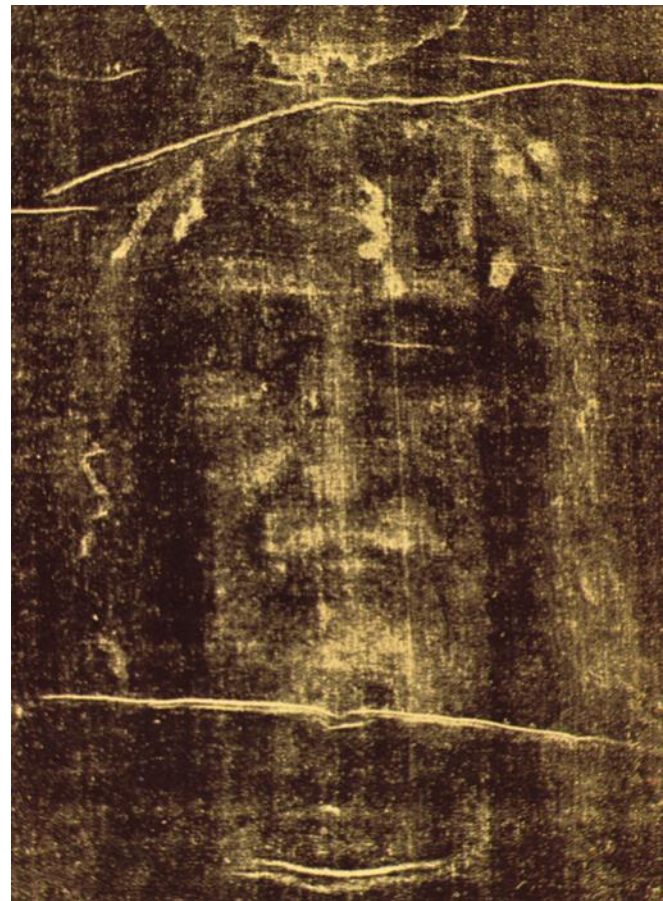


Chemical Kinetics

(Reaction rate + Reaction mechanism)



Chemical Kinetics

- Chemical kinetics:

Study how we can make reactions go faster or slower

- Why should we study this?

- Economics effects



1. Can it take place --> Feasibility
2. Fast or slow --> kinetics

- Who makes use of chemical kinetics?

- Biologist: metabolic reactions, food digestion, bone regeneration

- Automotive engineers: rate of combustion, rate of rusting, decrease pollutants

- Agriculture engineers: slow down food ripening

- Chemical engineers: design chemical reactors

- Pharmaceutical scientists: developing new drugs

Chemical Kinetics

Gibbs Free Energy

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

ΔG^θ Gibbs free-energy change
measured in kJ mol^{-1}

ΔH^θ Enthalpy change
measured in kJ mol^{-1}

T Temperature
measured in Kelvin

ΔS^θ Entropy change
measured in $\text{J K}^{-1}\text{mol}^{-1}$

Thermodynamics – does a reaction **take place**

Kinetics – how **fast** does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).



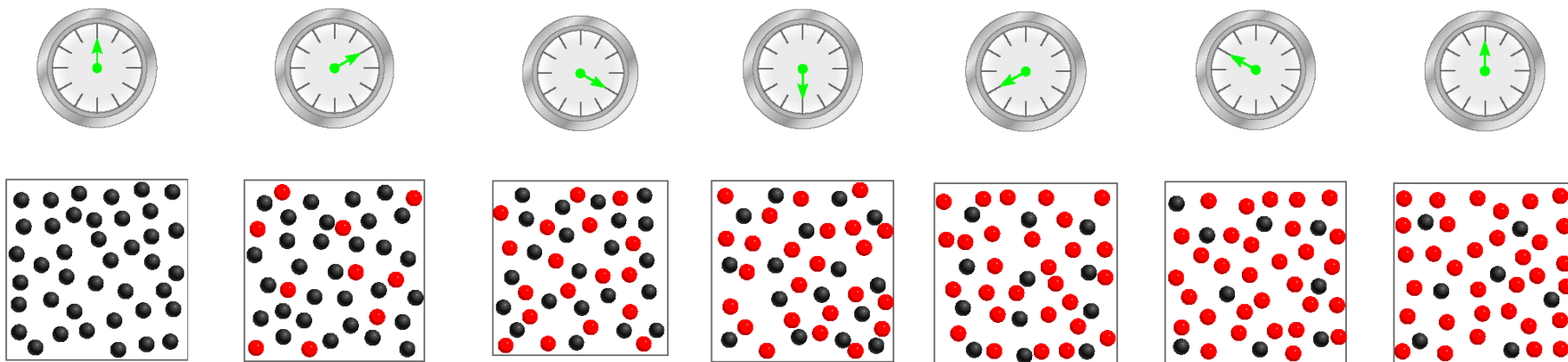
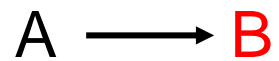
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over
time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

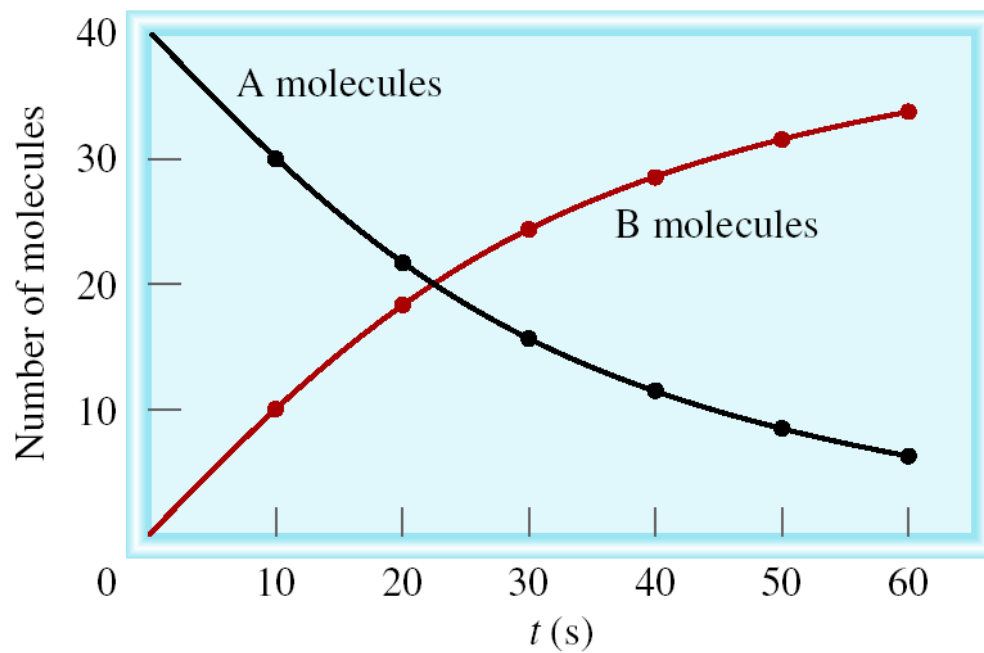
$\Delta[B]$ = change in concentration of B over
time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

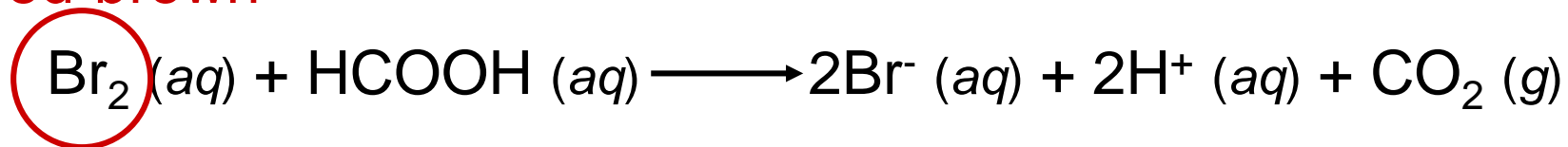


$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

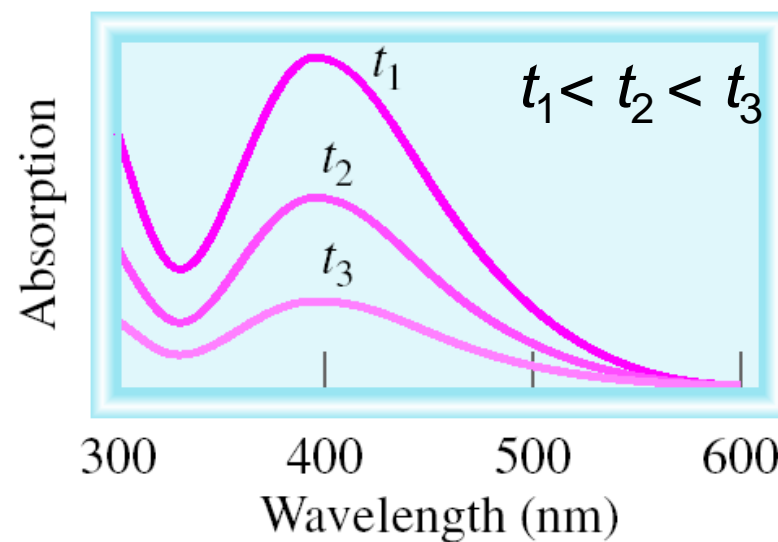
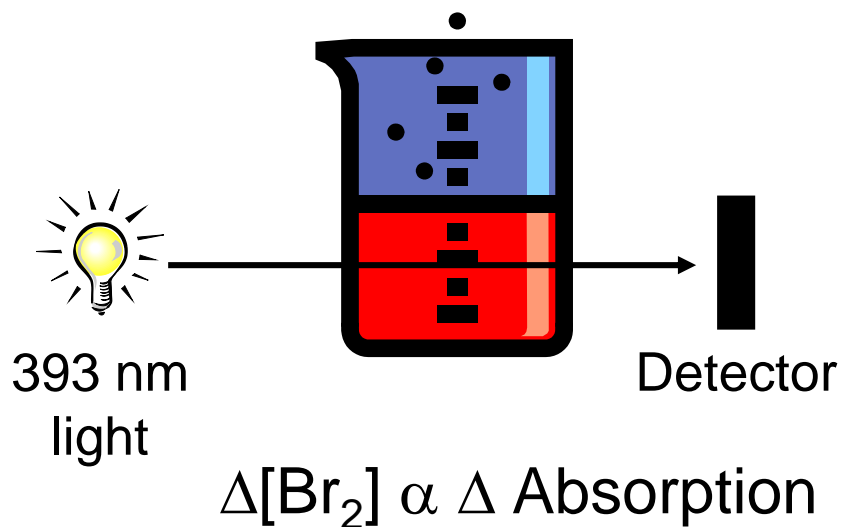
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

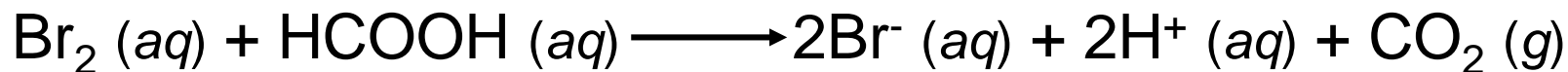


red-brown

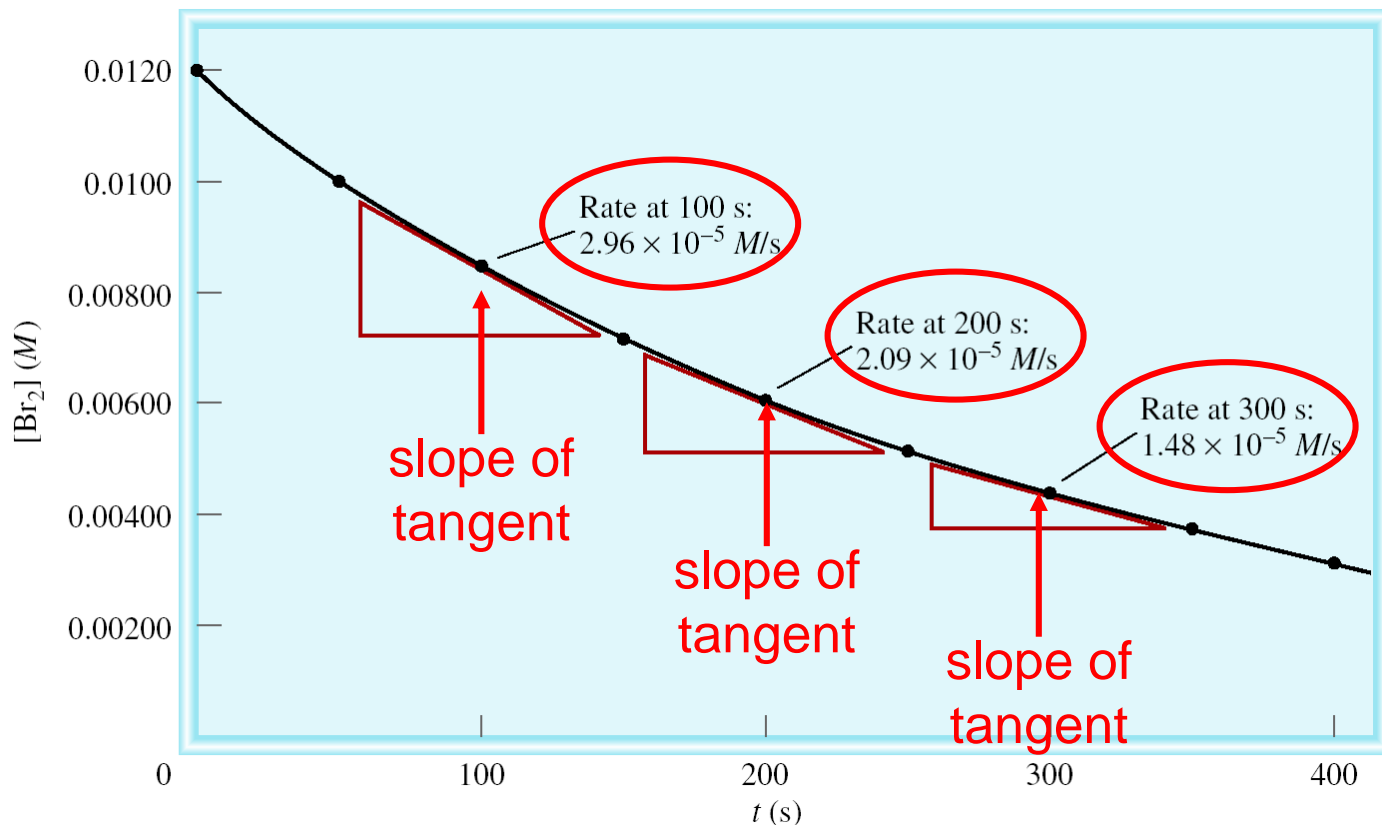


time





Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$$\text{average rate} = - \frac{\Delta[\text{Br}_2]}{\Delta t} = - \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

instantaneous rate = rate for specific instance in time

TABLE 13.1

Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

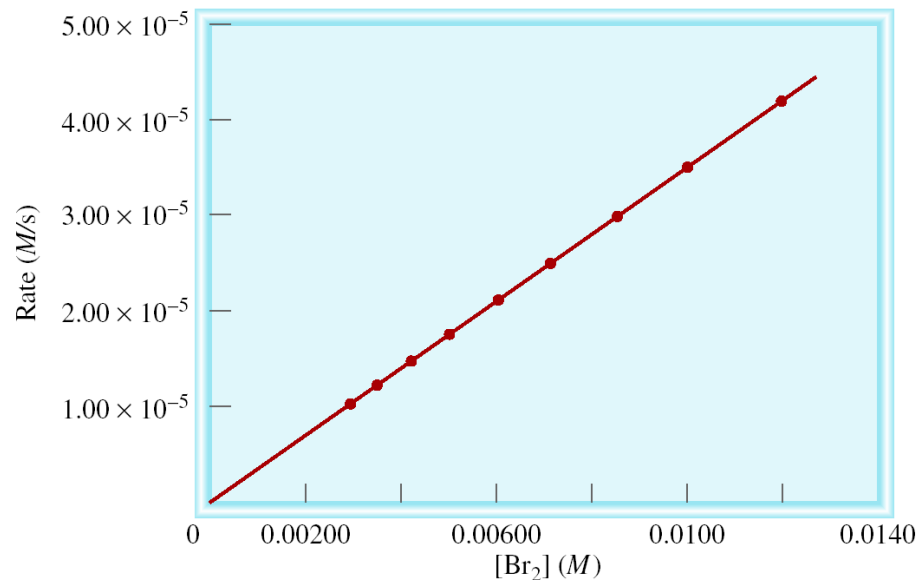
Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

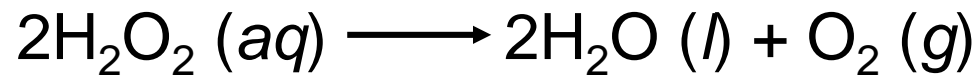
$$\text{rate} \propto [\text{Br}_2]$$

$$\text{rate} = k [\text{Br}_2]$$

$$k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}$$

$$= 3.50 \times 10^{-3} \text{ s}^{-1}$$





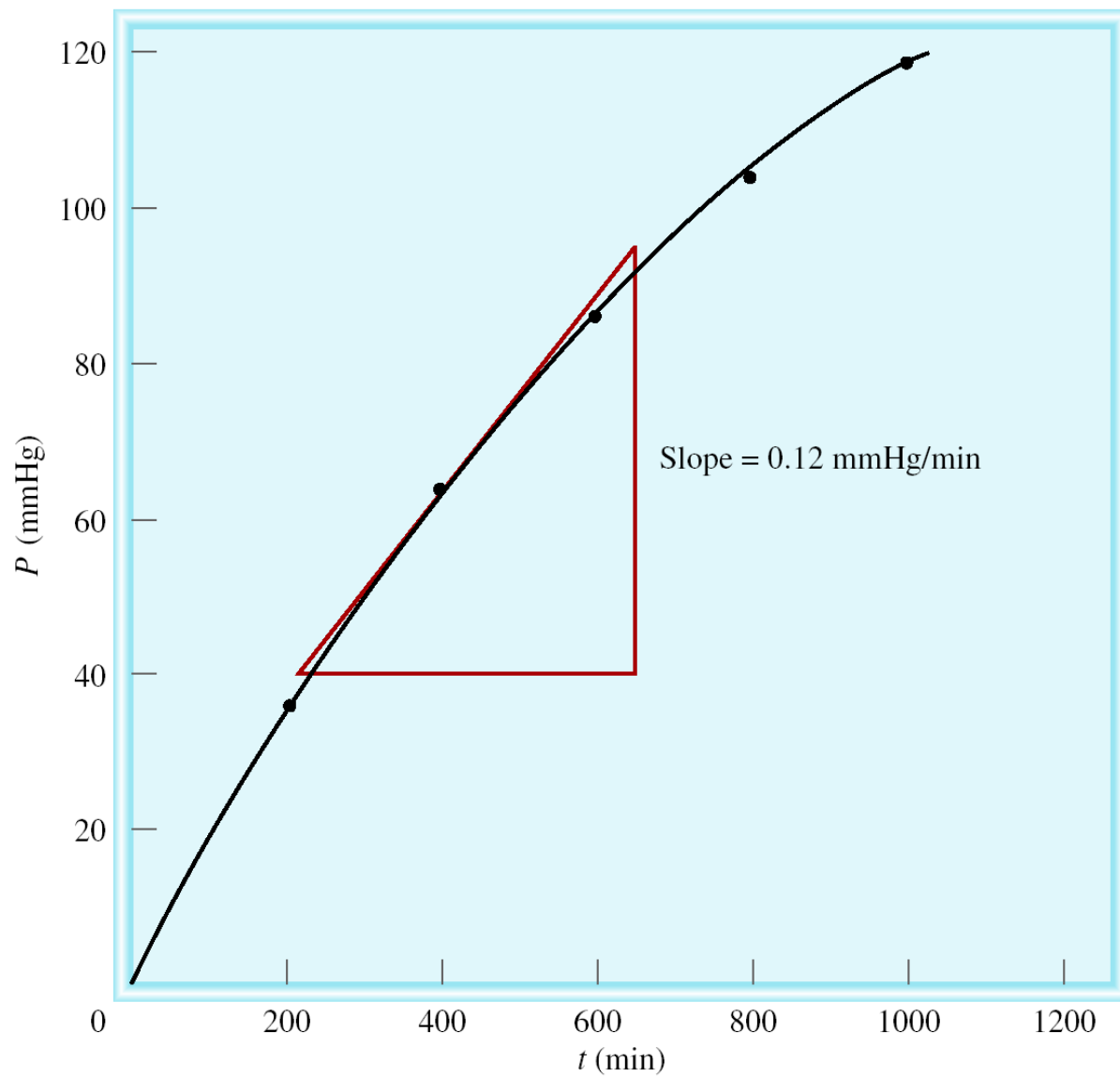
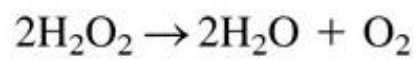
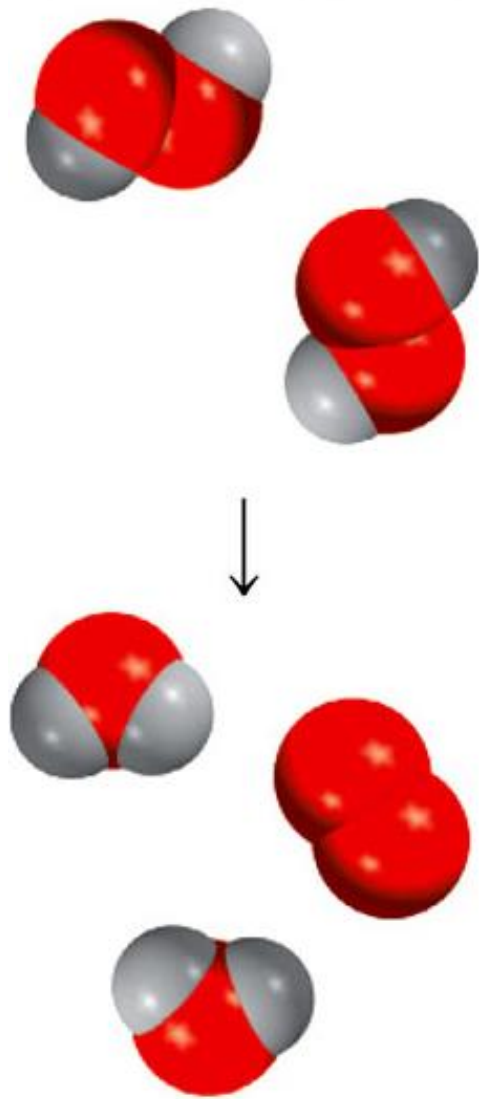
$$PV = nRT$$

$$P = \frac{n}{V} RT = [\text{O}_2] RT$$

$$[\text{O}_2] = \frac{1}{RT} P$$

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$

measure ΔP over time



Reaction Rates and Stoichiometry

Stoichiometry là nghiên cứu về các mối quan hệ định lượng hoặc tỷ lệ giữa các chất phản ứng và sản phẩm trong một phản ứng hóa học



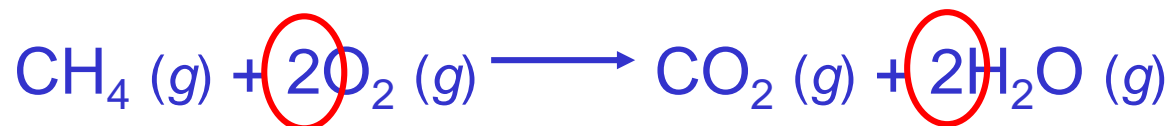
Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = - \frac{1}{2} \frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$



$$\text{rate} = - \frac{1}{a} \frac{\Delta[A]}{\Delta t} = - \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Write the **rate expression** for the following reaction:



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

The Rate Law

The **rate law** expresses the relationship of the rate of a **reaction** to the rate **constant** and **the concentrations of the reactants** raised to some powers.



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

Reaction is **xth order** in A

Reaction is **yth order** in B

Reaction is **(x + y)th order overall**

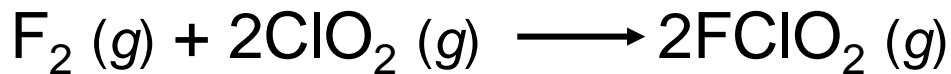


TABLE 13.2 Rate Data for the Reaction Between F_2 and ClO_2

	$[\text{F}_2] \text{ (M)}$	$[\text{ClO}_2] \text{ (M)}$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k [\text{F}_2]^x [\text{ClO}_2]^y$$

Double $[\text{F}_2]$ with $[\text{ClO}_2]$ **constant**

Rate doubles $\frac{\text{rate}_1}{\text{rate}_2} = \frac{k'[\text{F}_2]_1^x}{k'[\text{F}_2]_2^x} \Rightarrow \frac{1.2}{2.4} = \frac{[0.10]^x}{[0.20]^x} \Rightarrow x = 1$

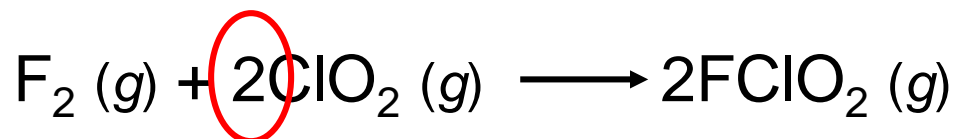
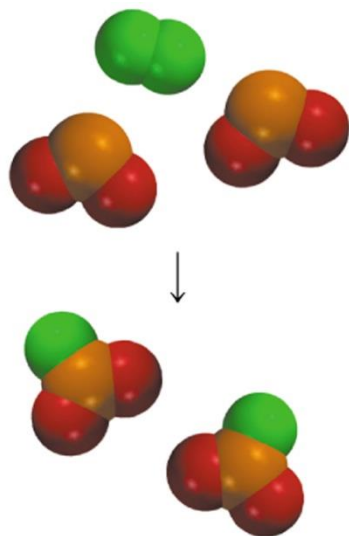
Quadruple $[\text{ClO}_2]$ with $[\text{F}_2]$ **constant**

Rate quadruples $\frac{1.2}{4.8} = \frac{[0.010]^y}{[0.040]^y} \Rightarrow y = 1$

Rate = $k [\text{F}_2][\text{ClO}_2]$ Overall rate order = $1 + 1 = 2$

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$\text{rate} = k [\text{F}_2][\text{ClO}_2]^1$$

Determine the rate law and calculate the rate constant for the following reaction from the following data:



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

$$y = 1$$

$$x = 1$$

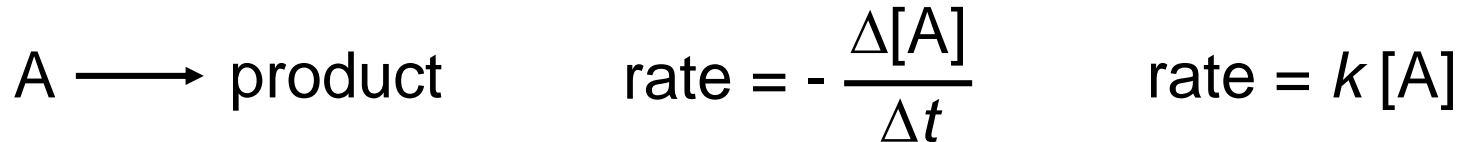
$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

Double $[\text{I}^-]$, rate doubles (experiment 1 & 2)

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M}\cdot\text{s}$$

First-Order Reactions

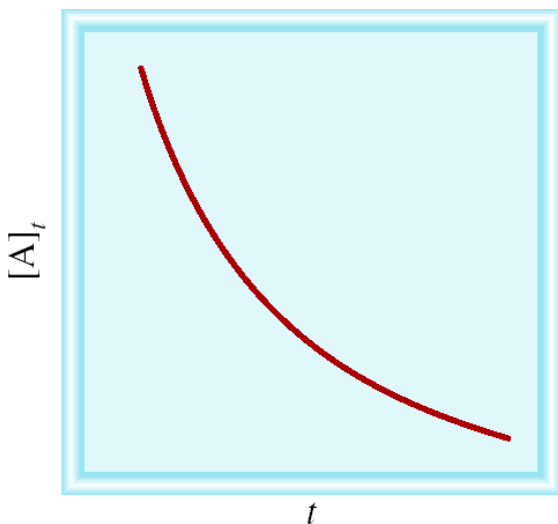


$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1} \quad - \frac{\Delta[A]}{\Delta t} = k[A]$$

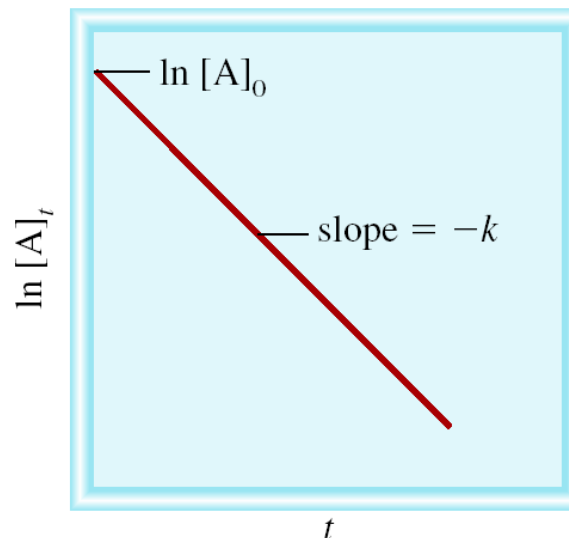
$[A]$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t=0$

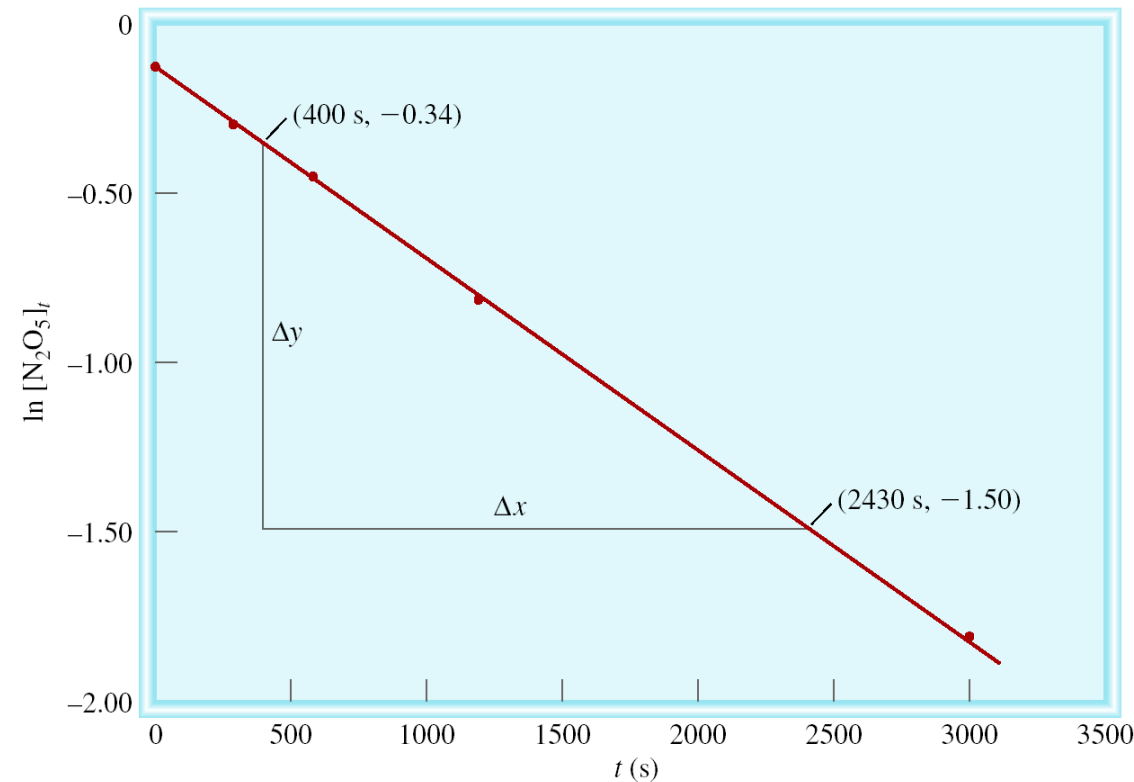
$$[A] = [A]_0 e^{-kt}$$



$$\ln[A] = \ln[A]_0 - kt$$



Graphical Determination of k



$$\begin{aligned}\text{slope } (m) &= \frac{\Delta y}{\Delta x} \\ &= \frac{-1.50 - (-0.34)}{(2430 - 400) \text{ s}} \\ &= -5.7 \times 10^{-4} \text{ s}^{-1}\end{aligned}$$

$$m = -k$$

$$k = 5.7 \times 10^{-4} \text{ s}^{-1}$$

The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at 80°C . How long will it take for A to decrease from 0.88 M to 0.14 M ?

$$\ln[A] = \ln[A]_0 - kt$$

$$[A]_0 = 0.88 \text{ M}$$

$$[A] = 0.14 \text{ M}$$

$$kt = \ln[A]_0 - \ln[A]$$

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 \cancel{\text{M}}}{0.14 \cancel{\text{M}}}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

First-Order Reactions

The **half-life, $t_{1/2}$** , is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

$$t_{1/2} = \frac{\ln \frac{\cancel{[A]}_0}{\cancel{[A]}_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

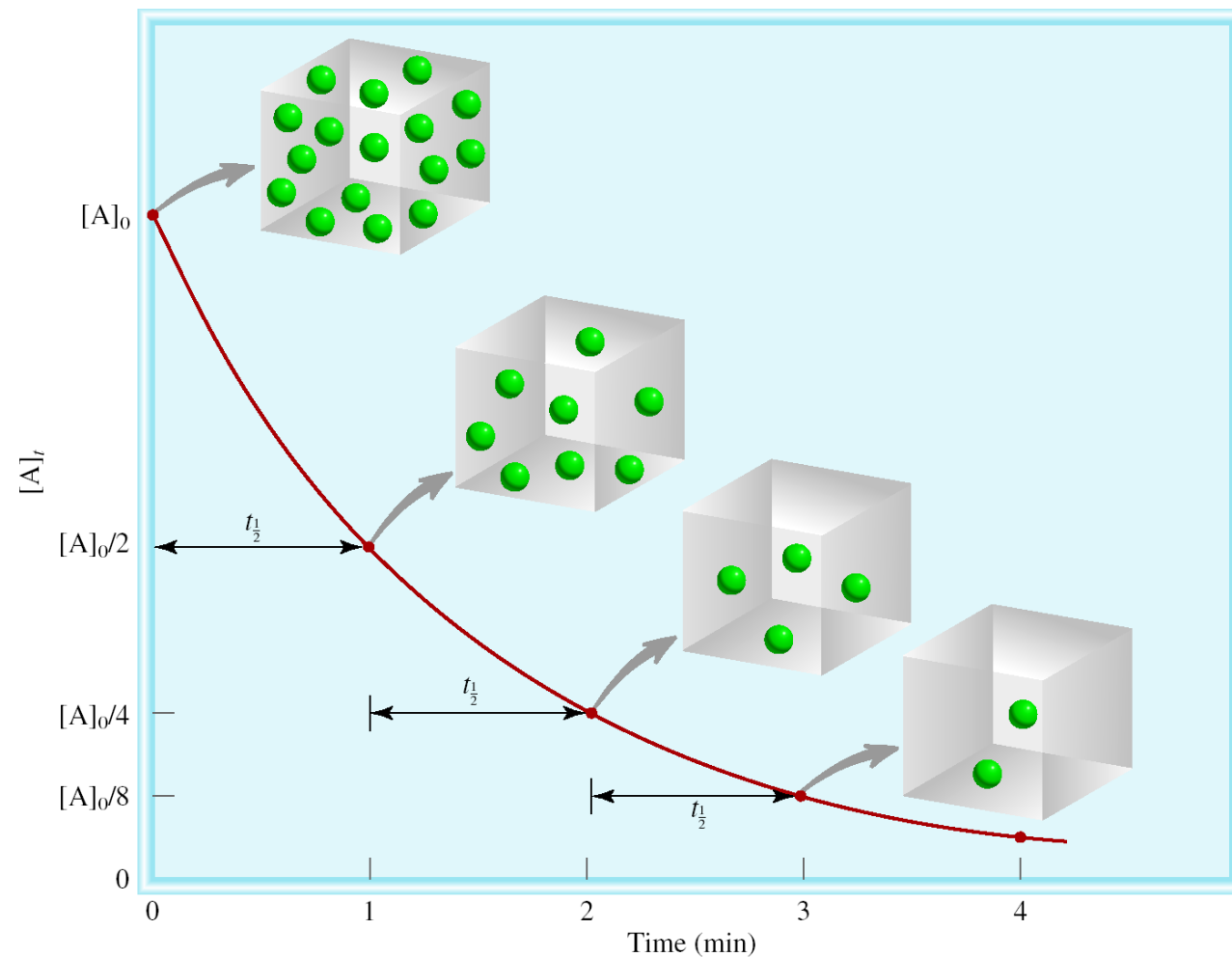
How do you know decomposition is first order?

units of $k \text{ (s}^{-1}\text{)}$ ¹⁹

First-order reaction

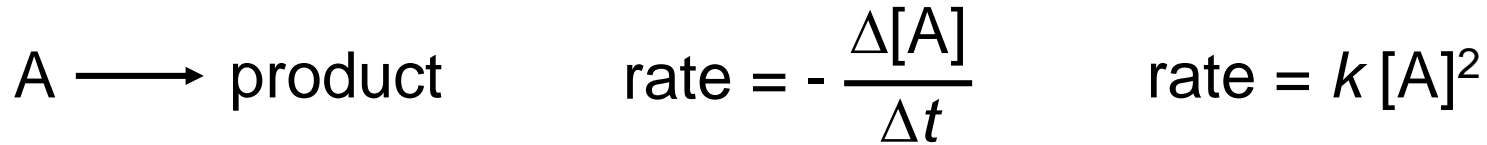


$$\frac{\# \text{ of half-lives}}{[A] = [A]_0 / n}$$



<u># of half-lives</u>	<u>$[A] = [A]_0 / n$</u>
1	2
2	4
3	8
4	16

Second-Order Reactions



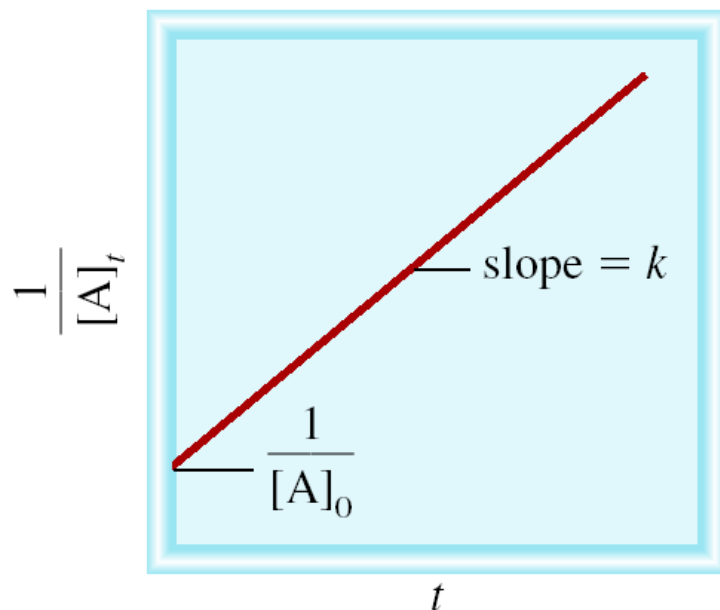
$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/(M \cdot s) \quad - \frac{\Delta[A]}{\Delta t} = k [A]^2$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

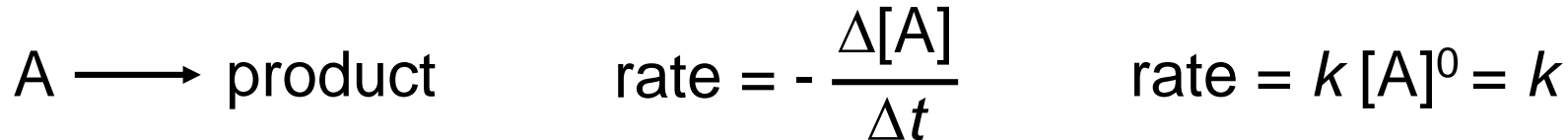
$[A]$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t=0$

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

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



Zero-Order Reactions



$$k = \frac{\text{rate}}{[A]^0} = M/s$$

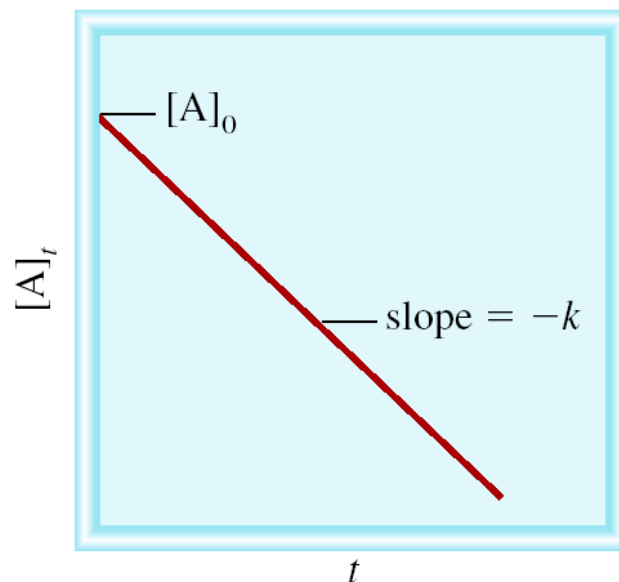
$$- \frac{\Delta[A]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

$[A]$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t = 0$

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

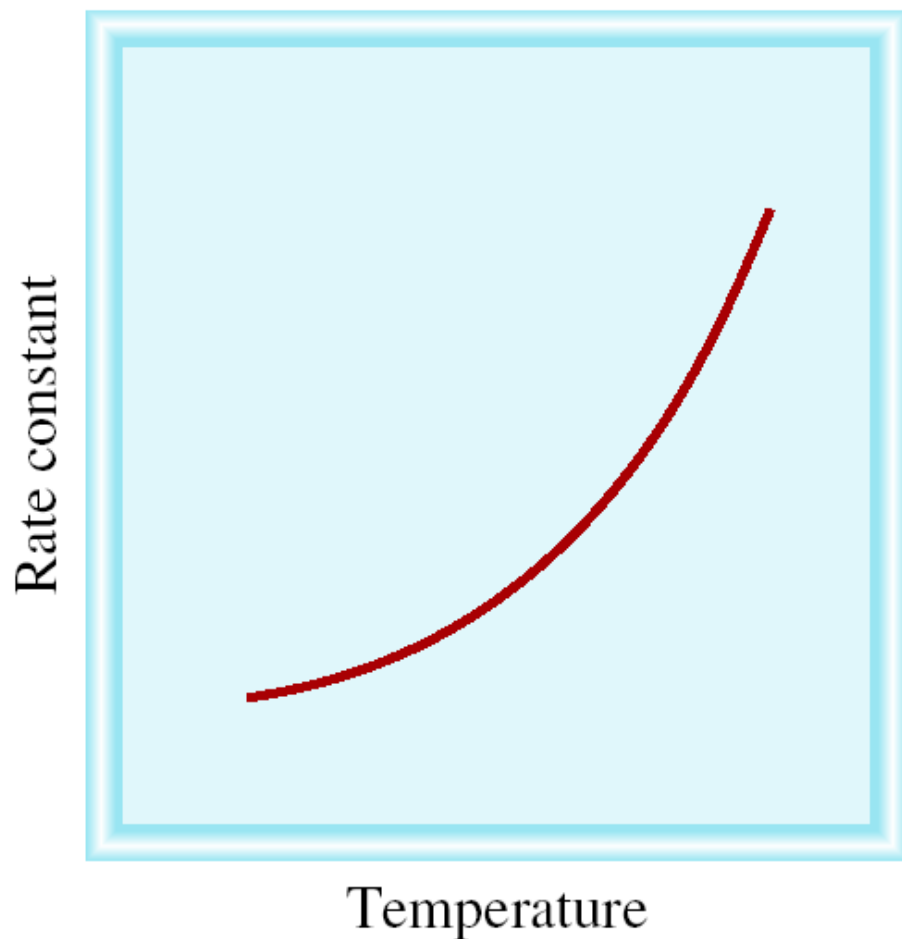
$$t_{1/2} = \frac{[A]_0}{2k}$$



Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life	k, unit
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$	M/s
1	rate = $k [A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$	1/(M·s)
2	rate = $k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$	1/s

Temperature Dependence of the Rate Constant



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

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

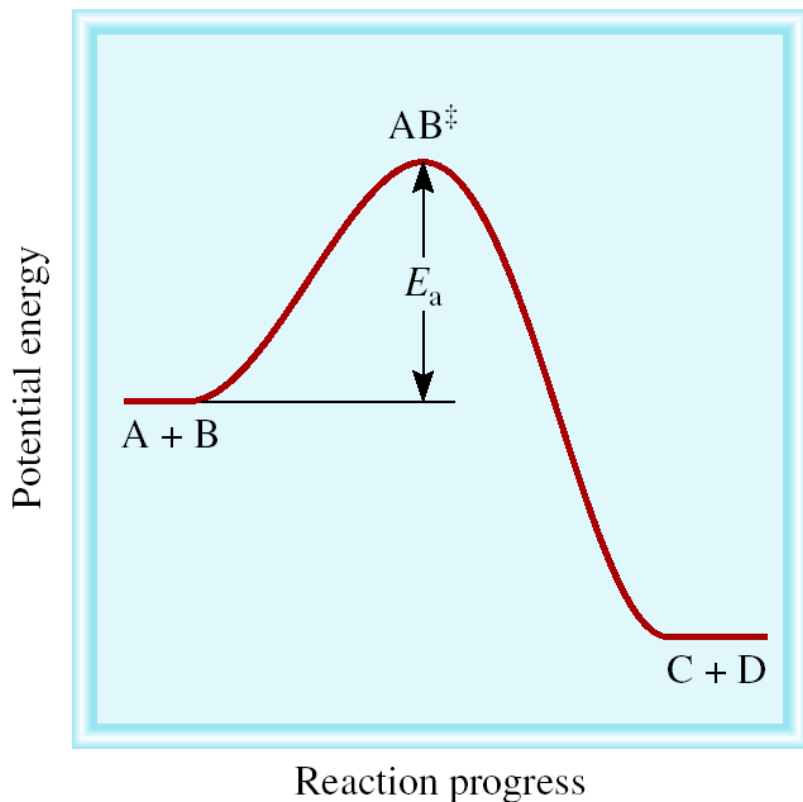
A is the frequency factor

Alternate format:

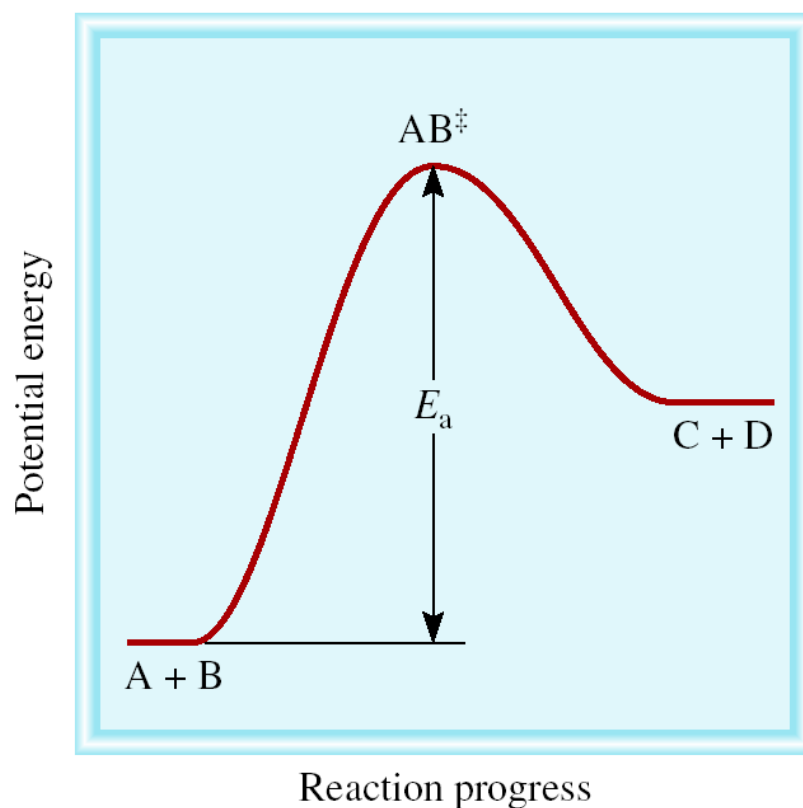
$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$



Exothermic Reaction



Endothermic Reaction



The **activation energy** (E_a) is the minimum amount of energy required to initiate a chemical reaction.

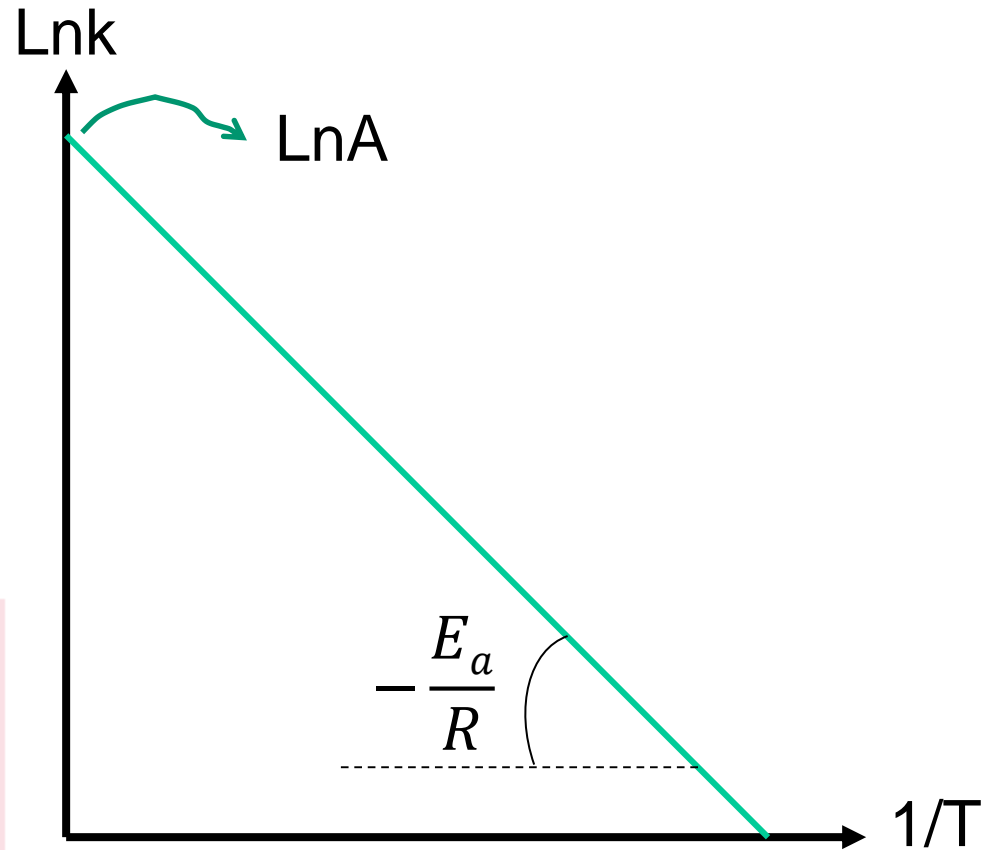
Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

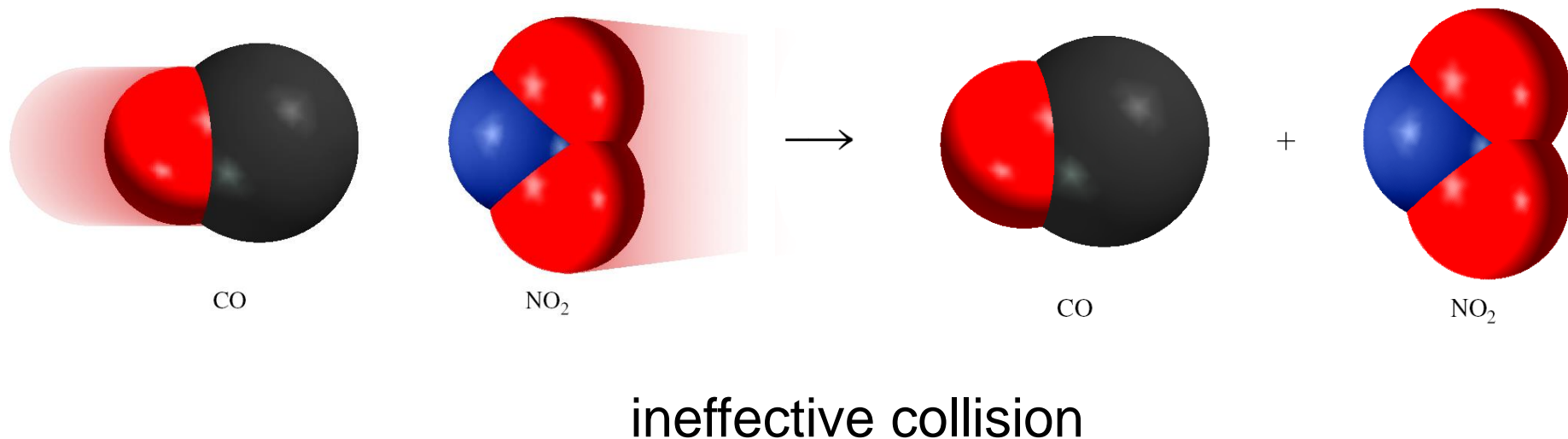
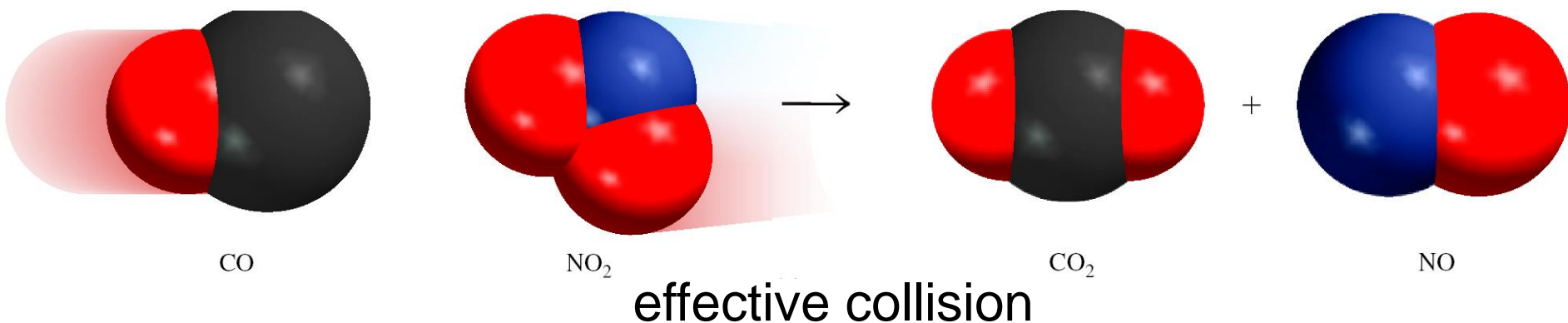
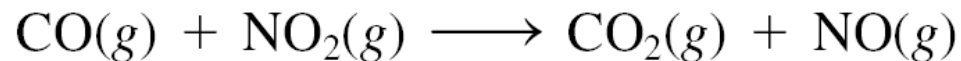
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

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



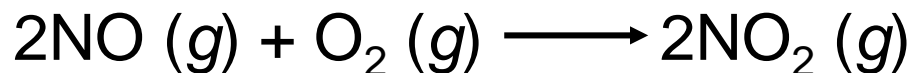
Importance of Molecular Orientation



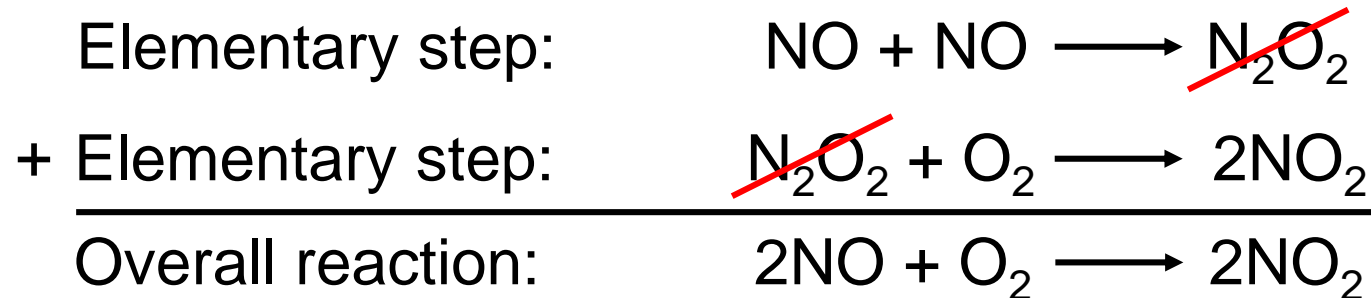
Reaction Mechanisms

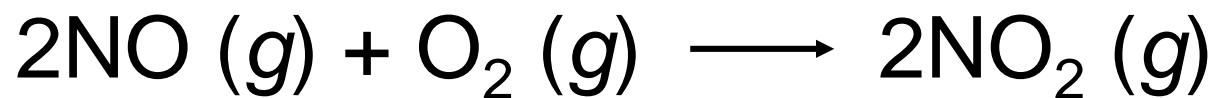
The overall progress of a chemical reaction can be represented at the molecular level by a series of simple ***elementary steps*** or ***elementary reactions***.

The sequence of ***elementary steps*** that leads to product formation is the ***reaction mechanism***.

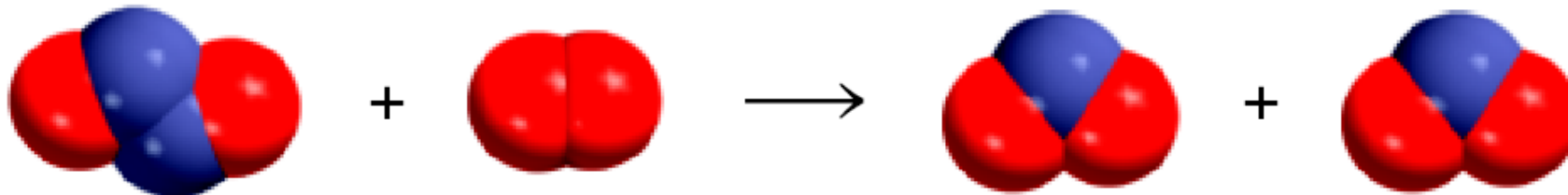
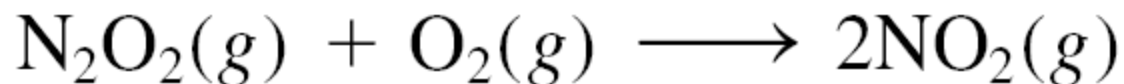
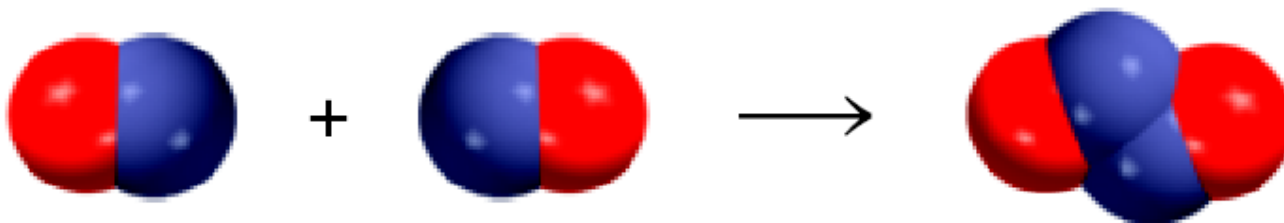
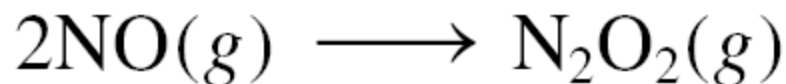


N_2O_2 is detected during the reaction!



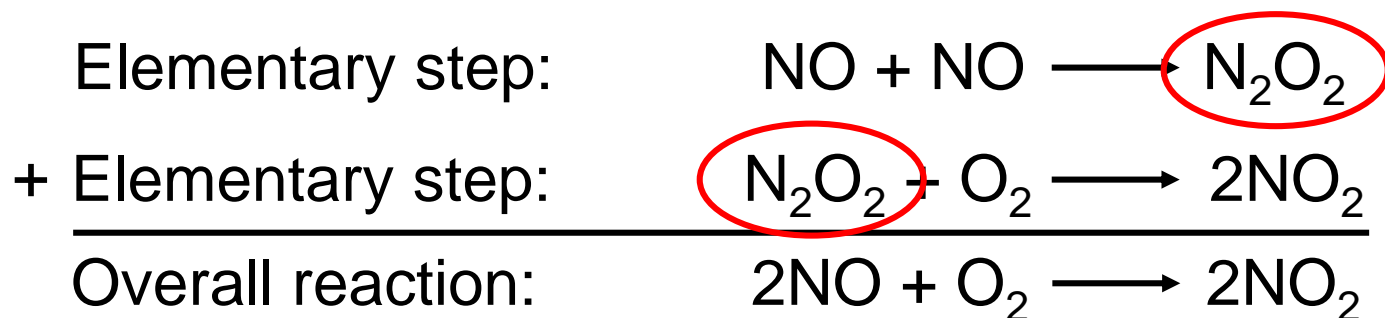


Mechanism:



Intermediates are species that appear in a reaction mechanism **but not** in the overall balanced equation.

An **intermediate** is always formed in an early elementary step and consumed in a later elementary step.



The **molecularity of a reaction** is the number of molecules reacting in an elementary step.

- **Unimolecular reaction** – elementary step with 1 molecule
- **Bimolecular reaction** – elementary step with 2 molecules
- **Termolecular reaction** – elementary step with 3 molecules

Rate Laws and Elementary Steps

Unimolecular reaction $A \longrightarrow \text{products}$ $\text{rate} = k [A]$

Bimolecular reaction $A + B \longrightarrow \text{products}$ $\text{rate} = k [A][B]$

Bimolecular reaction $A + A \longrightarrow \text{products}$ $\text{rate} = k [A]^2$

Writing plausible reaction mechanisms:

- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

The ***rate-determining step*** is the **slowest** step in the sequence of steps leading to product formation.

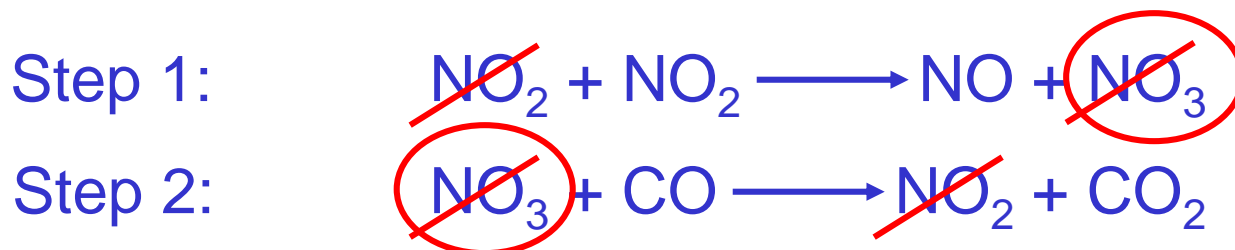
Sequence of Steps in Studying a Reaction Mechanism

Measuring
the rate of
a reaction

Formulating
the rate law

Postulating
a reasonable
reaction
mechanism

The experimental rate law for the reaction between NO_2 and CO to produce NO and CO_2 is $\text{rate} = k[\text{NO}_2]^2$. The reaction is believed to occur via two steps:



What is the equation for the overall reaction?



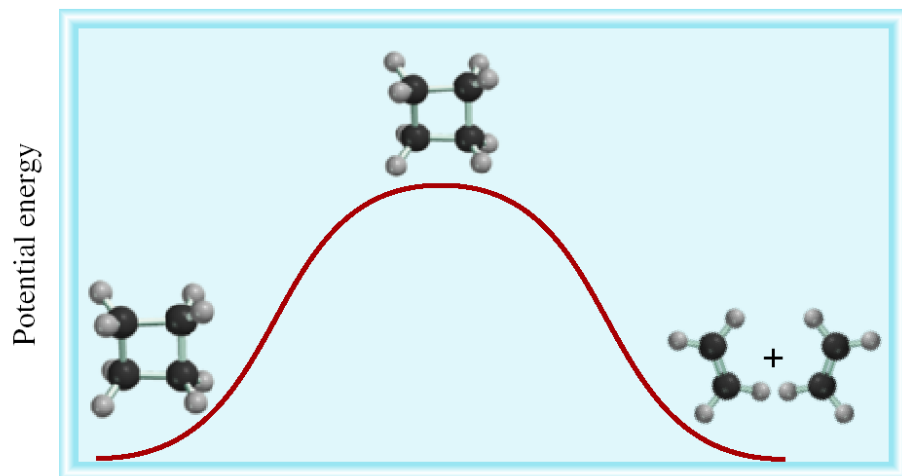
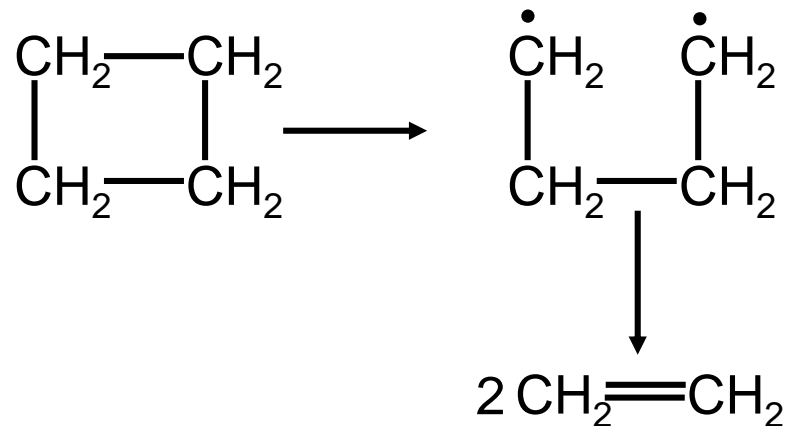
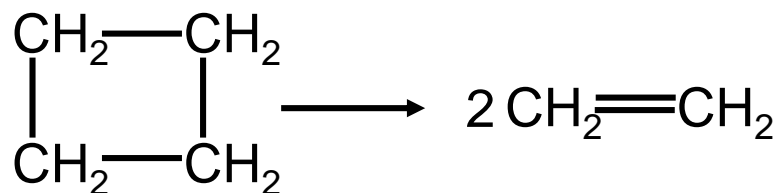
What is the intermediate?



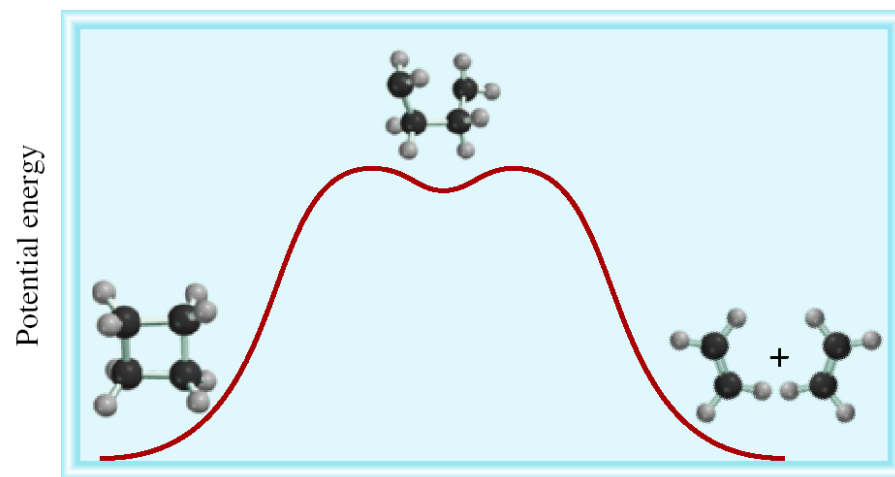
What can you say about the relative rates of steps 1 and 2?

$\text{rate} = k[\text{NO}_2]^2$ is the rate law for step 1 so
step 1 must be slower than step 2

Chemistry In Action: Femtochemistry



Reaction progress



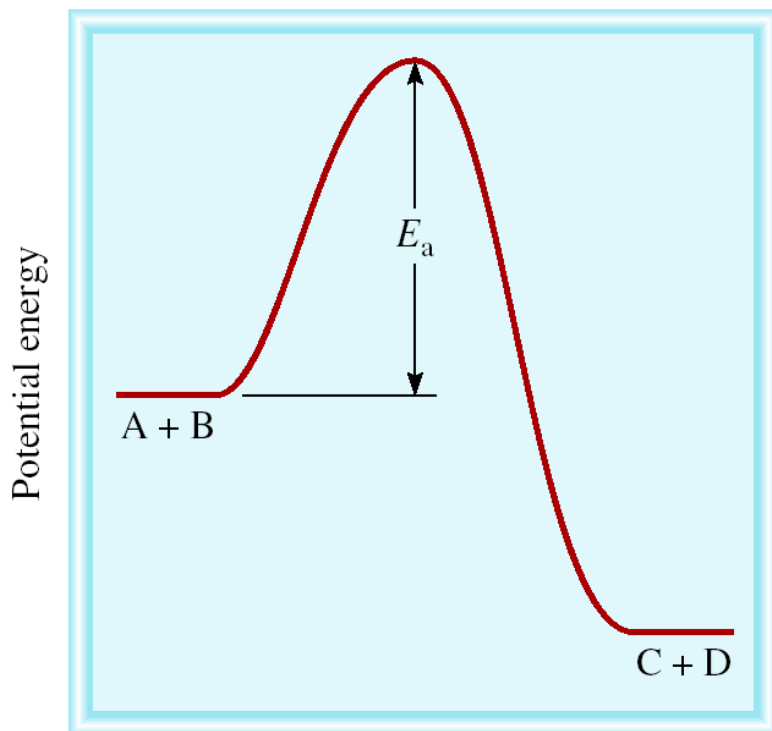
Reaction progress

A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

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

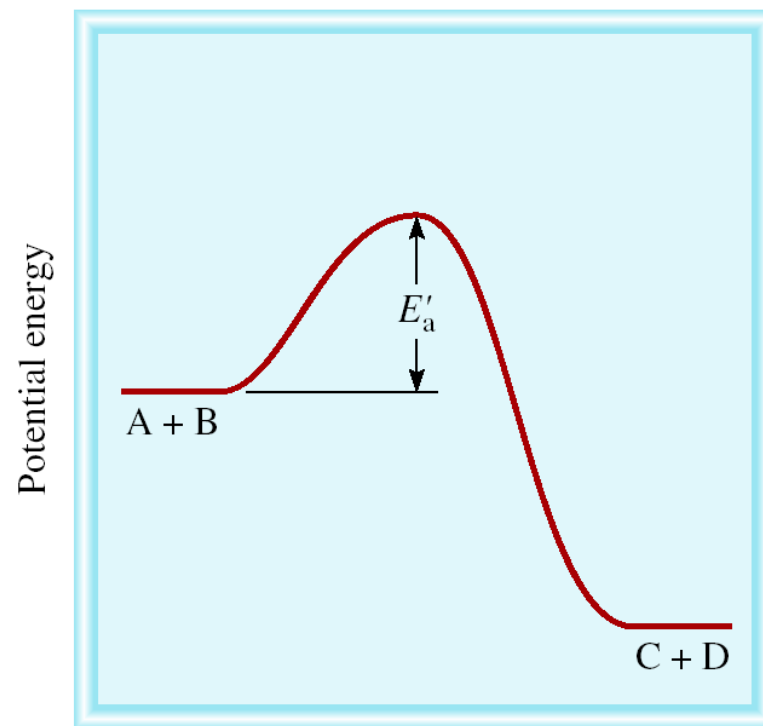
$$E_a \downarrow \quad k \uparrow$$

Uncatalyzed



Reaction progress

Catalyzed



Reaction progress

$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

$$E'_a < E_a$$

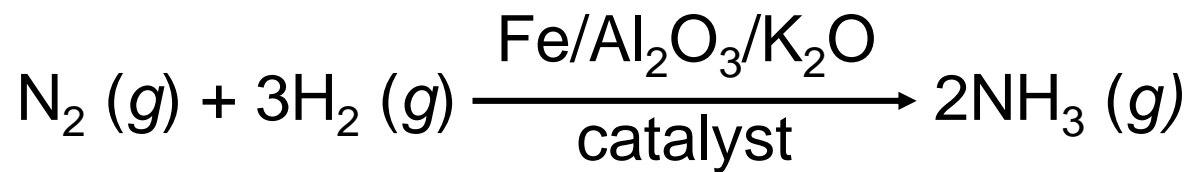
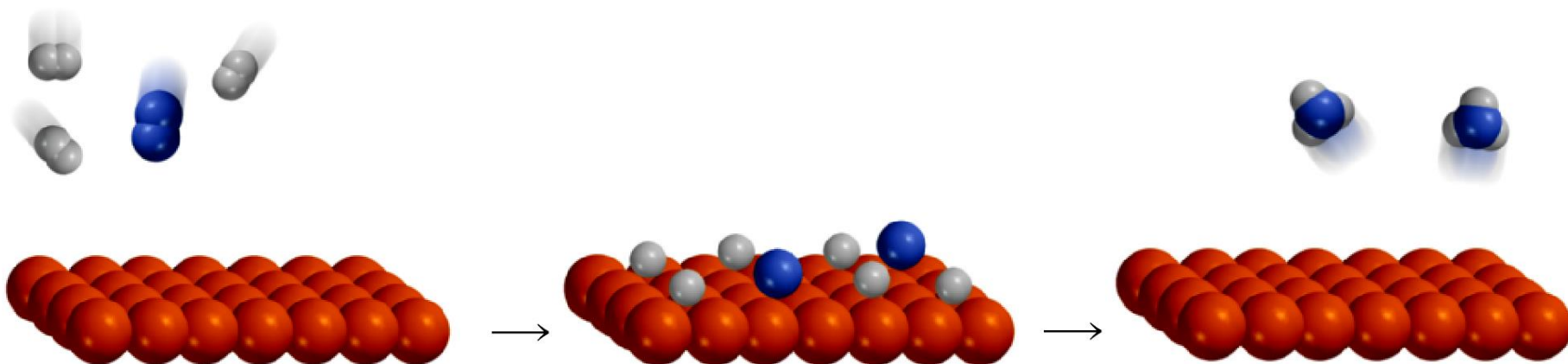
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

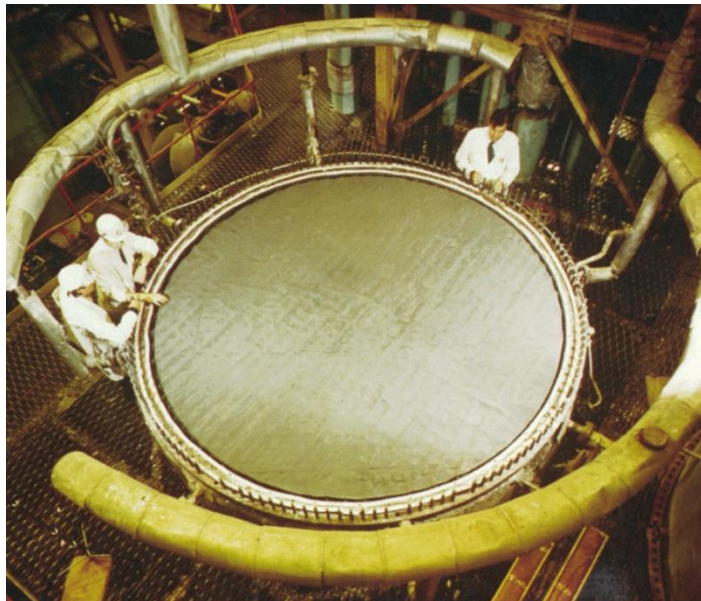
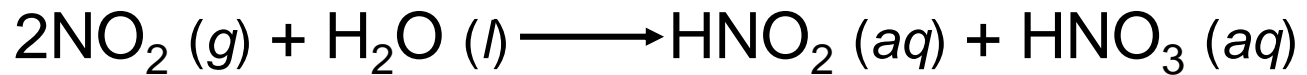
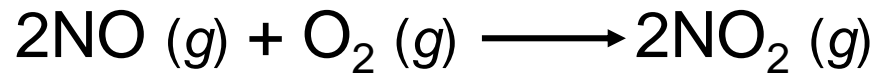
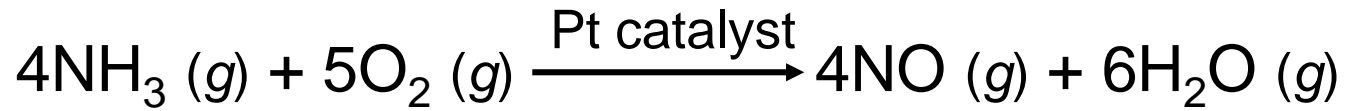
In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

Haber Process

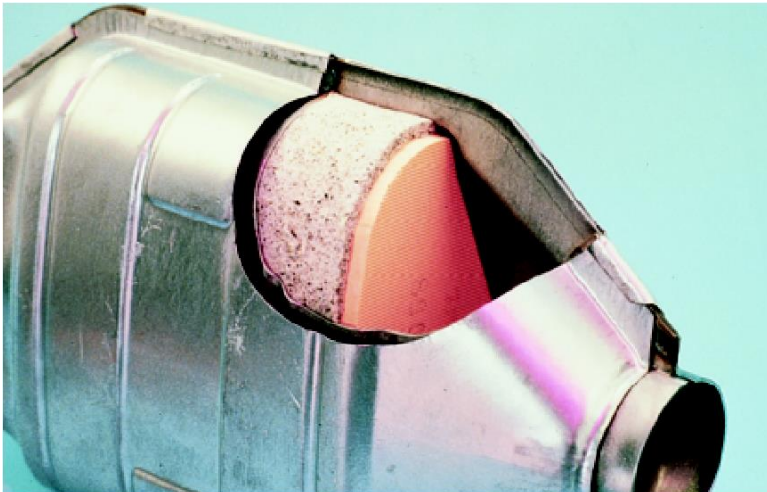
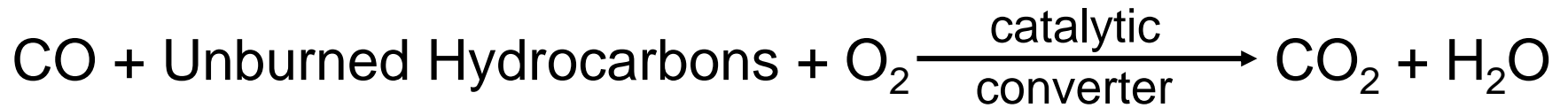
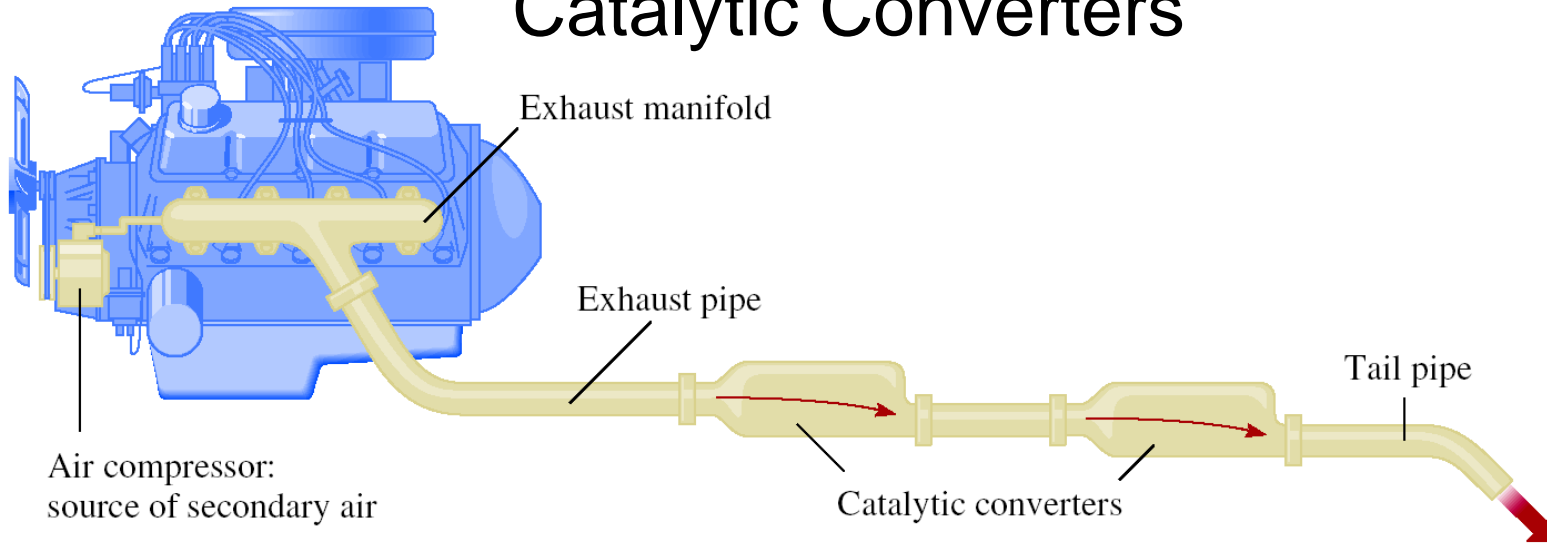


Ostwald Process

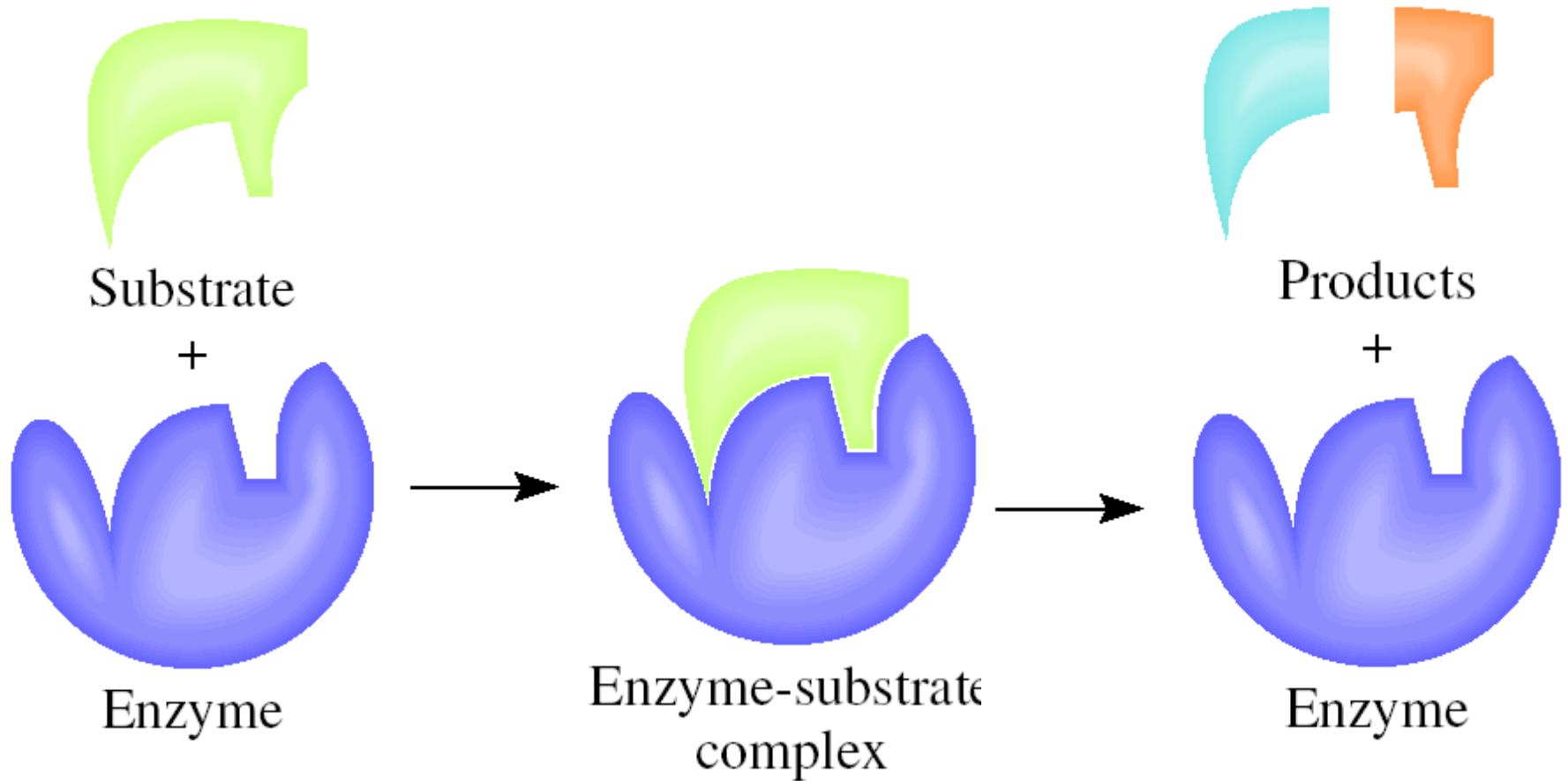


Pt-Rh catalysts used
in Ostwald process

Catalytic Converters



Enzyme Catalysis



Binding of Glucose to Hexokinase

