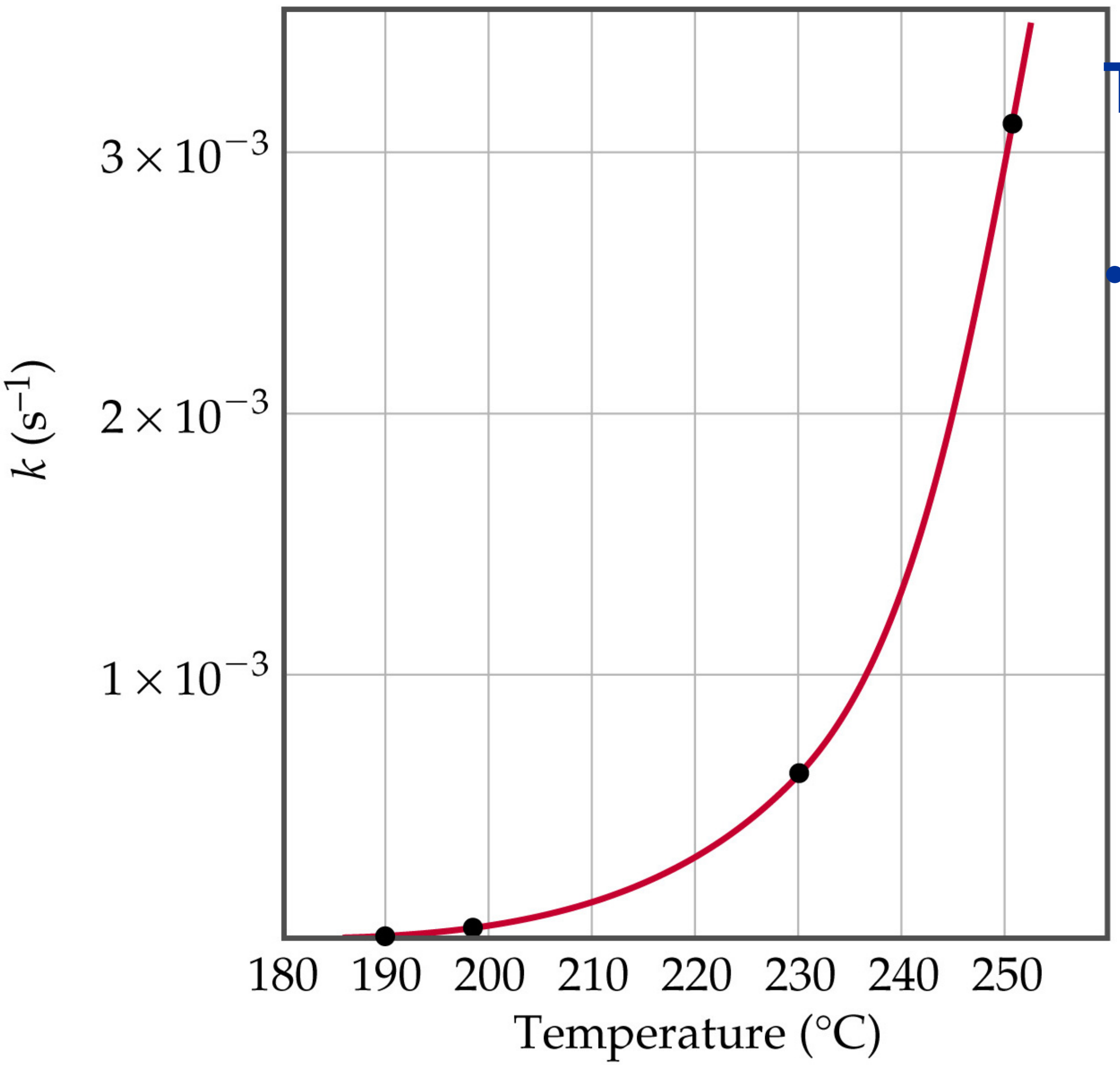
Collision Model

- Goal: develop a model that explains why rates of reactions increase as concentration and temperature increases.
- The collision model: in order for molecules to react they must collide.
- The greater the number of collisions the faster the rate.
- The more molecules present, the greater the probability of collision and the faster the rate.

Temperature and Rate

The Collision Model

- Most reactions speed up as temperature increases. (E.g. food spoils when not refrigerated.)
- When two light sticks are placed in water: one at room temperature and one in ice, the one at room temperature is brighter than the one in ice.
- The chemical reaction responsible for chemiluminescence is dependent on temperature: the higher the temperature, the faster the reaction and the brighter the light.



The Collision Model

- As temperature increases, the rate increases (exponentially).

- Since the rate law has no temperature term in it, the rate constant must depend on temperature.
- Consider the first order reaction $CH_3NC \rightarrow CH_3CN$.
  - As temperature increases from 190 °C to 250 °C the rate constant increases from $2.52 \times 10^{-5}\ s^{-1}$ to $3.16 \times 10^{-3}\ s^{-1}$.
- The temperature effect is quite dramatic. Why?
- Observations: rates of reactions are affected by concentration and temperature.

- The higher the temperature, the more energy available to the molecules and the faster the rate.
- Complication: not all collisions lead to products. In fact, only a small fraction of collisions lead to product.
- Effective Collision – A collision between molecules that leads to products (reaction occurs)

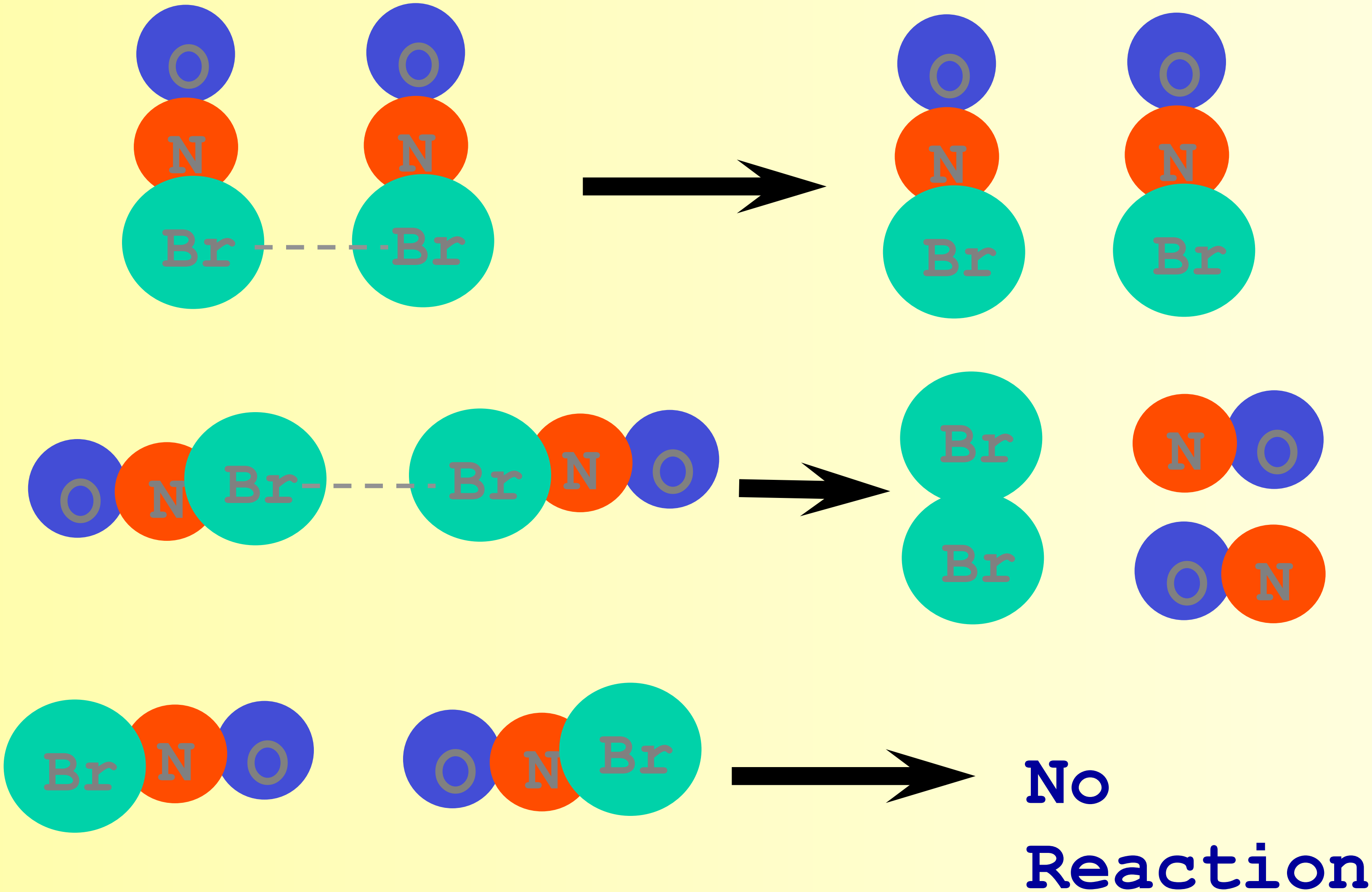
The Orientation Factor

- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

- Consider:

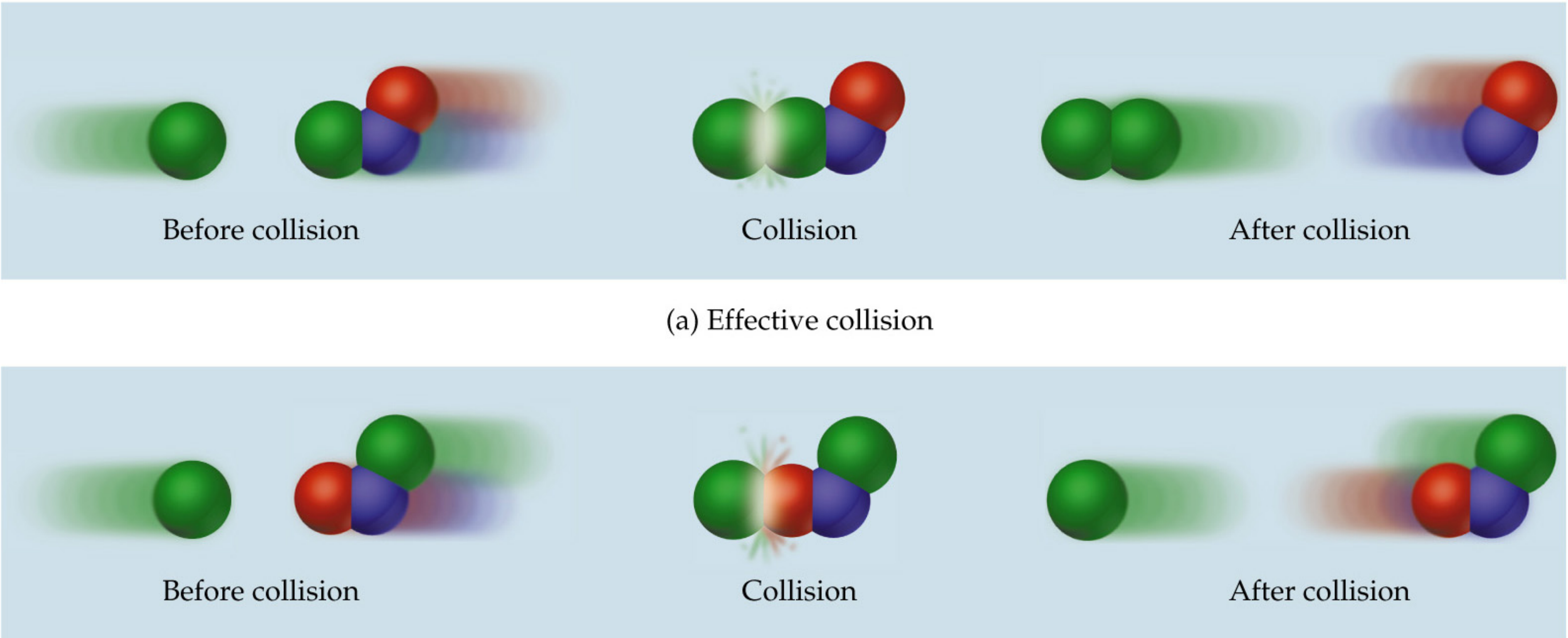
$$2\ NOBr \rightarrow 2\ NO + Br_2$$

- There are several possible ways that NOBr molecules can collide; one is effective and the others are not.


O
N
Br
O
N
Br
O
N
Br
O
N
Br
O N Br
Br N O
Br
Br
N O
O N
Br N O
O N Br
No
Reaction

The Orientation Factor

$$Cl + ClNO \longrightarrow Cl_2 + NO$$

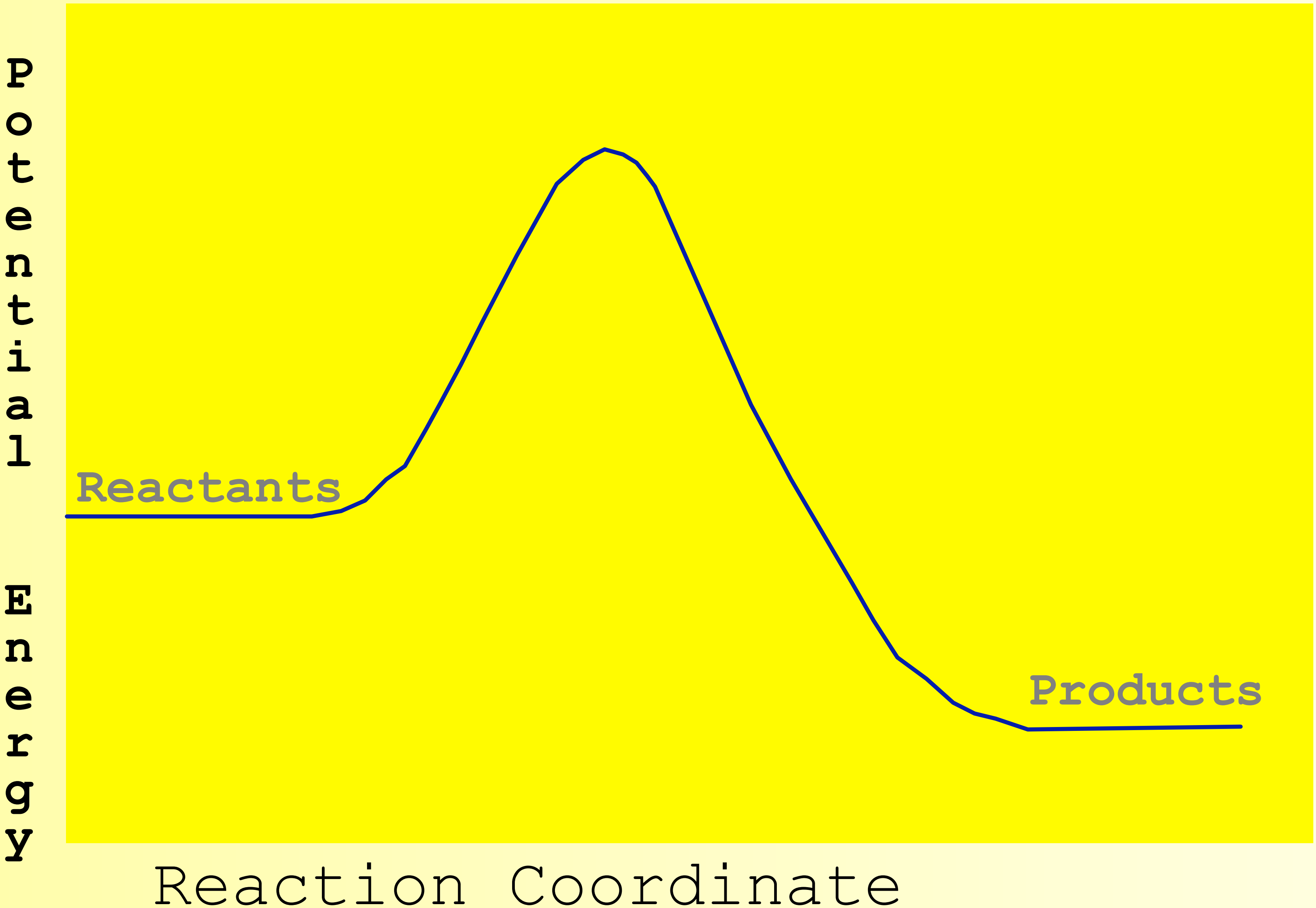


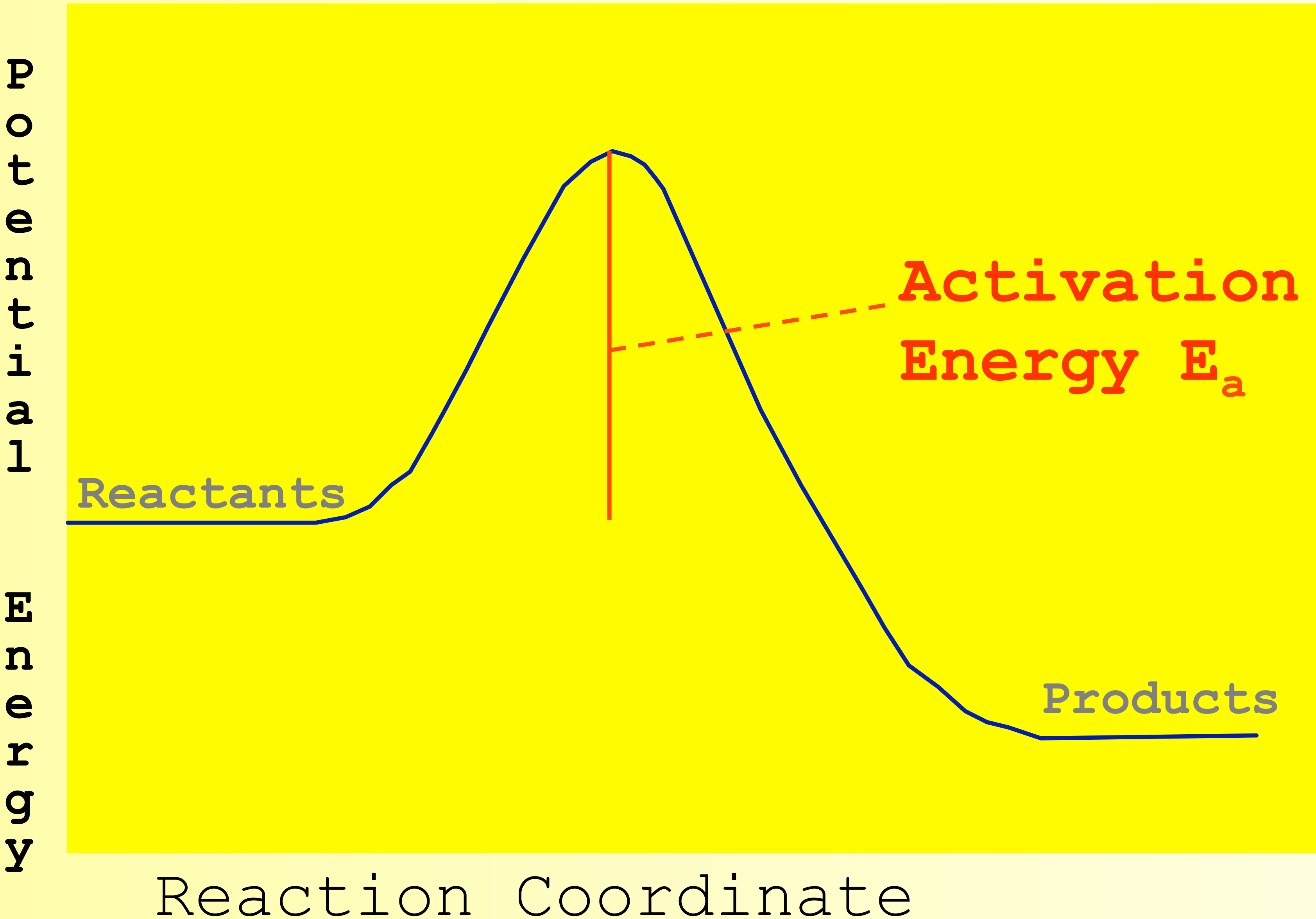
(a) Effective collision

(b) Ineffective collision

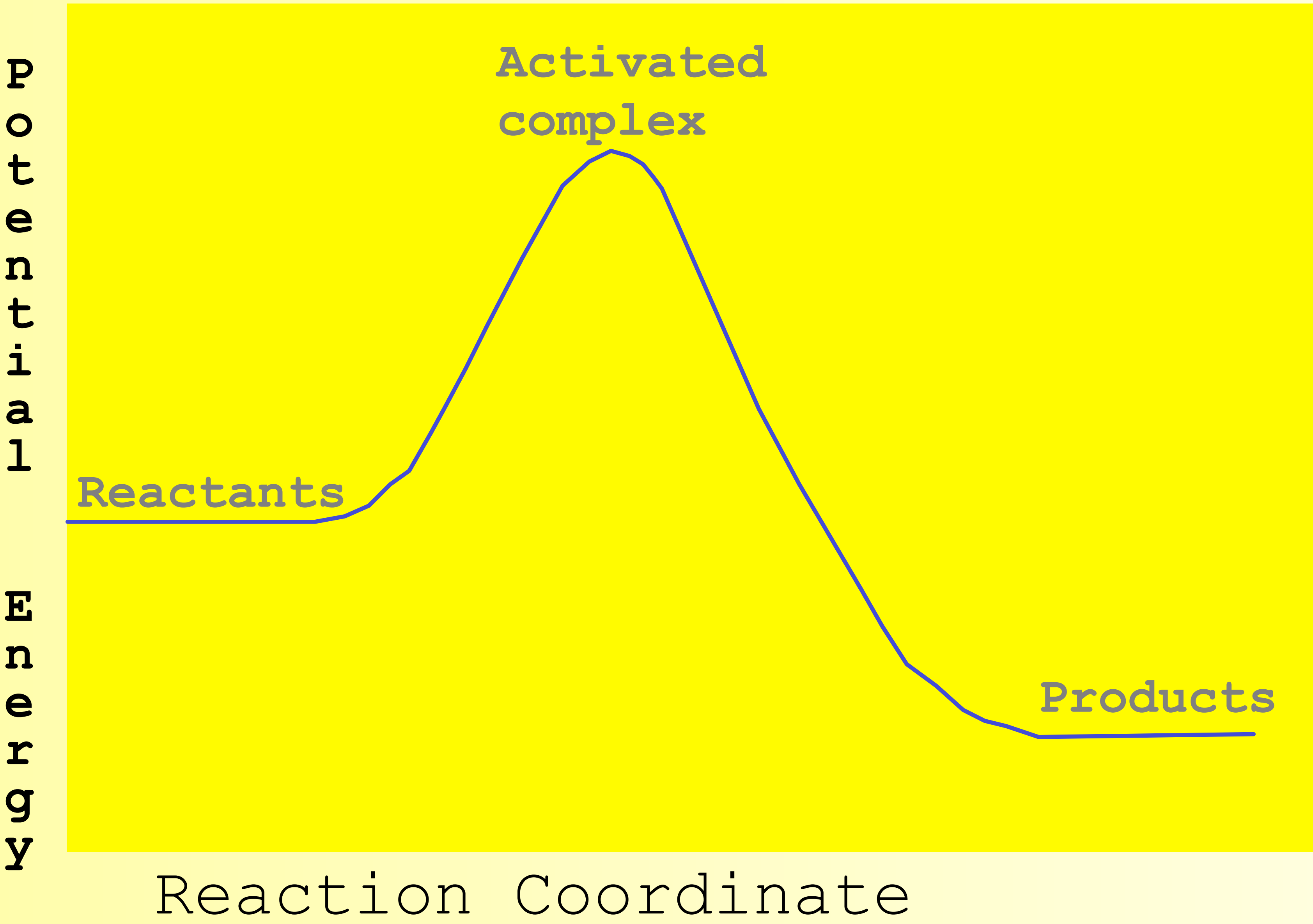
Activation Energy

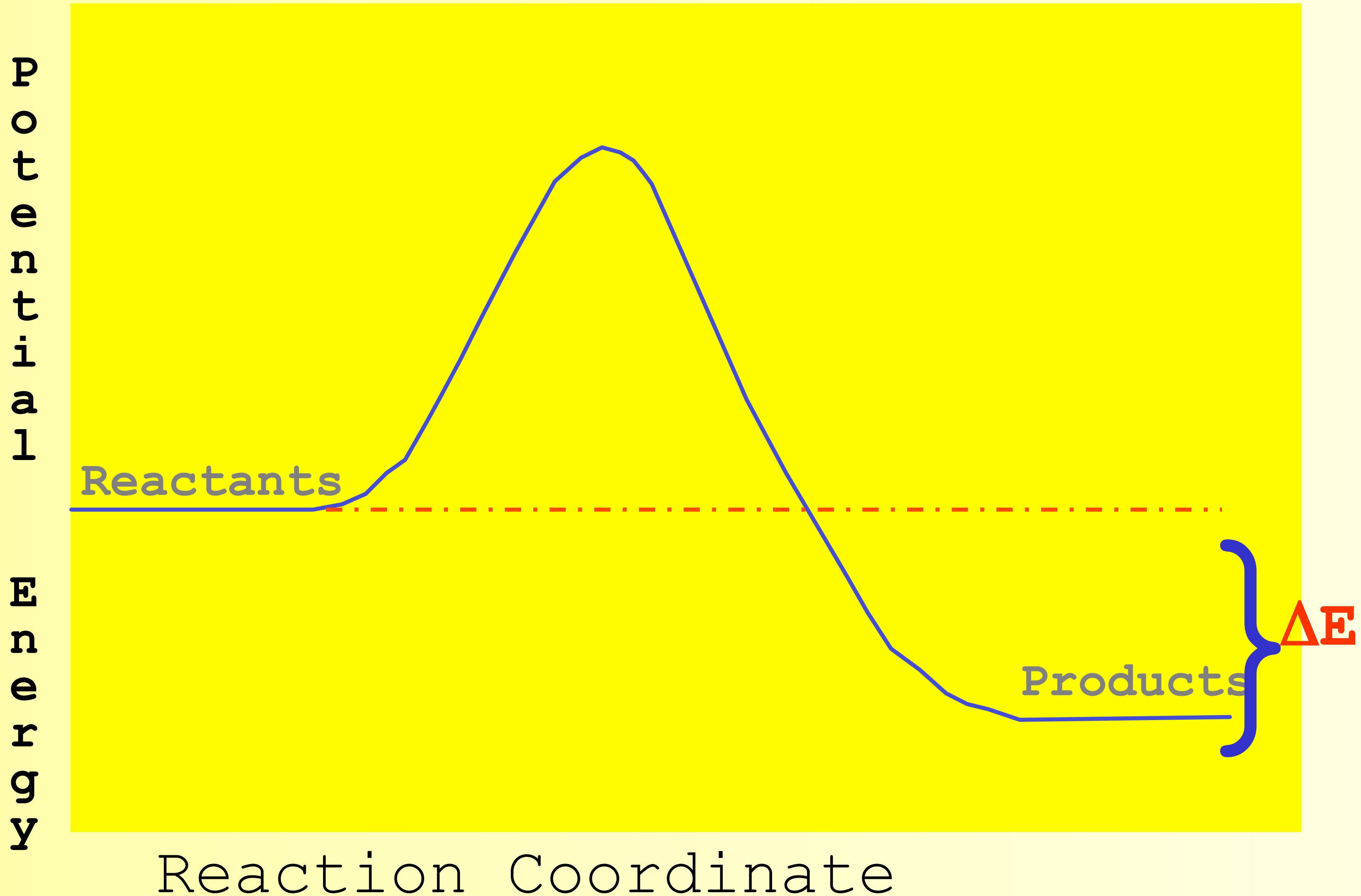
- Arrhenius: molecules must posses a minimum amount of energy to react. Why?
  - In order to form products, bonds must be broken in the reactants.
  - Bond breakage requires energy.
- Activation energy, E_a, is the minimum energy required to initiate a chemical reaction.

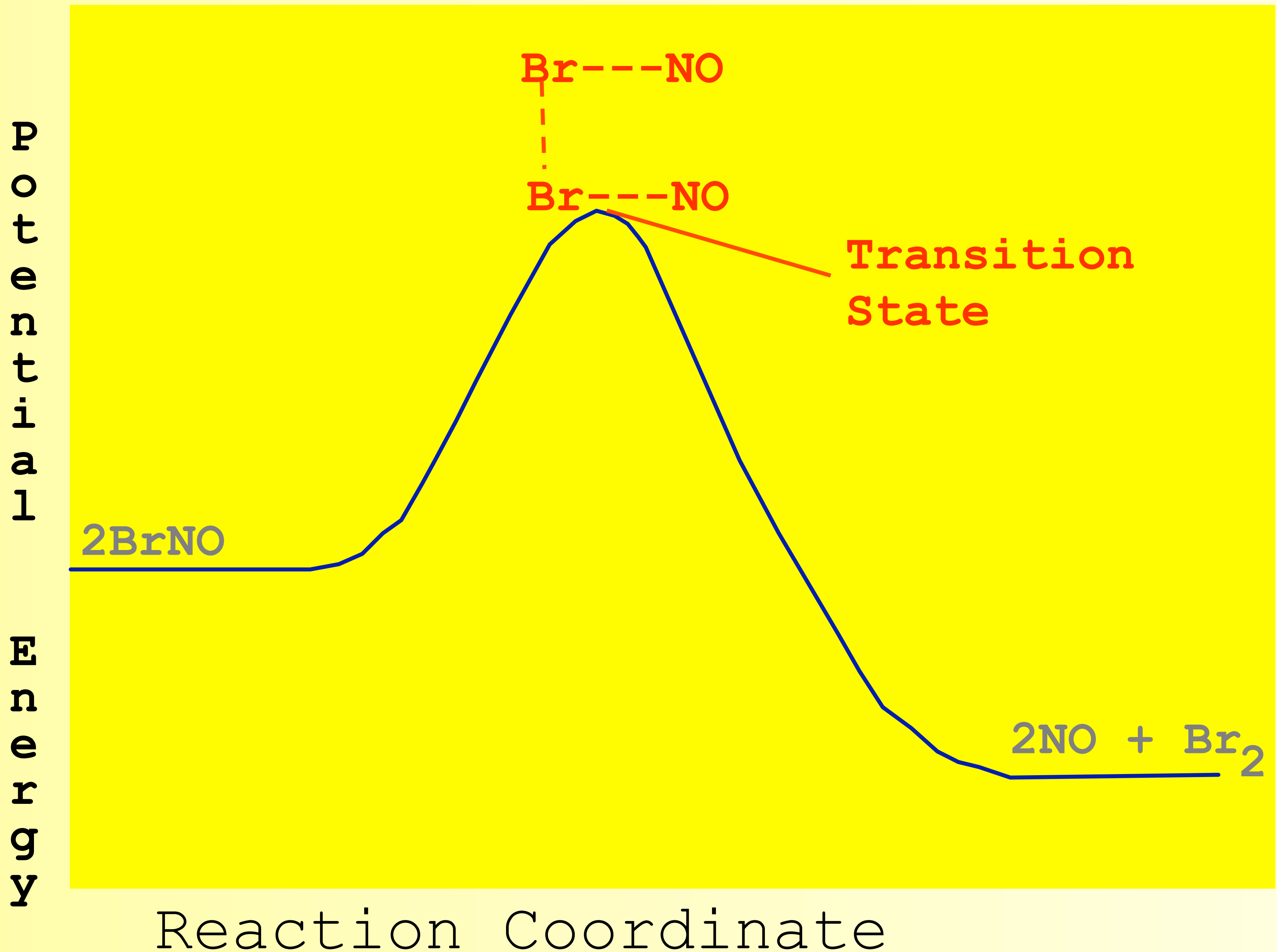

Potential Energy
Reactants
Products
Reaction Coordinate



Potential Energy
Reactants
Activation Energy E_a
Products
Reaction Coordinate


Activated complex
Reactants
Products
Potential Energy
Reaction Coordinate

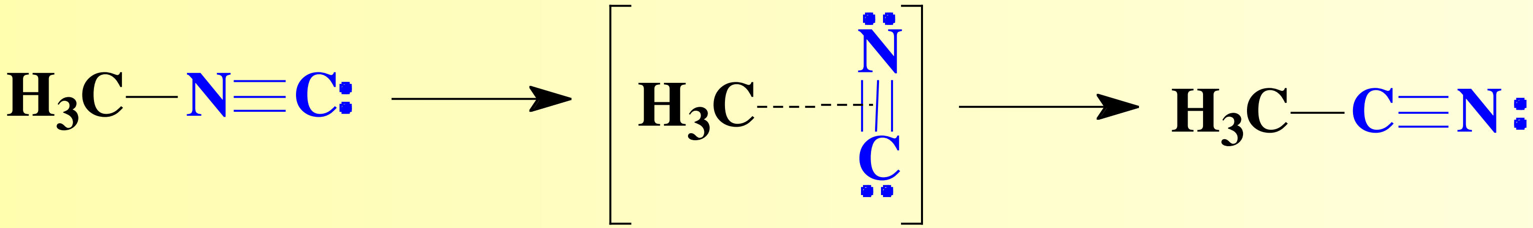

Potential Energy
Reactants
Products
ΔE
Reaction Coordinate


Br---NO
Br---NO
Transition State
2BrNO
2NO + Br2
Potential Energy
Reaction Coordinate

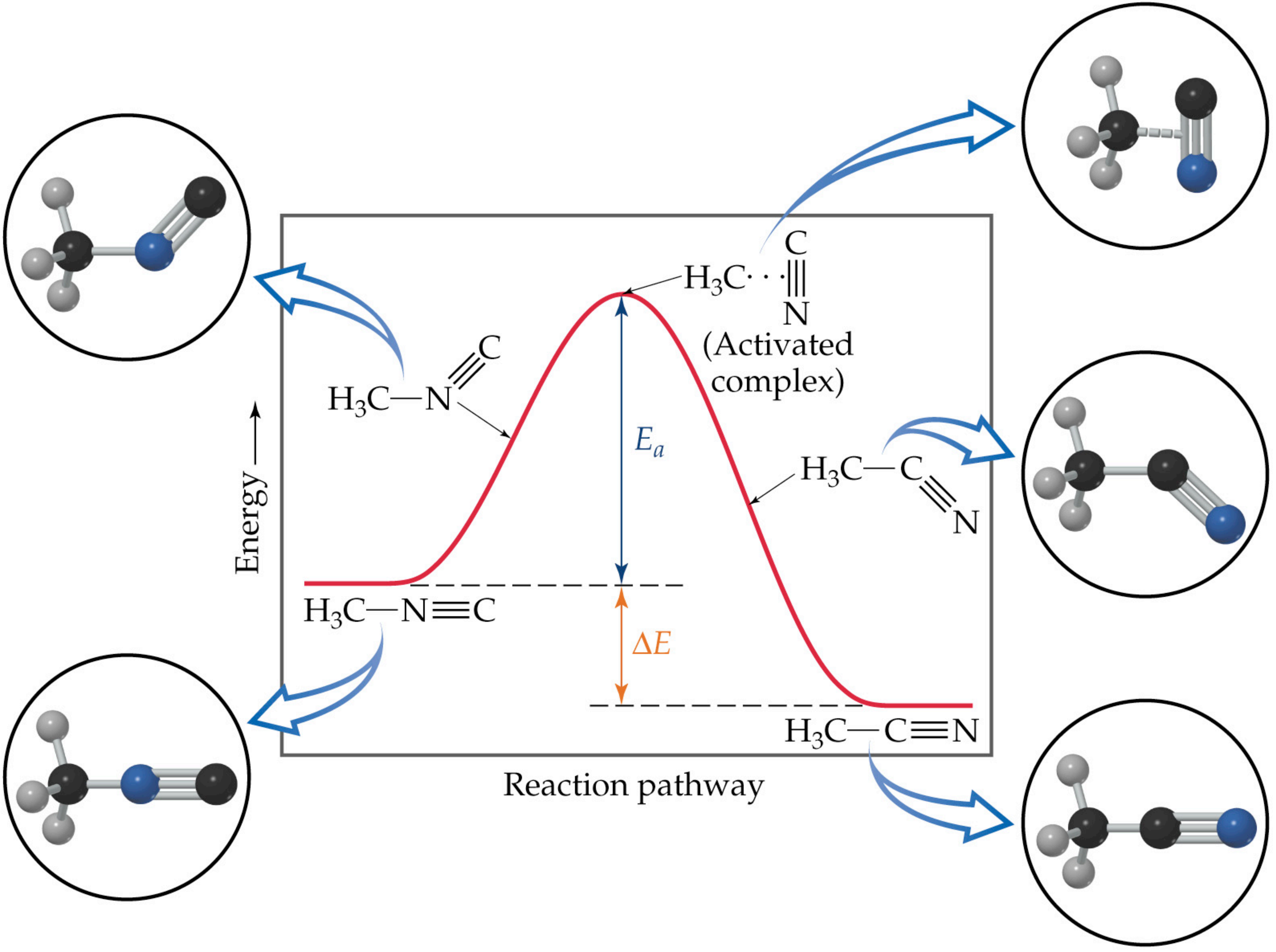
Terms

- Activation energy - the minimum energy needed to make a reaction happen.
- Activated Complex or Transition State - The arrangement of atoms at the top of the energy barrier.

- Consider the rearrangement of methyl isonitrile:



  – In H_3C-N≡C, the C-N≡C bond bends until the C-N bond breaks and the N≡C portion is perpendicular to the H_3C portion. This structure is called the activated complex or transition state.
  – The energy required for the above twist and break is the activation energy, E_a.
  – Once the C-N bond is broken, the N≡C portion can continue to rotate forming a C-C≡N bond.



C
H3C· · ·≡
N
(Activated complex)
H3C—N≡C
Ea
Energy ⟶
H3C—C≡N
ΔE
H3C—N≡C
H3C—C≡N
Reaction pathway

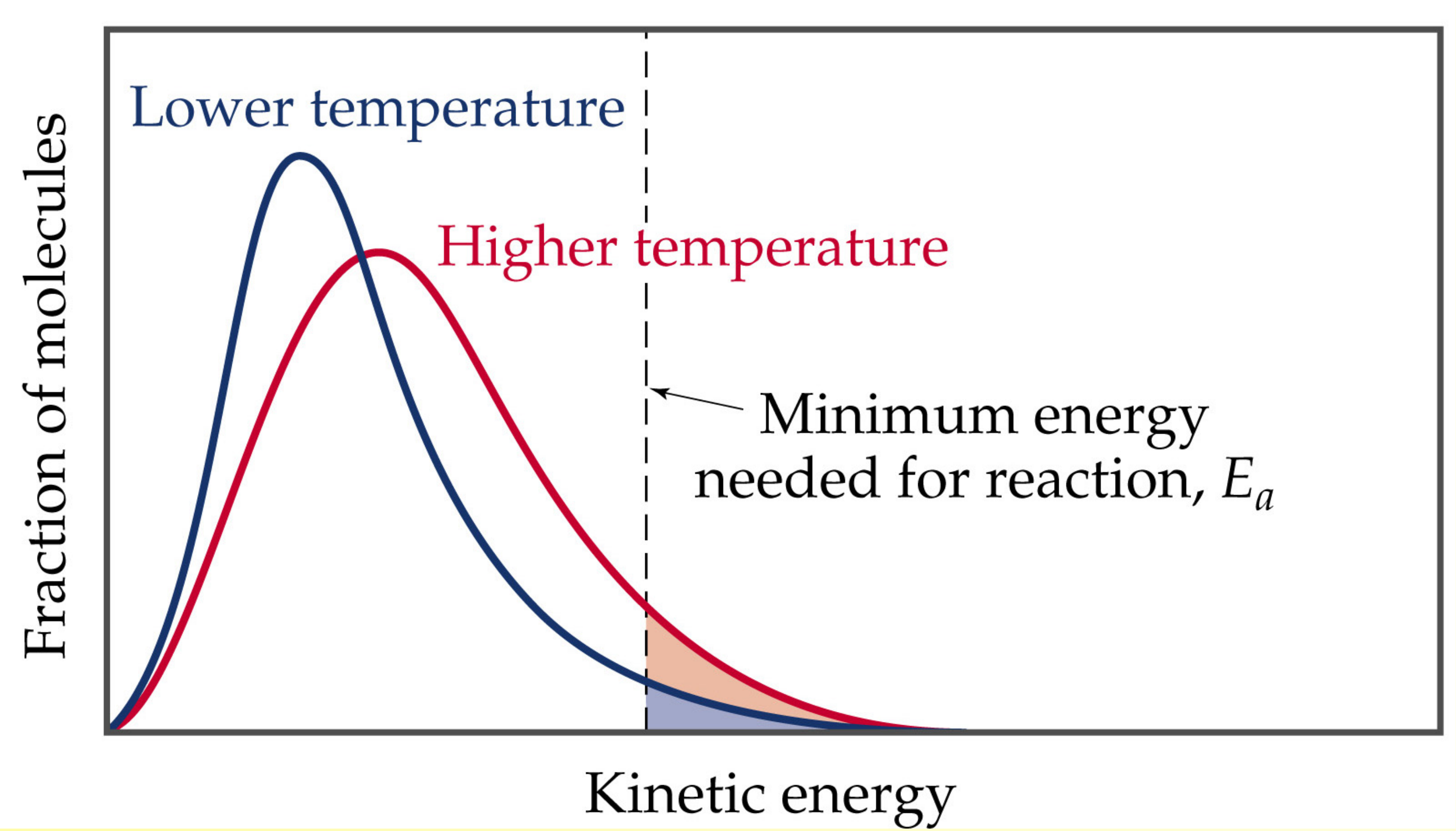
- The change in energy for the reaction is the difference in energy between CH_3NC and CH_3CN.
- The activation energy is the difference in energy between reactants, CH_3NC and transition state.
- The rate depends on E_a.
- Notice that if a forward reaction is exothermic ($CH_3NC \rightarrow CH_3CN$), then the reverse reaction is endothermic ($CH_3CN \rightarrow CH_3NC$).

- How does a methyl isonitrile molecule gain enough energy to overcome the activation energy barrier?
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases.
- We can show the fraction of molecules, *f*, with energy equal to or greater than E_a is

$$f = e^{-E_a/RT}$$

where *R* is the gas constant (8.314 J/mol·K).

Activation Energy



The Arrhenius Equation

- Arrhenius discovered most reaction-rate data obeyed the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

  - k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/K-mol) and T is the temperature in K.
  - A is called the frequency factor.
  - A is a measure of the probability of a favorable collision.
  - Both A and E_a are specific to a given reaction.

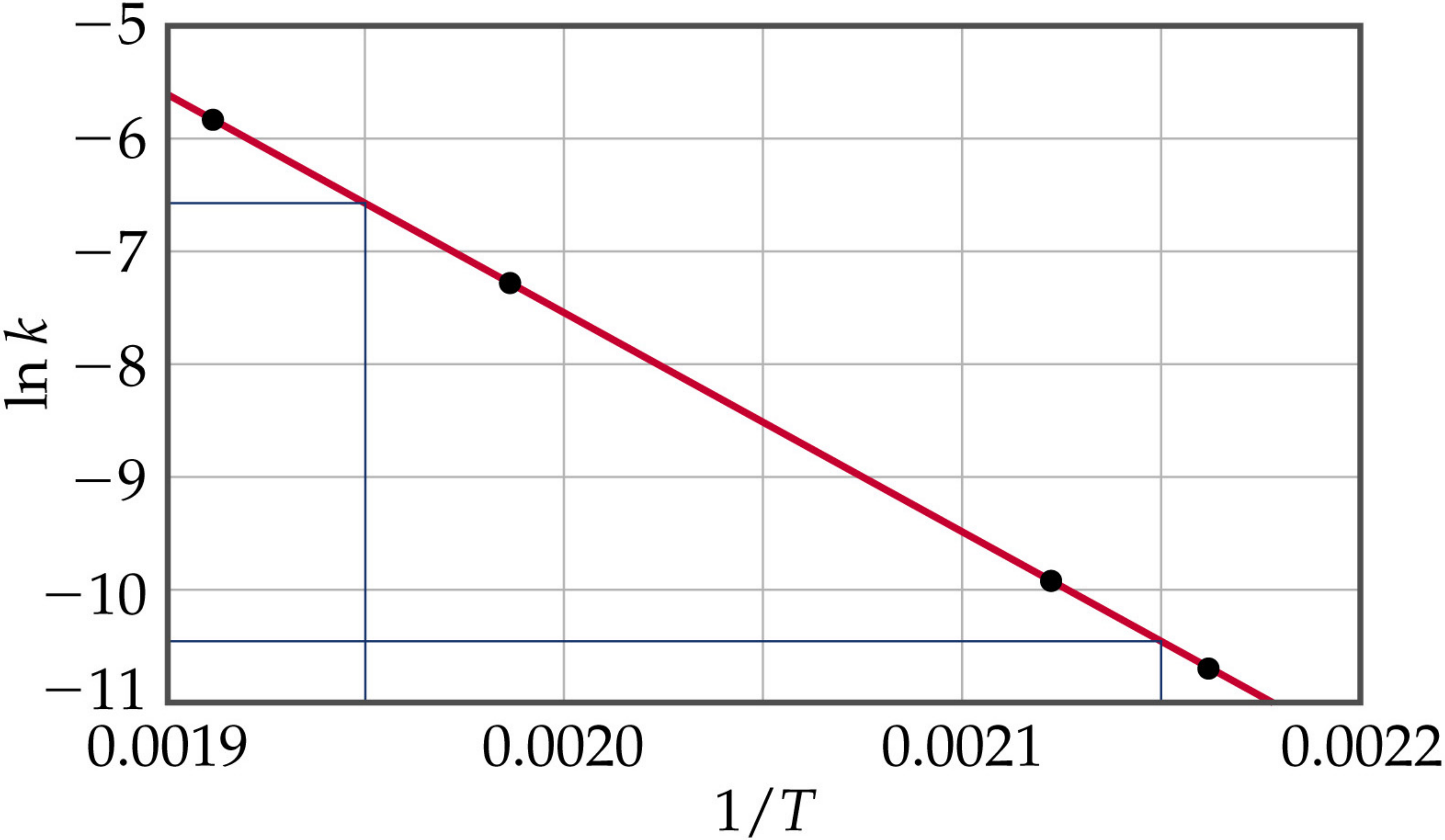
Determining the Activation Energy

- If we have a lot of data, we can determine E_a and A graphically by rearranging the Arrhenius equation:

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

- From the above equation, a plot of ln k versus $1/T$ will have slope of $-E_a/R$ and intercept of ln A.

Temperature and Rate



- If we do not have a lot of data, then we recognize

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

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