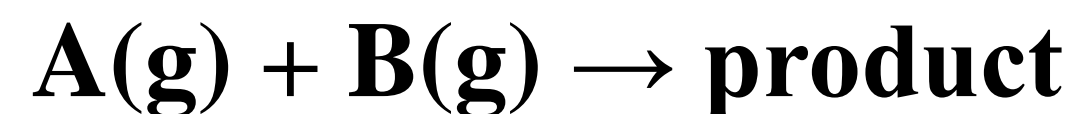
1. In the collision model, a reaction occur after two reactant molecules collide with sufficient energy
2. In collision theory, each approach to the activation of barrier is a collision between the reactant molecules.
3. This means, the frequency factor should be the number of collisions that occur per unit time (collision frequency, *z*).

- However, the frequency factor for most gas-phase reactions are observed to be smaller than collision frequency

$$k = Ae^{-E_a/RT}$$
$$= pze^{-E_a/RT}$$

Orientational factor   Collision frequency

Energetic collision
Leading to product

No reaction

Collision frequency: **Number of collisions that occur per unit time**, typically 10^9 per second.

Orientational factor: Fractions of collisions with an orientation that facilitates the reaction to occur (Ranges between 0 and 1)
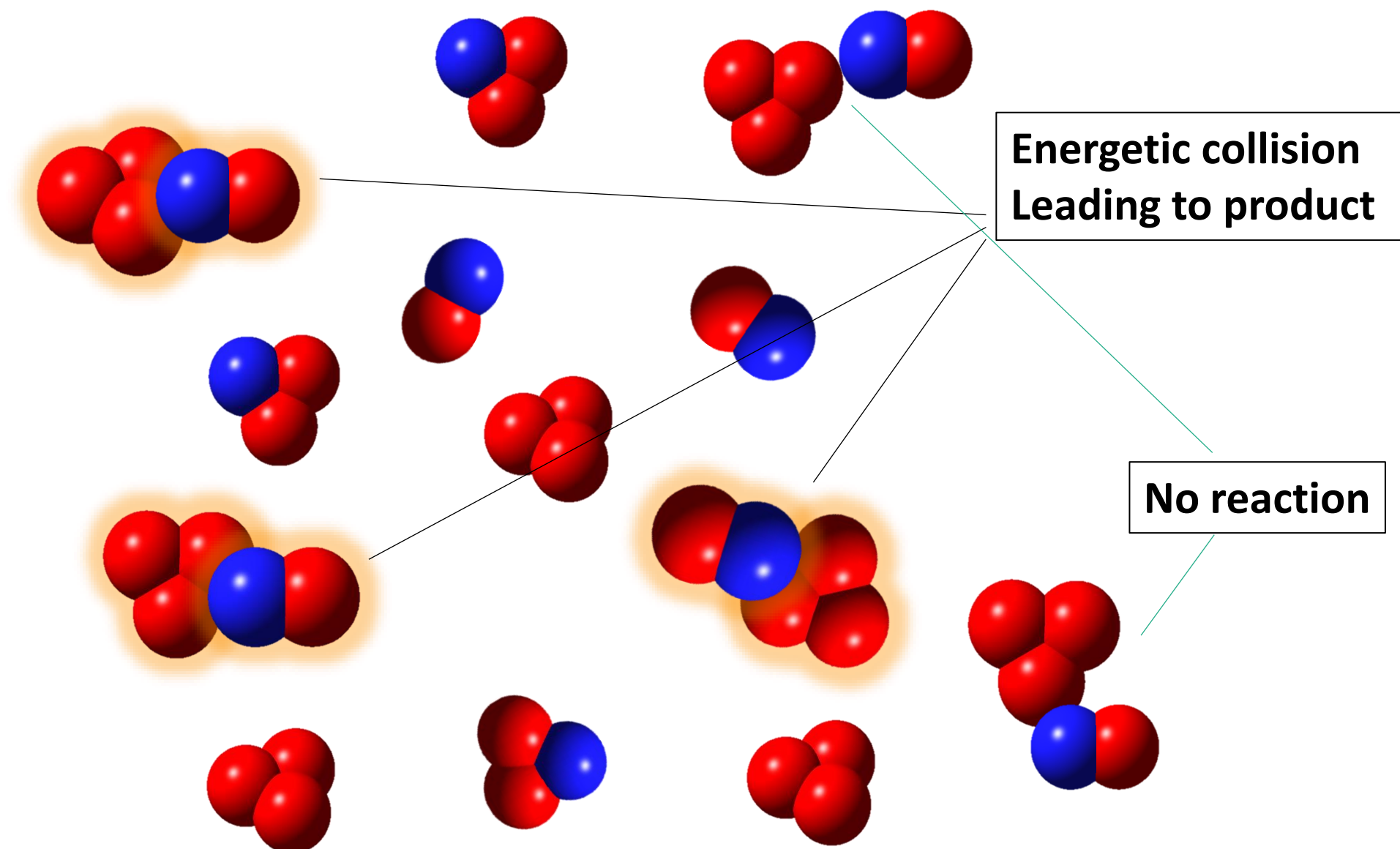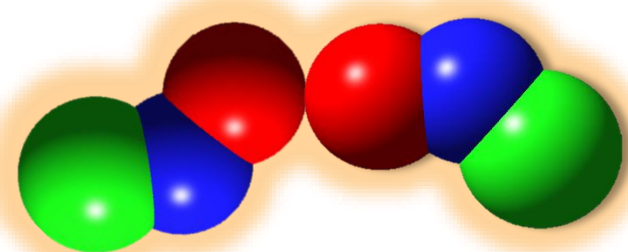
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The Frequency Factor (A closer look through collision model)

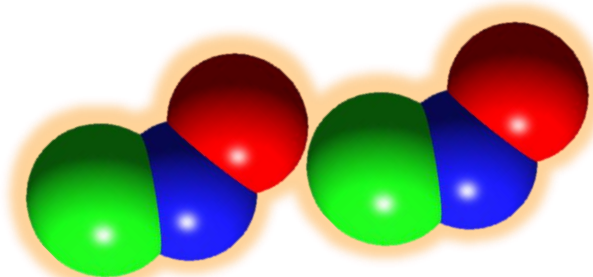$$NOCl(g) + NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$
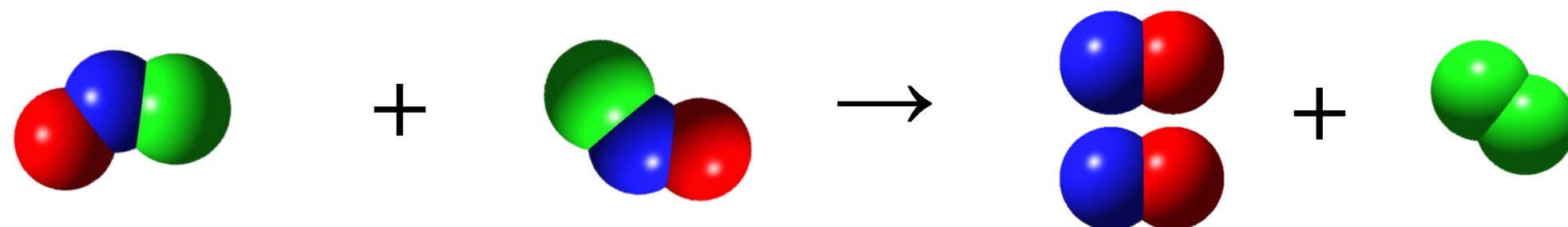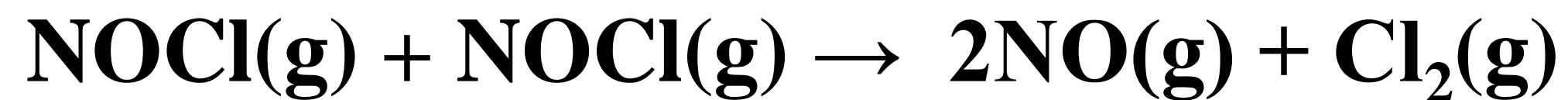
- For the reaction to occur, two NOCl molecules must collide with sufficient energy
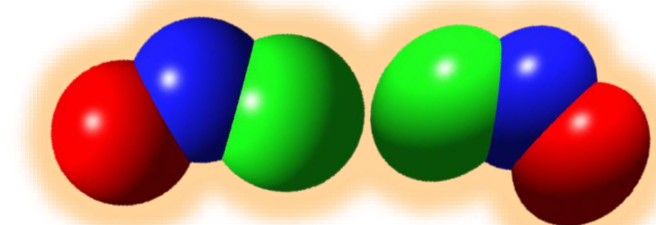
- Three possible collision orientations:

Ineffective collision

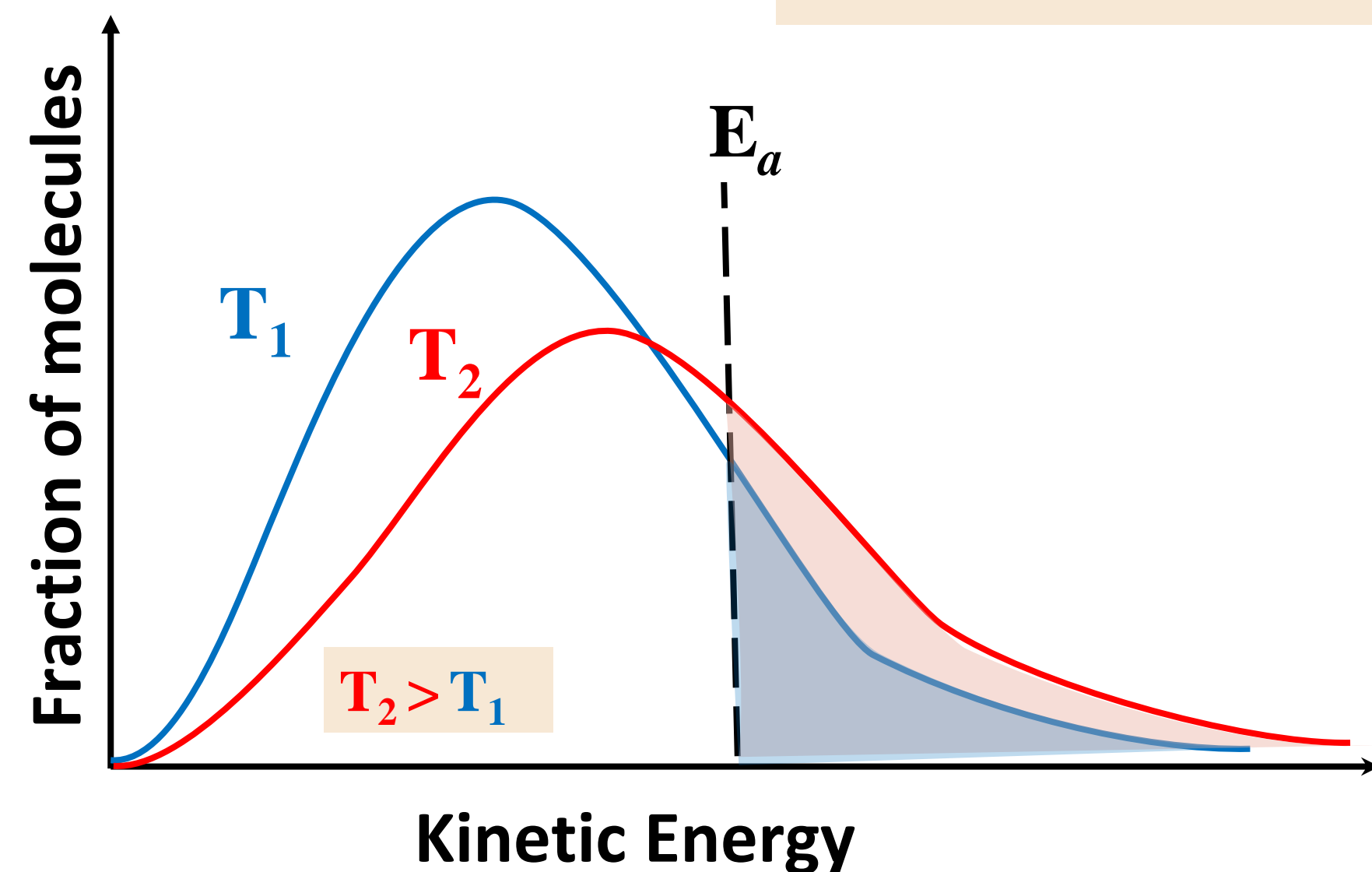Ineffective collision

Effective collision

- Even if the collision has sufficient energy, the orientation is not appropriate for the Cl atoms to bond

- For this reaction, $p = 0.16$ $(orientation\ factor)$
⇒ Only 16 out of 100 sufficiently energetic collisions are actually successful in forming the products

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The Exponential Factor ($e^{-E_a/RT}$)

$$k = Ae^{-E_a/RT}$$

Fraction of molecules vs **Kinetic Energy**

E_a

T_1
T_2
$T_2 > T_1$

1. When E_a is *low* and T is *high*: $e^{-E_a/RT} \rightarrow 1$
2. When E_a is *high* and T is *low*: $e^{-E_a/RT} \rightarrow 0$

$$0 \leq e^{-E_a/RT} \leq 1$$

- $e^{-E_a/RT}$ represents the fraction of molecules that have enough energy to make it over the activation barrier on a given approach.

- **In other words, the exponential factor signifies the fraction of approaches that are actually successful and result in the product**

- **Example:** If A = 10^9/s and $e^{-E_a/RT}$ = 10^{-7} at a certain temperature, then
  k= 10^9/s x 10^{-7} = 10^2/s
- Consider the previous example of conversion of CH_3NC to CH_3CN.
- If CN group wags at a rate of 10^9/s and with each wag, the activation barrier is approached. Then, for a given wag only **1** in 10^7 molecules has sufficient energy to actually reach or cross the activation barrier.
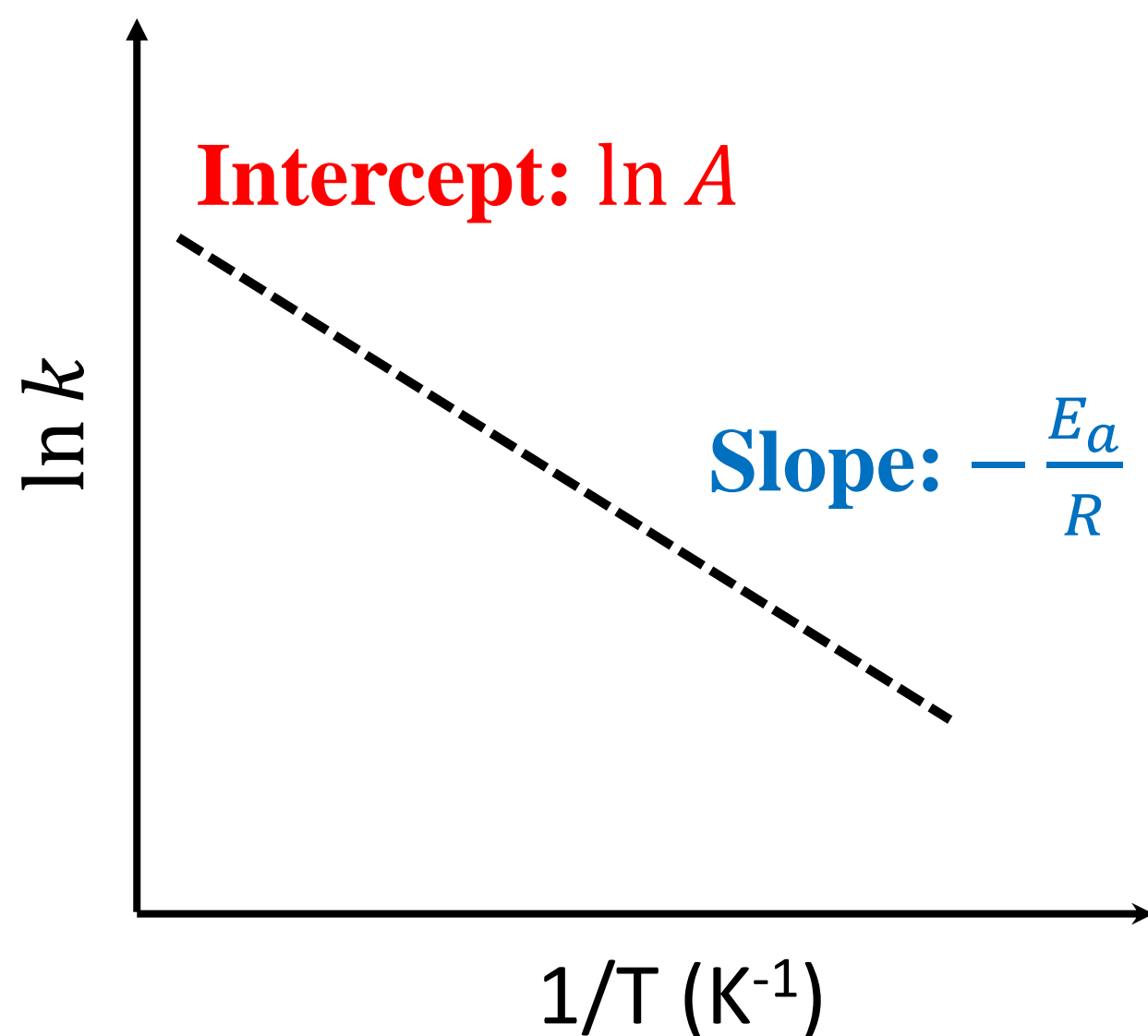
When the temperature increases, the number of molecules having enough thermal energy to surmount the activation barrier increases

- **Commonly, only small percentage of molecules have enough energy to surmount the barrier**

- **But, only small change in T makes huge difference in the number molecules which can surmount the barrier**

$$k = Ae^{-E_a/RT}$$

Intercept: $\ln A$

Slope: $-\dfrac{E_a}{R}$

$\ln k$

$1/T$ (K^{-1})

$$\ln k = \ln(Ae^{-E_a/RT})$$

- **Taking natural log of both sides**

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

- *y=mx + c* **form**

- **A plot of** $\ln k$ **vs** $\dfrac{1}{T}$ **yields a straight line with slope of** $-\dfrac{E_a}{R}$ **and intercept of** $\ln A$. **Such plot is called as an Arrhenius plot**

Arrhenius Plot: Experimental Measurements of A and E_a

- In some cases, when the data is limited or ploting tools are not available, we can still calculate A and E_a if we know the rate constants at just two temperatures

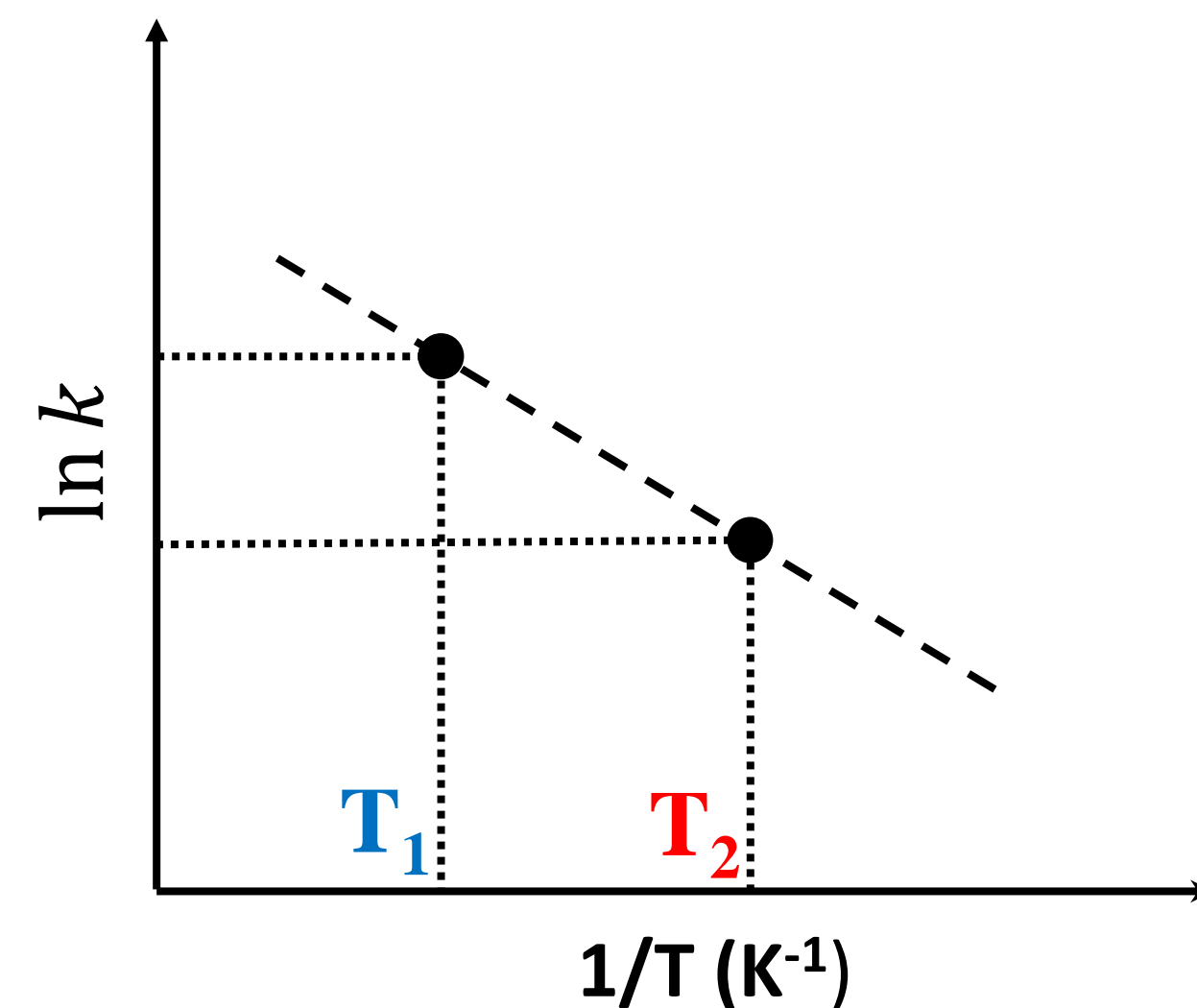$$\ln k_2 = -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A$$

- **rate at temperature T$_2$**

$$\ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A$$

- **rate at temperature T$_1$**

$$\ln k_2 - \ln k_1 = \left[-\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \ln A\right] - \left[-\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln A\right]$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- **Two-point form of Arrhenius equation**

$\ln k$

T_1 $\quad$ T_2

1/T (K^{-1})

Catalyst and Inhibitor

• A catalyst is substance which acts as both a reactant and a product of a reaction. Not consumed during the course of reaction and used to accelerates the reaction

• It's concentration enters into the kinetic equation but not into the equilibrium constant for the reaction

$$\mathbf{A} + \mathbf{B} + \text{catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{Y} + \mathbf{Z} + \mathbf{catalyst}$$
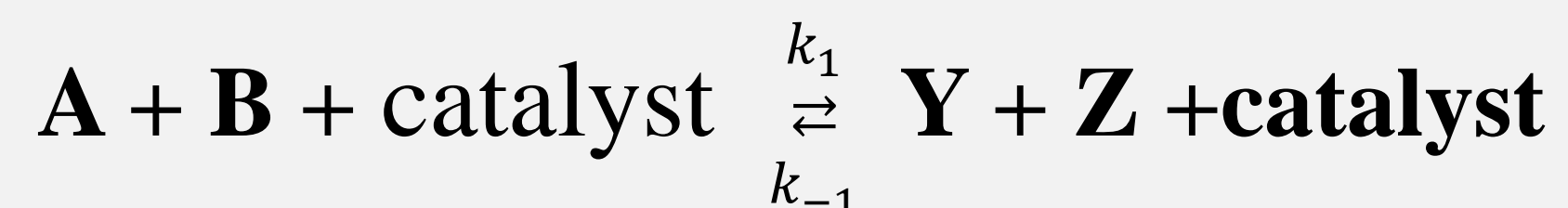
• **Rate from left to right:** $\upsilon_1 = k_1[\text{A}][\text{B}][\text{catalyst}]$

• A catalyst increases the rates to the same extent in forward and reverse directions

• **Rate from right to left:** $\upsilon_{-1} = k_{-1}[\text{Y}][\text{Z}][\text{catalyst}]$

• **At equilibrium, the rates are same in the two directions**
$$k_1[\text{A}][\text{B}][\text{catalyst}] = k_{-1}[\text{Y}][\text{Z}][\text{catalyst}]$$

• **At equilibrium,**
$$\text{K} = \frac{k_1}{k_{-1}} = \left(\frac{[\text{Y}][\text{Z}][\text{catalyst}]}{[\text{A}][\text{B}][\text{catalyst}]}\right)_{eq} = \left(\frac{[\text{Y}][\text{Z}]}{[\text{A}][\text{B}]}\right)_{eq}$$

• **Catalyst does not modify the standard Gibb's free energy change for the reaction:** $\Delta G^0 = -RT\ln \text{K}$

Effect of catalyst on the activation energy and rate constant
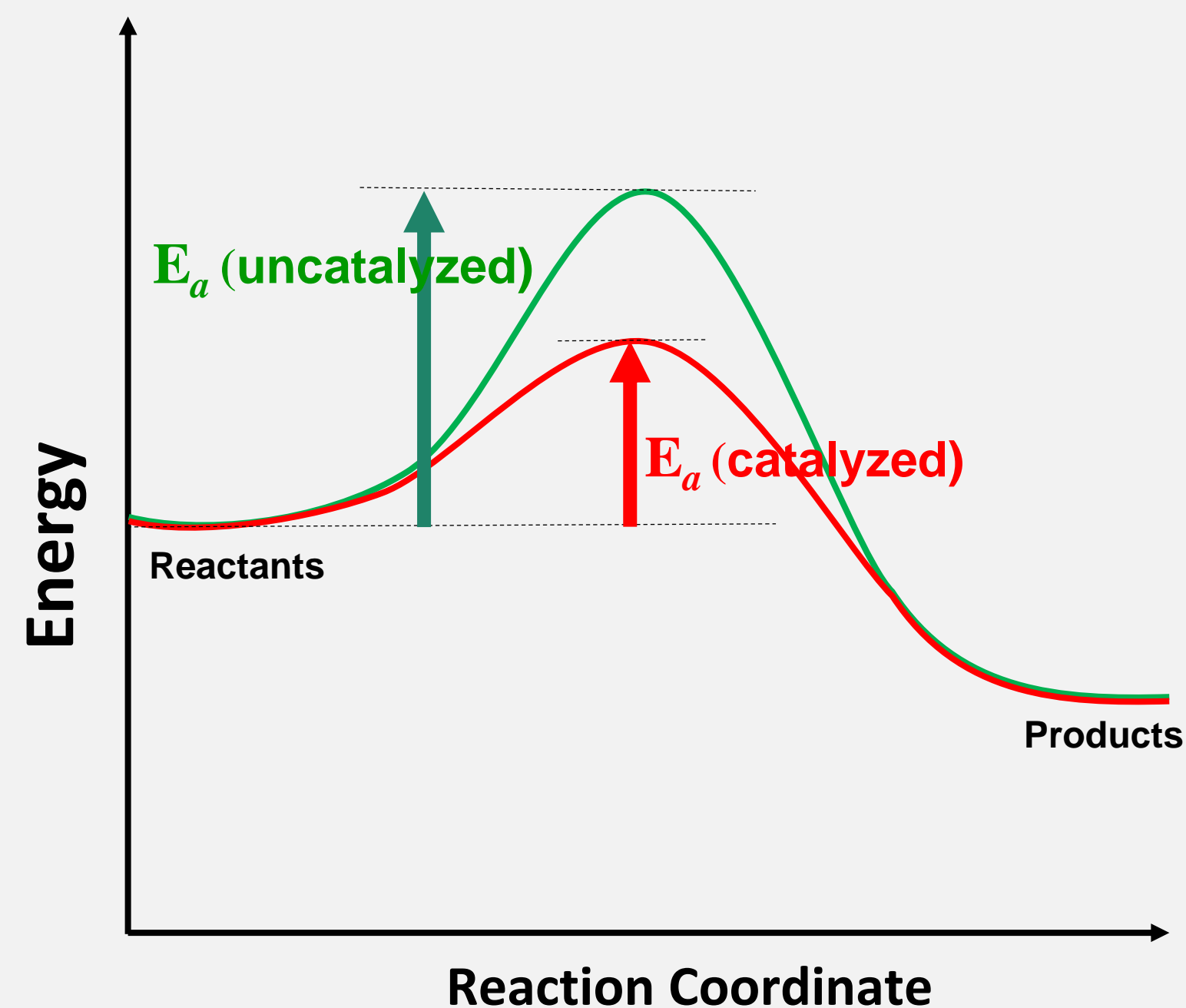
- **Effect on E_a :** A catalyst lowers the activation energy and provides an alternative path to accelerate the reaction

Effect on k:

$$\frac{k_{catalyzed}}{k_{uncatalyzed}} = \frac{A\, e^{-E_{a,catalyzed}/RT}}{A\, e^{-E_{a,uncatalyzed}/RT}} = e^{-(E_{a,catalyzed}-E_{a,uncatalyzed})/RT}$$

$$k_{catalyzed} = k_{uncatalyzed}\, e^{-\Delta E_a/RT}$$

Even a small change in E_a leads to significant change in the rate, some times by orders of magnitude

- **Example:** Enzyme catalase reduces the activation energy for the decomposition of hydrogen peroxide from 76 kJ/mol to 8 kJ/mol
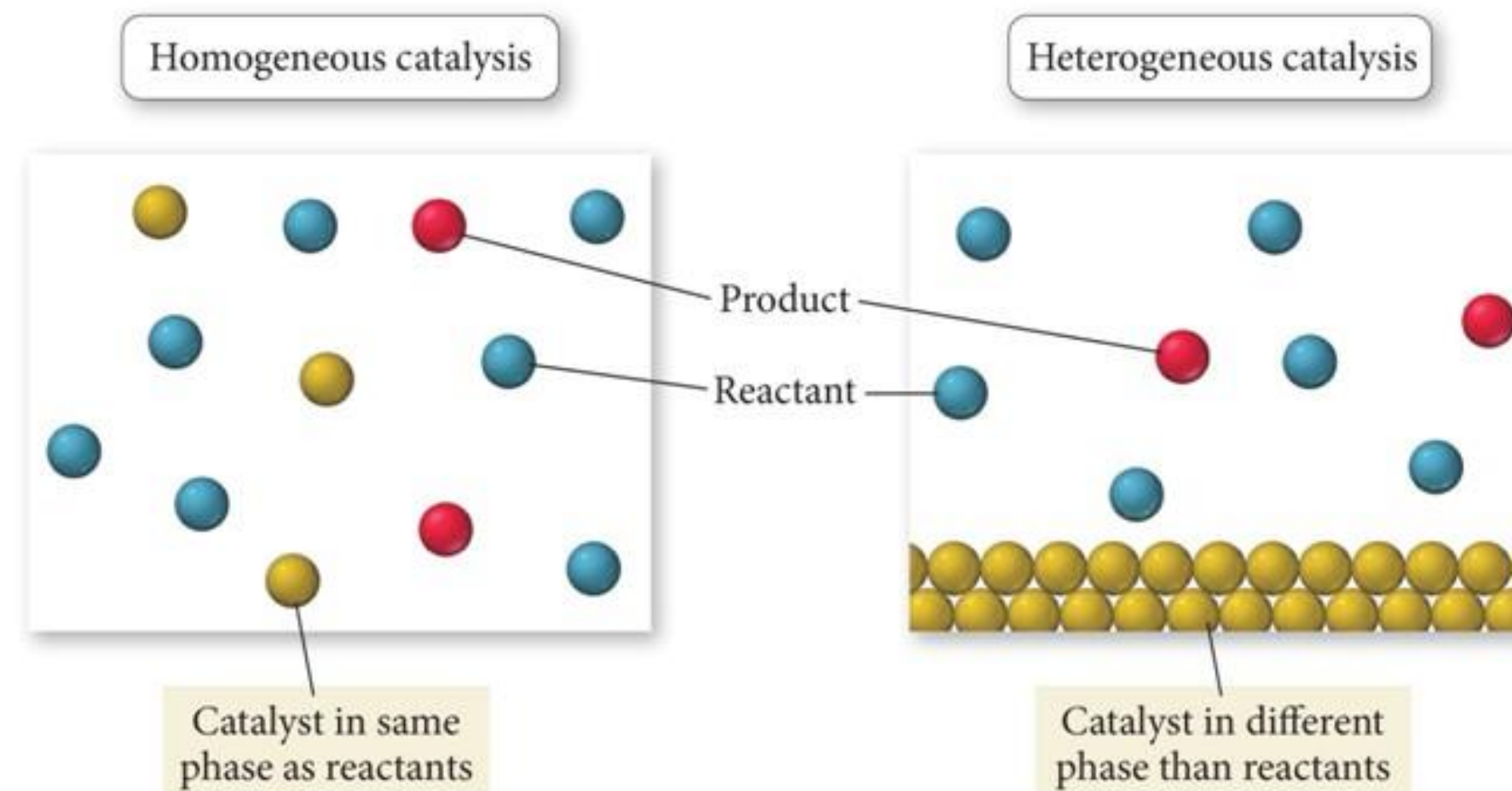
➢ $\frac{k_{catalyzed}}{k_{uncatalyzed}}$ =8.3 x 10^{11}
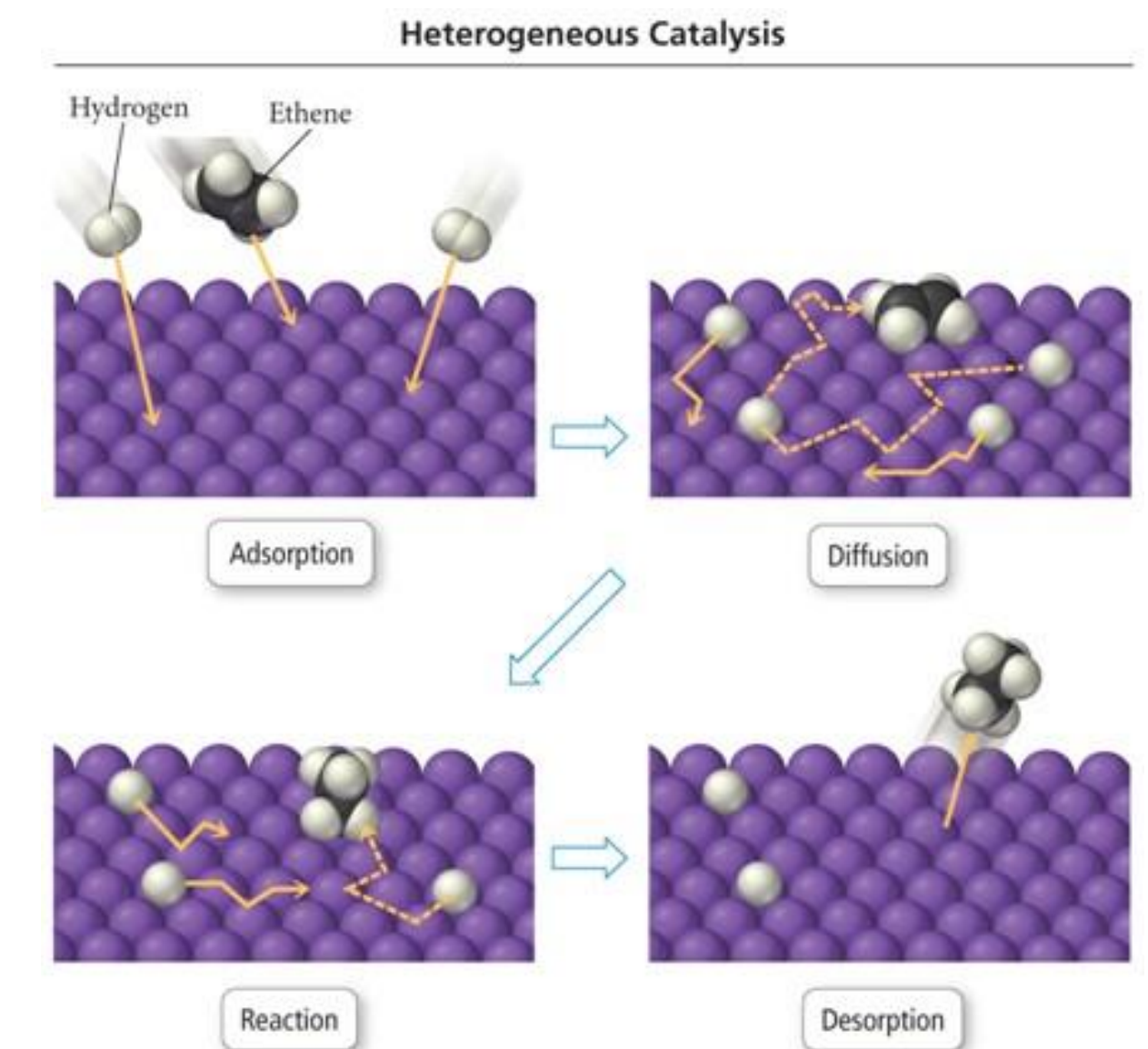
Catalyst and Inhibitor

Catalysis

Homogeneous Catalysis

Only one phase is involved (reactants, products and catalyst all in one phase)

Heterogeneous Catalysis

Reaction occurs at an interface between phases

Homogeneous catalysis

Product
Reactant

Catalyst in same phase as reactants

Heterogeneous catalysis

Catalyst in different phase than reactants

Heterogeneous Catalysis

Hydrogen   Ethene

Adsorption   Diffusion

Reaction   Desorption

Inhibitor: An inhibitor is a substance that diminishes the rate of chemical reaction and may be consumed during the course of reaction

Degree of inhibition:
$$\epsilon_i = \frac{\upsilon_0 - \upsilon}{\upsilon_0} = 1 - \frac{\upsilon}{\upsilon_0}$$

υ_0 rate without inhibitor
υ rate with inhibitor