Chemistry 102(001) Spring 2015

Instructor: Dr. Upali Siriwardane

e-mail: upali@latech.edu
Office: CTH 311
Phone 257-4941

Office Hours: M,W 8:00-9:30 & 11:00-12:30 am; Tu,Th, F 8:00 - 10:00 am. or by appointment.;

Test Dates:

March 30, 2015 (Test 1): Chapter 13
April 22, 2015 (Test 2): Chapter 14 &15
May 81, 2015 (Test 3): Chapter 16 &7
May 20, 2015 (Make-up test) comprehensive: Chapters 13-17

Chapter 13. Chemical Kinetics

A Nanoscale View: Elementary Reactions

Most reactions occur through a series of simple steps or elementary reactions.

Elementary reactions could be

unimolecular - rearrangement of a molecule

bimolecular - reaction involving the collision of two molecules or particles

termolecular - reaction involving the collision of three molecules or particles

Elementary Reactions and Mechanism

$$2NO_{2\,(g)} + F_{2\,(g)} \longrightarrow 2NO_2F_{(g)}$$

If the reaction took place in a single step the rate law would be: rate = $k\,[NO_2]_2\,[F_2]$

Observed: rate = $k_1\,[NO_2]\,[F_2]$

If the observed rate law is not the same as if the reaction took place in a single step that more than one step must be involved

Elementary Reactions

A possible reaction mechanism might be:

Step one $NO_2 + F_2 \longrightarrow NO_2F + F$ **(slow)**

Step two $NO_2 + F \longrightarrow NO_2F$ **(fast)**

Overall $2NO_2 + F_2 \longrightarrow 2NO_2F$

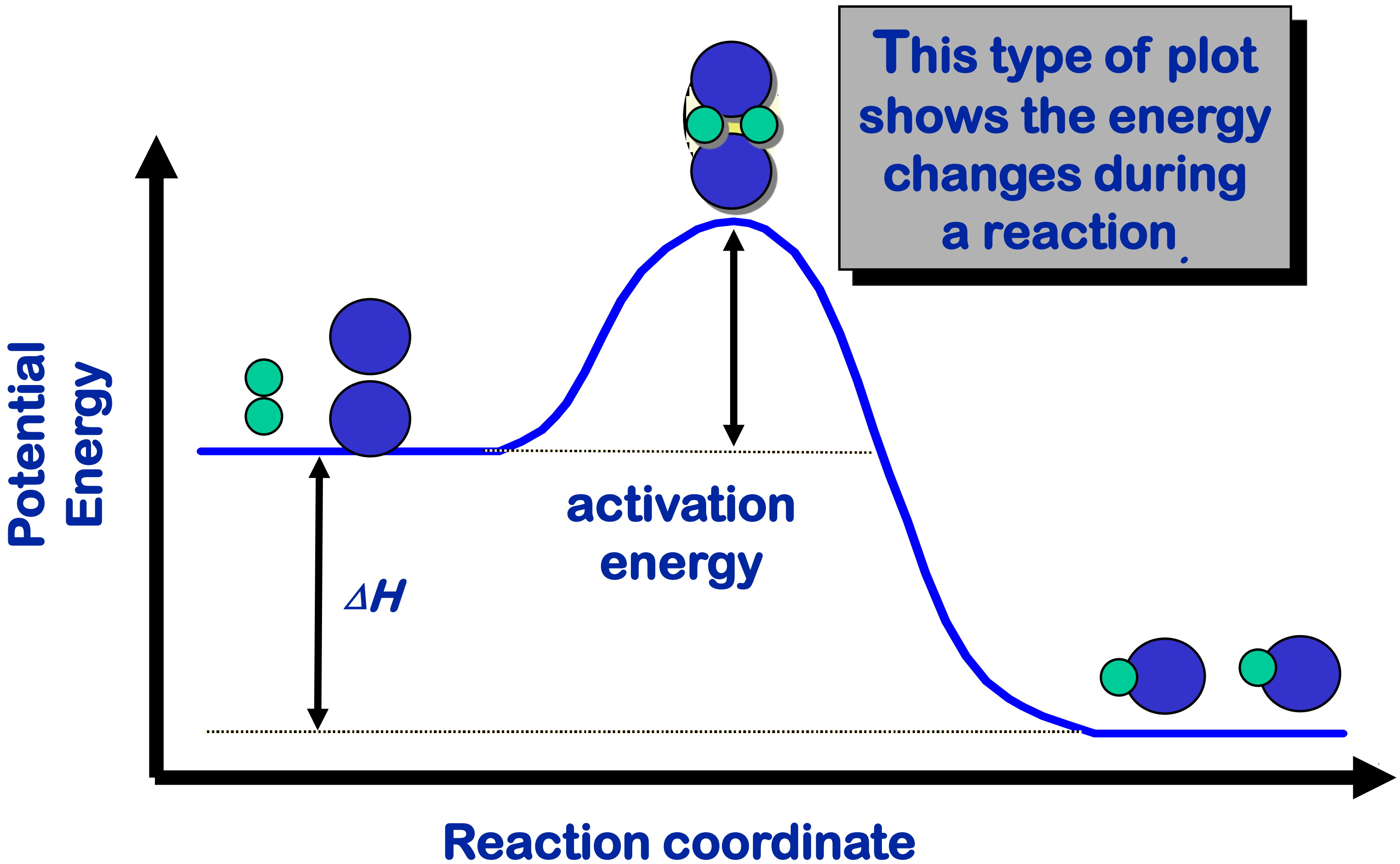
Rate Determining Step

slowest step in a multi-step mechanism

the step which determines the overall rate of the reaction

$$\text{rate} = k_1 [NO_2] [F_2]$$

Reaction profile of rate determining step



What Potential Energy Curves Show

Exothermic Reactions

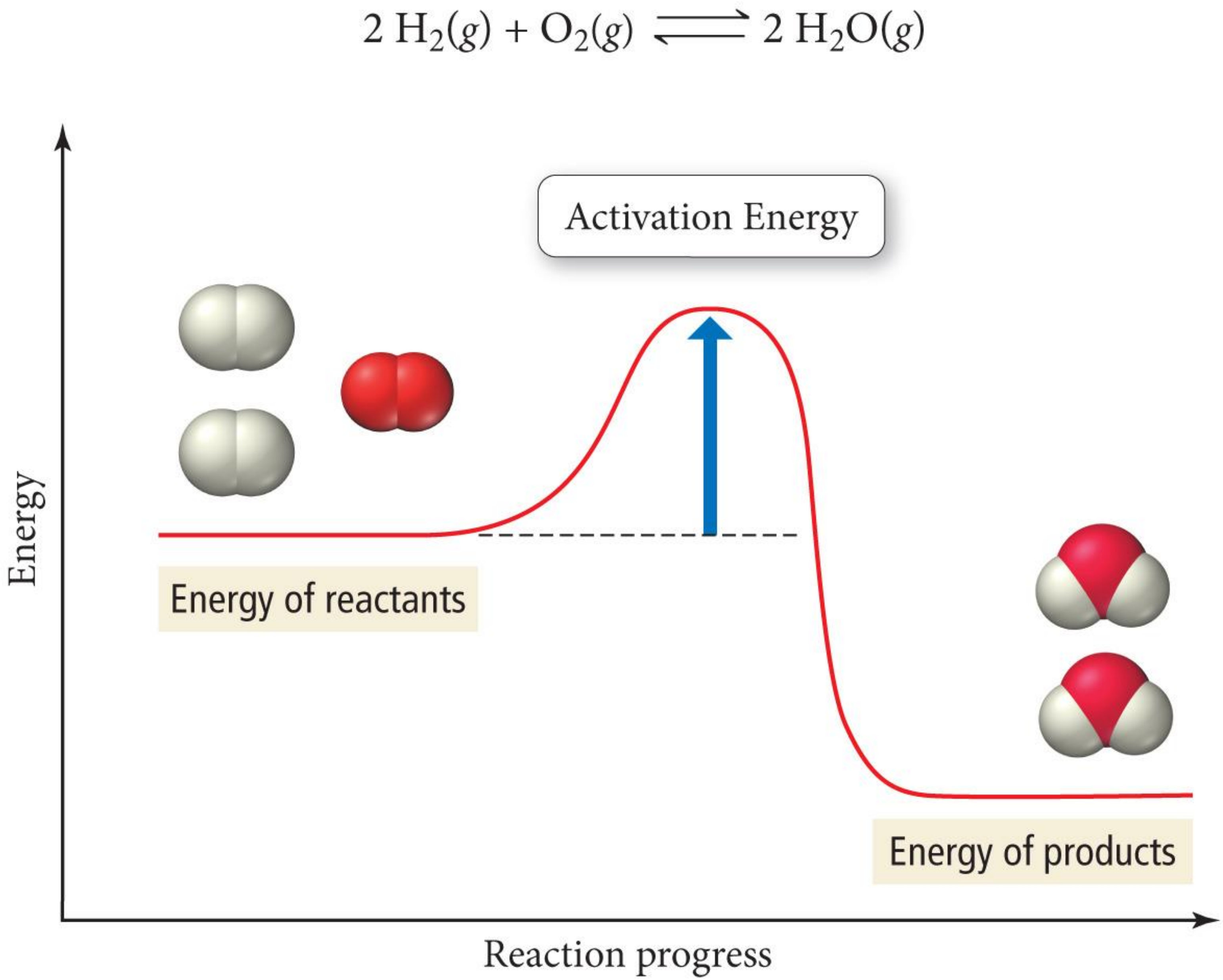
Endothermic Reactions

Activation Energy (E_a) of reactant or the minimum energy required to start a reaction

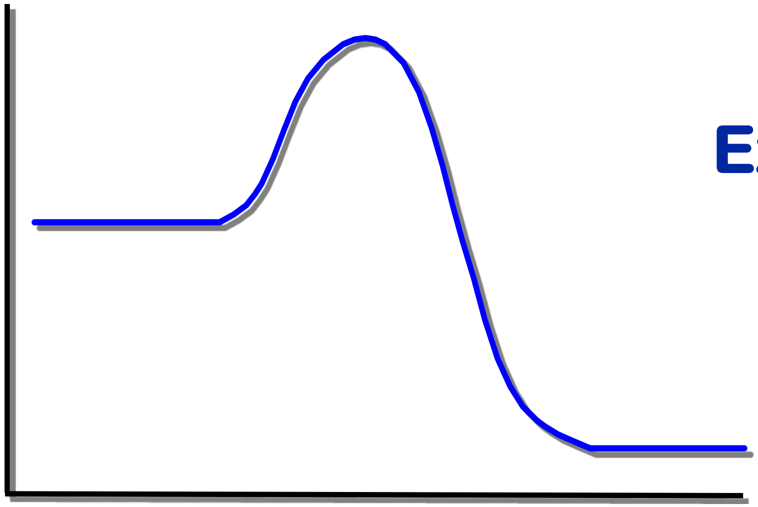
Effect of catalysts

Effect of temperature

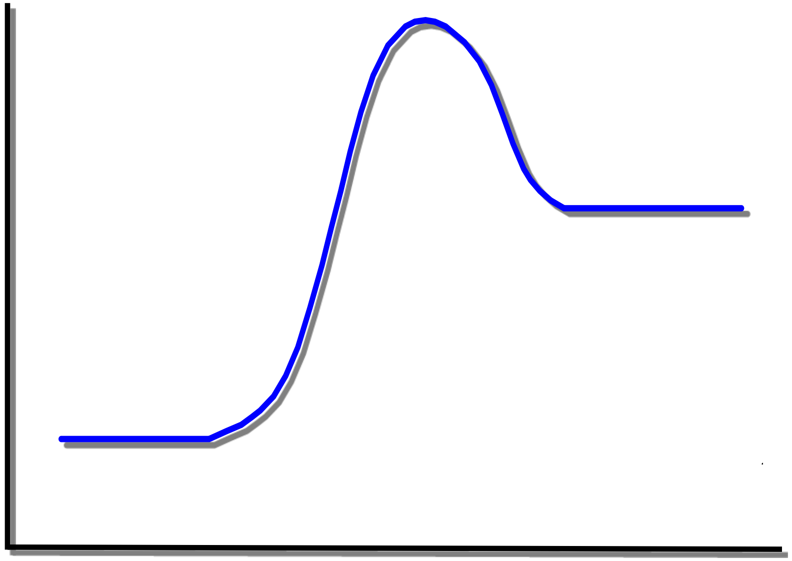
Activation Energy



Examples of reaction profiles

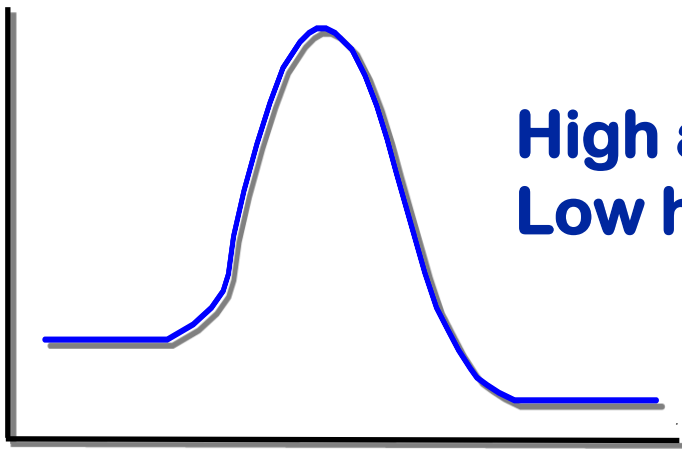


Exothermic reaction

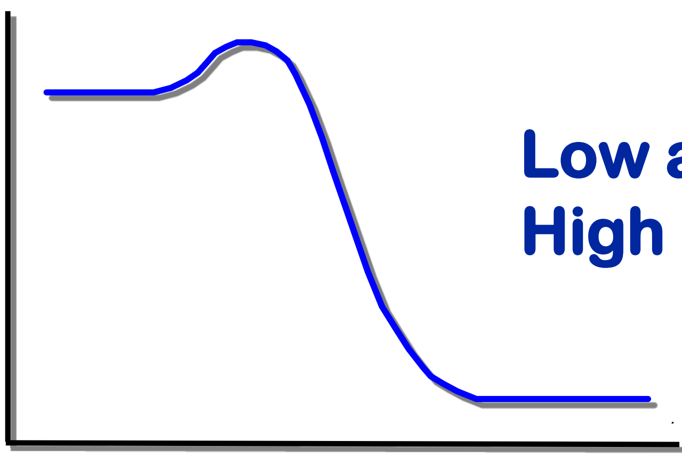


Endothermic reaction

Examples of reaction profiles



High activation energy **(kinetic)**
Low heat of reaction **(thermodynamic)**



Low activation energy **(kinetic)**
High heat of reaction **(thermodynamic)**

Catalysts Lowers E_a

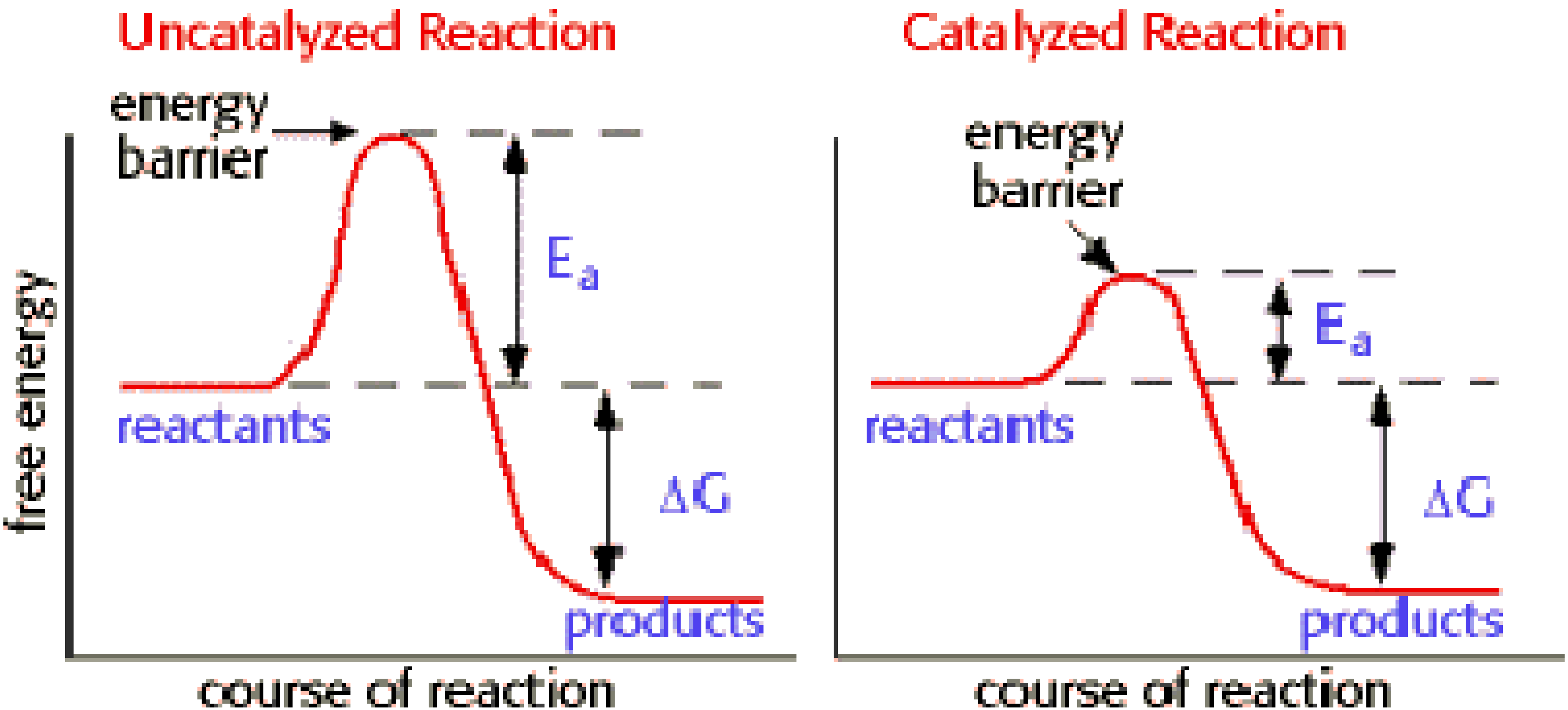


TABLE 13.2 Rate Laws for Elementary Step

Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ products	1	$\text{Rate} = k[A]$
$A + A \longrightarrow$ products	2	$\text{Rate} = k[A]^2$
$A + B \longrightarrow$ products	2	$\text{Rate} = k[A][B]$
$A + A + A \longrightarrow$ products	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \longrightarrow$ products	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + A + C \longrightarrow$ products	3 (rare)	$\text{Rate} = k[A][B][C]$

1. **Given the chemical reaction:**

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, and the mechanism:

$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$; slow step

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$; fast step

a) How many elementary steps are in the mechanism?

b) Does the elementary steps adds up to overall chemical reaction? (Show your work)

c) What's is the molecularity of the slowest step?

1. **Given the chemical reaction:**

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, and the mechanism:

$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$; slow step

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$; fast step

d) What is the rate determining step in the mechanism?

e) What is(are) the intermediates in the mechanism?

1. **Given the chemical reaction:**

$NO_2(g) + CO(g) \rightarrow NO (g) + CO_2 (g)$, and the mechanism:

$NO_2(g) + NO_2 (g) \rightarrow NO_3 (g) + NO (g)$; fast step

$NO_3(g) + CO (g) \rightarrow NO_2 (g) + CO_2 (g)$; slow step

f) What's the rate law for the chemical reaction?

g) Rate law of what elementary step would agree with the experimentally determined the rate law?

1. **Given the chemical reaction:**

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, and the mechanism:

$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$; slow step

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$; fast step

f) What's the rate law for the chemical reaction?

g) Rate law of what elementary step would agree with the experimentally determined the rate law?

2) Draw potential energy diagrams to show:

a) **An Exothermic Reaction:**

b) **Endothermic Reaction:**

c) **Label Activation Energy (E_a) on both diagrams a) and b) above.**

2) Draw potential energy diagrams to show:

d) the effect of a catalyst in a chemical reaction.

3) The chemical reaction:

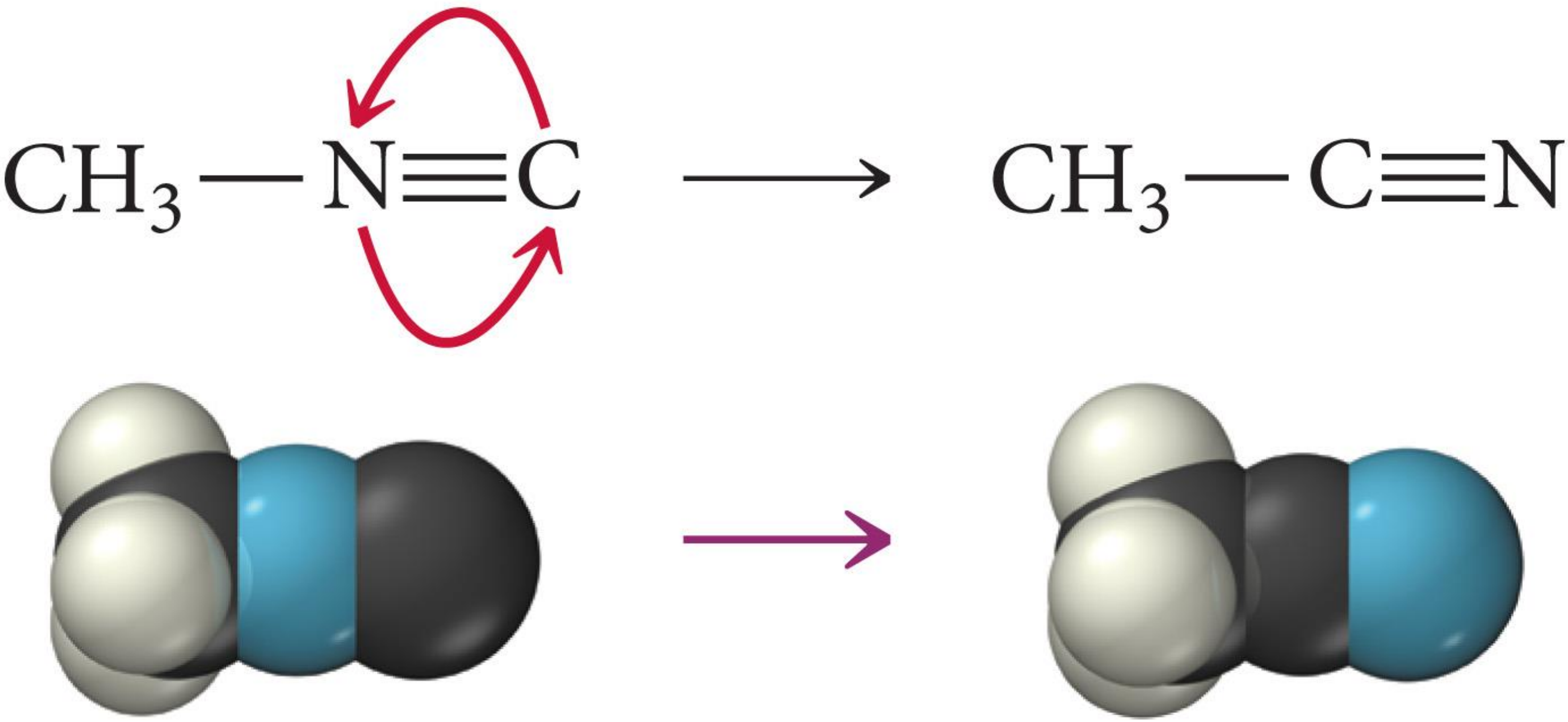
$$2NO_2\,(g) + F_2(g) \rightarrow 2NO_2F(g)$$

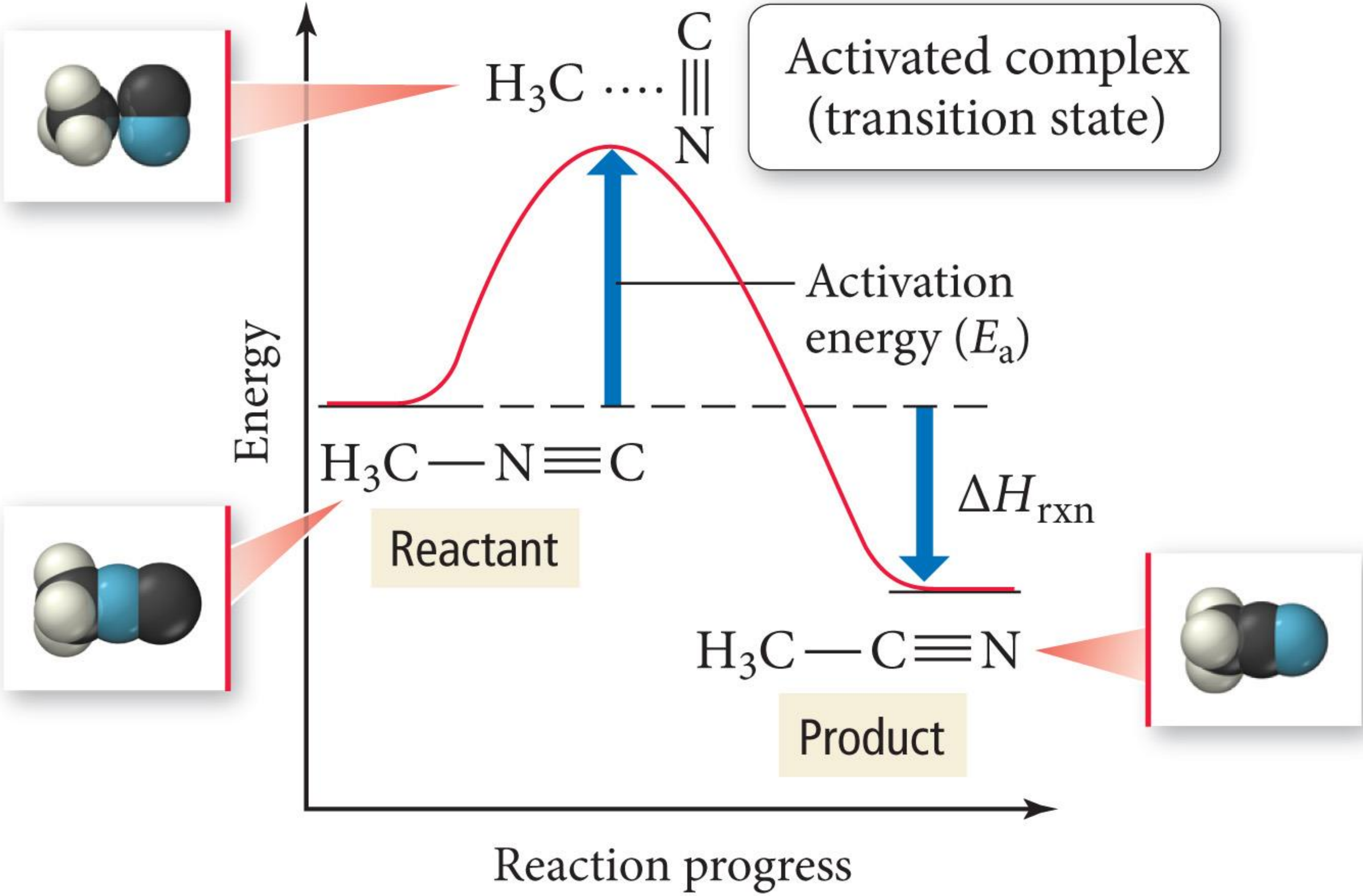
follows Rate Law: $\text{rate} = k\,[NO_2]\,[F_2]$

What would be the molecularity of the rate determining step in the mechanism?

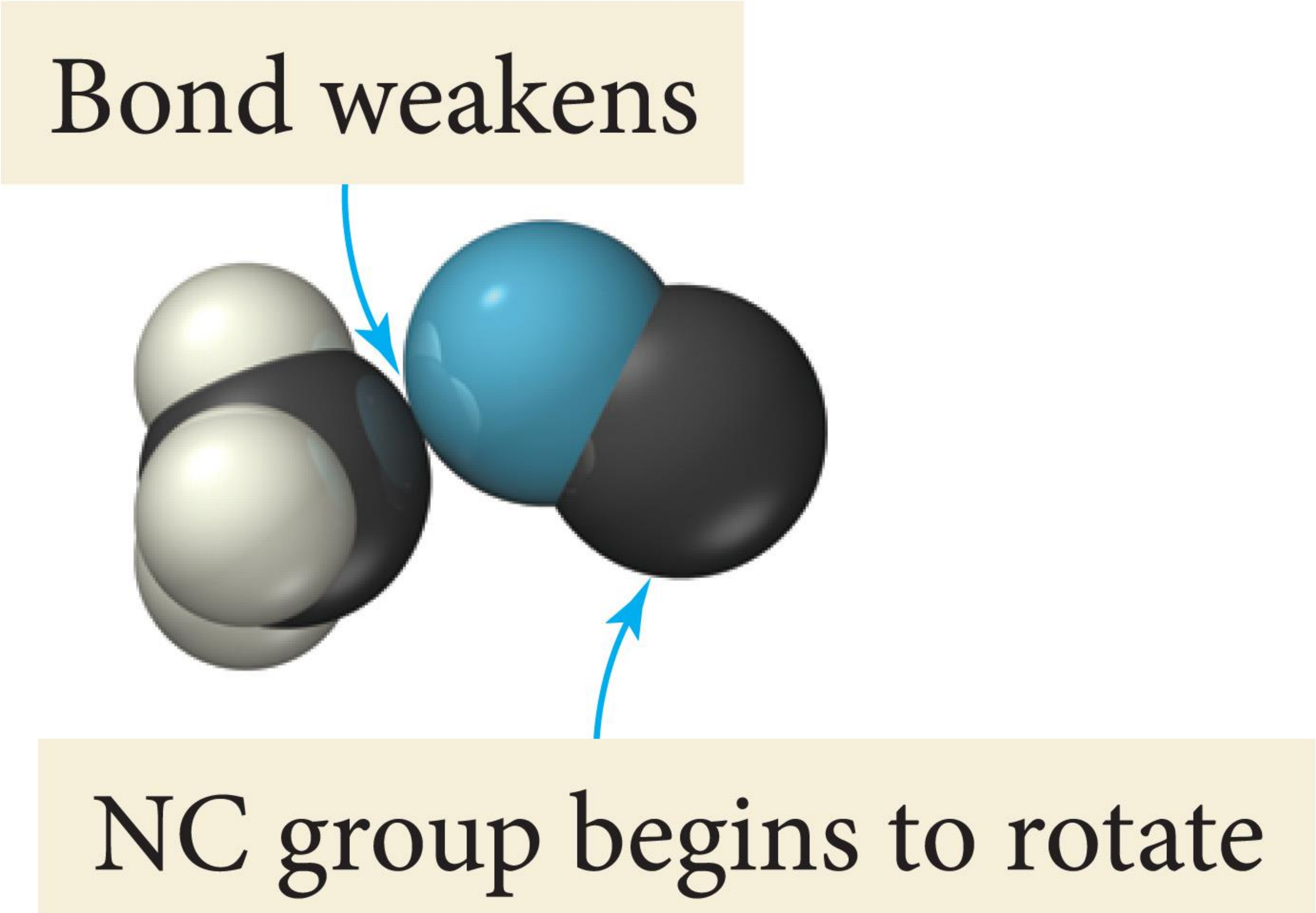
Reaction Mechanism

A set of elementary reactions which represent the overall reaction

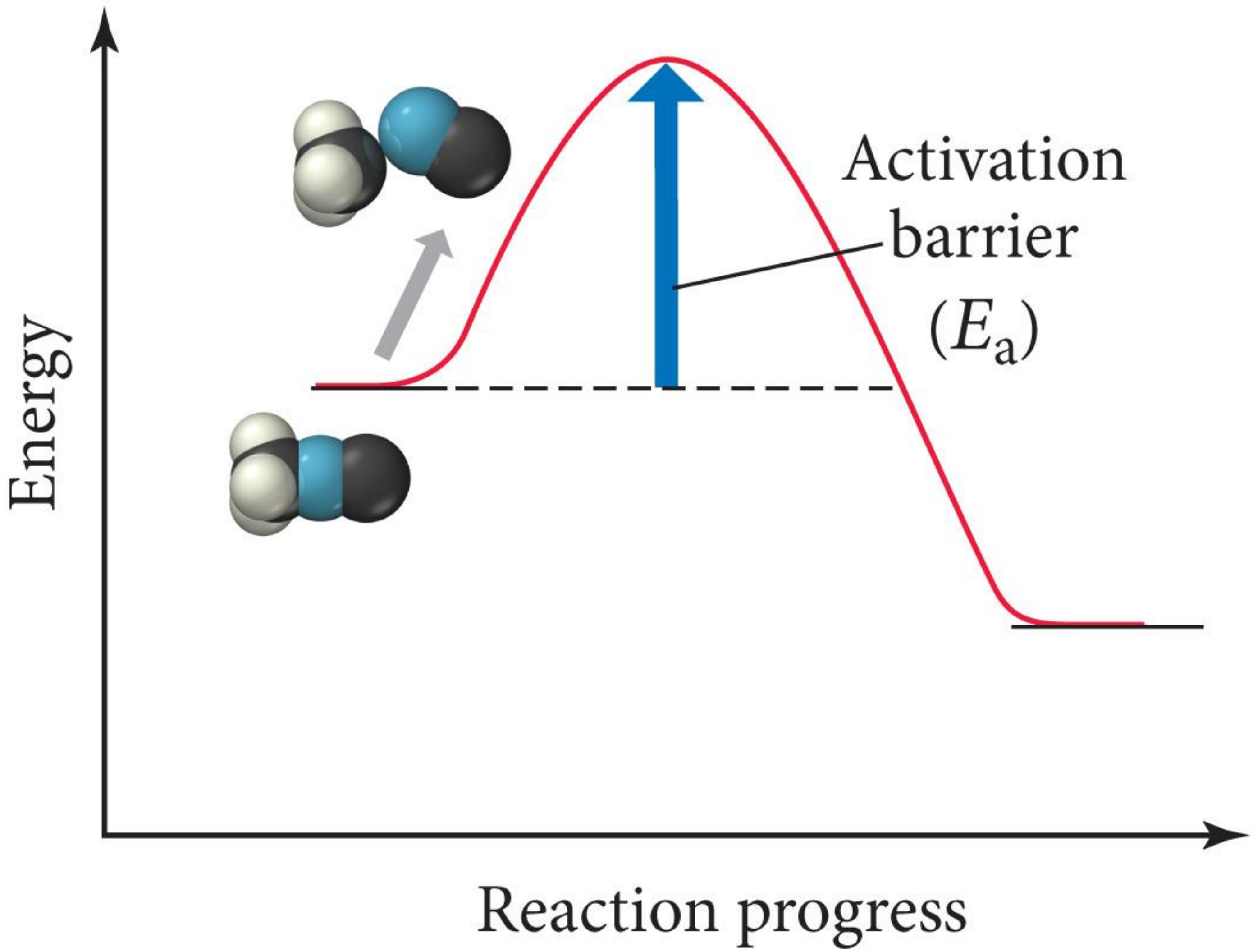

CH3—N≡C
CH3—C≡N



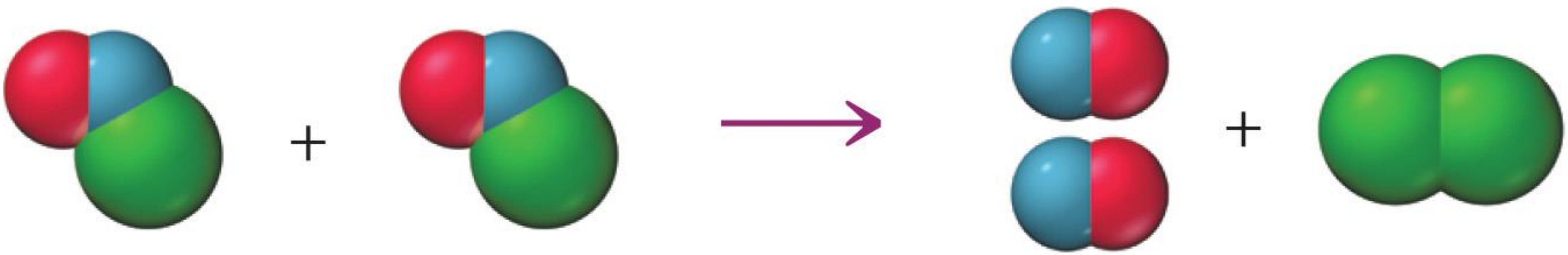
C
$H_3C \cdots$
N
Activated complex
(transition state)
Activation
energy (E_a)
Energy
$H_3C—N≡C$
Reactant
ΔH_{rxn}
$H_3C—C≡N$
Product
Reaction progress

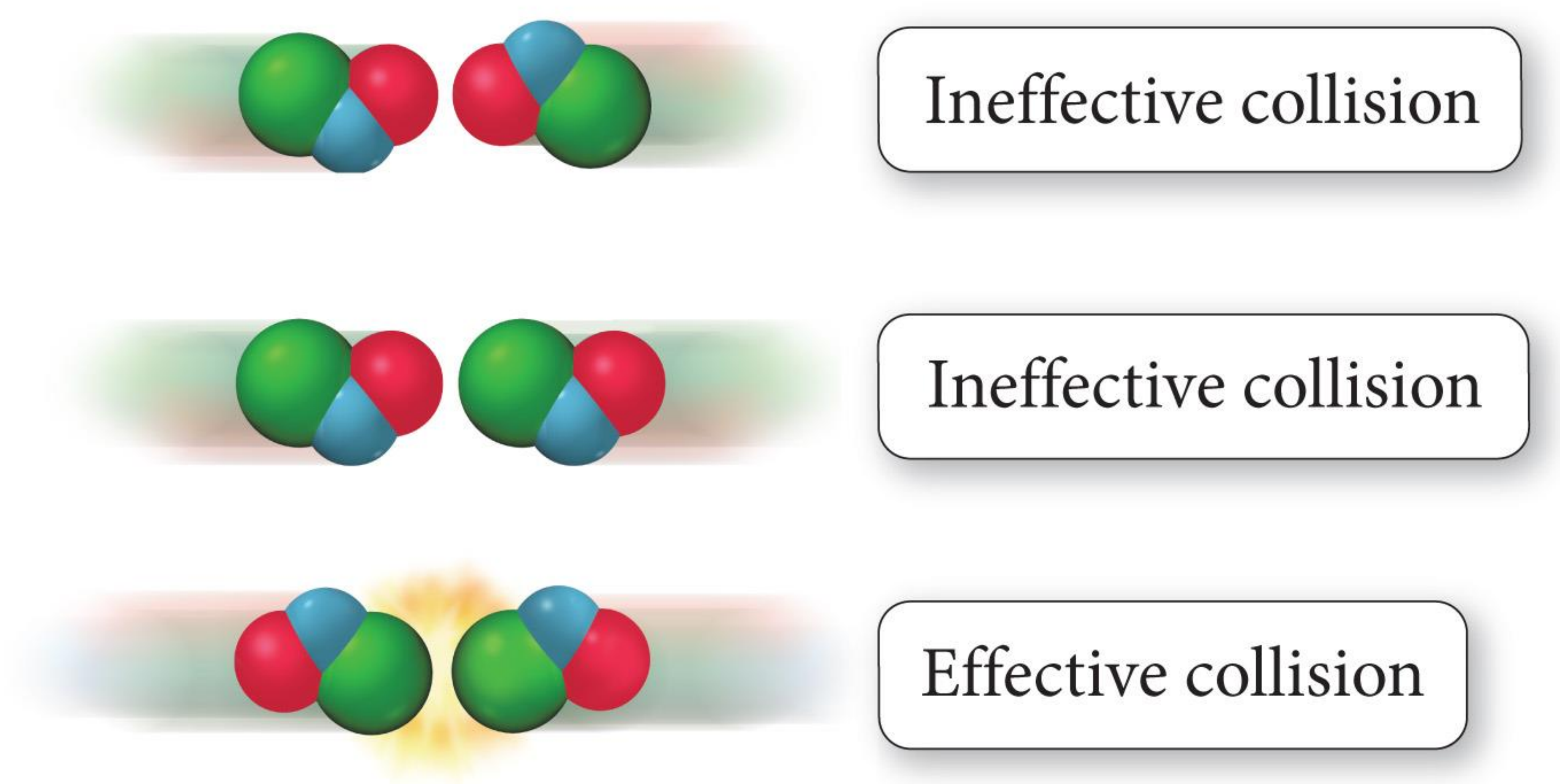

Bond weakens
NC group begins to rotate

Each wag is an approach to the activation barrier.



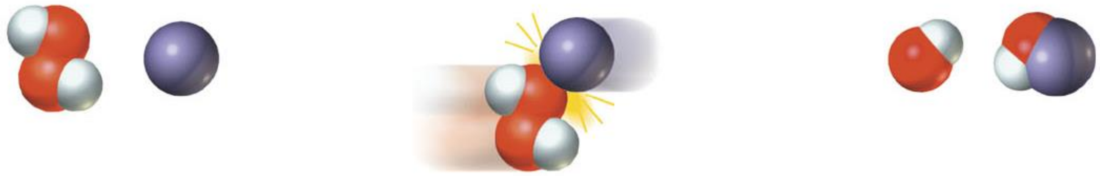
$$NOCl(g) + NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$



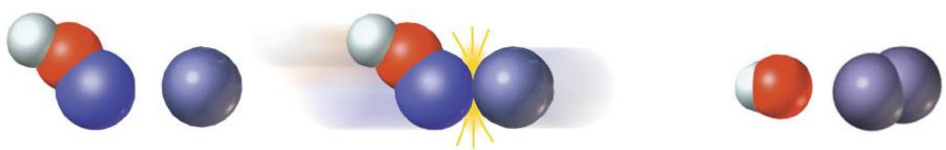

Ineffective collision
Ineffective collision
Effective collision

Mechanism Oxidation of Iodide Ion by Hydrogen Peroxide

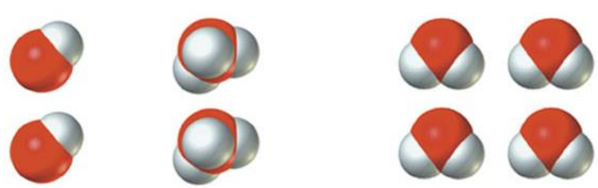
$$HOOH + I^- \xrightarrow{\text{slow}} OH^- + HOI$$



$$HOI + I^- \xrightarrow{\text{fast}} OH^- + I_2$$



$$2\ OH^- + 2\ H_3O^+ \xrightarrow{\text{fast}} 4\ H_2O$$



Rate Law of Oxidation of Iodide Ion by Hydrogen Peroxide

Step 1.

$HOOH + I^- \rightarrow HOI + OH^-$

slow step - rate determining step, suggests that the reaction is first order with regard to hydrogen peroxide and iodide ion

rate = $k[HOOH][I^-]$

4) The mechanism of a reaction is shown below.

$$HOOH + I^- \rightarrow HOI + OH^- \quad \text{(slow)}$$

$$HOI + I^- \rightarrow I_2 + OH^- \quad \text{(fast)}$$

$$2OH^- + 2H_3O^+ \rightarrow 4\,H_2O \quad \text{(fast)}$$

a) What is the overall reaction?

b) Which compounds are intermediates?

4) The mechanism of a reaction is shown below.

$$HOOH + I^- \rightarrow HOI + OH^- \quad \text{(slow)}$$

$$HOI + I^- \rightarrow I_2 + OH^- \quad \text{(fast)}$$

$$2OH^- + 2H_3O^+ \rightarrow 4\,H_2O \quad \text{(fast)}$$

c) Predict the rate law based on this mechanism.

d) What is the overall order of the reaction?

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

Activation energy

Frequency factor

Exponential factor

Arrhenius Equation: Dependence of Rate Constant (k) on T

Rate constant (k)

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

A = frequency factor: A = p x z

E_a = Activation energy

R = gas constant

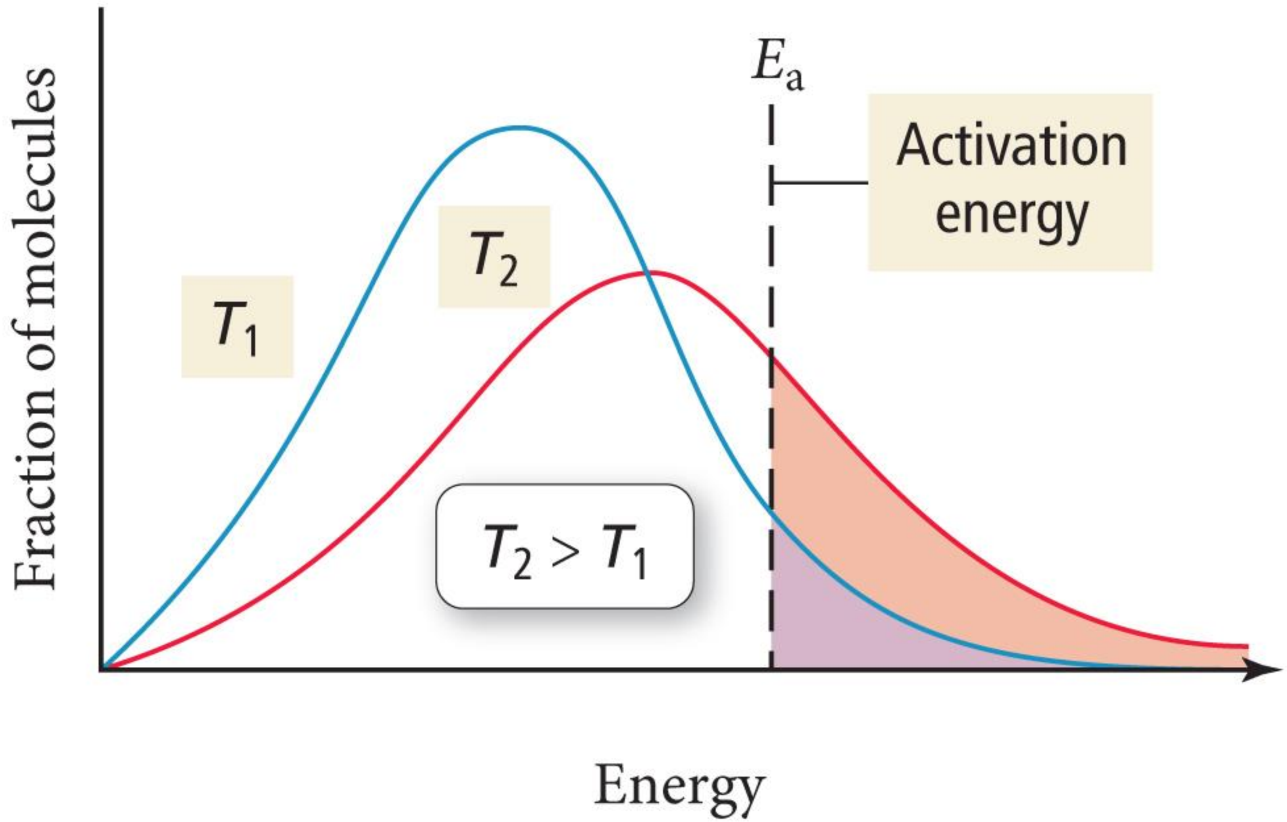
T = Kelvin temperature

p = collision factor

z = Orientation factor

Thermal Energy Distribution

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



Arrhenius Equation: ln form

An alternate form of the Arrhenius equation:

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

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

If ln k is plotted against 1/T, a straight line of slope -Ea/RT is obtained.

Activation energy - E_a

The energy that molecules must have in order to react.

5) For the reaction A + B $\rightarrow$ C, the rate constant at 215 ^oC is 5.0 x 10^{-3} and the rate constant at 452^o C is 1.2 x 10^{-1}.

a) How the rate constant is affected by increasing the temperature?

b) Write the form of Arrhenius equation and define the variables that fit the data for this problem:

5) For the reaction A + B $\rightarrow$ C, the rate constant at 215 ^{o}C is 5.0 x 10^{-3} and the rate constant at 452^{o} C is 1.2 x 10^{-1}.

c) What is the activation energy in kJ/mol?

d) What is the rate constant at 100^{o}C.

Arrhenius Equation: Dependence of Rate Constant (k) on T

Rate constant (k)

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

E_a = Activation energy

R = gas constant

T = Kelvin temperature

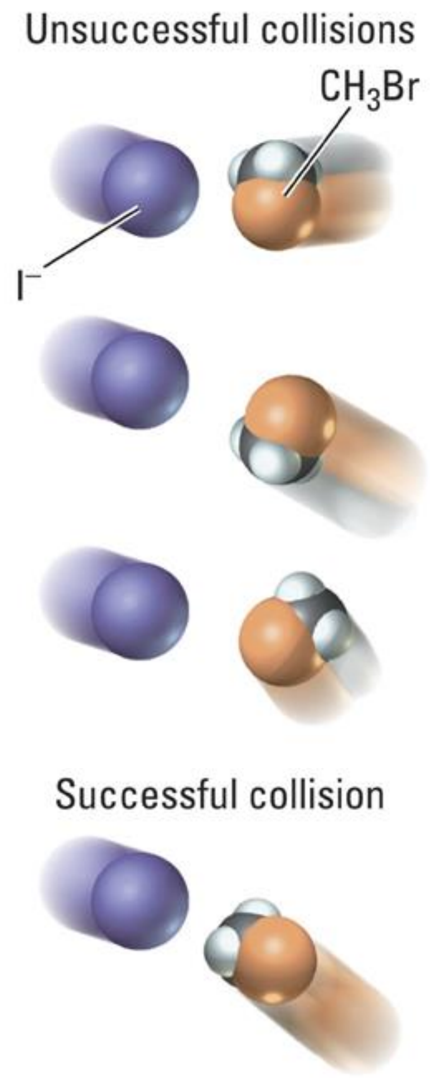
A = frequency factor: A = p x z

p = collision factor

z = Orientation factor

Orientation Factor: Some Unsuccessful Collisions

$$I^- + CH_3Br \longrightarrow ICH_3 + Br^-$$



Calculation of E_a

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

$\ln k = \ln A - E_a/RT$

$\log k = \log A - E_a/\ 2.303\ RT$

using two set of values

$\log k_1 = \log A - E_a/\ 2.303\ RT_1$

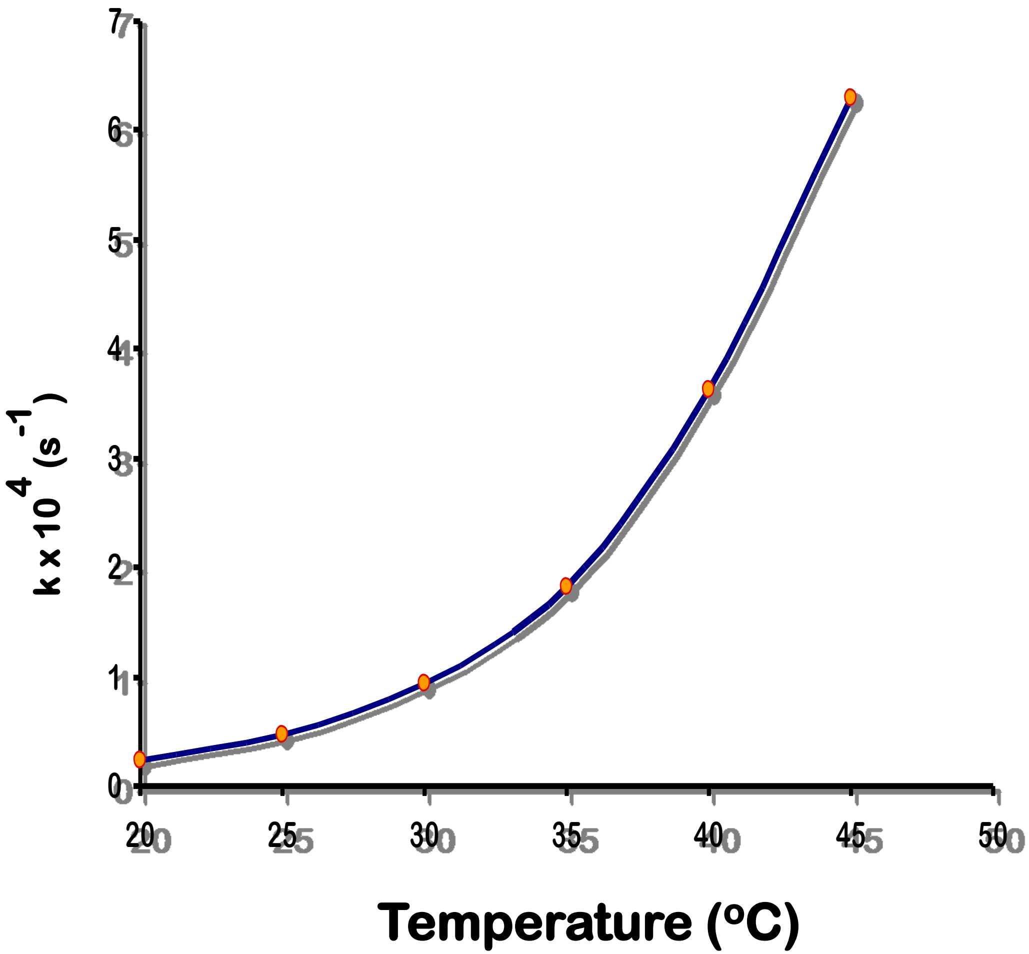
$\log k_2 = \log A - E_a/\ 2.303\ RT_2$

$\log k_1 - \log k_2 = - E_a/\ 2.303\ RT_2 + E_a/\ 2.303\ RT_1$

$\log k_1/\ k_2 = E_a/\ 2.303\ R[\ 1/T_1 - 1/T_2\ ]$

Rate vs Temperature plot

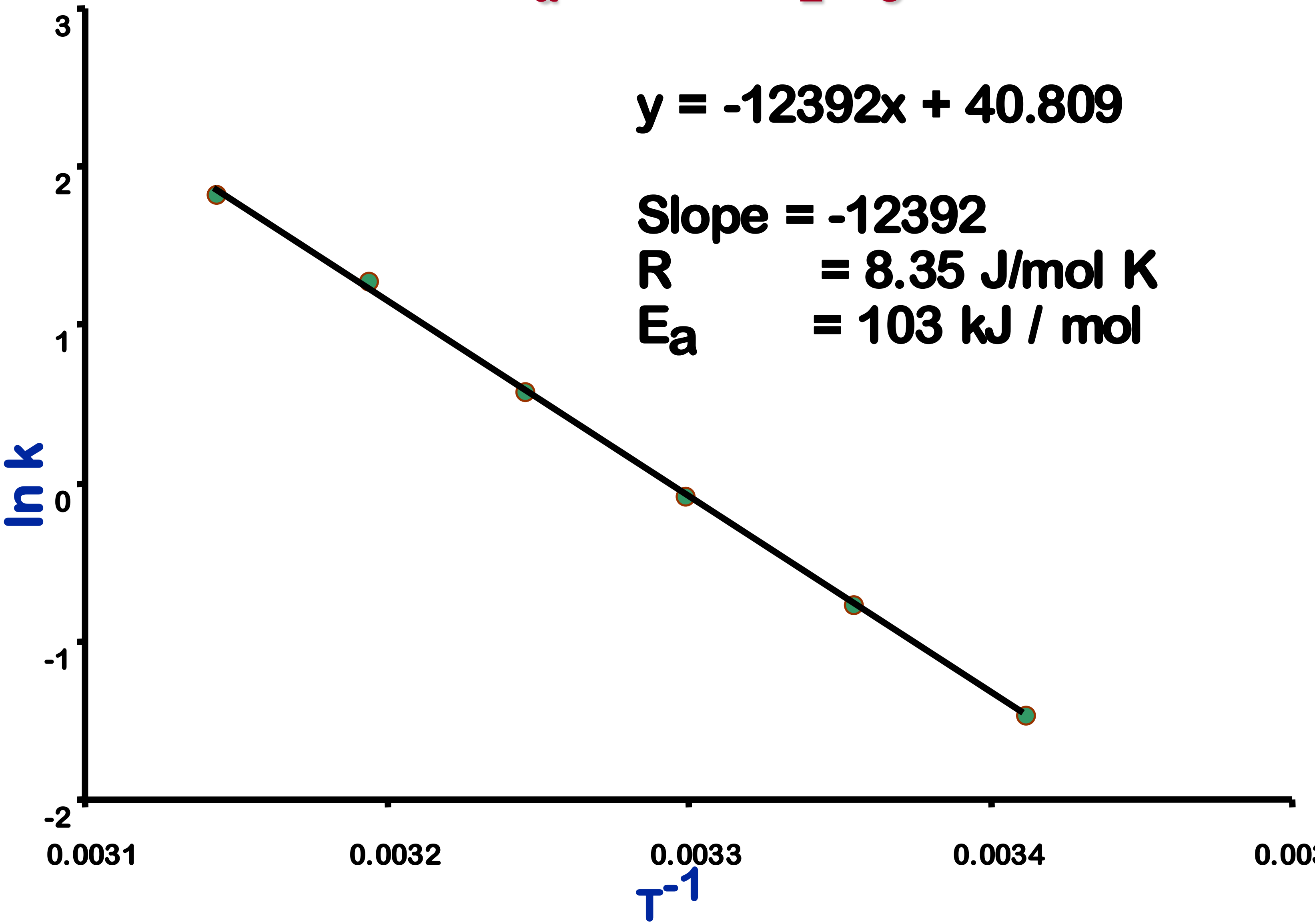
Reaction rates are temperature dependent.



Here are rate constants for N_2O_5 decomposition at various temperatures.

T, °C	k x 10^4, s^{-1}
20	0.235
25	0.469
30	0.933
35	1.82
40	3.62
45	6.29

Calculation of E_a from N_2O_5 data



Collision Model

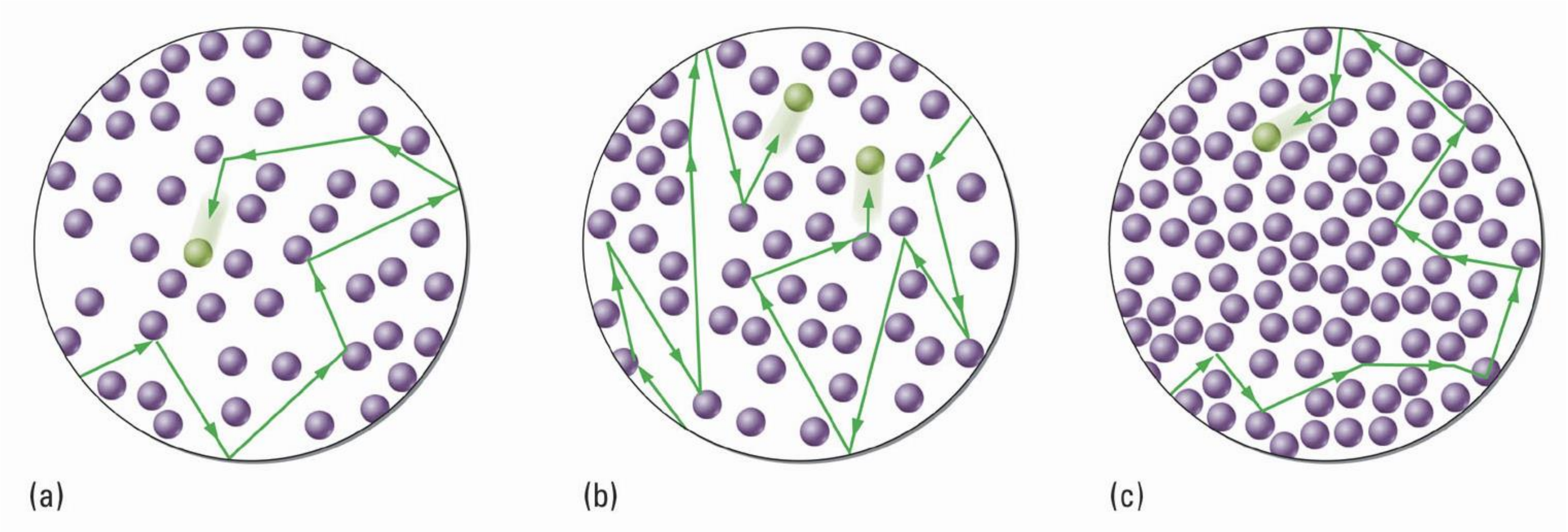
Three conditions must be met at the nano-scale level if a reaction is to occur:

the molecules must *collide;*

they must be positioned so that the reacting groups are together in a *transition state* between reactants and products;

and the collision must have enough *energy* to form the transition state and convert it into products.

Effect of Concentration on Frequency of Bimolecular Collisions



Transition State: Activated Complex or Reaction Intermediates

an unstable arrangement of atoms that has the highest energy reached during the rearrangement of the reactant atoms to give products of a reaction

Catalyst

A substance which speeds up the rate of a reaction while not being consumed

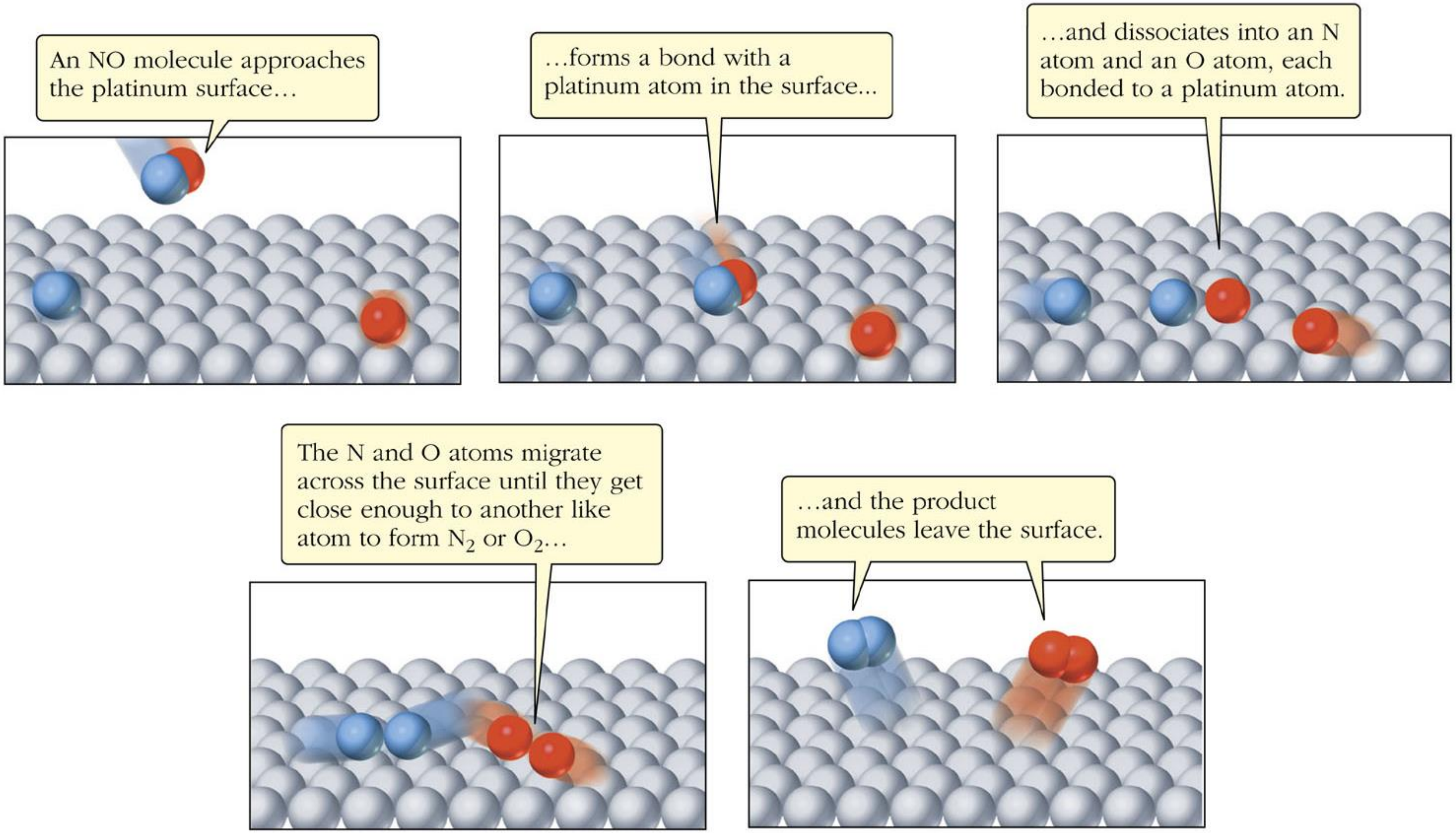
Homogeneous Catalysis - a catalyst which is in the same phase as the reactants

Heterogeneous Catalysis- a catalyst which is in the different phase as the reactants

catalytic converter

- solid catalyst working on gaseous materials

Conversion of NO to N_2 + O_2



Catalytic Converter

$$H_2O_{(g)} + HCs \xrightarrow{\text{catalyst}} CO_{(g)} + H_{2(g)}$$ (unbalanced)

$$2\ H_{2(g)} + 2\ NO_{(g)} \xrightarrow{\text{catalyst}} N_{2(g)} + 2\ H_2O_{(g)}$$

$$HCs + O_{2(g)} \xrightarrow{\text{catalyst}} CO_{2(g)} + H_2O_{(g)}$$ (unbalanced)

$$CO_{(g)} + O_{2(g)} \xrightarrow{\text{catalyst}} CO_{2(g)}$$ (unbalanced)

catalyst = Pt-NiO
HCs = unburned hydrocarbons

Enzymes: Biological catalysts

Biological catalysts

Typically are very large proteins.

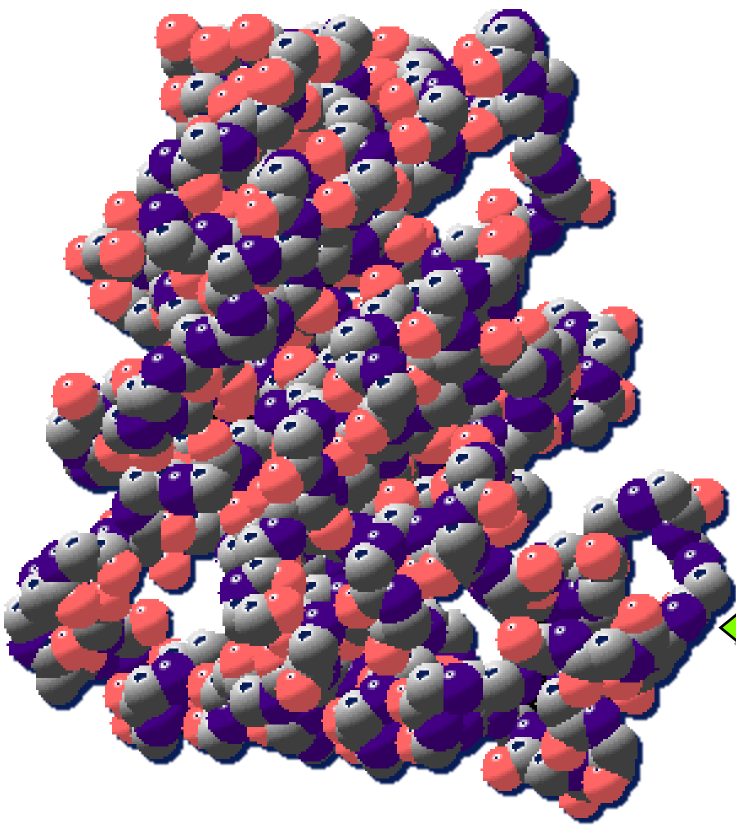
Permit reactions to 'go' at conditions that the body can tolerate.

Can process millions of molecules every second.

Are very specific - react with one or only a few types of molecules (substrates).

The active site

Enzymes are typically HUGE proteins, yet only a small part is actually involved in the reaction.

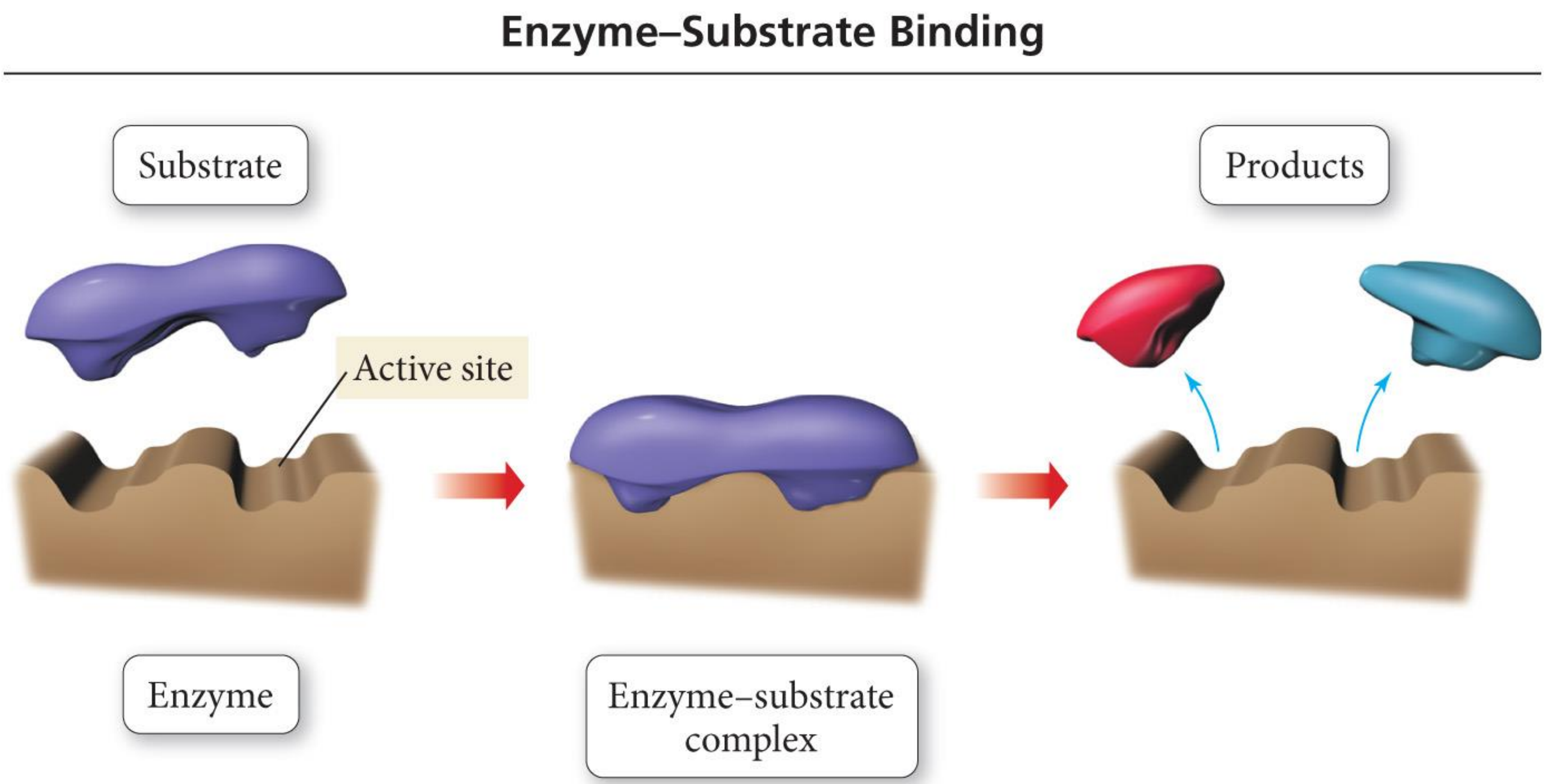


The active site has two basic components.

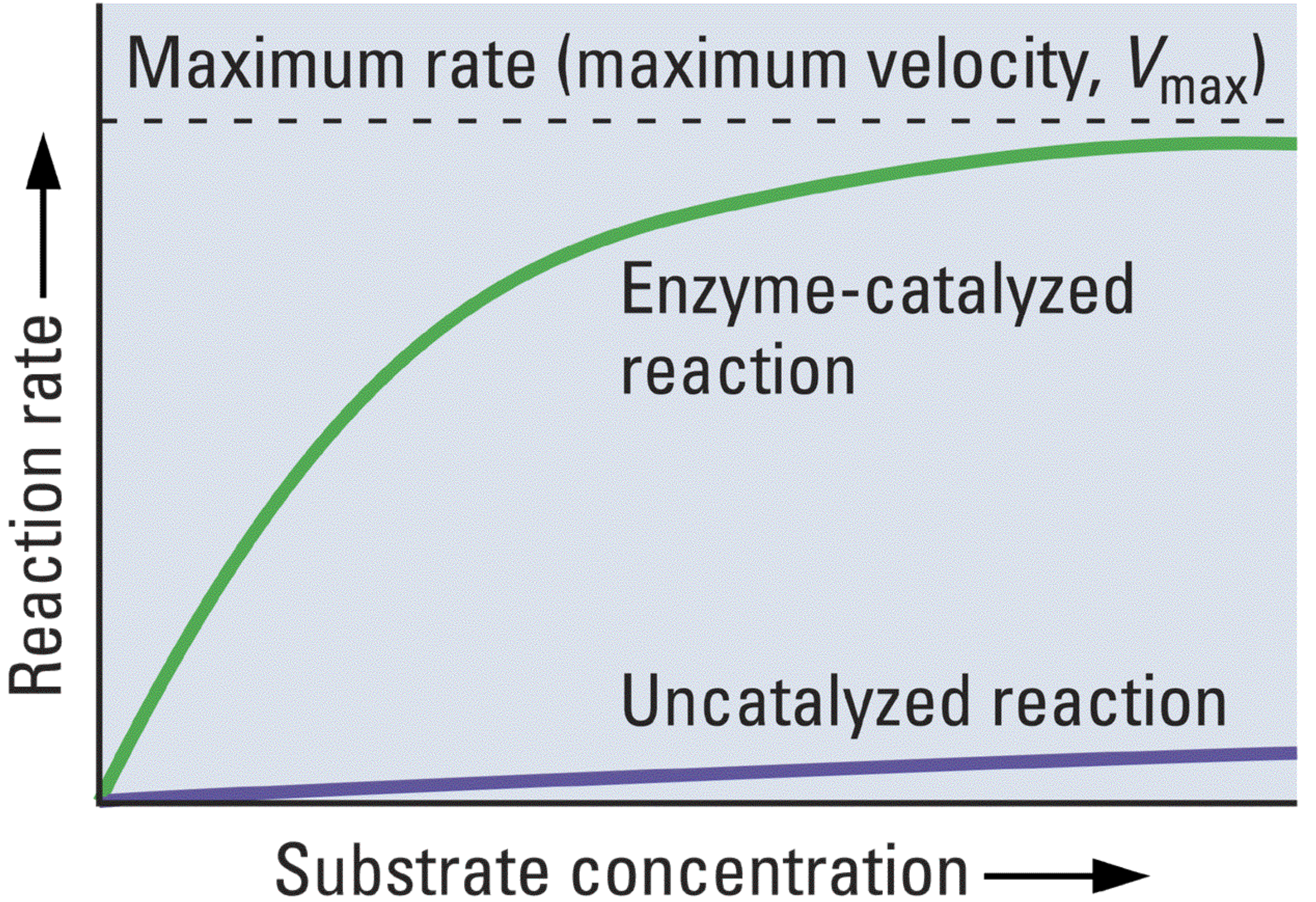
catalytic site

binding site

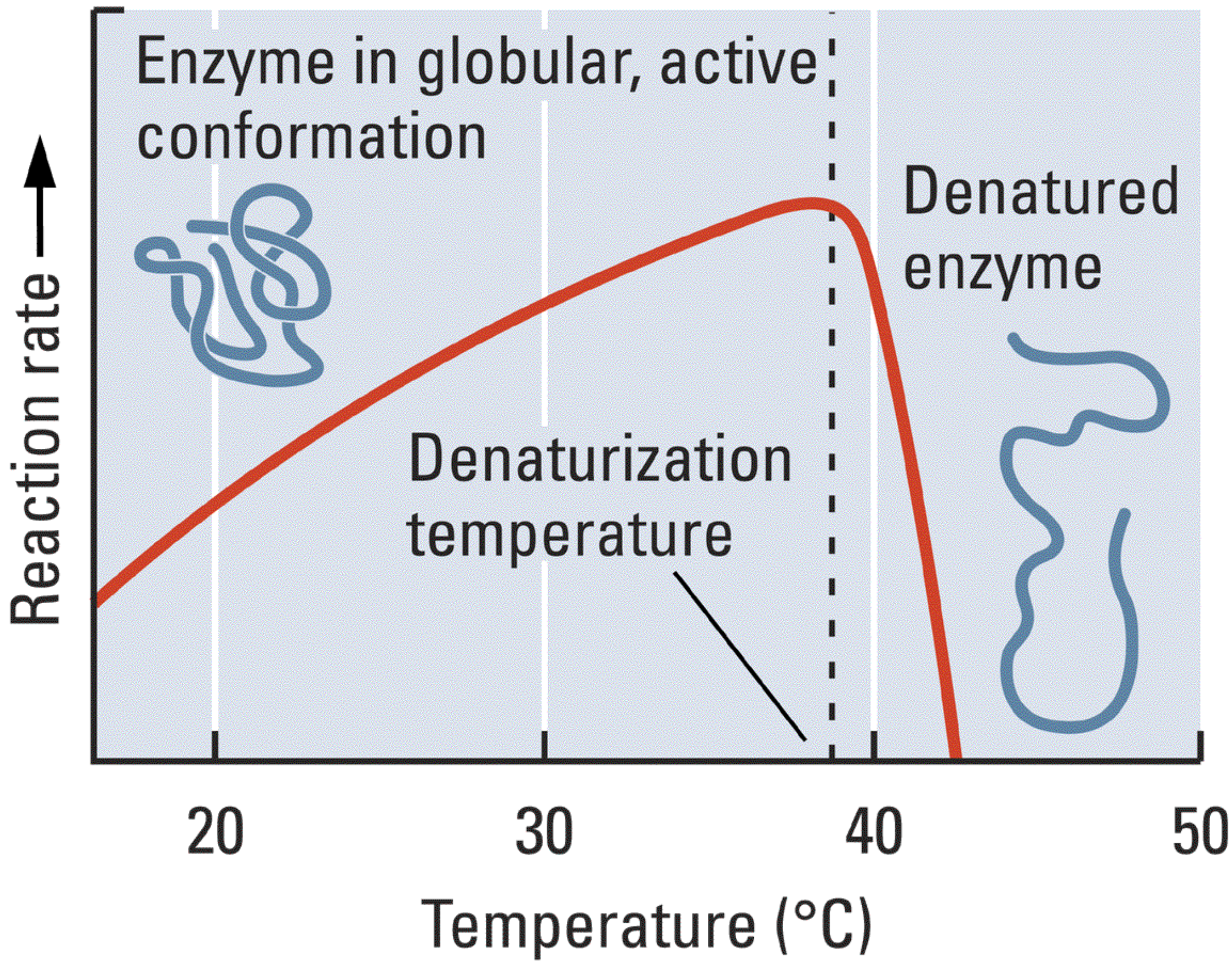
Model of trios-phosphate-isomerase


Enzyme–Substrate Binding
Substrate
Products
Active site
Enzyme
Enzyme–substrate complex

Maximum Velocity for an Enzyme Catalyzed Reaction



Enzyme Activity Destroyed by Heat



Mechanisms with a Fast Initial Step

$$2\,NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$$

$$rate_{experimental} = k[NO]^2[Br_2]$$

Mechanism of NO + Br_2

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g) \qquad \text{fast}$$

$$NOBr_2(g) + NO(g) \longrightarrow 2\ NOBr(g) \qquad \text{slow}$$

Rate = k[$NOBr_2$][NO]

Rate Constants for NO + Br_2

Step +1(forward), rate constant k_1

Step -1(backward), rate constant k_{-1}

Step 2, rate constant k_2

$$rate_{Step+1} = rate_{Step-1} + rate_{Step2}$$

$$k_1[NO][Br_2] = k_{-1}[NOBr_2] - k_2[NOBr_2]$$

Relationships of Rate Constants

$k_1[NO][Br_2] \sim k_{-1}[NOBr_2]$

thus

$[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$

substituting into

$rate = k_2[NOBr_2][NO]$

$rate = k_2((k_1/k_{-1})[NO][Br_2])[NO]$

$rate = (k_2k_1/k_{-1})[NO]^2[Br_2]$

Chain Mechanisms

chain initiating step

- - the step of a mechanism which
- starts the chain chain

propagating step(s)

- the step or steps which keeps the chain going

chain terminating step(s)

- the step or steps which break the chain

Chain Mechanisms

combustion of gasoline in an internal combustion engine

chain initiating step - additives which generate free radicals, particles with unpaired electrons

chain propagating step(s) - steps which generate new free radicals

chain terminating step(s)

- steps which do not generate new free radicals