Chemical Kinetics 3

Reading:	Ch 13 sections 5-7	Homework:	Chapter 13: 57*, 59*, 61*, 63*, 65*, 69, 73, 75 Excel assignment* (see assignments for link)

* = ‘important’ homework question

Temperature and Rate – Transition State Theory and the Arrhenius Equation

Background: Recall that the number of ‘fruitful’ collisions per unit time among the reactant(s) determine the overall rate of reaction.

Discussion: What factors determine if a *single* collision will be fruitful?

1.	
2.	
3.	

The above are the three basic assumptions of *collision theory*

Collision Theory

For a reaction to occur, the reactant molecules must collide with energy greater than some minimum value (E_a) and have the correct spatial orientation. E_a is the activation energy.

Recap: At a defined temperature, a reaction rate is described by the rate equation:

Generically: $\mathbf{aA + bB \rightarrow cC + dD}$ **Rate = k[A]^m[B]^n**

Observation: Rates of reaction typically increase *substantially* for a relatively small elevation of temperature.

Discussion: How does increasing temperature effect the rate equation?

(see slide of k v temp)

The makeup of *k*

The three collision theory variables (*energy of reactants*, *frequency of collisions* and *orientation of reactants*), when combined, give rise to the rate constant k. Clearly, the value of k varies with temperature(!)

Mathematically:

$$k = Zpf$$

where: k = rate constant

Z = frequency of collisions

p = fraction of molecules with correct orientation

f = fraction of molecules with E_a or greater

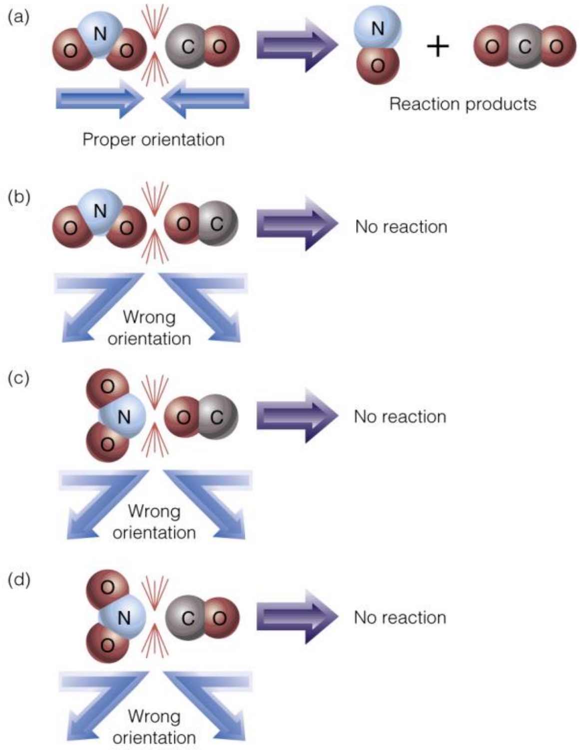
Discussion: To what extent are Z, p and f affected by temperature?

Collision Frequency (Z) – recall *Chemical Kinetics 1*

KE = $\frac{1}{2} mv^2$ = kT (k is the Boltzmann constant). **i.e. Temp $\propto v^2$**

Reactant Orientation (p)

Random (see slide) – temp has NO effect, some *fixed* fraction of reactant(s) will have the correct orientation



Transition State Theory

Only reactants colliding with the correct orientation (a) may give rise to an *activated complex*, or *transition state* species

The reactants must also have greater than a minimum amount of ‘collision energy’ (E_a, see next) in order to form an activated complex (see additional slide).

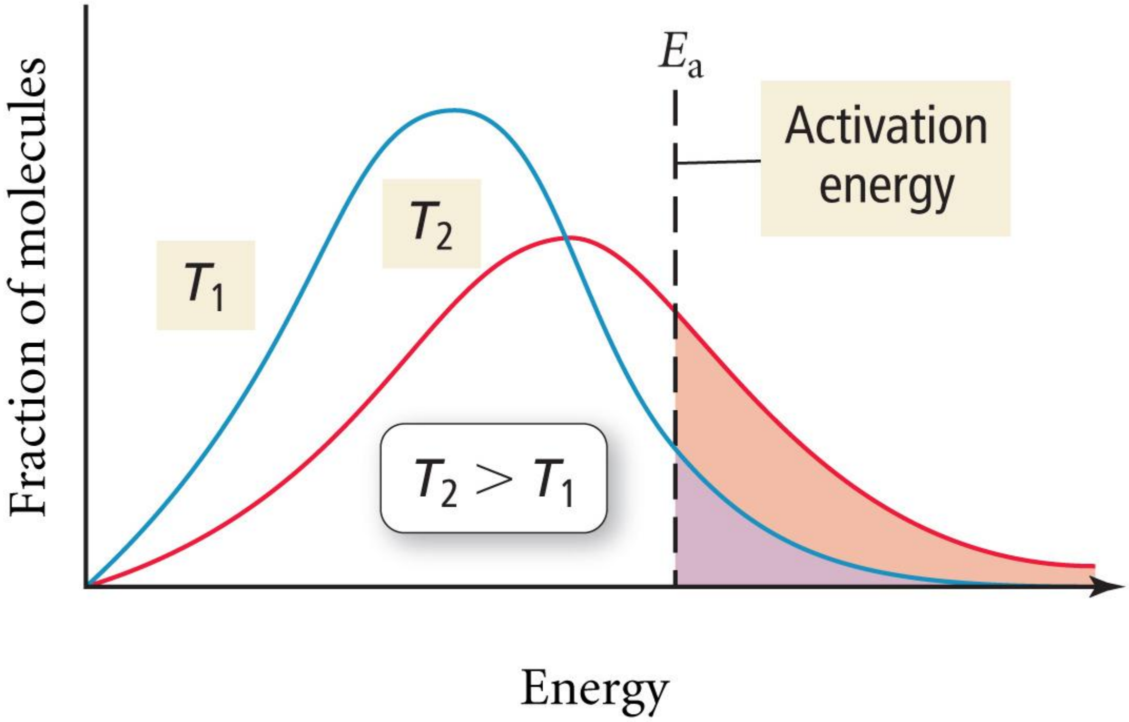
We will return to this topic later in the handout

Fraction of molecules with E_a or greater (f)

Q: Do all molecules of a compound have the same speed at, say, room temperature?

A:

The distribution of molecular speeds - the Boltzmann distribution



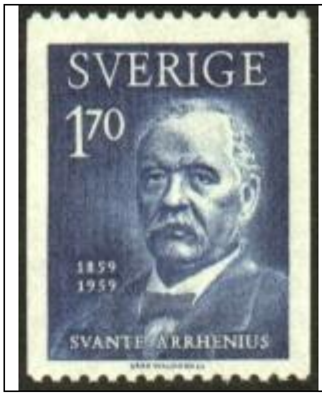
Features

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

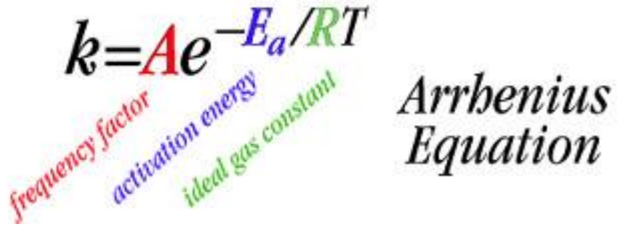
Due to the line shape of the Boltzmann distribution, the fraction of molecules with E_a or greater has an exponential relationship with temperature:

Since the fraction of molecules with the correct orientation (p) is fixed and the frequency of collisions (Z) does not vary significantly for a small change in temperature, these two variables are combined into a single constant called the ‘frequency factor’ (A):

The Arrhenius Equation



The *Arrhenius Equation* combines the above variables and, so, relates *k* to activation energy and temperature for any reaction



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

We will return to the Arrhenius equation soon, but first, more on transition state theory and activated complexes….

Definition of an Activated Complex

An unstable grouping of atoms, formed during a fruitful collision, that breaks apart to form reaction product(s)

A short lived activated complex (transition state) is formed during a fruitful collision

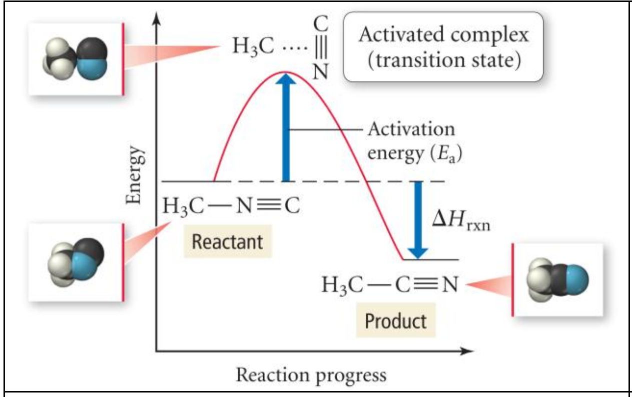
The activated complex, once formed, quickly decomposes to give reaction products

The energy needed to form an activated complex is equal to or greater than the respective reaction's activation energy (E_a)

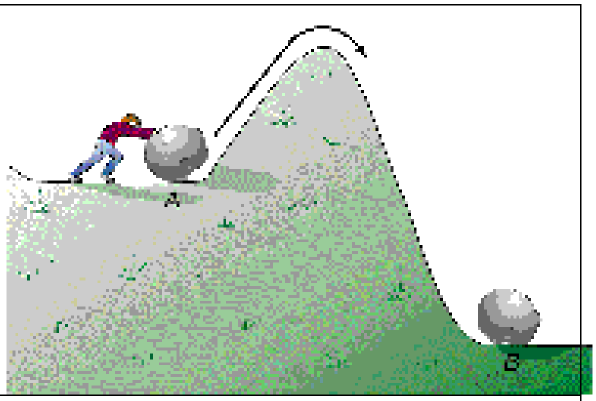
"If you think about it, reactions are *really* all about making activated complexes"

Example: The isomerization of methylisonitrile (see slide and appendix)

$$CH_3NC\ (g) \rightarrow [\text{activated complex }]^{\ddagger} \rightarrow CH_3CN\ (g)$$



Reaction Pathway (coordinate) diagram

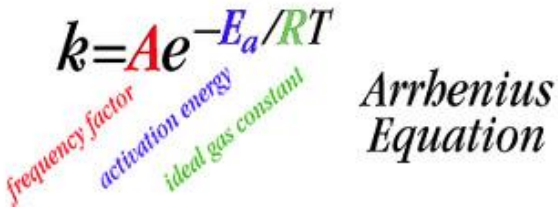


Analogy

"Activation energy gets you over the 'hump' needed to start a reaction" - think about this in terms of why you have to strike a match or spark your stove.

A reaction cannot proceed unless the reactants have achieved or surpassed the necessary activation energy (E_a) for the chemical process

OK, back to the Arrhenius Equation….



A LINEAR version of the Arrhenius Equation, in terms of *k* and T, is required to determine the activation energy (E_a) for a chemical process.

Derivation: The two linear forms of the Arrhenius equation

Interpretation

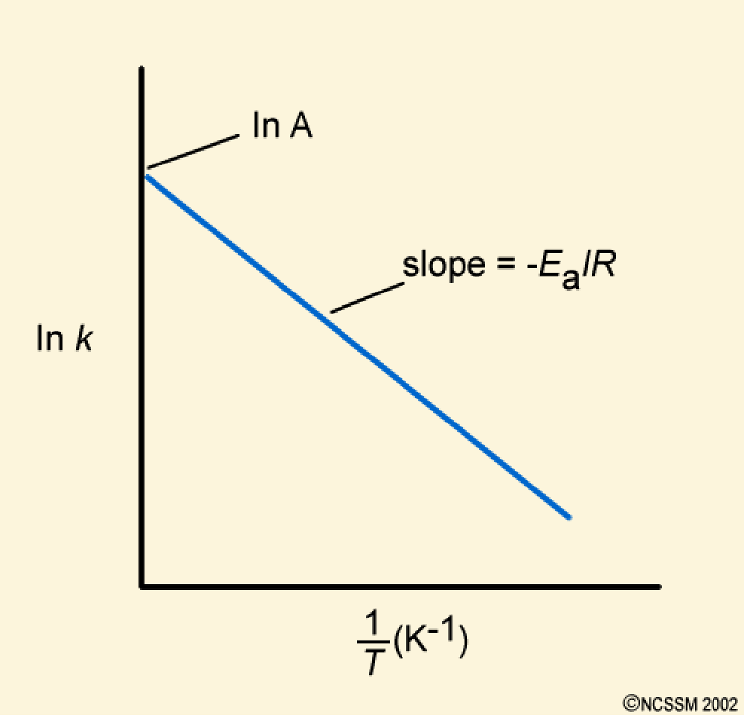
$$\ln k = \frac{-Ea}{R}\,\frac{1}{T} + \ln A \qquad \underline{\text{OR}} \qquad \ln k_2 - \ln k_1 = \frac{-Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$y = m \quad x + b \qquad\qquad (y_2 - y_1) = m \quad (x_2 - x_1)$$

A plot of ln *k* v 1/T (for *k* determined at different temperatures) for any chemical process will yield a LINEAR plot with slope equal to $-E_a/R$. OR

Two points from the Arrhenius data (ln k_1, $1/T_1$) and (ln k_2, $1/T_2$) may be used to find E_a mathematically

Generic Arrhenius Plot of ln k v 1/T



The following data was determined:

Experiment	k	T (K)		
1.	1.05×10^{-3}	759		
2.	2.14×10^{-2}	836		

Questions: What is E_a? What is k at 865 K?

Discussion: How would you solve these problems (there are two general methods)?

Plan and execution:

"Standard question"

The following question is a great example of the type asked on standardized tests like the MCAT etc. Again, as is often the case, once you know the trick they are easy….

The rate of a particular reaction is quadrupled when the temperature was increased from $55^{o}C \rightarrow 60^{o}C$. What is E_a for this process?

<u>Work in groups of 3 or 4 – try to figure out the 'trick'</u>

Reaction Mechanisms

Definition of Reaction Mechanism: A combination of *elementary steps* resulting in the formation of product(s) from reactant(s)

Example: The following reaction has a single, *bimolecular*, *elementary step*:

$$NO\ (g) + O_3\ (g) \rightarrow [NOO_3]^{\ddagger} \rightarrow NO_2\ (g) + O_2\ (g)$$

bimolecular – involves the collision of two reactant molecules (NO and O_3)

elementary step – ONE collision or other molecular scale event

molecularity – the number of molecules involved in an elementary step

Note: Reactions can also feature *unimolecular* (e.g. isomerization of methylisonitrile, any nuclear decay) or (rarely, why?) *termolecular* elementary steps.

Elementary Steps and their rate laws (fill in the blanks)

Molecularity	Elementary Step	Rate Law
*Uni*molecular	$A \rightarrow$ products	Rate = $k[A]^1$
*Bi*molecular	$A + A \rightarrow$ products	Rate = $k[A]^2$
*Bi*molecular	$A + B \rightarrow$ products	Rate = $k[A]^1[B]^1$
*Ter*molecular	$A + A + A \rightarrow$ products	Rate = $k[A]^3$
*Ter*molecular	$A + A + B \rightarrow$ products	Rate =
*Ter*molecular	$A + B + C \rightarrow$ products	Rate =

Discussion: For the above reactions, which feature single elementary steps, do you see any correlation between the molecularity and the overall order in each case?

DANGER! DANGER! WILL ROBINSON…

DO NOT assume molecularity (stoichiometry) and reaction order are numerically identical for all reactions. This IS true for elementary steps, but ***not*** for multi-step reactions (discussed below).

Recall from *Chemical Kinetics 2* that orders of reaction must be determined from initial rate (experimental) data

Multiple Step Reactions

Most reactions feature two or more elementary steps – these are called multi-step reactions

The mechanism (and balanced chemical equation) for a multi-step reaction is the sum of its individual elementary steps.

Example: The formation of NO and CO_2 from NO_2 and CO

Elementary step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

Elementary step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Combine steps: $NO_2 + NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$

What's that itch??

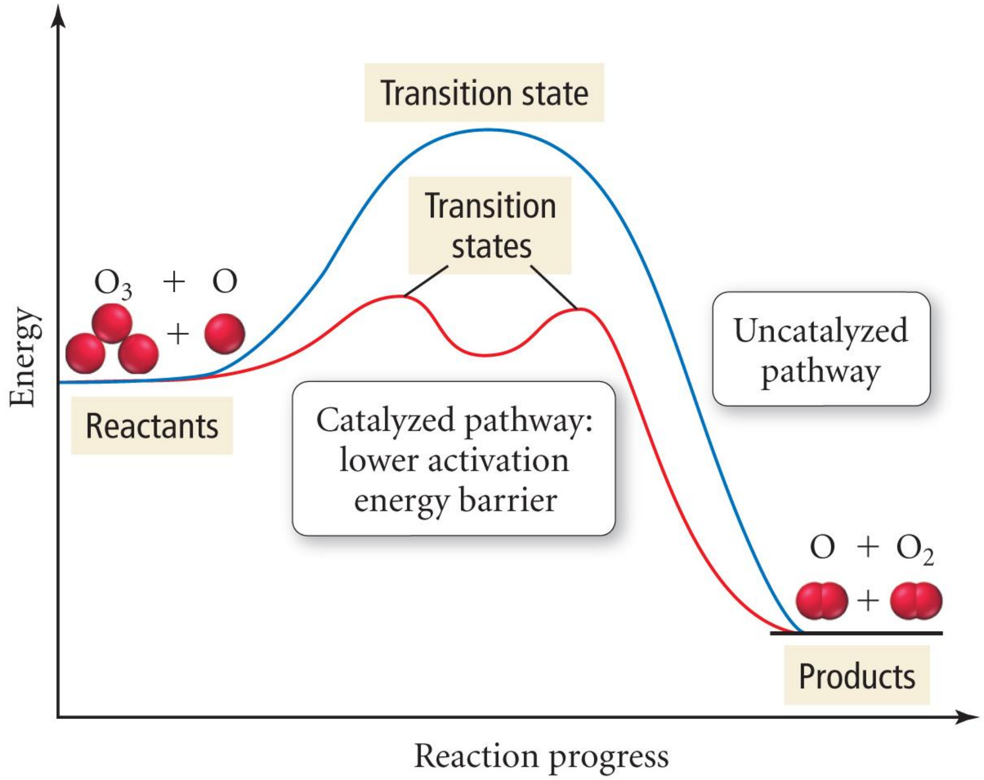
Net Reaction:

The overall rate of a multi-step reaction is limited by its slowest single elementary step (the *rate limiting step*) – this fact was utilized in your recent clock reaction lab. How?

Analogy: A production line is only as fast as its slowest person – "quit showing off Frank, these pies need to go in the oven!"

Catalysis

Background: As we saw in *Chemical Kinetics 1*, a catalyst speeds up the rate of reaction without being consumed in the process. We discovered that, in part, this is due to the catalyst (be it homogeneous *or* heterogeneous) increasing the *local* reactant concentration. However, this is only part of the story - what's really going on behind the curtain?

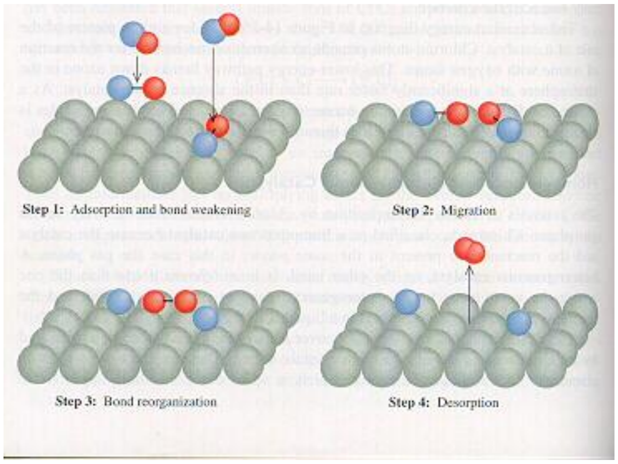


A catalyst provides an ***alternate reaction pathway***, which, in turn, consists of two or more elementary steps.

While the *total* activation energies for the uncatalyzed and catalyzed pathways are the same, that of the catalyzed process is made up from the sum of each elementary step's activation energies.

A greater fraction of molecules (recall the Boltzmann distribution) will have kinetic energy greater than, or equal to, that of the largest E_a for the catalyzed reaction's elementary steps

Case study: The conversion of NO_2 (g)→ N_2 (g) + O_2 (g) by your car's catalytic converter



The (catalyzed) reaction is now composed of four(+) individual processes, each with its own E_a, that occur at the catalyst surface:

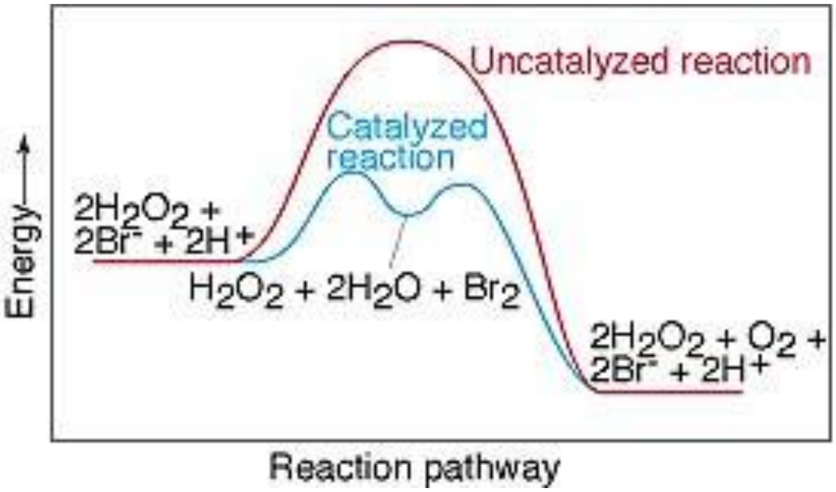
a. NO_2 (g) → NO_2 (ads)
b. 2 NO_2 (ads) → O_2(ads) + 2 N (ads)
c. O_2 (ads) → O_2(g)
d. 2 N (ads) → N_2(ads) (not shown)
e. N_2 (ads) → N_2(g) (not shown)

The sum of these reactions E_as equals that of the uncatalyzed reaction

Homogeneous Catalysis

Homogeneous catalysts 'do the same job' as heterogeneous catalysts, *but are in the same phase as the reactants* – typically in solution.

Examples of homogeneous catalysts include aqueous ions, such as H^+, or aqueous transition metal complexes, such as $TiCl_4$.



“Arrhenius”

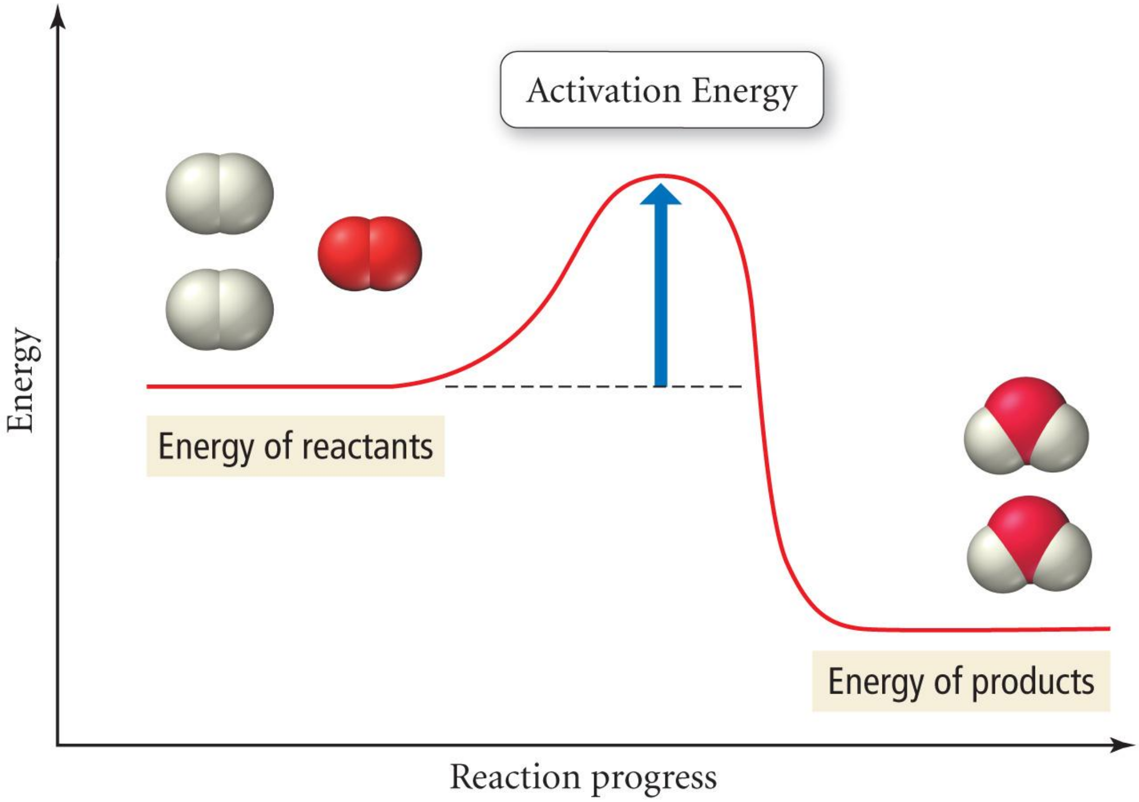
The following question was taken from your 2nd practice midterm:

Question 1 (25 points): The activation energy for a certain reaction is 65.7 kJ/mol. How many times faster will the reaction occur at 50°C than 0°C?

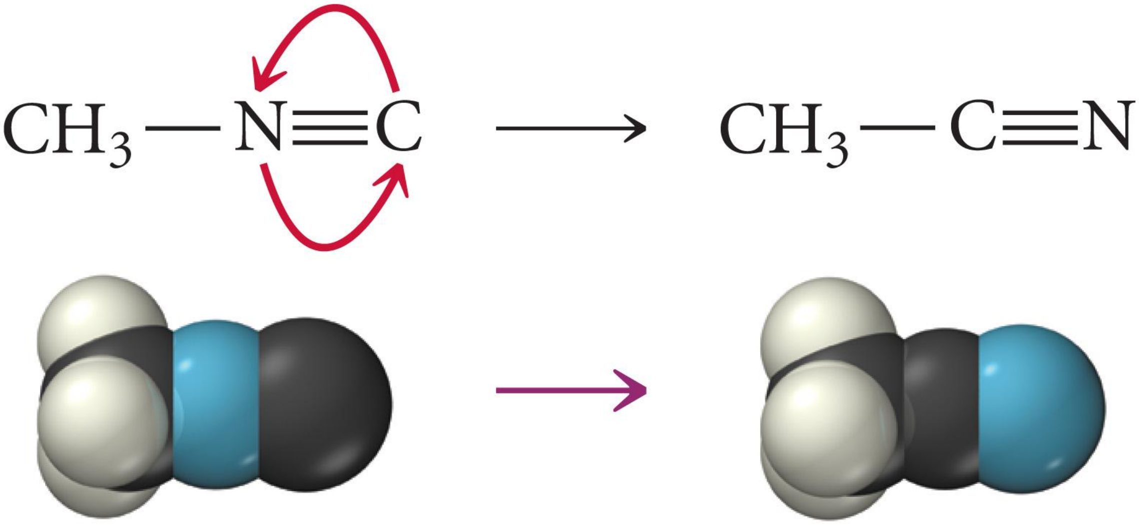
Appendix

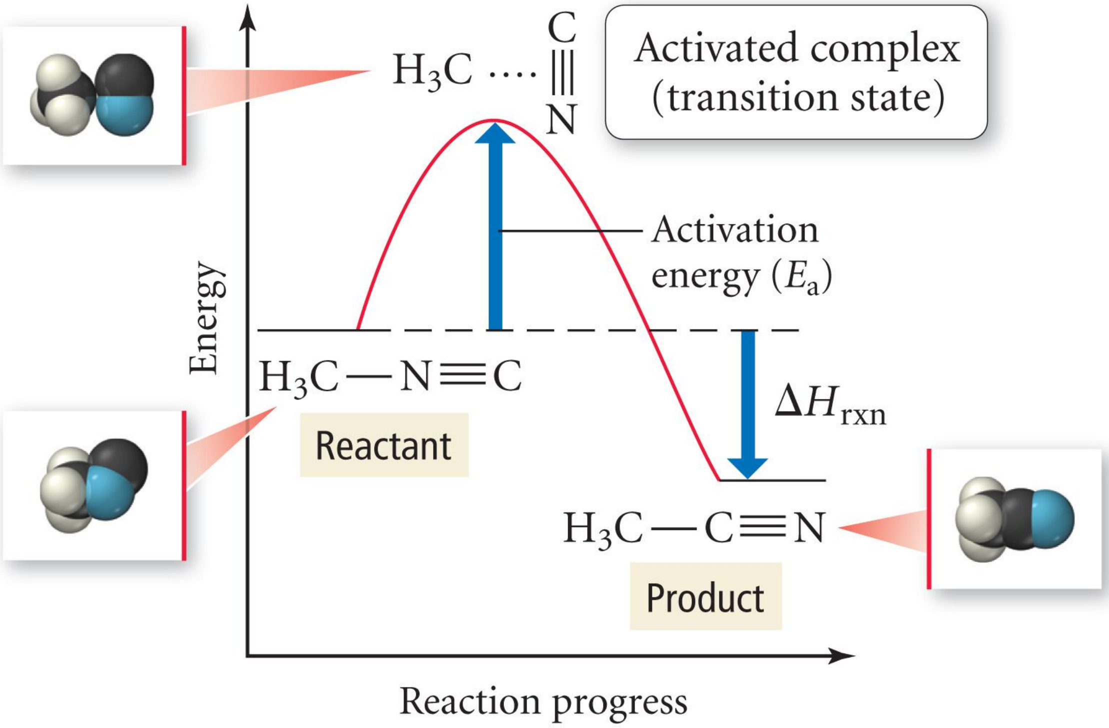
Activation Energy

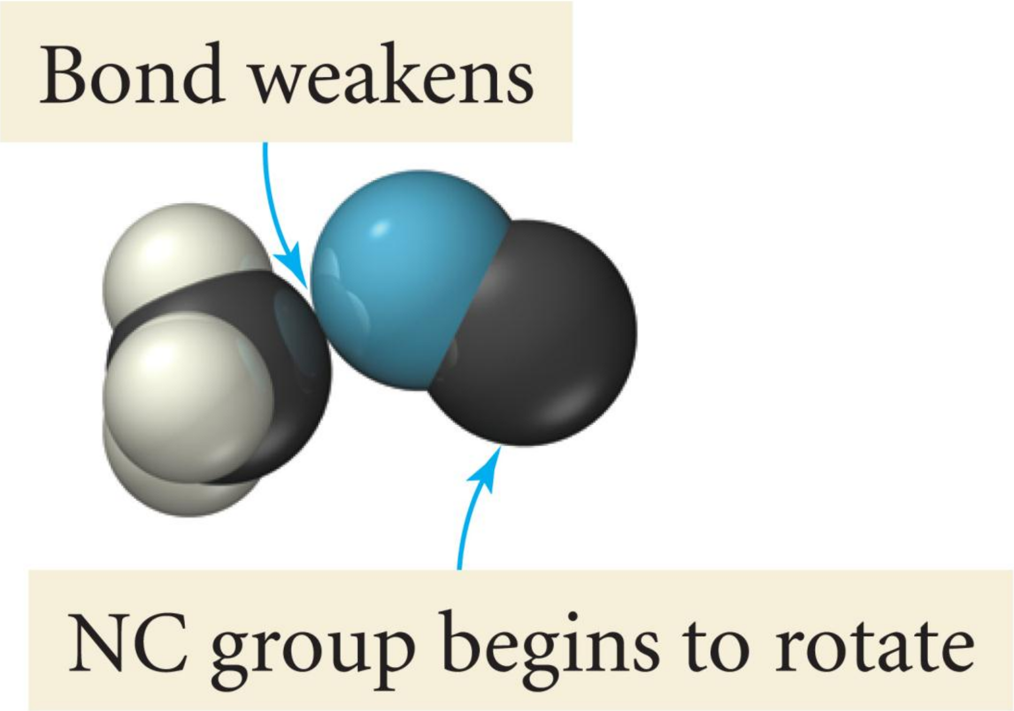
$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

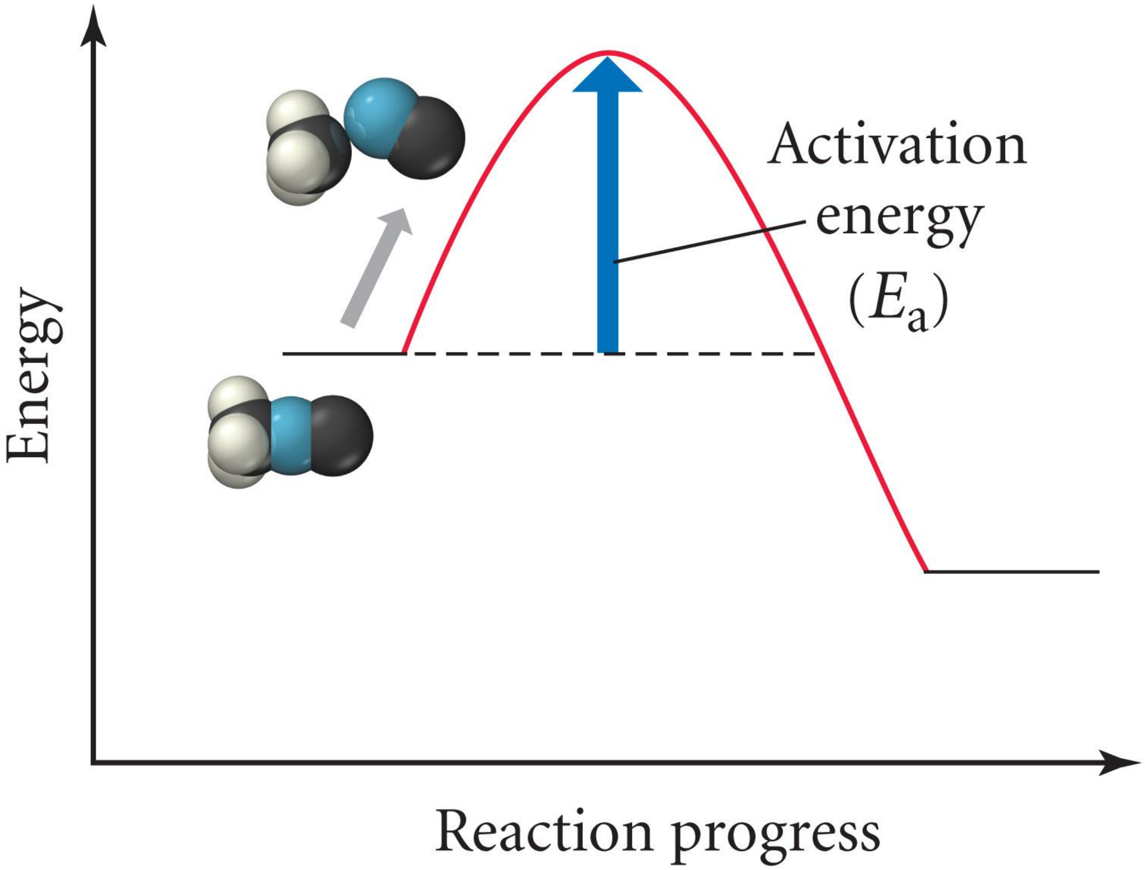


$$k = \underbrace{A}_{\text{Frequency factor}}\,\underbrace{e^{\frac{-\overset{\text{Activation energy}}{E_a}}{RT}}}_{\text{Exponential factor}}$$


CH3—N≡C
→
CH3—C≡N

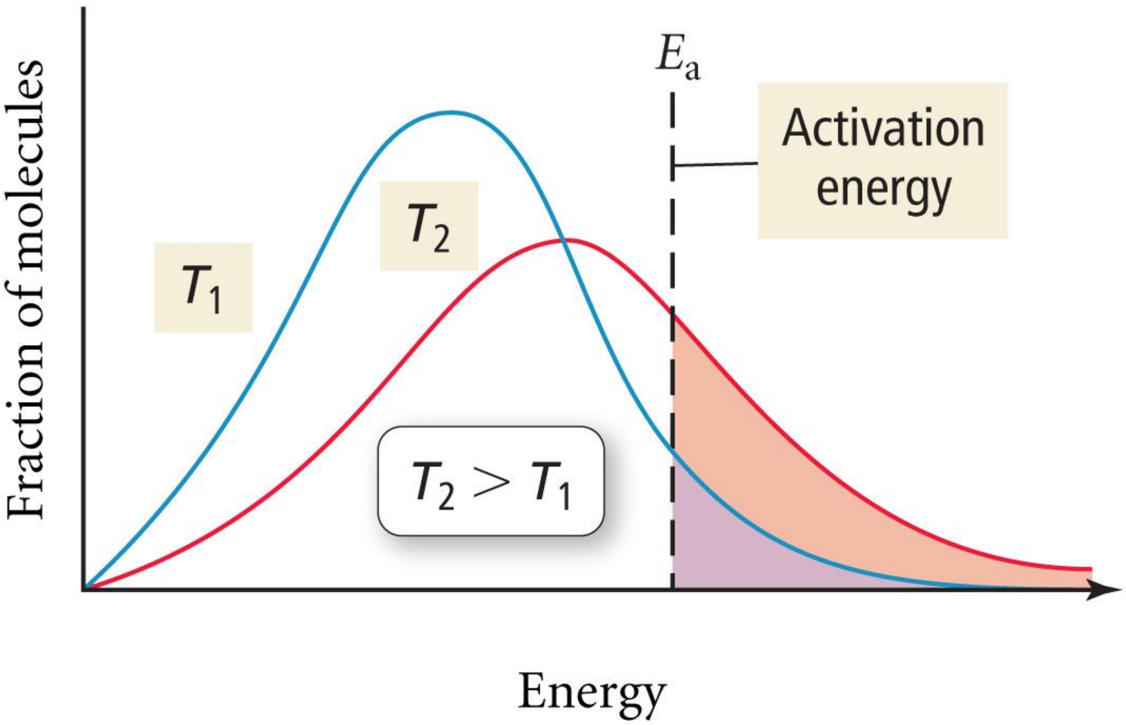

H3C ···· C≡N
Activated complex (transition state)
Activation energy (Ea)
Energy
H3C—N≡C
Reactant
ΔHrxn
H3C—C≡N
Product
Reaction progress

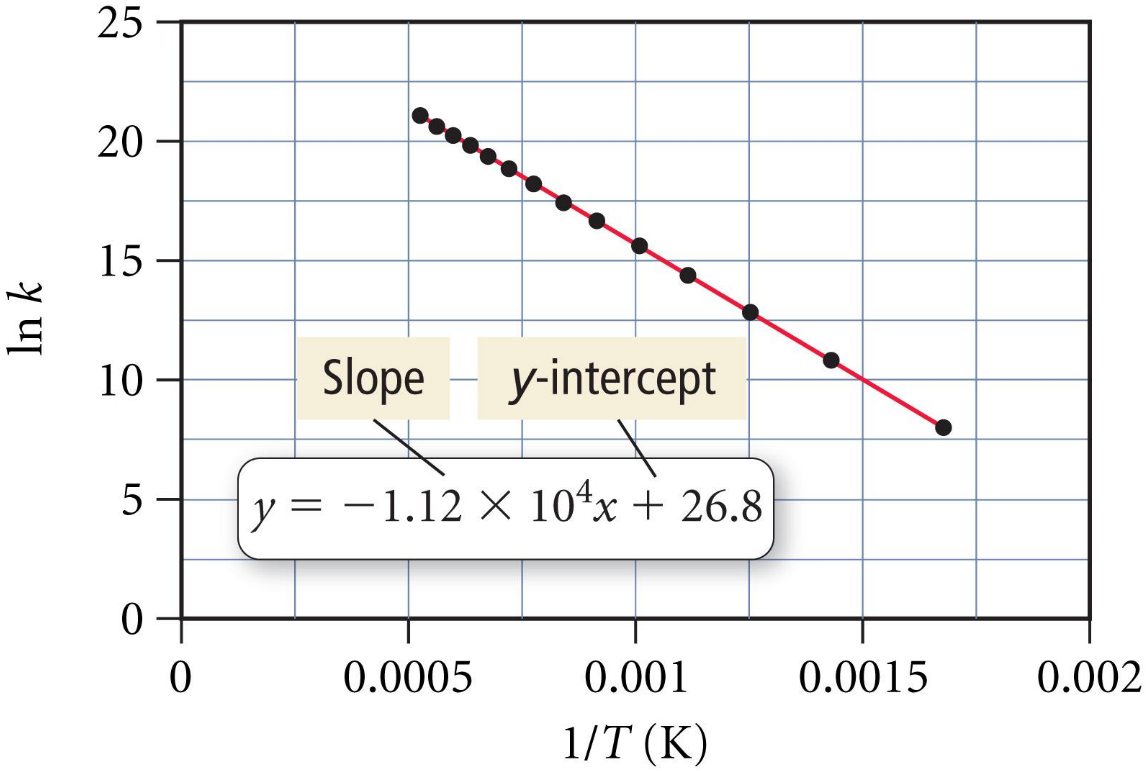

Bond weakens
NC group begins to rotate


Activation energy (E_a)
Energy
Reaction progress

Thermal Energy Distribution

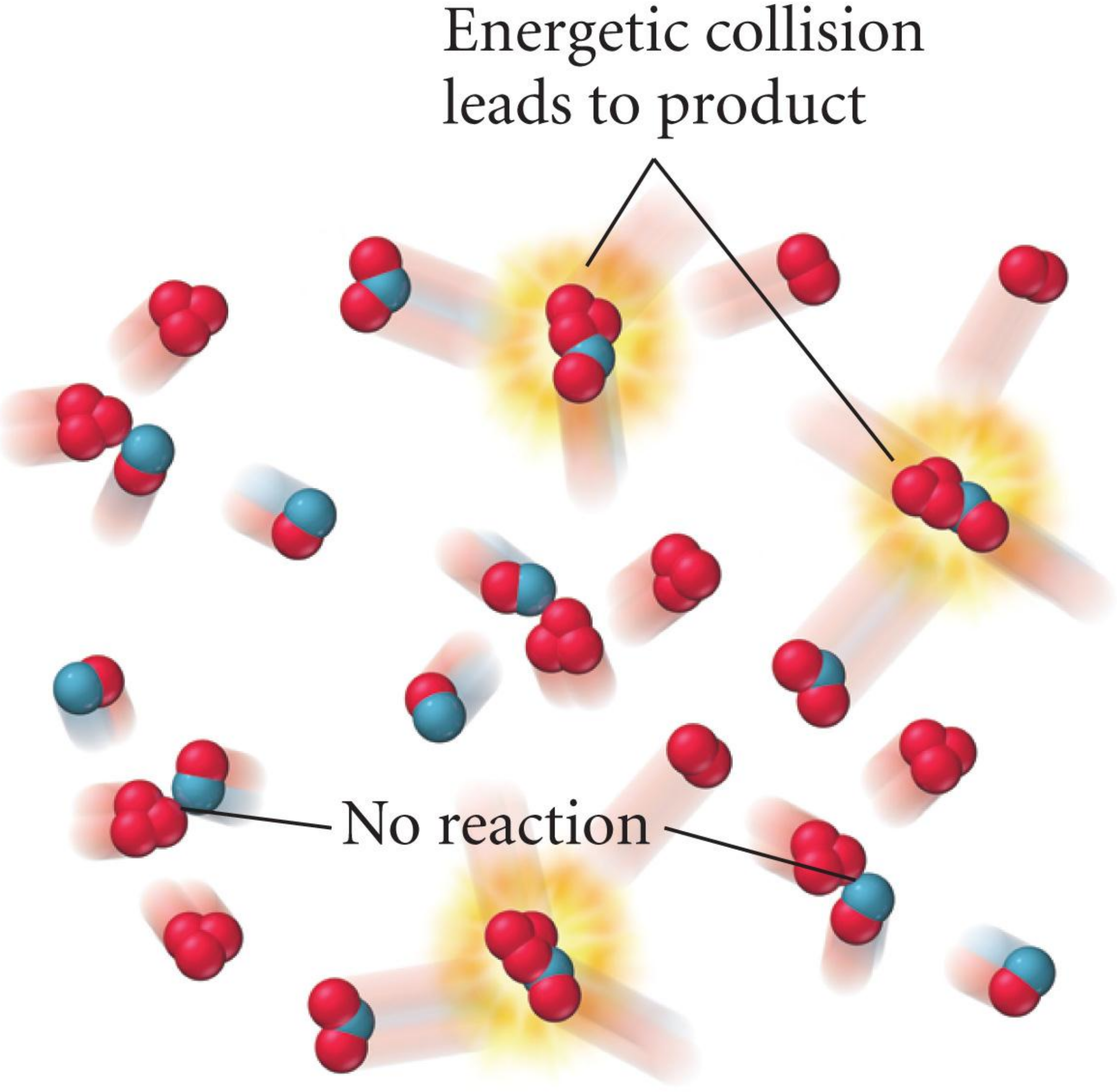
As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



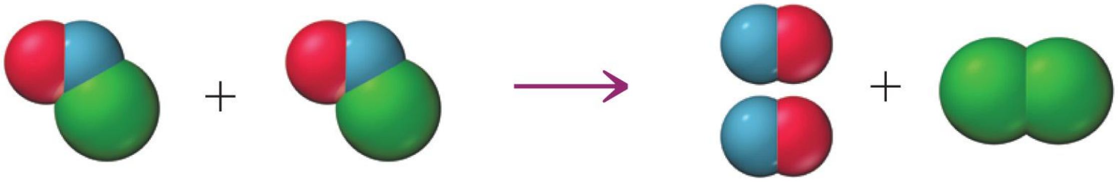


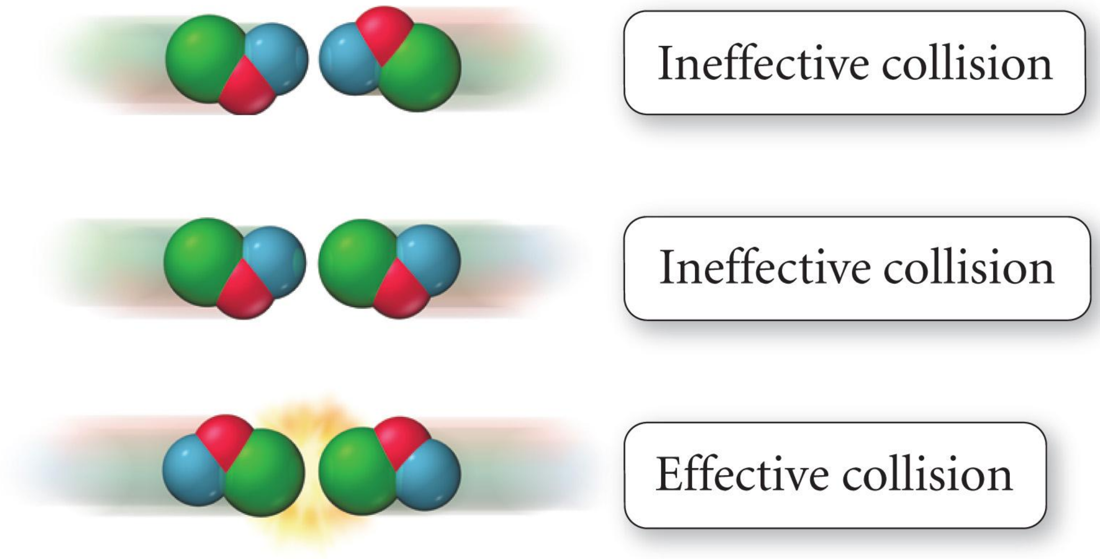
$$k = Ae^{\frac{-E_a}{RT}}$$

$$= \underbrace{p}_{\text{Orientation factor}}\underbrace{z}_{\text{Collision frequency}}e^{\frac{-E_a}{RT}}$$

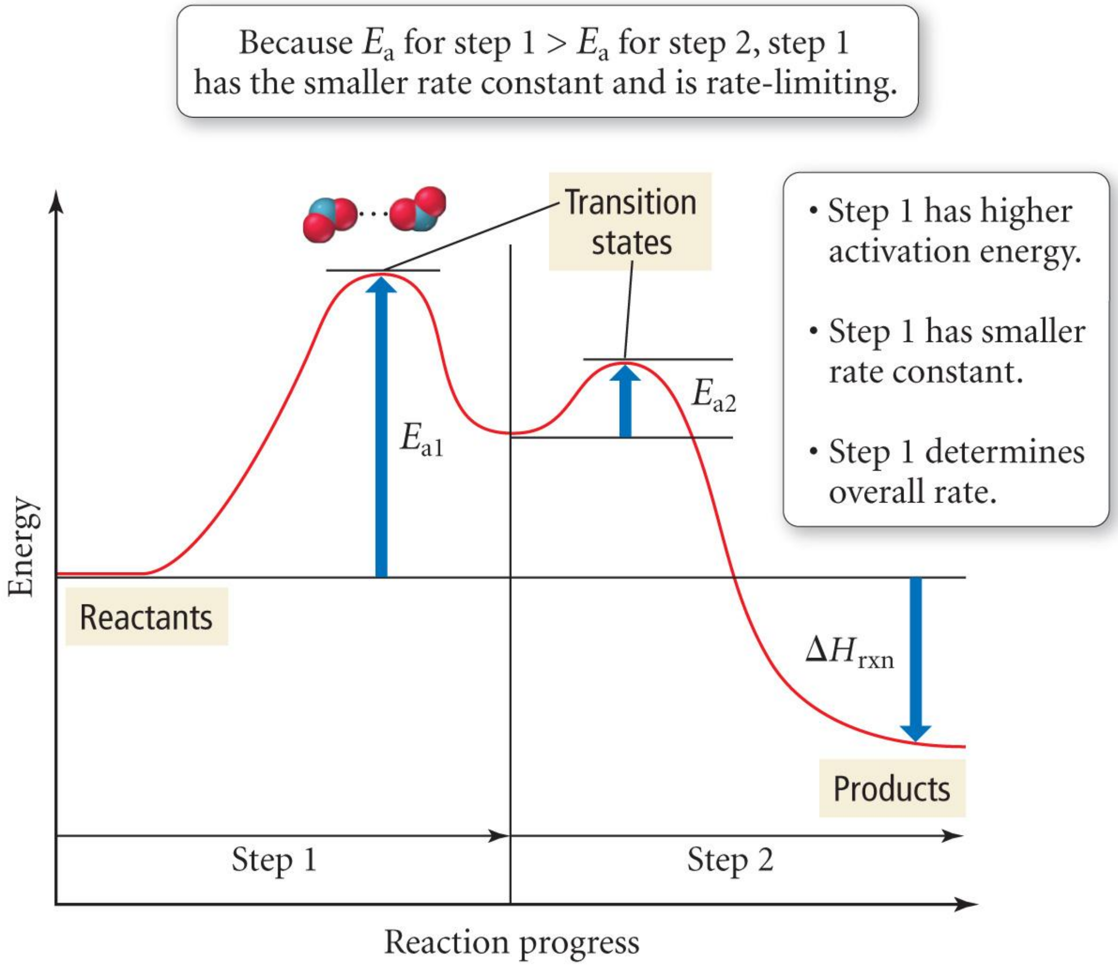

Energetic collision leads to product
No reaction

$$\mathrm{NOCl}(g) + \mathrm{NOCl}(g) \longrightarrow 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g)$$





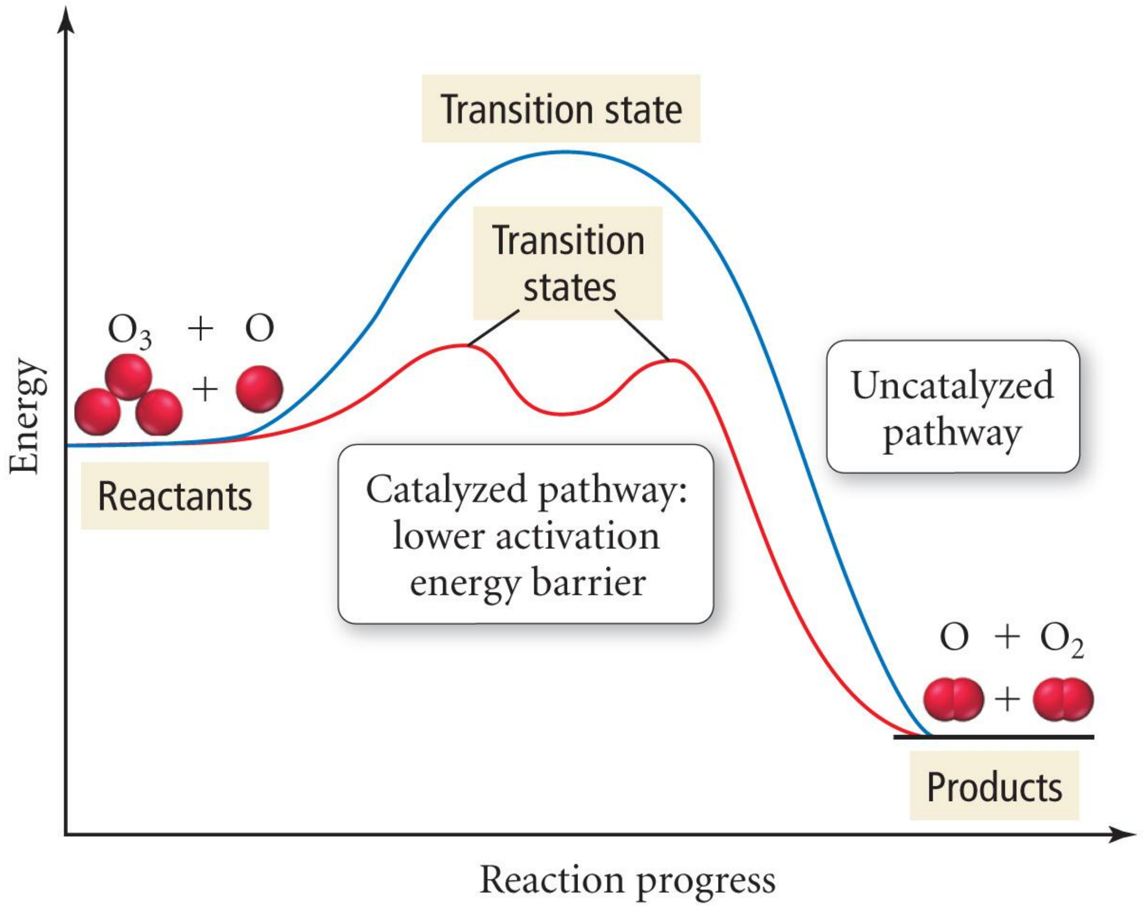
Energy Diagram for a Two-Step Mechanism



Because E_a for step 1 > E_a for step 2, step 1 has the smaller rate constant and is rate-limiting.

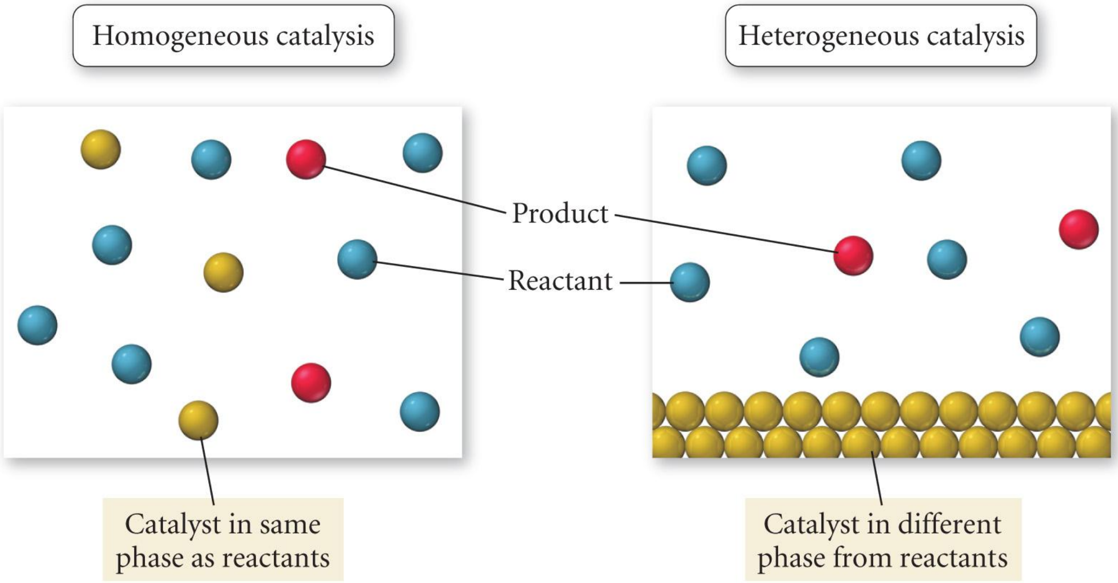
- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

Energy Diagram for Catalyzed and Uncatalyzed Pathways



$$CH_3CH_2CH_3(g) + 5\ O_2(g) \xrightarrow[\text{catalyst}]{} 3\ CO_2(g) + 4\ H_2O(g)$$

Fuel fragment



Heterogeneous Catalysis