

Why would k (along with the rate) increase with temperature?
Let's go back to *Kinetic Molecular Theory* to understand...

The Collision Model: In order for molecules to react they must collide.

As temperature increases, the molecules move faster and the collision frequency increases.

Therefore, the greater the number of collisions the faster the rate.

Thus reaction **rate** should **increase** with an increase in temperature.

Also, the more molecules present, the greater the probability of collision and the faster the rate.

Thus reaction **rate** should **increase** with an increase in the concentration of reactant molecules.

Activation Energy

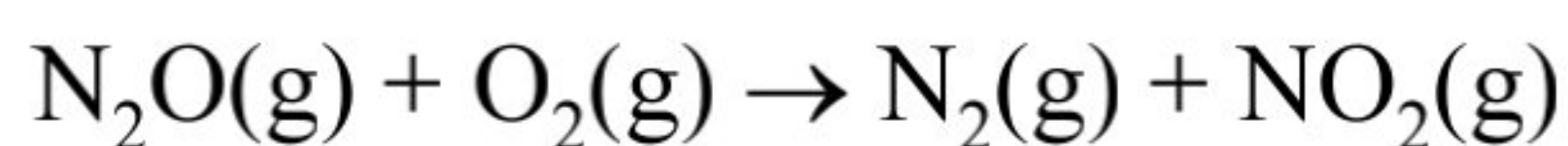
Arrhenius: Molecules must possess a minimum amount of energy to react. Why?

- (1) In order to form products, bonds must be broken in the reactants.
- (2) Bond breakage requires energy.
- (3) Molecules moving too slowly, with too little kinetic energy, don't react when they collide.

The Activation energy, E_a , is the minimum energy required to initiate a chemical reaction.

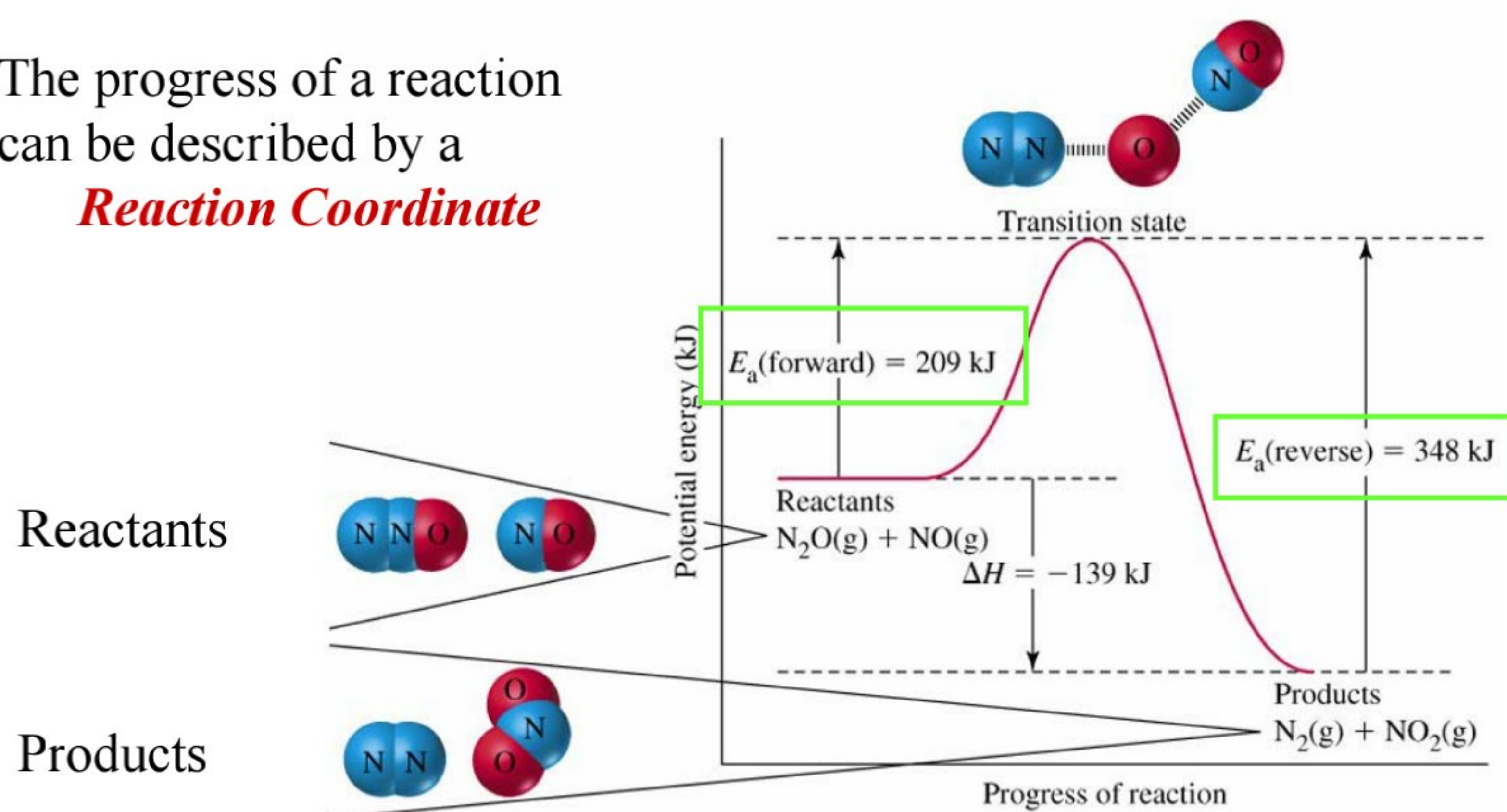
E_a is specific to a particular reaction.

Consider the reaction:

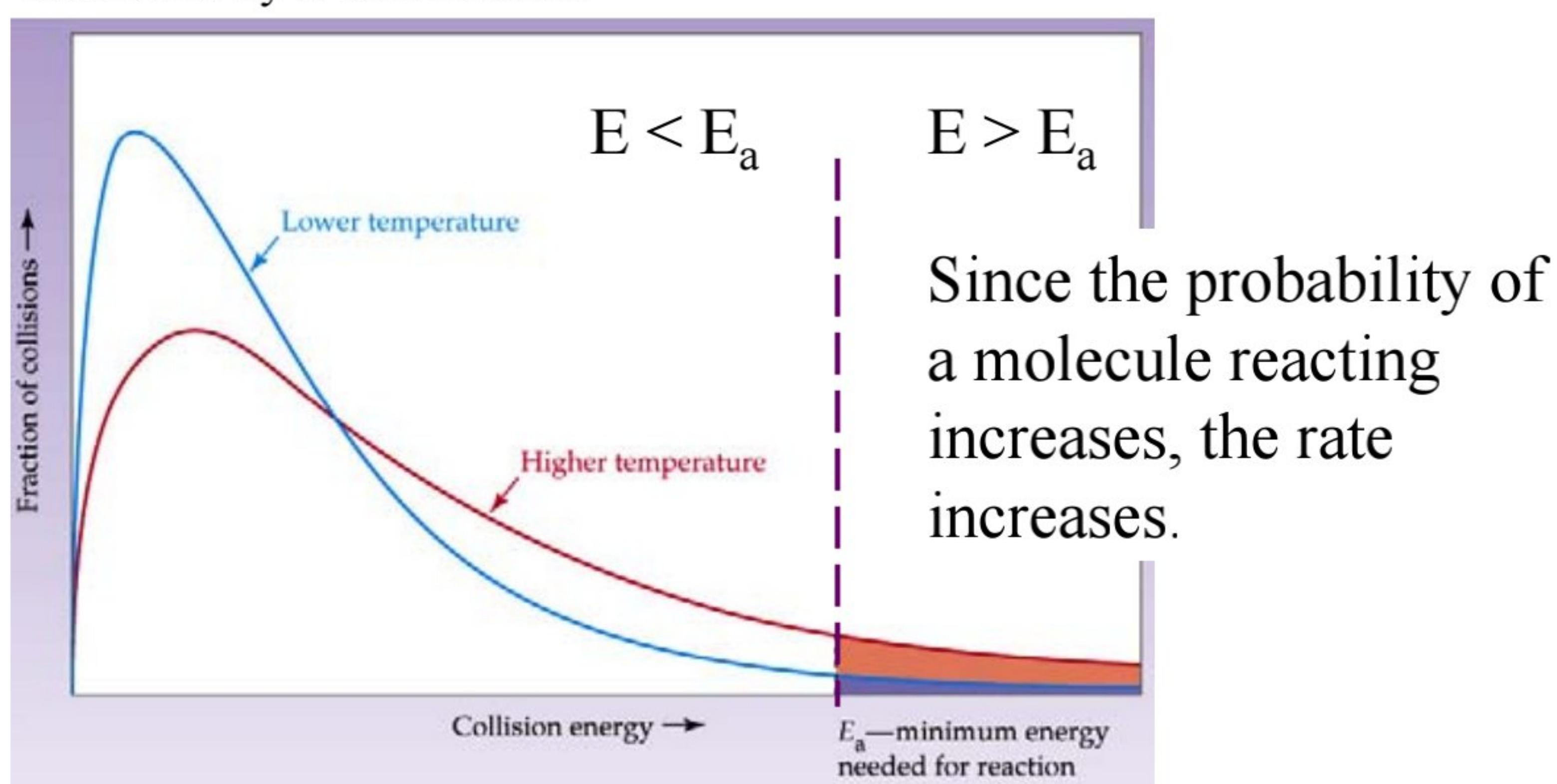


The progress of a reaction can be described by a

Reaction Coordinate



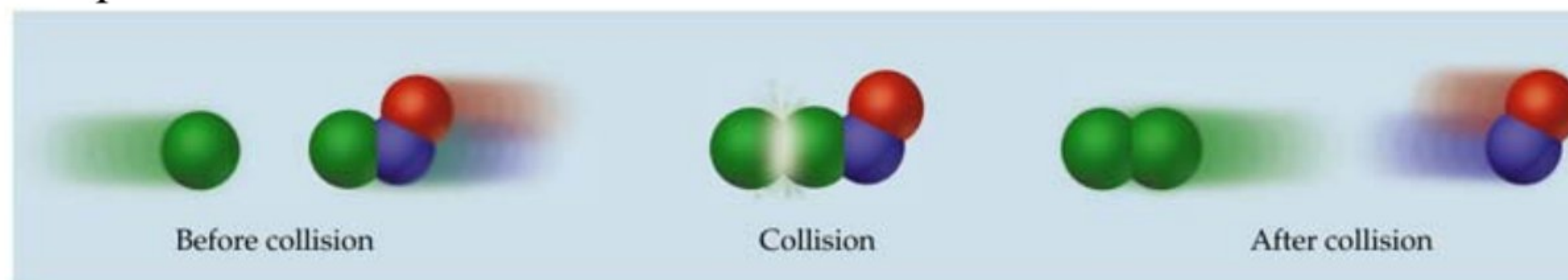
Recall for KMT that the temperature for a system of particles is described by a distribution.



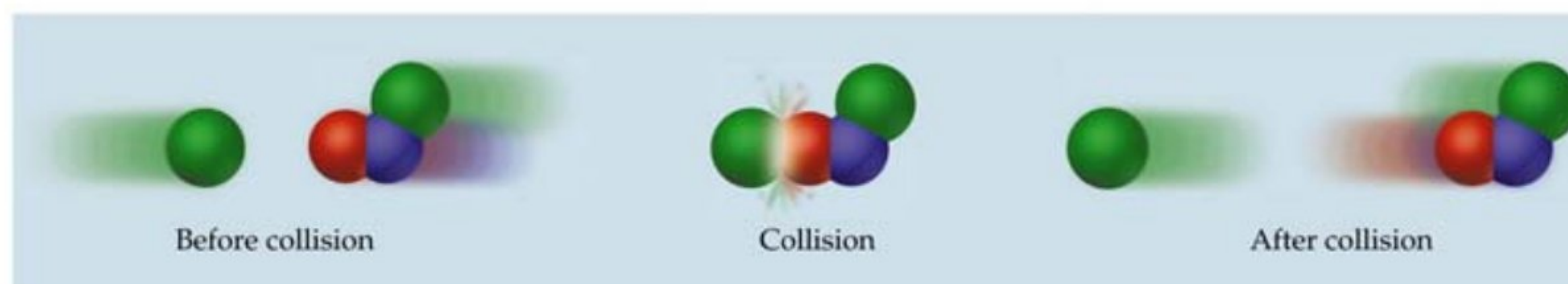
At higher temps, more particles have enough energy to go over the barrier.

Orientation factors into the equation

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.



(a) Effective collision



(b) Ineffective collision

Some collisions do not lead to reaction even if there is sufficient energy.

The Arrhenius Equation

Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- (1) The number of collisions per unit time.
- (2) The fraction of collisions that occur with the correct orientation.
- (3) The fraction of the colliding molecules that have an energy greater than or equal to E_a .

From these observations Arrhenius developed the aptly named ***Arrhenius equation***.

Arrhenius equation

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

k is the rate constant

T is the temperature in K

E_a is the activation energy

R is the ideal-gas constant (8.314 J/Kmol)

A is known the *frequency or pre-exponential factor*

In addition to carrying the units of the rate constant, “ A ” relates to the frequency of collisions and the orientation of a favorable collision probability

Both A and E_a are *specific to a given reaction*.

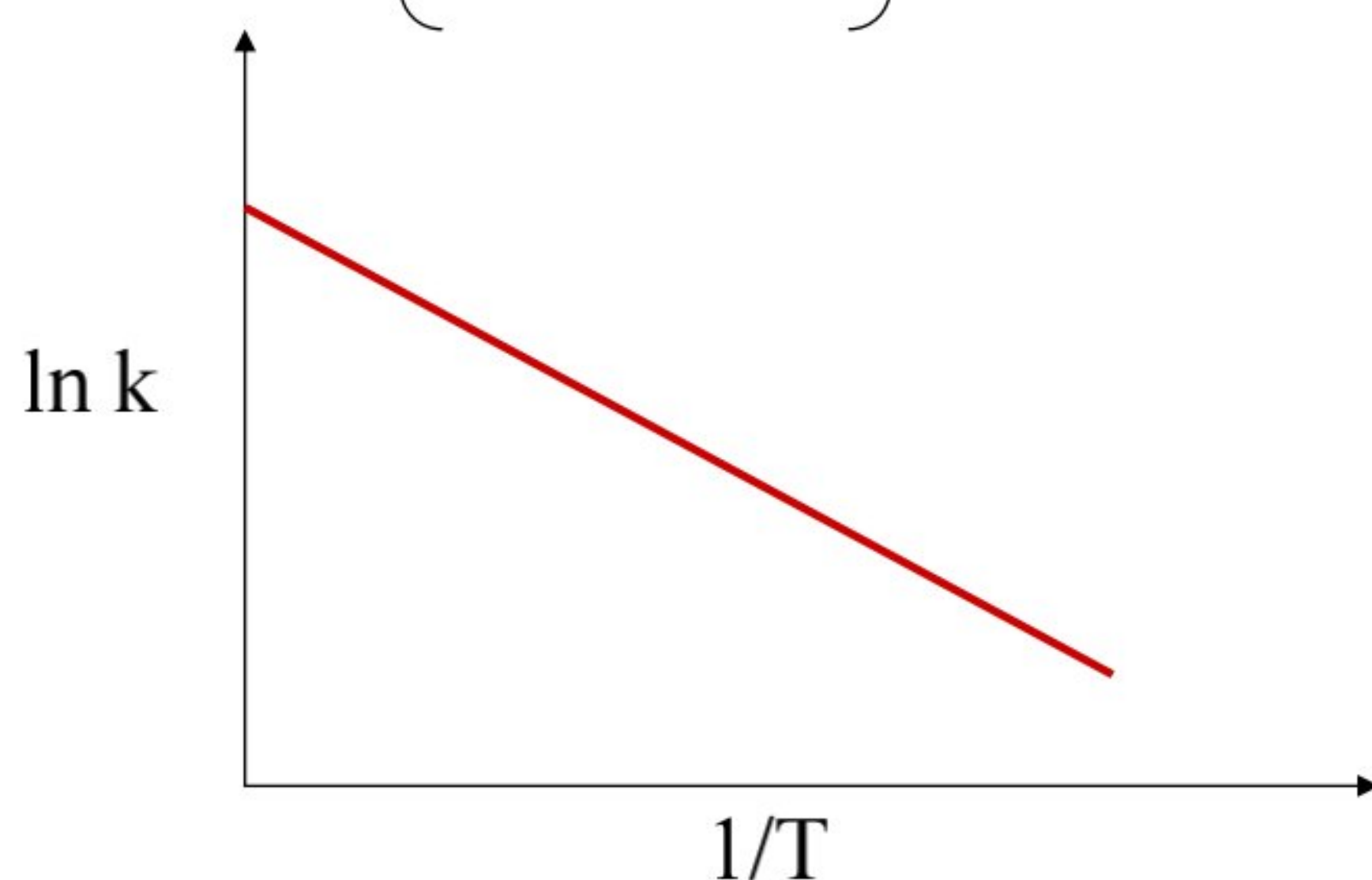
Determining the Activation Energy

E_a may be determined experimentally.

First take natural log of both sides of the Arrhenius equation:

$$\ln \left(k = Ae^{\frac{-E_a}{RT}} \right) \longrightarrow \ln k = -\frac{E_a}{RT} + \ln A$$

Golly-gee, what do we have once again...



A plot of $\ln k$ vs $1/T$ will have a slope of $-E_a/R$ and a y-intercept of $\ln A$.

Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

$$(1) \quad k_2 = 2k_1 \qquad (2) \quad \ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(3) \quad \frac{E_a}{R} = \frac{50.2 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} = 6.04 \times 10^3 \text{ K}$$

$$(4) \quad \ln(2) = 0.693 = 6.04 \times 10^3 \text{ K} \times \left(\frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

A 10°C change of temperature doubles the rate!!

$$(5) \quad \frac{1}{T_2} = 3.24 \times 10^{-3} \text{ K}^{-1} \longrightarrow \boxed{T_2 = 308 \text{ K}}$$