Chemical Kinetics

Study of the

TIME vs RATE

of Chemical Change

CHEMICAL KINETICS DEALS WITH

1. How **FAST**

{Speed like miles per hour}

and

2. By what **MECHANISM**

does a reaction happen?

Part I

How Fast (RATE) Does a Chemical Reaction "Go" ?

What does the speed (RATE) depend upon?

Reaction Rates

- The change in the concentration of a **reactant** or **product** with time (M/s)

for $A \rightarrow B$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} \qquad \text{Rate} = \frac{\Delta[B]}{\Delta t}$$

Rate disappearance = Rate of formation

STOICHIOMETRY AFFECTS THE RATE

$$2A \rightarrow B$$

A disappears at twice the rate B forms

$$\text{Rate} = -\tfrac{1}{2}\ \Delta[A] = \Delta[B]$$

Rate disappearance $\neq$ Rate of formation

For $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$

If rate of decomposition of $N_2O_5 = 4.2 \times 10^{-7}$ M/s

What is the rate of APPEARANCE of

(a) NO_2 ?

Twice rate of decomposition = __________ M/s

(b) O_2 ?

½ the rate of decomposition = __________ M/s

How is the rate of the disappearance of the reactants related to the appearance of the products for

$$\mathbf{CH_4(\mathit{g}) + 2O_2(\mathit{g}) \rightarrow CO_2(\mathit{g}) + 2H_2O(\mathit{g})}$$

$$\text{rate} = -\frac{1}{1}\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{1}\frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{H}_2]}{\Delta t}$$

Consider the reaction 3A --> 2B

The average rate of appearance of B is given by [B]/*t*.

How is the average rate of appearance of B related to the average rate of disappear-ance of A?

(a) -2[A]/3*t*   (b) 2[A]/3*t*   (c) -3[A]/2*t*

(d) [A]/*t*   (e) -[A]/*t*

Answer on Text Book's Web Site

THE RATES OF REACTION DEPENDS ON

1. **Nature of *Reactants*** {fixed
2. **Concentration of *Reactants*** {variable
3. **Temperature** {variable
4. **Etc.** {variable
   - **Catalysts**
   - **Particle Size**
   - **Photochemical**

The “things” that affect the rate of reaction are

Considered
one at a time

I. NATURE OF REACTING SUBSTANCES

$Zn(s) + HCl(aq) \rightarrow H_2 + ZnCl_2(aq)$ Fast Reaction

Iron "Rusts" but not very fast

$Fe(s) + O_2 \rightarrow$ Slow Reaction

Whereas Silver does not react at all

$Ag(s) + O_2 \rightarrow$ No Reaction

THE NATURE OF REACTANTS IS FIXED

II. CONCENTRATION OF REACTANTS

$$\text{Reactant} \rightarrow \text{Products}$$

$$R \rightarrow P$$

$$\text{rate} \propto [R]$$

$$A + B \rightarrow P + Q$$

$$\text{rate} \propto [A]\,[B]$$

$$A + B + C \rightarrow P + Q + Z$$

$$\text{rate} \propto \underline{\hspace{5cm}}$$

Rate constant: k

A constant of proportionality between the reaction rate and the concentration of reactants.

$$R \rightarrow P$$

$$\text{rate} \propto [R]$$

$$\text{rate} = k\,[R]$$

REACTION ORDER

$$R \rightarrow P$$

To complete the equation

Concentrations are raised to a power of **x**

$$\text{rate} = k\ [R]^{x}$$

[**x** is determined experimentally]

Reaction order is determined experimentally

Reaction order =

to the sum of the powers to which all reactant concentrations in the rate law are raised

REACTION ORDER

- Zero Order Reactions
- First Order Reactions
- Second Order Reactions
- Third Order Reactions

RATE LAW

- **Rate Law:** Shows the relationship of the rate of a reaction to the rate constant & the concentration of the reactants raised to some powers.

- For the general reaction: $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\text{rate} = \text{k}\,[\text{A}]^{x}\,[\text{B}]^{y}$$

REACTION ORDER

Order = $x + y$

The sum of the powers to which all reactant concentrations appearing in the rate law are raised

x & y MAY OR MAY NOT BE THE STOICHIOMETRIC COEFFICIENTS

Reaction order is determined experimentally

A reaction $A + B \rightarrow C$ obeys the following rate law $\text{Rate} = k[A]^2[B]$

(a) If [A] is doubled, how will the rate change? ______

(b) Will the rate constant change? ______

(c) What are the reaction orders for A and B? ______

(d) Overall order ? ______

(e) Units of rate constant ______

The reaction $A + B \rightarrow C$

obeys the following rate law :

$$\text{Rate} = k[A]^2[B]$$

(a) What is the order of the reaction

(i) With respect to A ? (a) 1st (b) 2nd (c) 3rd

(ii) With respect to B ? (a) 1st (b) 2nd (c) 3rd

(iii) Overall order (a) 1st (b) 2nd (c) 3rd

$$Rate = k[A]^2[B]$$

(b) How does the rate change if

(i) [A] is doubled ?

(a) doubles (b) triples (c) quadruples (d) no change

(ii) [B] is doubled ?

(a) doubles (b) triples (c) quadruples (d) no change

(iii) [C] is doubled ?

(a) doubles (b) triples (c) quadruples (d) no change

Method of Initial Rates

Uses Initial Rates to Determine Rate Law

Nitrogen monoxide reacts with hydrogen to form nitrogen gas and water

1st Write reaction

$$NO(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$$

2nd balance reaction

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Write Rate Law: Rate = k $[NO]^x[H_2]^y$

Determine x and y using method of Initial rates

What can you measure INITIALLY ? _______

How many UNKNOWNS in Rate Law? ______

How many experiments are needed ? ______

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

$$Rate = k\,[NO]^x[H_2]^y$$

METHOD OF INITIAL RATES

Experiment	$[NO]_{initial}$	$[H_2]_{initial}$	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

$$2\ NO(g) + 2\ H_2(g) \rightarrow\ N_2(g) + 2\ H_2O(g$$

$$\text{Rate} = k\ [NO]^x\ [H_2]^y$$

Exp 1: $1.3 \times 10^{-5} = k\ (5.0\times10^{-3})^x\ (2.0\times10^{-5})^y$

Exp 2: $5.0 \times 10^{-5} = k\ (10\times10^{-3})^x\ (2.0\times10^{-5})^y$

Exp 3: $10.0 \times 10^{-5} = k\ (10\times10^{-3})^x\ (4.0\times10^{-5})^y$

Experiment	$[NO]_{initial}$	$[H_2]_{initial}$	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

$$\text{Rate} = k\,[NO]^x\,[H_2]^y$$

Exp 1: $1.3 \times 10^{-5} = k\,(5.0 \times 10^{-3})^x\,(2.0 \times 10^{-5})^y$

Exp 2: $5.0 \times 10^{-5} = k\,(10 \times 10^{-3})^x\,(2.0 \times 10^{-5})^y$

Exp 3: $10.0 \times 10^{-5} = k\,(10 \times 10^{-3})^x\,(4.0 \times 10^{-5})^y$

Take RATIO of Exp 2 to Exp 1

$$\frac{\exp 2}{\exp 1} : \quad \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{k}{k}\,\frac{(10 \times 10^{-3})^x}{(5.0 \times 10^{-3})^x}\,\frac{(2.0 \times 10^{-5})^y}{(2.0 \times 10^{-5})^y}$$

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

Exp 1: $1.3 \times 10^{-5} = k\ (5.0 \times 10^{-3})^x\ (2.0 \times 10^{-5})^y$

Exp 2: $5.0 \times 10^{-5} = k\ (10 \times 10^{-3})^x\ (2.0 \times 10^{-5})^y$

$$\frac{\exp 2}{\exp 1} : \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{k}{k} \frac{(10 \times 10^{-3})^x}{(5.0 \times 10^{-3})^x} \frac{(2.0 \times 10^{-5})^y}{(2.0 \times 10^{-5})^y}$$

$$3.9 = \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{(10 \times 10^{-3})^x}{(5.0 \times 10^{-3})^x} = (2)^x$$

What is x ? (a) 0 (b) 1 (c) 2 (d) 3

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

Exp 1: $1.3 \times 10^{-5} = k\,(5.0 \times 10^{-3})^x\,(2.0 \times 10^{-5})^y$

Exp 2: $5.0 \times 10^{-5} = k\,(10 \times 10^{-3})^x\,(2.0 \times 10^{-5})^y$

Exp 3: $10.0 \times 10^{-5} = k\,(10 \times 10^{-3})^x\,(4.0 \times 10^{-5})^y$

Take RATIO of Exp 3 to Exp 2 to find y

$$\frac{\text{exp 3}}{\text{exp 2}} : \quad \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{k}{k}\,\frac{(10 \times 10^{-3})^x}{(10 \times 10^{-3})^x}\,\frac{(4.0 \times 10^{-5})^y}{(2.0 \times 10^{-5})^y}$$

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Exp 2: $5.0 \times 10^{-5} = k\ (10x10^{-3})^x\ (2.0x10^{-5})^y$

Exp 3: $10.0 \times 10^{-5} = k\ (10x10^{-3})^x\ (4.0x10^{-5})^y$

$$\frac{\exp 3}{\exp 2} : \quad \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{k}{k}\frac{(10x10^{-3})^x}{(10x10^{-3})^x}\frac{(4.0x10^{-5})^y}{(2.0x10^{-5})^y}$$

$$2 = \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{(4.0x10^{-3})^y}{(2.0x10^{-3})^y} = (2)^y$$

What is y = ? (a) 0 (b) 1 (c) 2 (d) 3

METHOD OF INITIAL RATES

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

$$\text{Rate} = k\ [NO]^x\ [H_2]^y$$

The order with respect to NO is 2nd order

The order with respect to H_2 is 1^{st} order

$$\text{Rate} = k\ [NO]^2\ [H_2]^1$$

The overall order of the reaction is $2 + 1 = 3$

$$2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

$$\text{Rate} = k\,[NO]^2\,[H_2]^1$$

What is the rate constant ?

$$\text{Exp 1:} \quad 1.3 \times 10^{-5} = k\ (5.0\text{x}10^{-3})^2\ (2.0\text{x}10^{-5})^1$$

$$\text{Exp 2:} \quad 5.0 \times 10^{-5} = k\ (10\text{x}10^{-3})^2\ (2.0\text{x}10^{-5})^1$$

$$\text{Exp 3:} \quad 10.0 \times 10^{-5} = k\ (10\text{x}10^{-3})^2\ (4.0\text{x}10^{-5})^1$$

Solve for k from any of the equations

$k = 2.5 \times 10^4$ Units????

EXAMPLE 2

$$S_2O_8^{2-}(aq) + 3\,I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

$$\text{Rate} = k\,[S_2O_8^{2-}]^X\,[I^-]^Y$$

Determine

– the rate law

– the order

– and rate constant

$$S_2O_8^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$Rate_1$ = ______________________________

$Rate_2$ = ______________________________

$Rate_3$ = ______________________________

Experiment	$[S_2O_8^{2-}]$	[I–]	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

Divide Rate 1 by Rate 2 to find Y

$$\frac{R_1}{R_2} = \frac{k}{k}\frac{[.08]^X}{[.08]^X}\frac{[.034]^Y}{[.017]^Y} = \left[\frac{.034}{.017}\right]^Y = [2]^Y$$

$$\frac{R_2}{R_1} = \frac{k}{k}\frac{[.08]^X}{[.08]^X}\frac{[.034]^Y}{[.017]^Y} = \left[\frac{.034}{.017}\right]^Y = [2]^Y$$

Now put in values for Rates:

$$\frac{R_2}{R_1} = \frac{2.2 x 10^{-4}}{1.1 x 10^{-4}} = 2 = [2]^Y$$

and guess what Y is

(a) Y = 0 (b) Y = 1 (c) Y = 2 (d) Y = 3

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

Divide Rate 3 by Rate 2 to find X

$$\frac{R_3}{R_2} = \frac{k}{k}\frac{[.16]^X}{[.08]^X}\frac{[.017]^Y}{[.017]^Y} = \left[\frac{.16}{.08}\right]^X = [2]^X$$

$$\frac{R_3}{R_2}=\frac{k}{k}\frac{[.16]^X}{[.08]^X}\frac{[.017]^Y}{[.017]^Y}=\left[\frac{.16}{.08}\right]^X=[2]^X$$

Now put in values for Rates:

$$\frac{R_3}{R_2}=\frac{2.2x10^{-4}}{1.1x10^{-4}}=2=[2]^X$$

and guess what X is

(a) X = 0 (b) X = 1 (c) X = 2 (d) X = 3

For the Reaction

$S_2O_8^{2-}(aq) + 3\,I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$

the rate law : $\text{Rate} = k\,[S_2O_8^{2-}]\,[I^-]$

the order : $X + Y = 1 + 1 = 2$

and rate constant :

$$R_1 = 2.2 \times 10^{-4} = k\,(0.08)(0.034)$$

$$k = 8.0882353 \times 10^{-2}$$

Really ?

Problem 14.26 page 566

$$\mathbf{S_2O_8^{2-}(\mathit{aq}) + 3I^-(\mathit{aq}) \rightarrow 2SO_4^{2-}(\mathit{aq}) + I_3^-(\mathit{aq})}$$

Exp	$[S_2O_8]$	$[I^-]$	Rate(M/s)
1	0.018	0.036	2.6×10^{-6}
2	0.027	0.036	3.9×10^{-6}
3	0.036	0.054	7.8×10^{-6}
4	0.050	0.072	1.4×10^{-5}

How is this problem different from the previous example ?

Additional Topics:

I. Integrated form of rate equation

II. Half-life

III. Temperature

IV. Catalyst

For 1st Order Reactions: A → B

Instead of $\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[A]$

use $Rate = -\frac{d[A]}{dt} = \text{k}\,[\text{A}]$

or $-\frac{d[A]}{[A]} = \text{k}\,dt$

Integrated form of rate equation

$$-\int_{\text{initial}}^{\text{final}} \frac{d[A]}{[A]} = \int_0^{\text{t}} \text{k}\ dt$$

$[A]_0$ = initial concentration at time t = 0

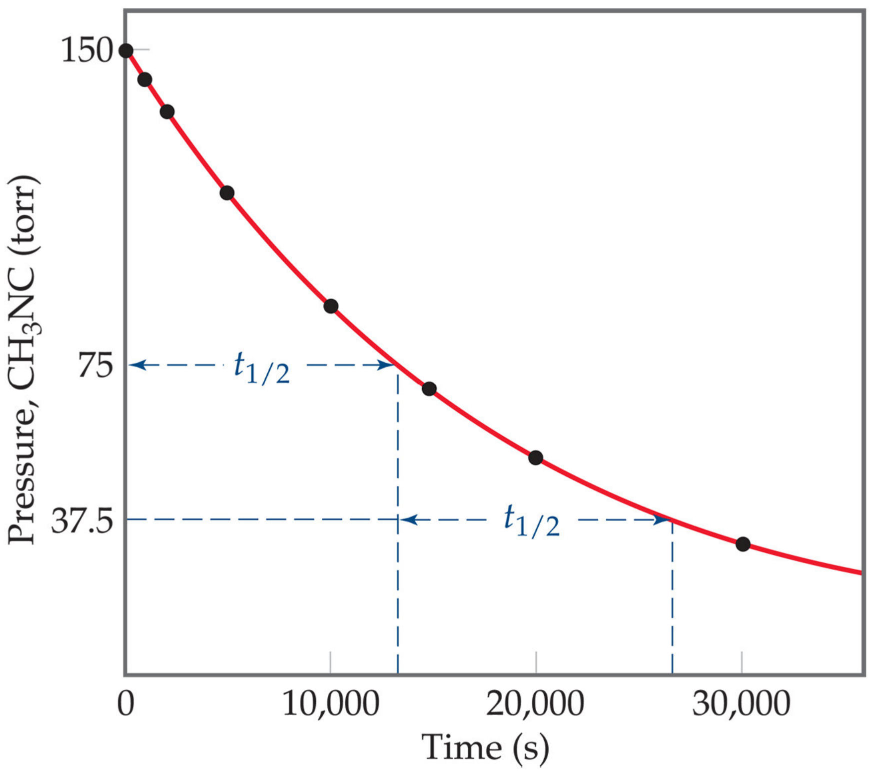
[A] = concentration at time t

$$\ln\frac{[A]_0}{[A]} = \text{k t}$$

II. Reaction Rates & Half-Life

The half-life (**$t_{1/2}$**) of a reaction is the TIME required for the concentration of a reactant to decrease to one half its initial value

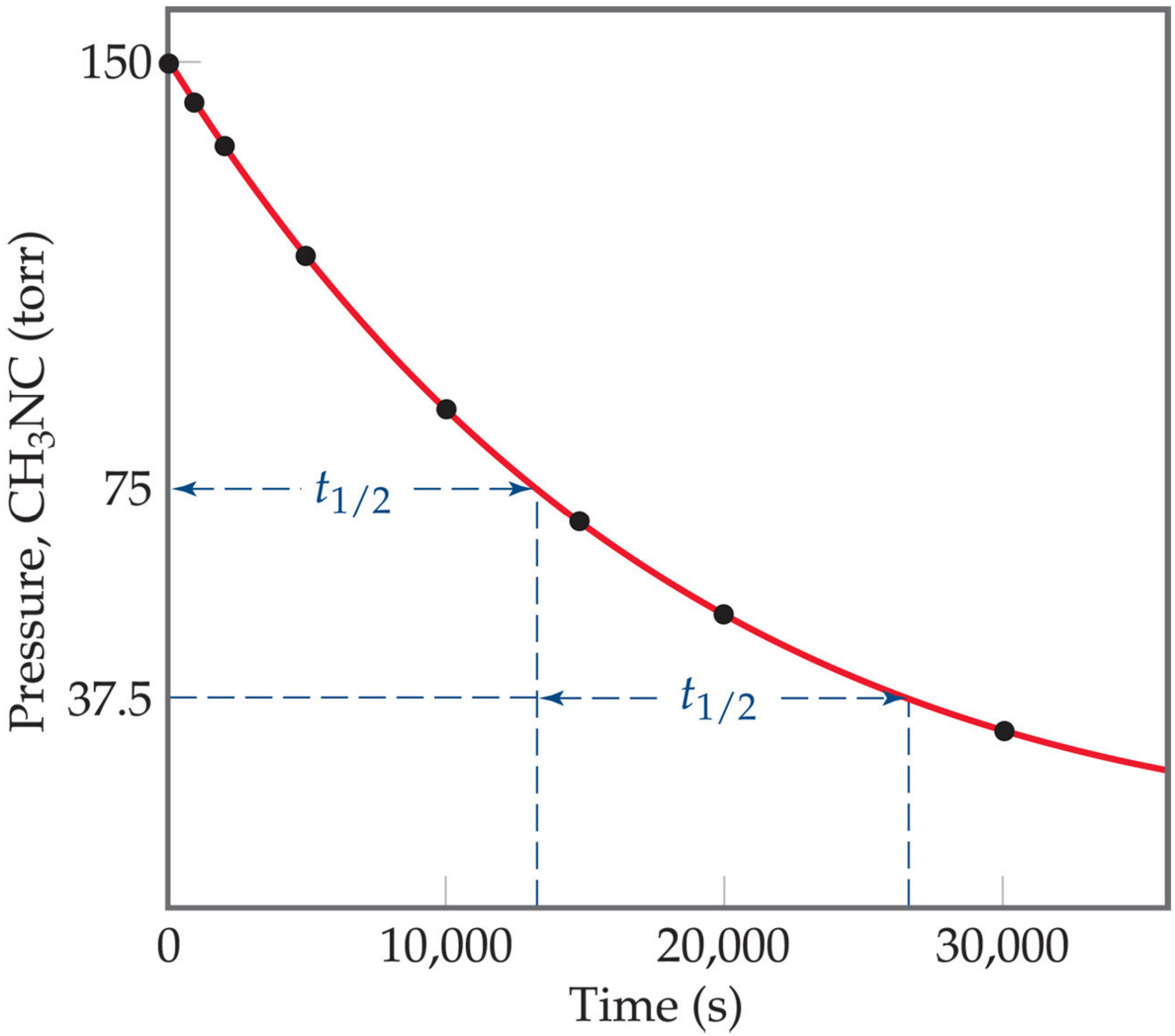
Half-life is defined as the time required for one-half of a reactant to react.



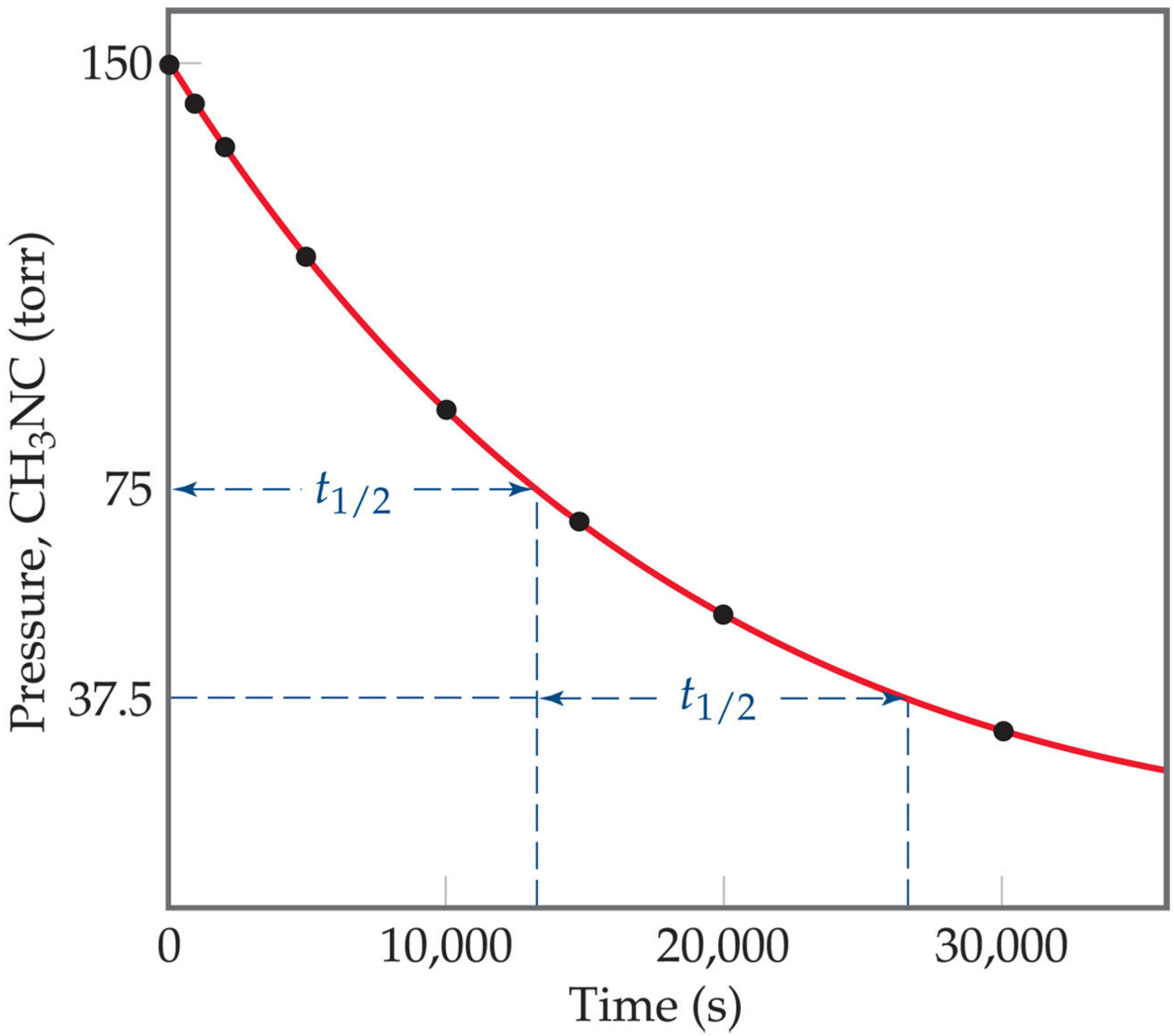
- Because [A] at $t_{1/2}$ is one-half of the original [A],

$$[A]_t = 0.5\ [A]_0.$$

The concentration of A at $t_{1/2}$ is one half the original concentration $[A]_t = 0.5\ [A]_0$



[A] is one-half of the original $[A]_o$ at $t_{1/2} = 13{,}500$ sec



The Concentration [A] is one-half of that at two half lives {28,000 sec

Consider the Reaction

$$2\ H_2O_2\,(aq) \rightarrow H_2O\,(liq) + O_2\,(g)$$

What will the concentration of Hydrogen Peroxide be after 3 half-lives ? **The half-life** ($t_{1/2}$) of the decomposition of Hydrogen Peroxide is 654 mins

If the initial concentration of H_2O_2 is 0.020 M

How long will it take for the concentration of Hydrogen Peroxide to drop to 0.010 ?

654 mins = one half-life

What will the concentration of Hydrogen Peroxide be after 3 half-lives? _________

All radioactive decay is 1st order

$$\ln \frac{[A]_0}{[A]} = k\,t$$

At $t_{1/2}$ concentration is ½ initial

$$\ln \frac{[A]_0}{[\tfrac{1}{2} A]_0} = k\,t_{1/2}$$

$$\ln 2 = k\,t_{1/2}$$

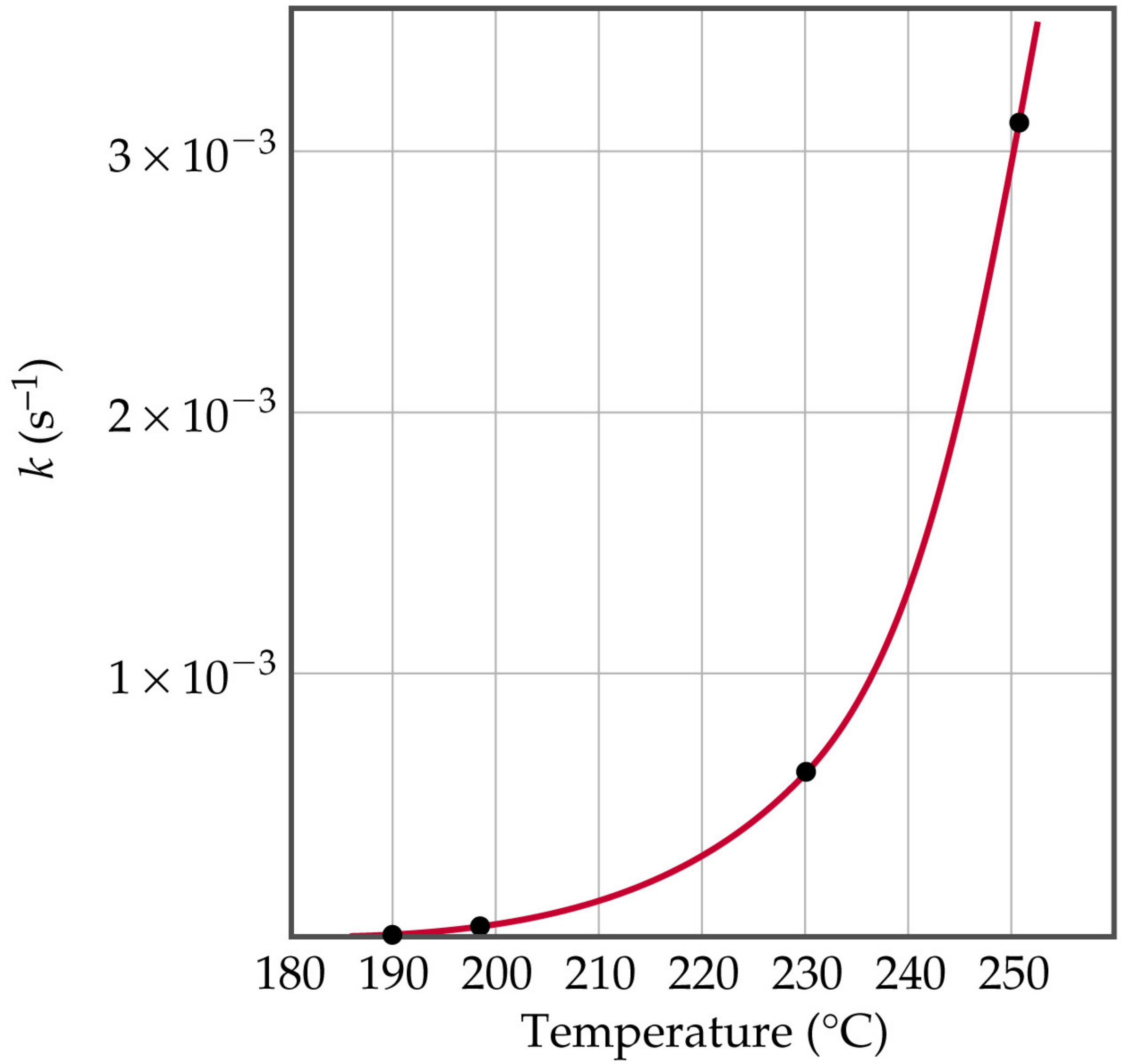
III. Temperature and Rate

Rates of reactions are affected by

1. concentration
2. and temperature.

Since the rate law has no temperature term in it, ***the rate constant must depend on temperature.***

Temperature and Rate



As temperature increases, the rate increases.

Rule of Thumb for
Reaction Rates & Temperature

Ten degree increase in temperature

Doubles Rate of Reaction

Energy of Activation

- 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

a ball cannot get over a hill if it does not roll up the hill with enough energy

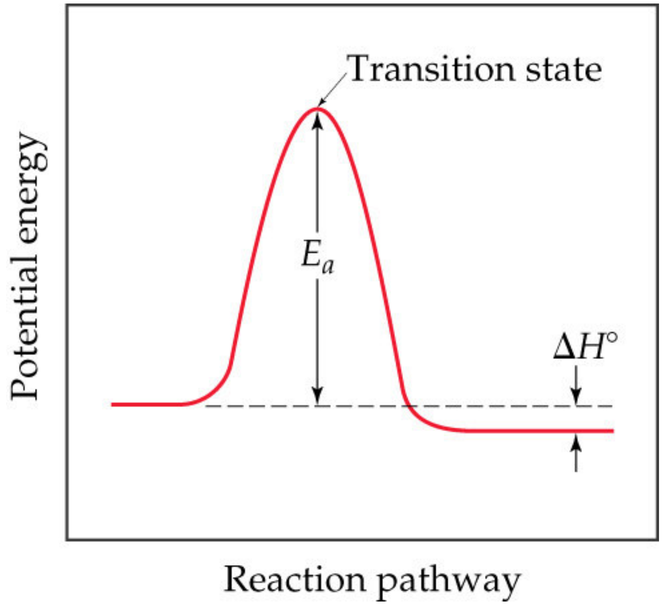
Activation Energy

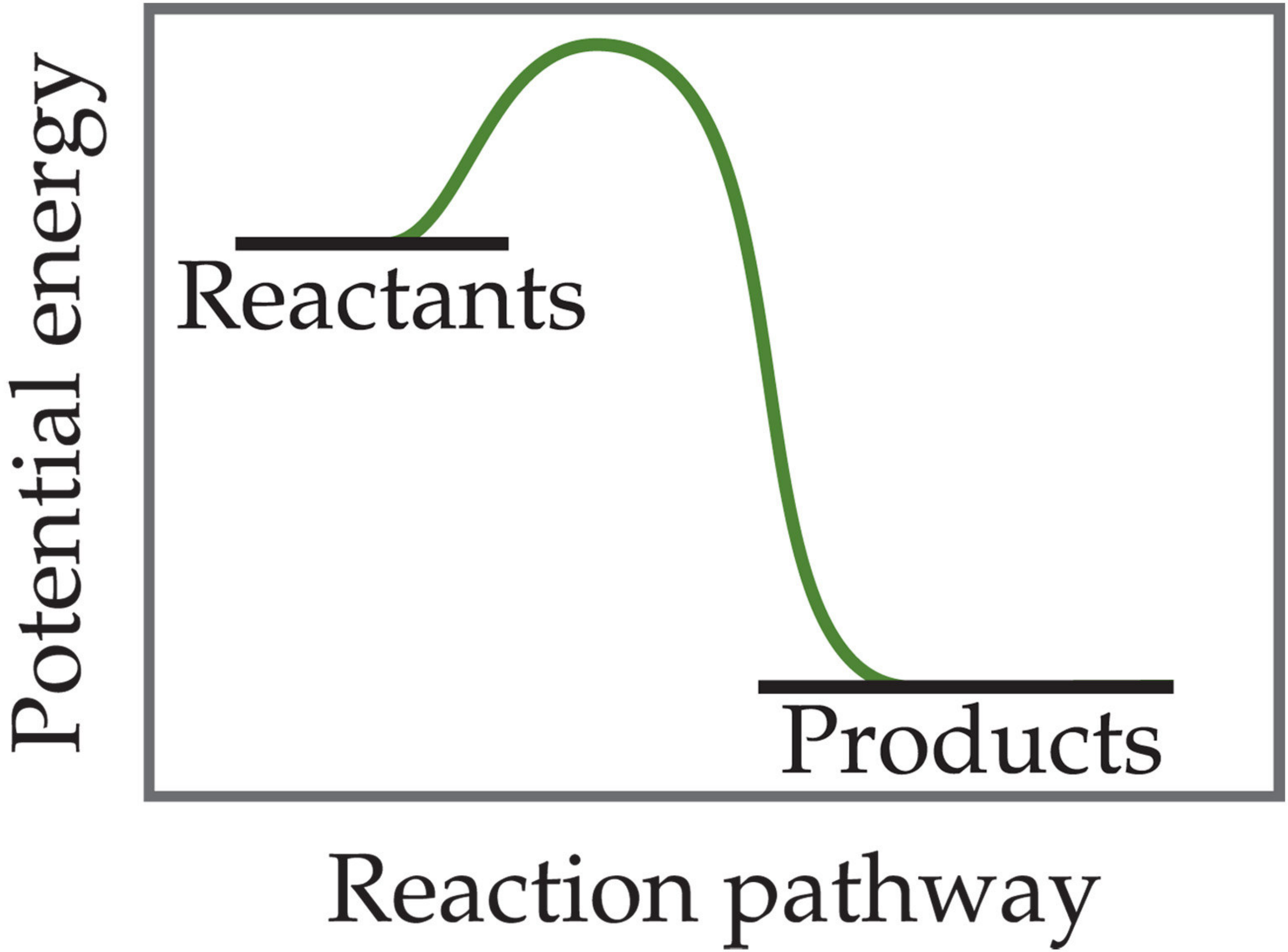
- In other words, there is a minimum amount of energy required for reaction: the activation energy, E_a.
- a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

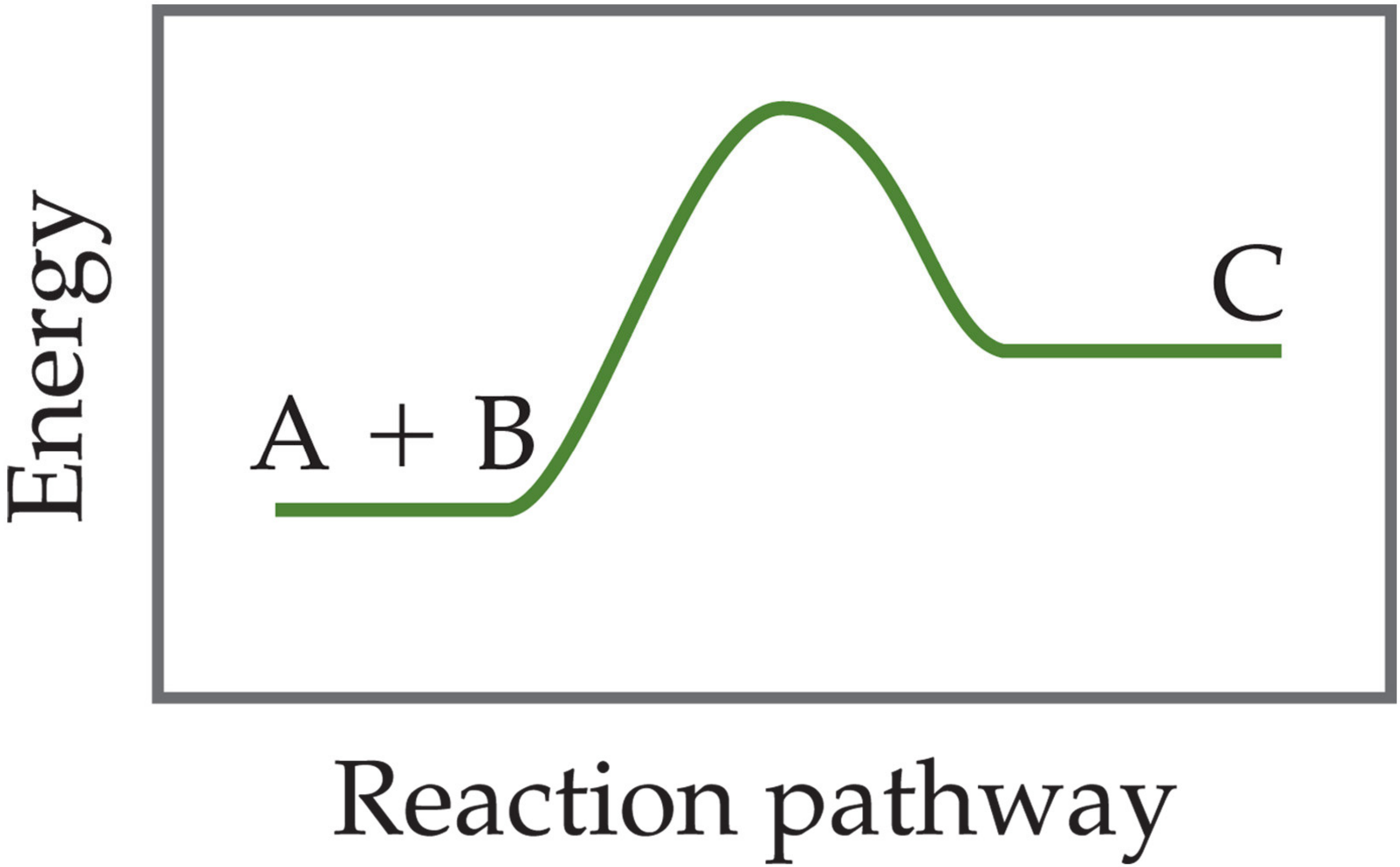
Energy of Activation E_a

the minimum energy required to initiate a chemical reaction.

Figure 14.15.

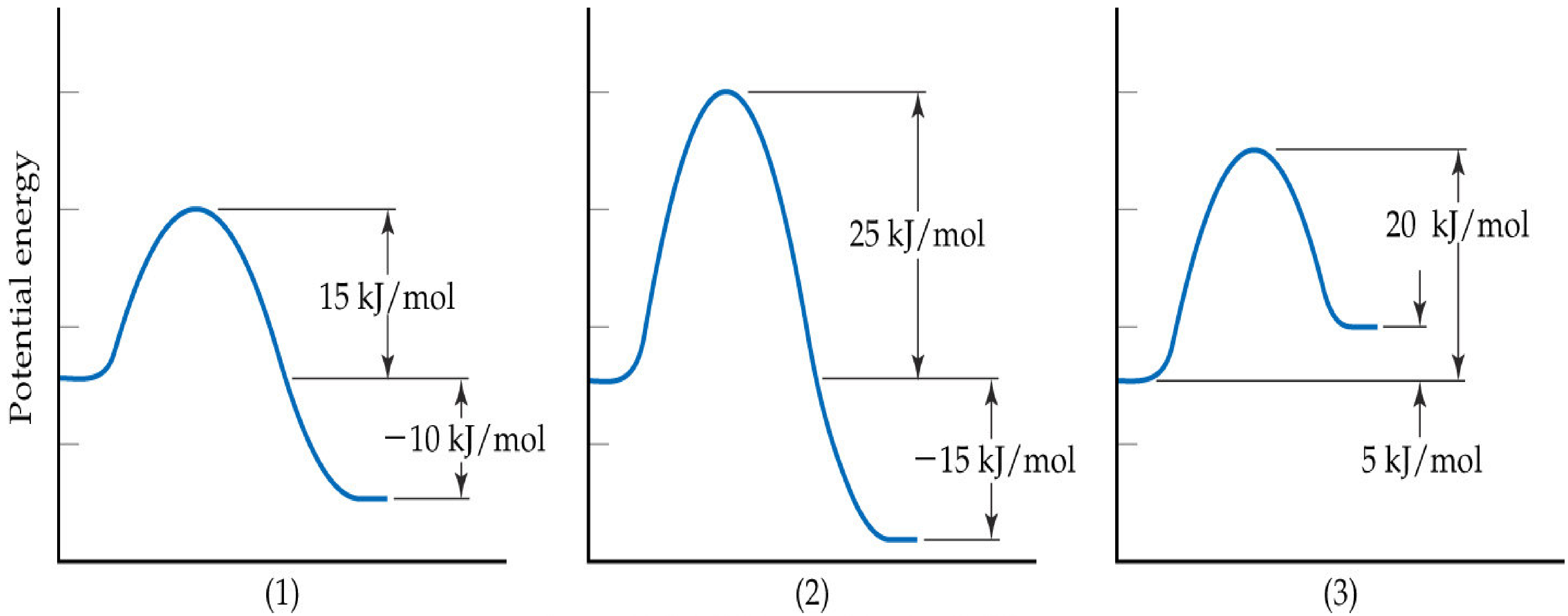

Transition state
E_a
$\Delta H°$
Potential energy
Reaction pathway


Potential energy
Reactants
Products
Reaction pathway


Energy
A + B
C
Reaction pathway

Energy Profiles- determine

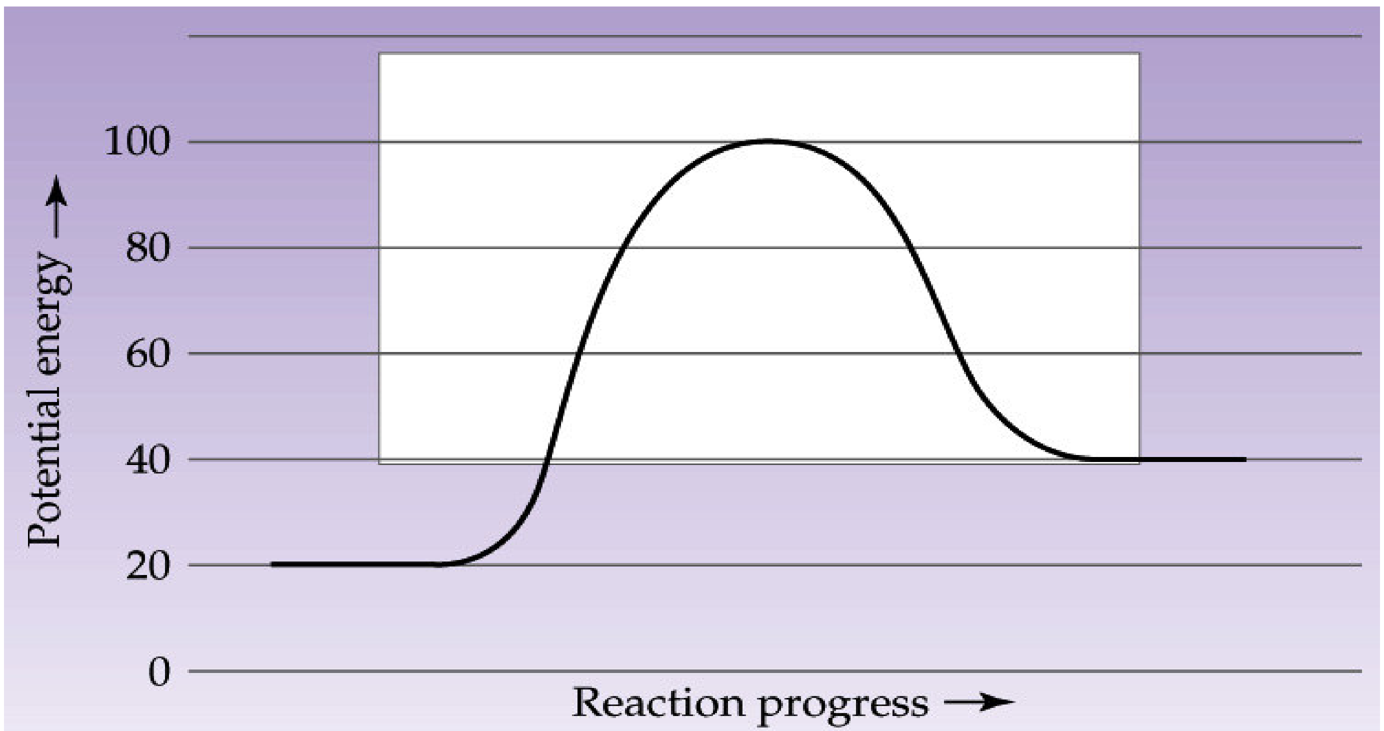
1. Energy of Activation
2. Heat of Reaction



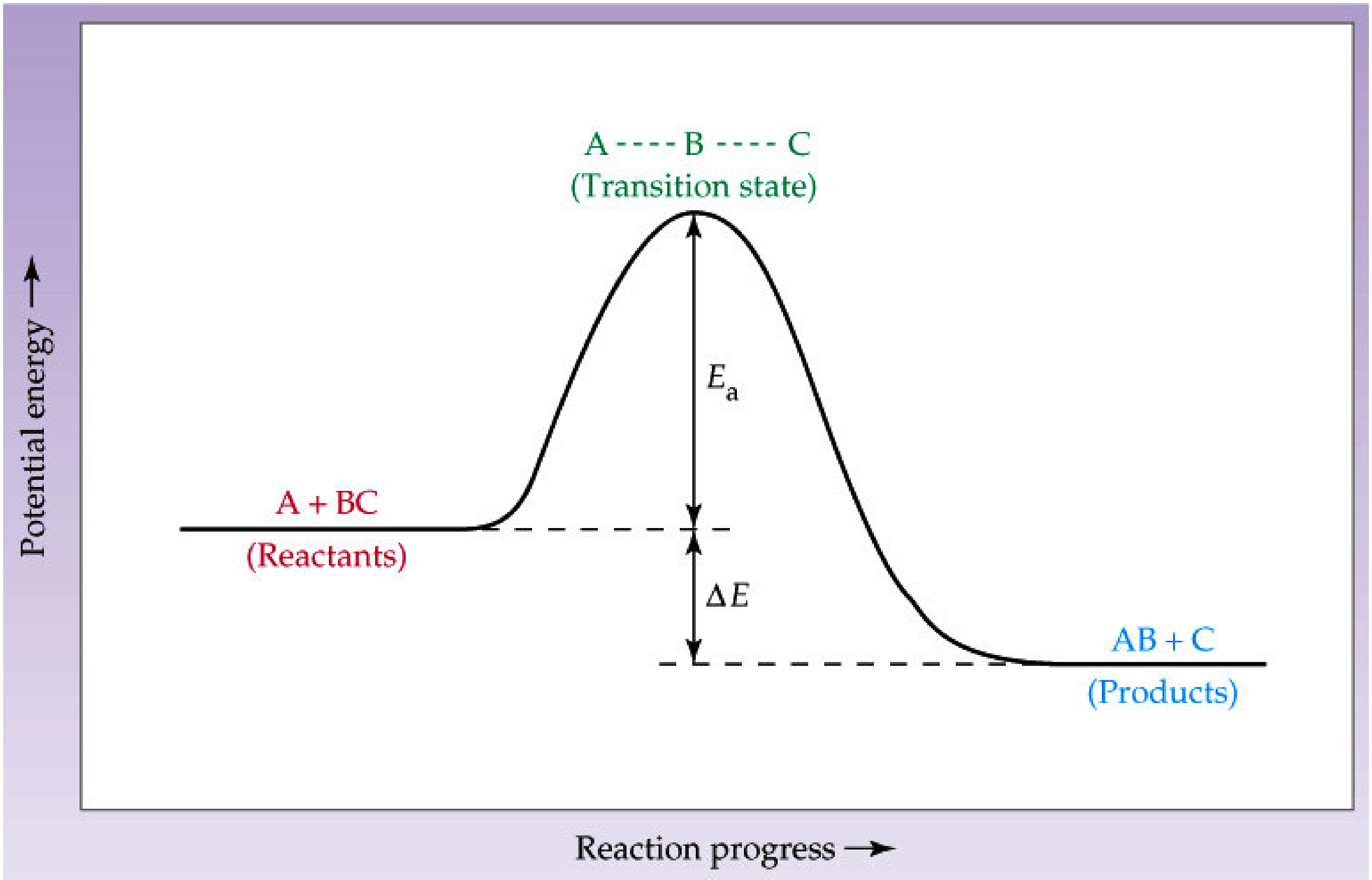
Consider the reaction A → D

(a) What is the value of E_a?

(b) Is the reaction exothermic, or endothermic?



Is this an Endo or Exo Thermic Process ?



Reaction Rates and Catalysis

Increases Rate

Takes Part in Reaction

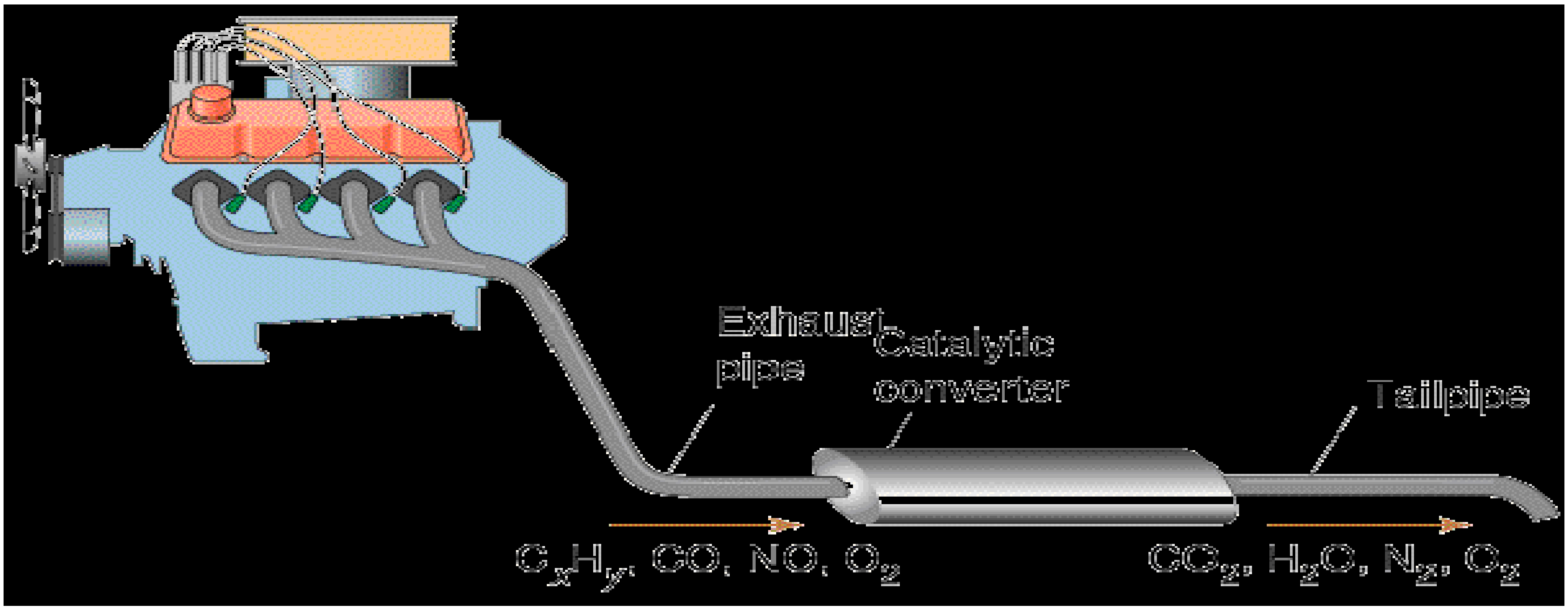
Is not consumed

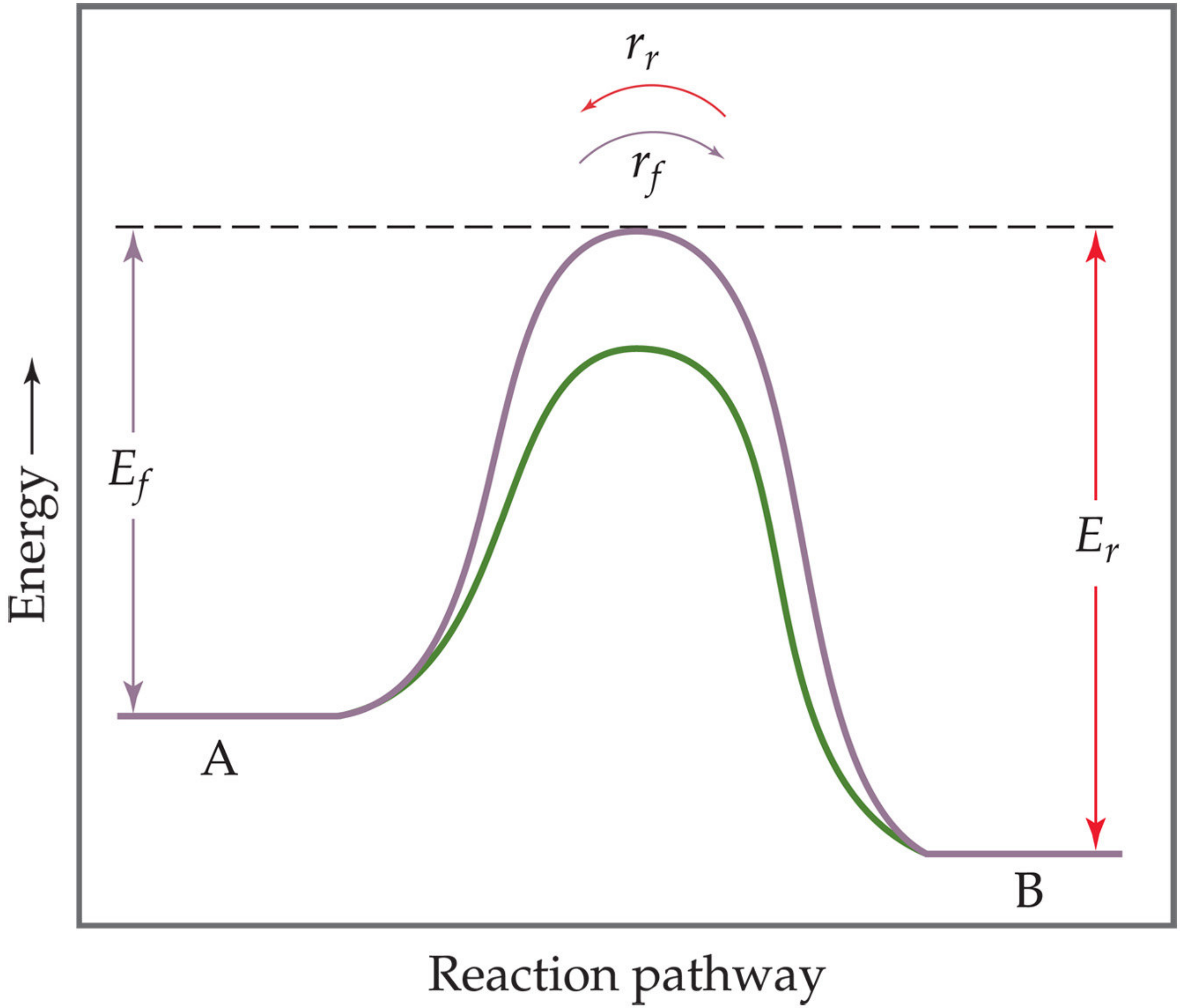
CATALYSTS

- A **catalyst** is a substance that increases the rate of a reaction without being consumed in the reaction.
- Catalysts change the mechanism by which the process occurs.
- Enzymes are catalysts in biological systems

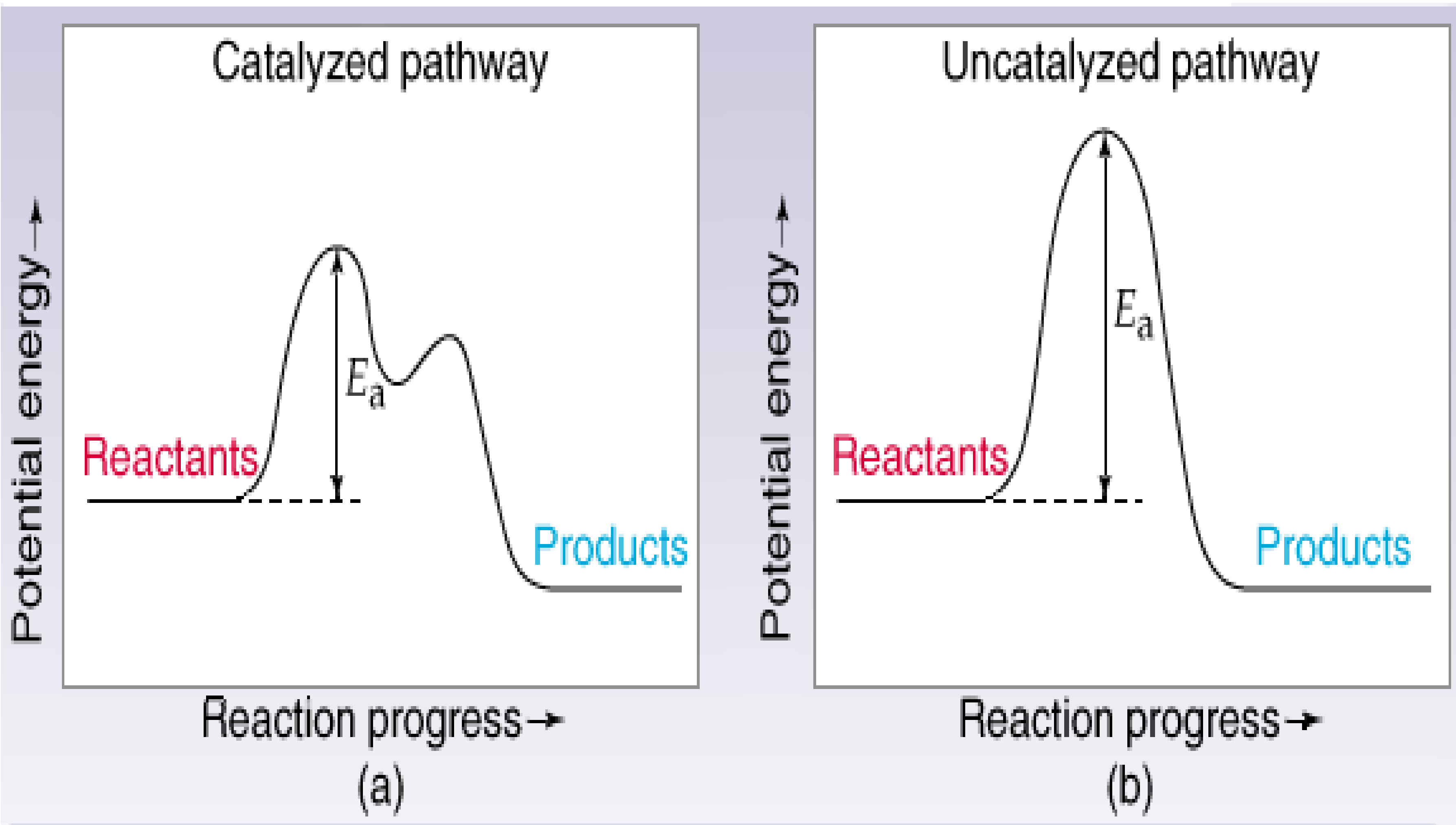
Homogeneous catalyst: Exists in the SAME phase as the reactants.

Heterogeneous catalyst: Exists in DIFFERENT phase to the reactants.

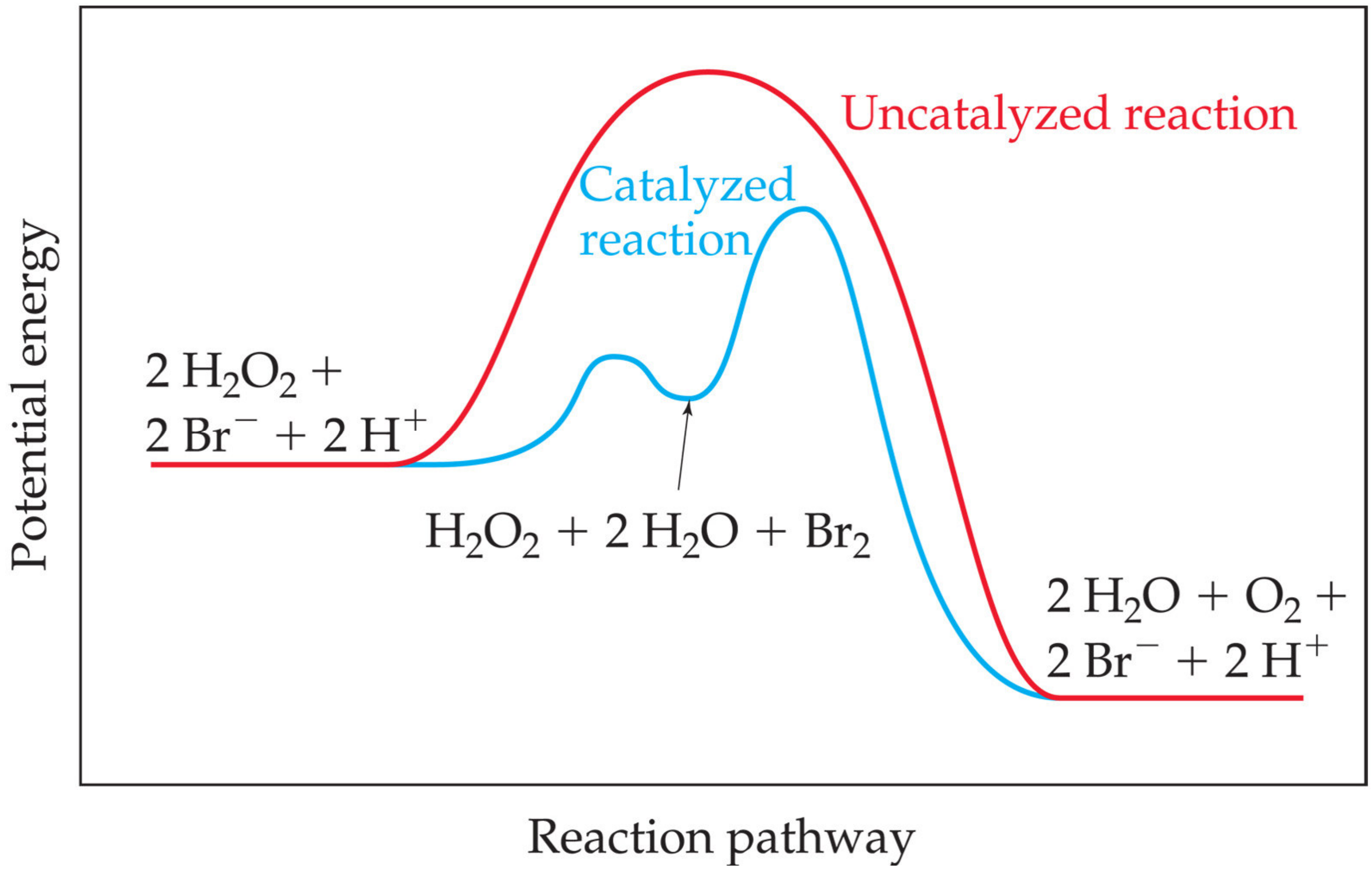



r_r
r_f
E_f
E_r
Energy ⟶
A
B
Reaction pathway

Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.



CATALYSTS


Uncatalyzed reaction
Catalyzed reaction
Potential energy
$2\,H_2O_2$ +
$2\,Br^-$ + $2\,H^+$
$H_2O_2 + 2\,H_2O + Br_2$
$2\,H_2O + O_2$ +
$2\,Br^- + 2\,H^+$
Reaction pathway

PART II
Mechanism

How does the reaction go from
Reactants to Products

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

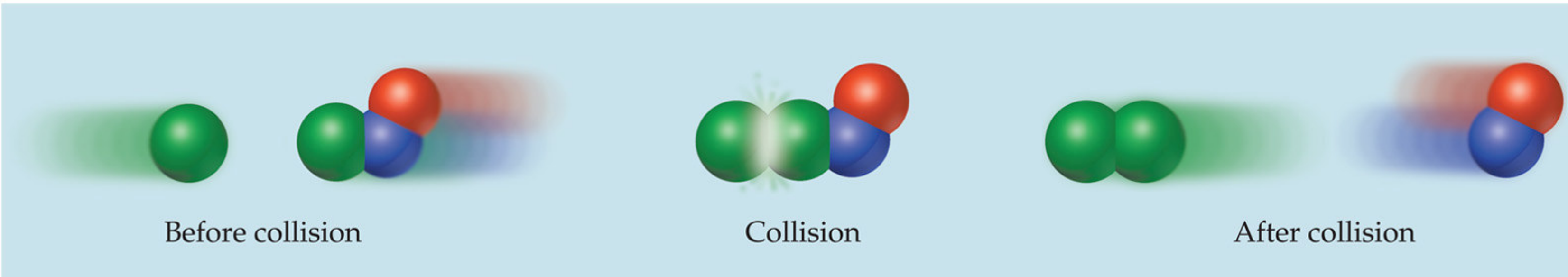
Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

The Collision Model



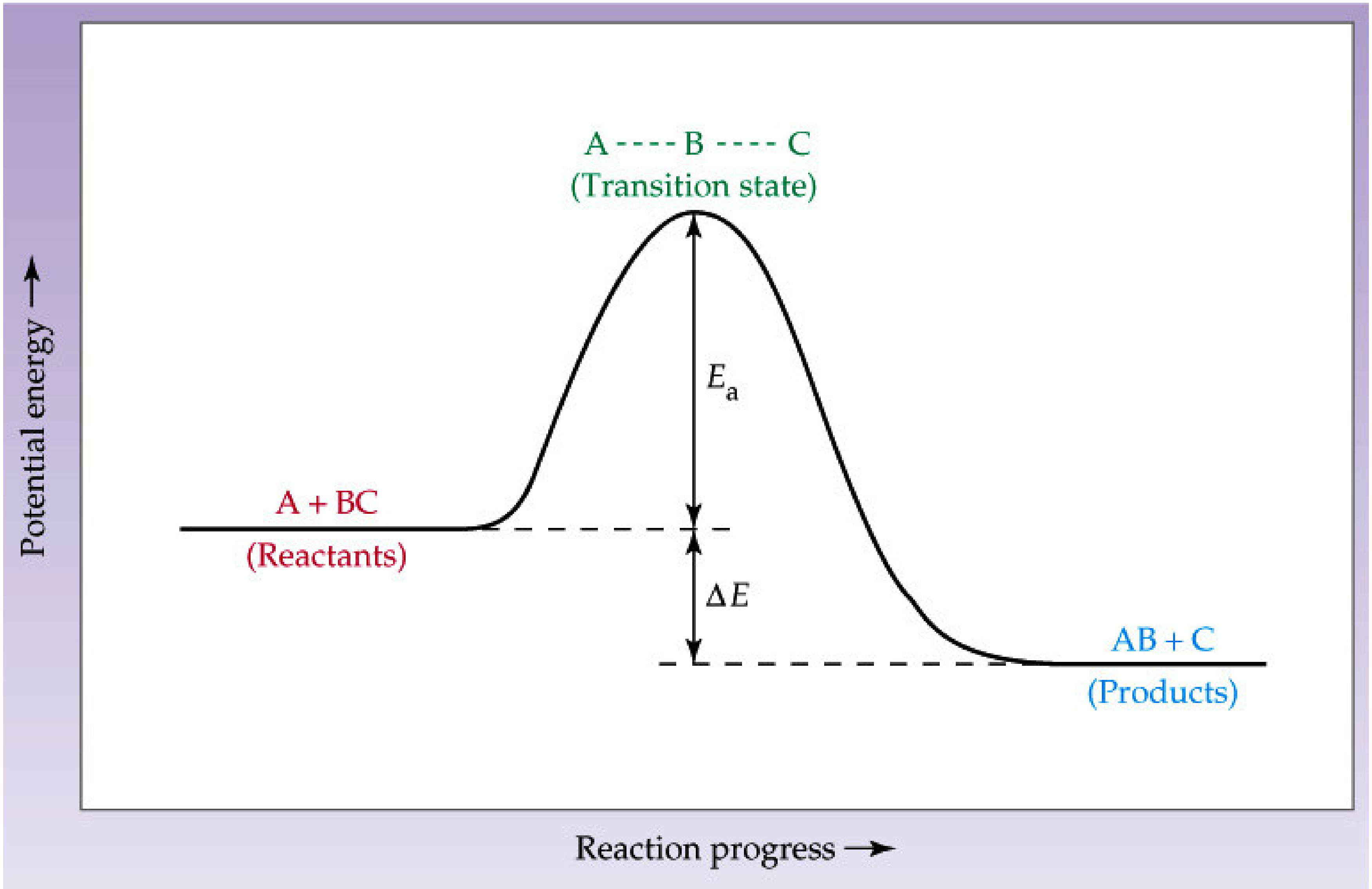
Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.

Collision Theory

1. molecules MUST collide
2. collide with sufficient energy. *
3. correctly oriented molecules

***Activation Energy (E_a):** The energy barrier that must be surmounted before reactants can be converted to products.

Activation Energy

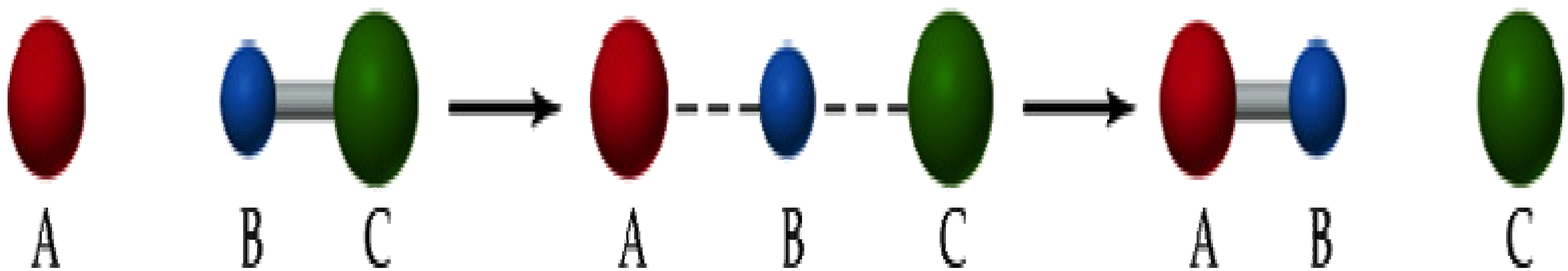


The Collision Theory

- Not all collisions lead to products.
- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.
- The higher the temperature, the more energy available to the molecules and the faster the rate.

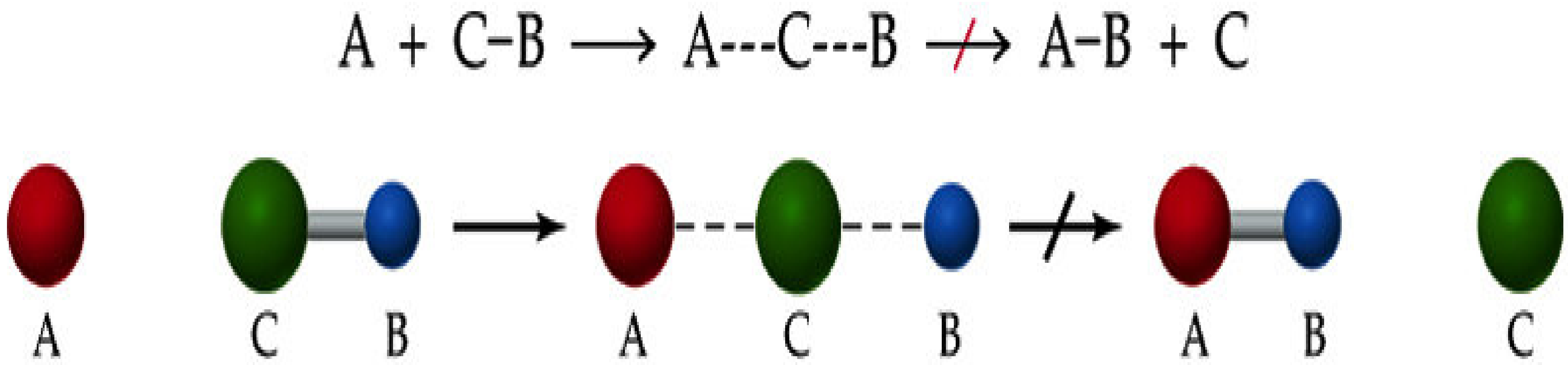
Collision Theory

$$A + B\text{–}C \longrightarrow A\text{---}B\text{---}C \longrightarrow A\text{–}B + C$$

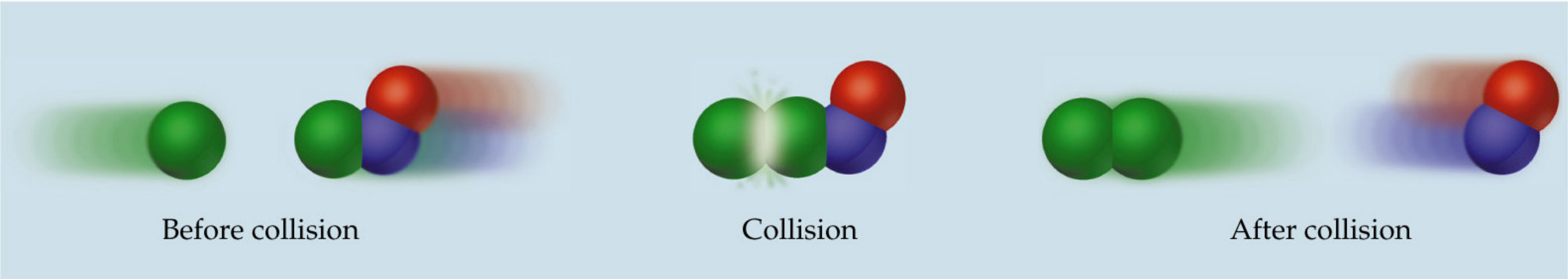


The fraction of collisions having correct orientation is called the ***steric factor***, *p*.

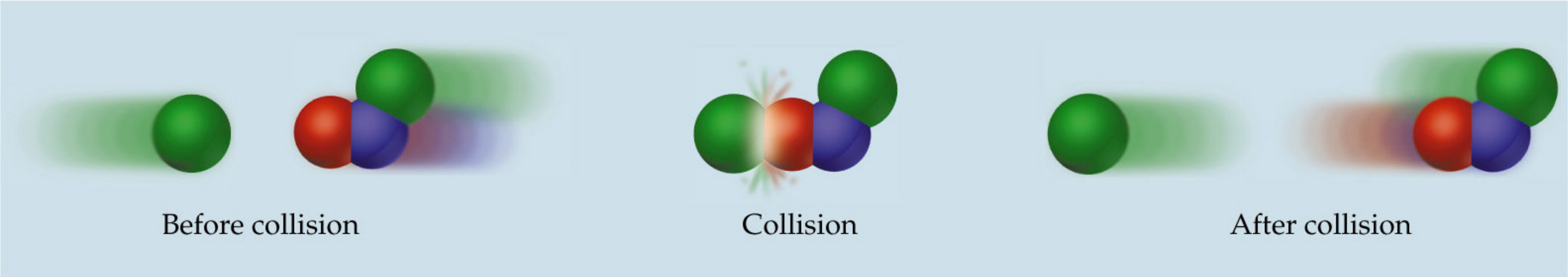
- The fraction of collisions leading to product is further reduced by an orientation requirement.



The Orientation Factor



(a) Effective collision



(b) Ineffective collision

REACTION MECHANISMS

Most Chemical Reactions
DO NOT Occur In A Single Step

Chemical Equations Normally
Represent the OVERALL Reaction
Not the Series of INDIVIDUAL Steps
By Which The Reaction Actually Occurs

HOW DOES

OZONE "turn into" OXYGEN ?

$$2\ O_3\ \text{-----?????}\rightarrow\ 3\ O_2$$

What is "BETWEEN" Reactants and Products

HOW DOES

The reaction of Hydrogen with
Iodine monochloride
form Hydrogen Chloride and Iodine ?

$H_2(g)$ + Cl_2 (g) ---- ???? → HCl (g) + I_2 (g)

What Happens BETWEEN Reactants & Products ?

REACTION MECHANISM

The SEQUENCE Of Reaction

STEPS That Defines

The PATHWAY

From Reactants To Products

ELEMENTARY STEPS

- Single steps in a mechanism are called **<u>elementary steps</u>** (reactions).
- An **<u>elementary step</u>** describes the behavior of individual molecules.
- An **<u>overall reaction</u>** describes the reaction stoichiometry.

Terms You Need To Know

Molecularity: is the number of molecules (or atoms) on the reactant side of the chemical equation.

Unimolecular Reactions: Single reactant molecule.

Bimolecular Reactions: Two reactant molecules.

Termolecular: Three reactant molecules.

Rate Laws and Reaction Mechanisms

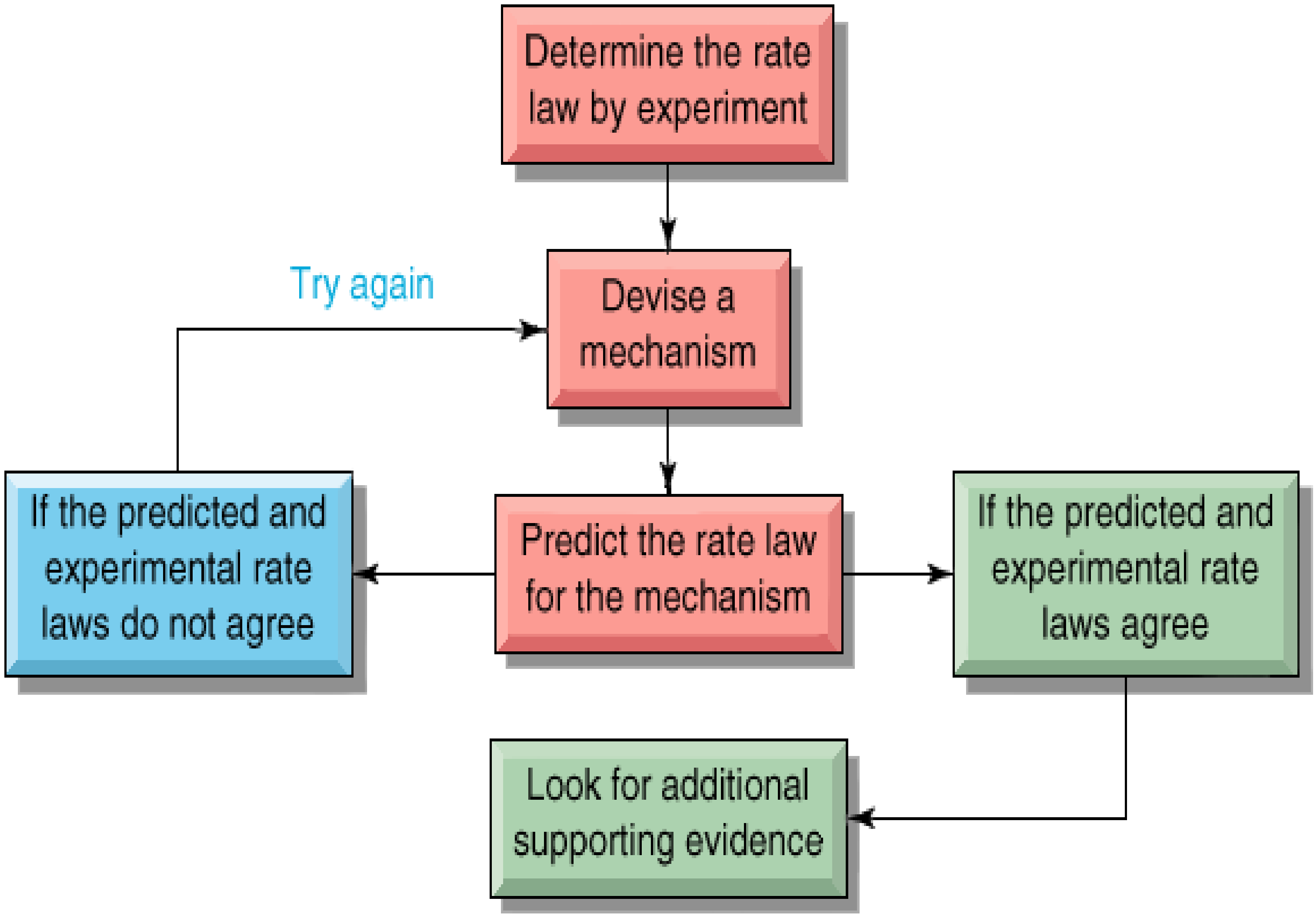
- Rate law for an **overall reaction** MUST be determined **experimentally**.
- Rate law for **elementary steps** follows from its molecularity.
- Elementary steps: Processes in a chemical reaction that occur in a single event or step

Rate Laws and Reaction Mechanisms

- The **rate law** of each **elementary step** follows its **molecularity.**
- The **overall reaction** is a sequence of elementary steps called the ***reaction mechanism*.**

Rate Laws and Reaction Mechanisms

Therefore, the experimentally observed **rate law** for an **overall reaction** must depend on the **reaction mechanism**.


Determine the rate law by experiment
Devise a mechanism
Try again
Predict the rate law for the mechanism
If the predicted and experimental rate laws do not agree
If the predicted and experimental rate laws agree
Look for additional supporting evidence

"How" does ozone "turn into" oxygen?

$$2\,O_3 \;\; \text{-???}\rightarrow \;\; 3\,O_2$$

It has been proposed that the mechanism of ozone into O_2 proceeds by a two-step :

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

$$O_3(g) + O(g) \longrightarrow 2O_2(g)$$

(a) Describe the molecularity of each elementary reaction in this mechanism.
(b) Write the equation for the overall reaction
(c) Identify the intermediate(s).

SAMPLE EXERCISE 14.14 Determining the Rate Law

For the decomposition of nitrous oxide, N_2O

$$N_2O(g) \longrightarrow N_2(g) + O(g) \quad \text{(slow)}$$

$$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) \quad \text{(fast)}$$

(a) Write the equation for the overall reaction.
(b) Write the rate law for the overall reaction.

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

The reaction is believed to occur in two steps

$$O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$$

$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

1. Write the overall reaction
2. Is the proposed mechanism possible ?
3. Identify the intermediate(s) ?

NO catalyzes the decomposition of N_2O by the following mechanism

$$NO\ (g) + N_2O\ (g) \rightarrow N_2 + NO_2\ (g)$$

$$2\ NO_2(g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

(a) Write the balanced equation for the reaction

(b) Why is NO considered a catalyst and not an intermediate ?

(c) Identify intermediates in mechanism