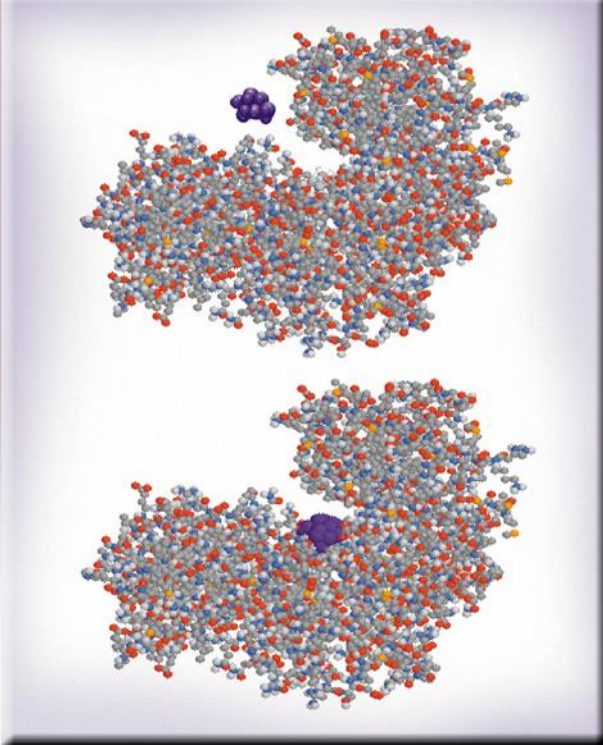
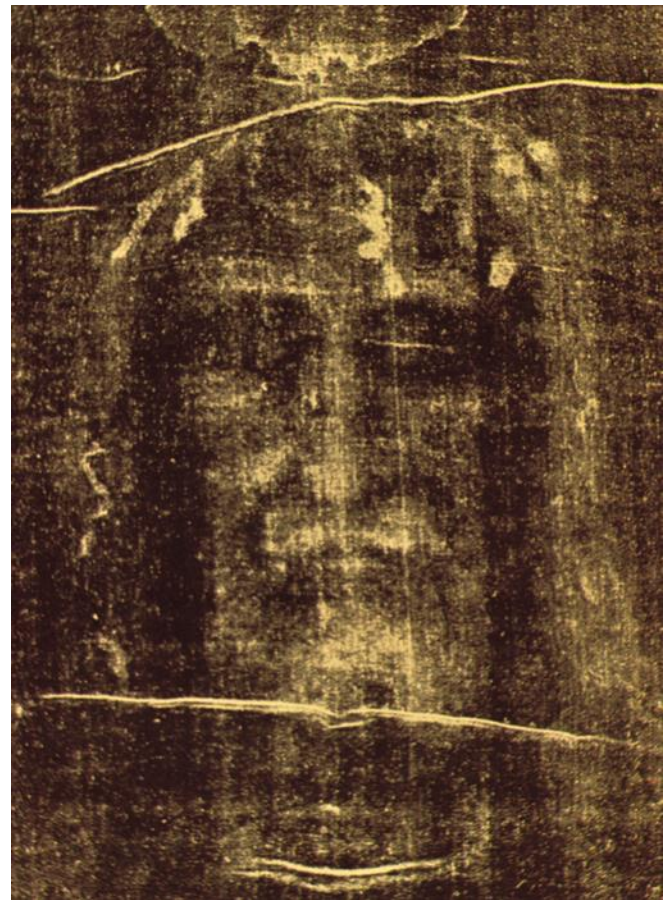




Chemical Kinetics

Chapter 13



Chemical Kinetics

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).



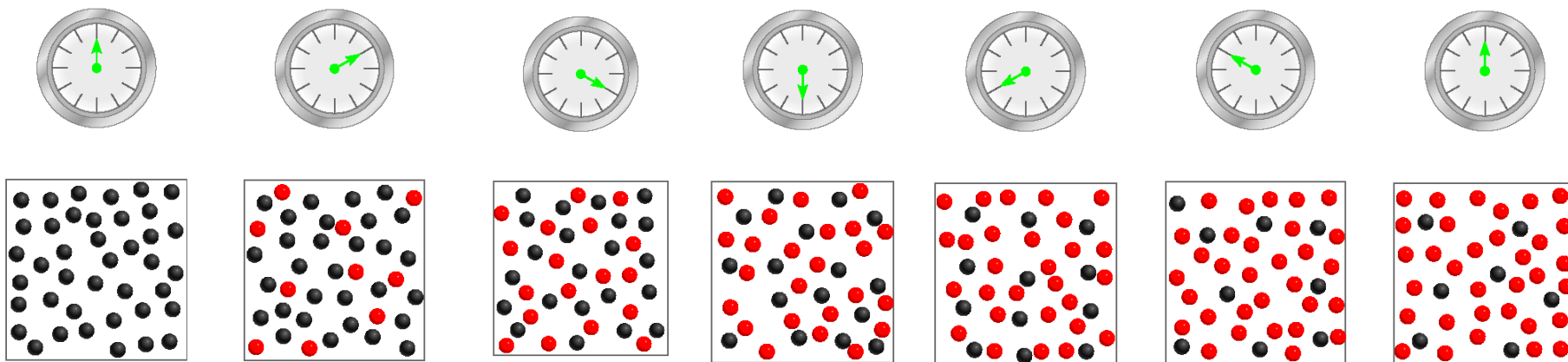
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

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

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

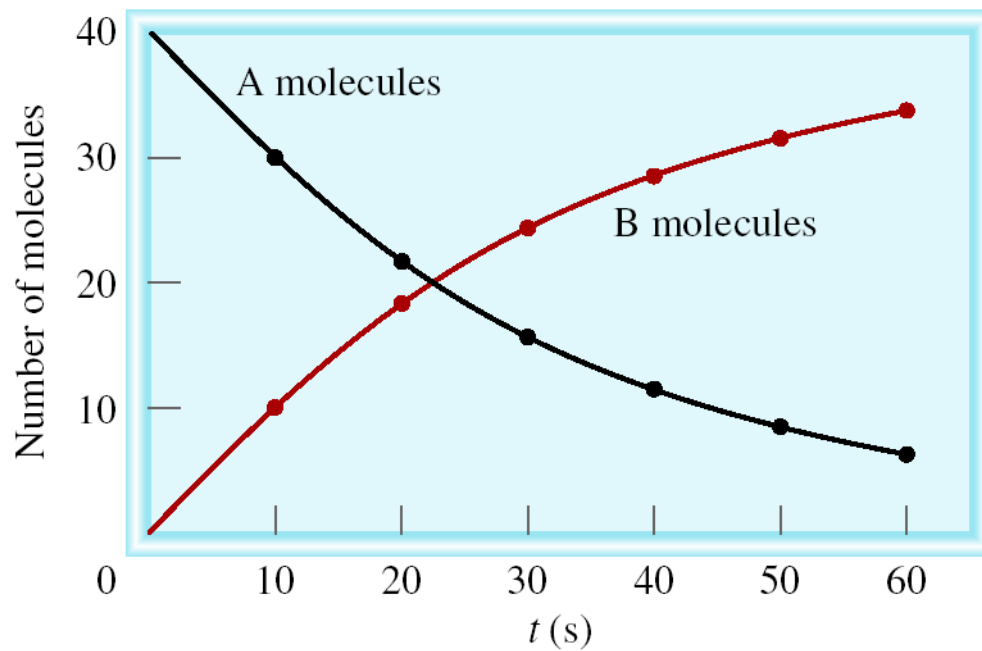
$\Delta[B]$ = change in concentration of B over time period Δt

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

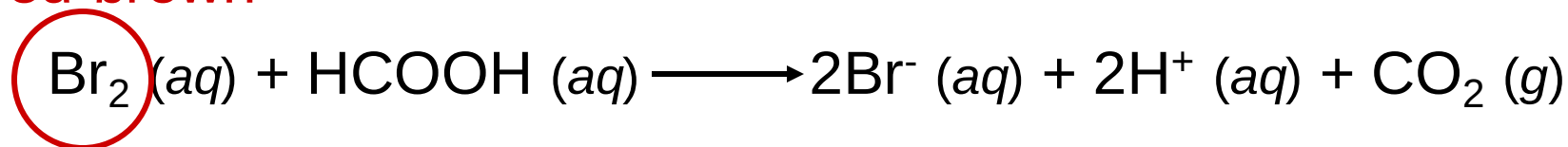


$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

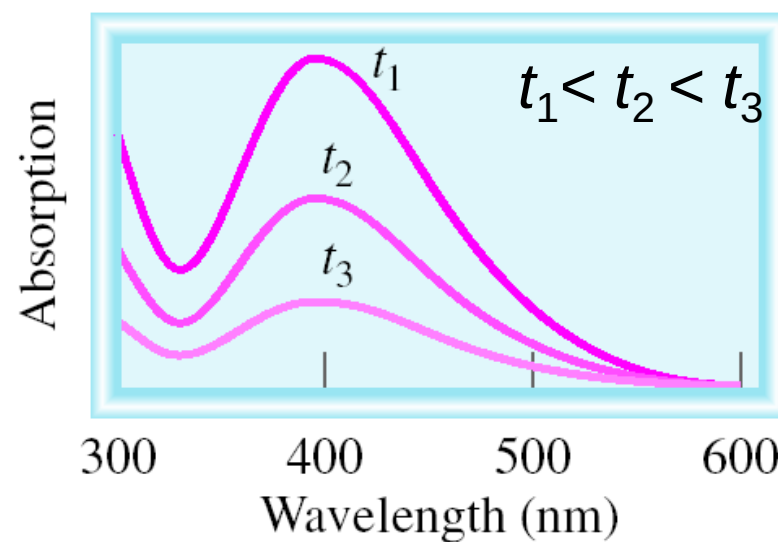
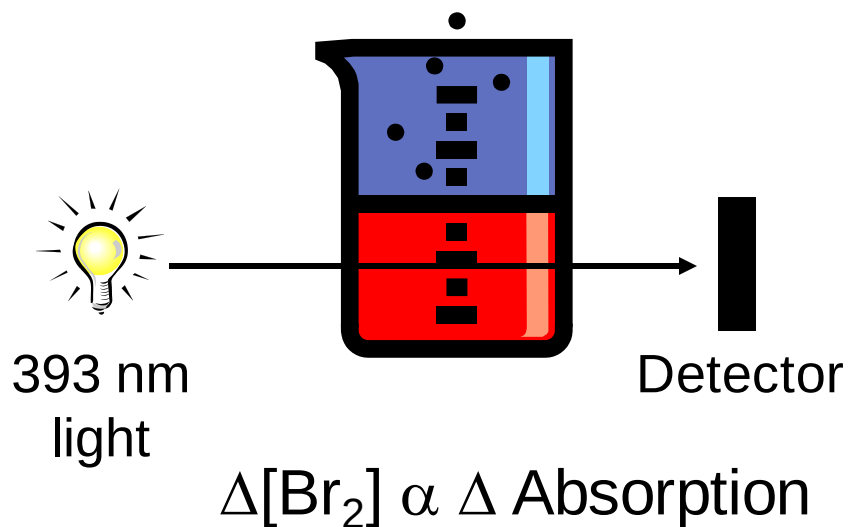
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

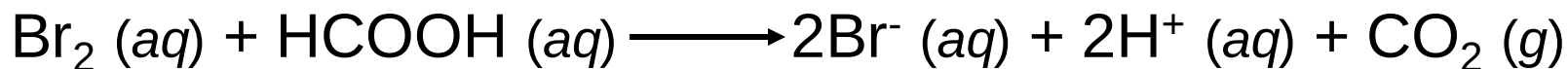


red-brown

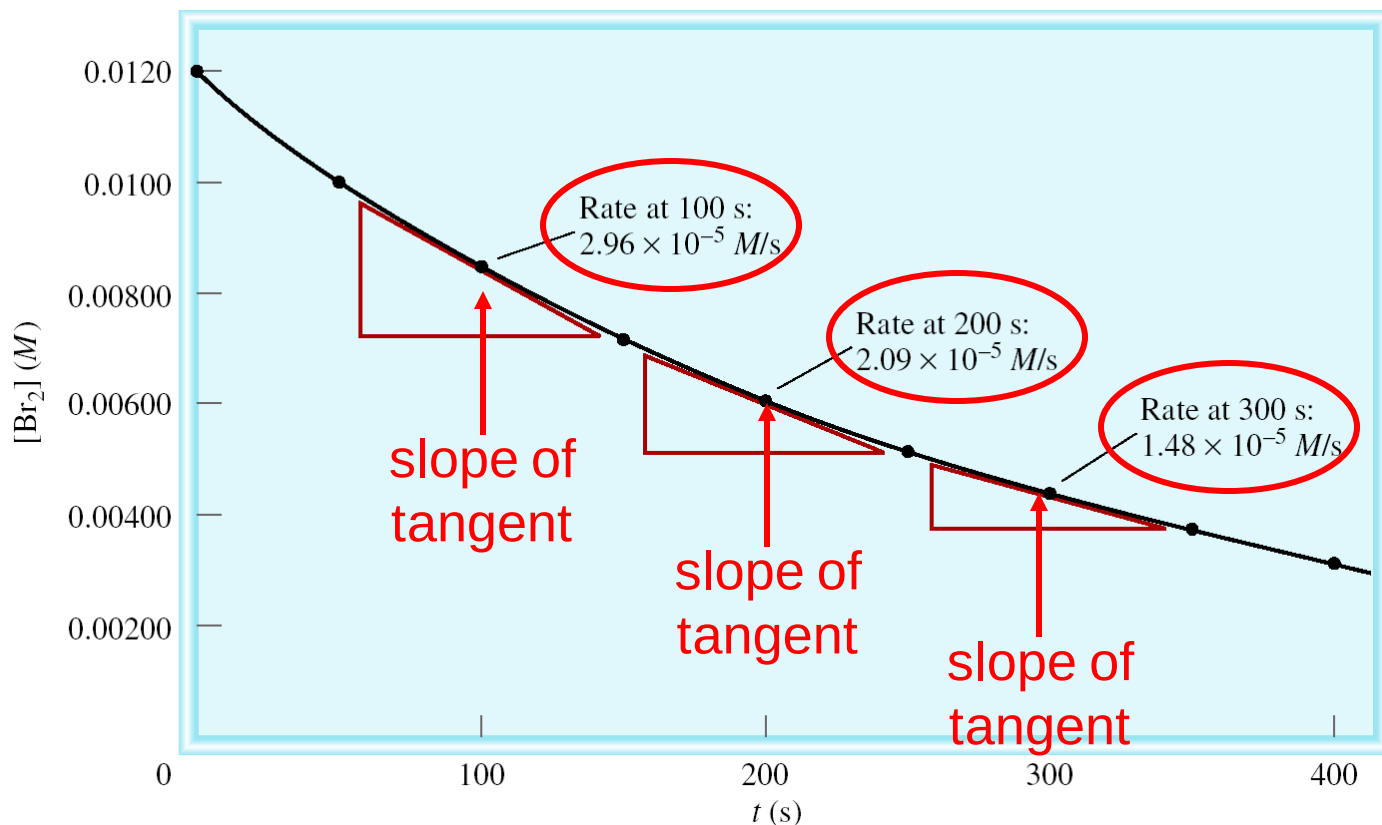


time





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

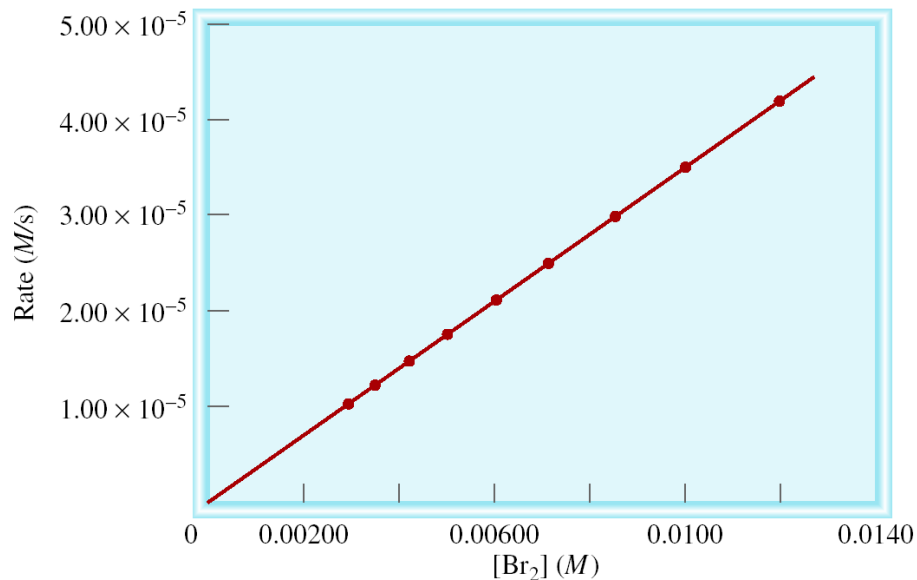
Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500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

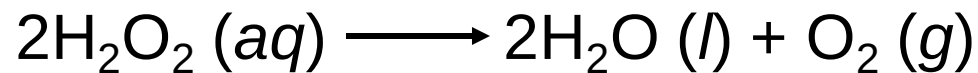
$$\text{rate} \propto [\text{Br}_2]$$

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

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

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





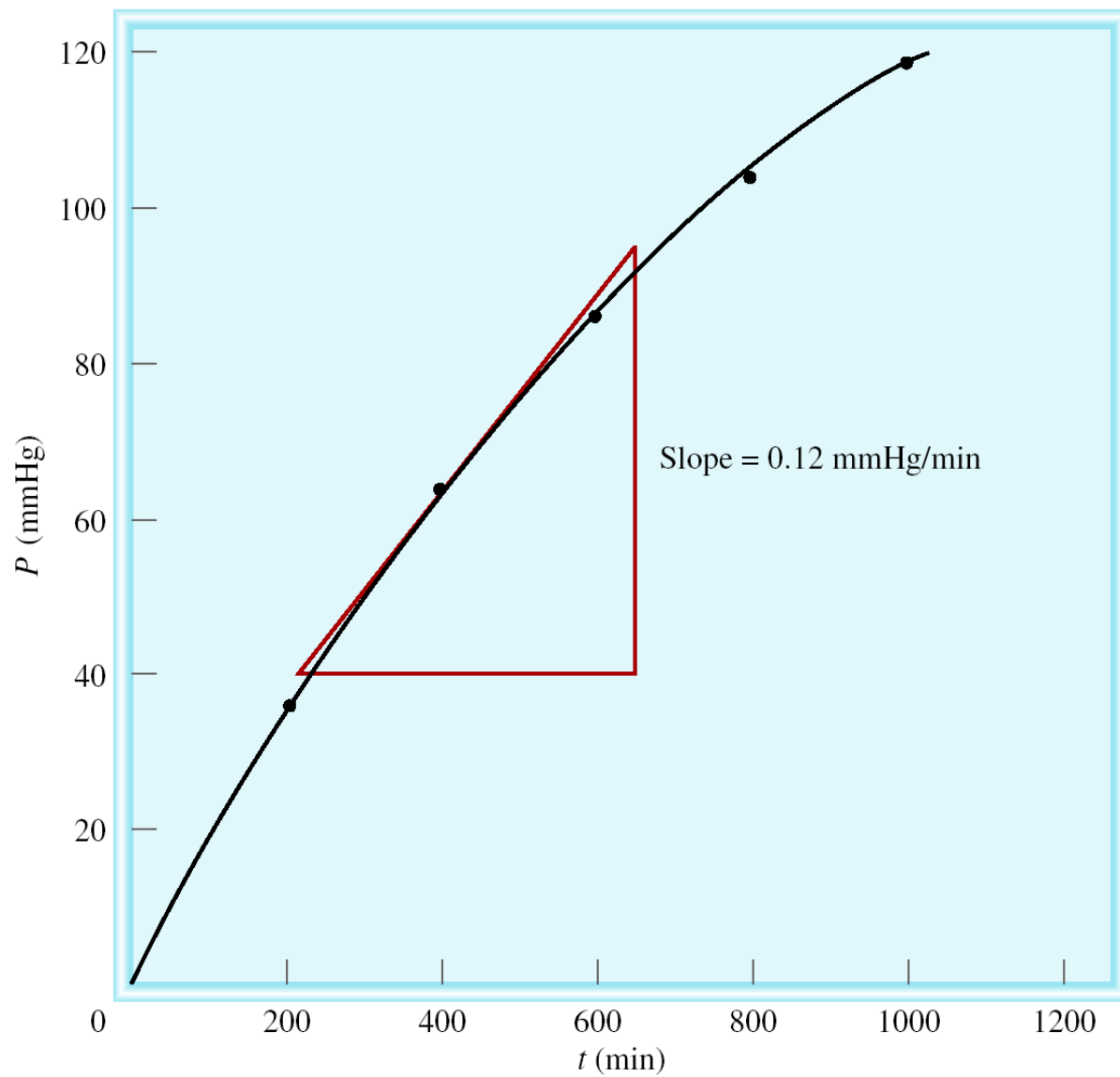
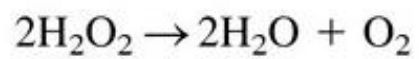
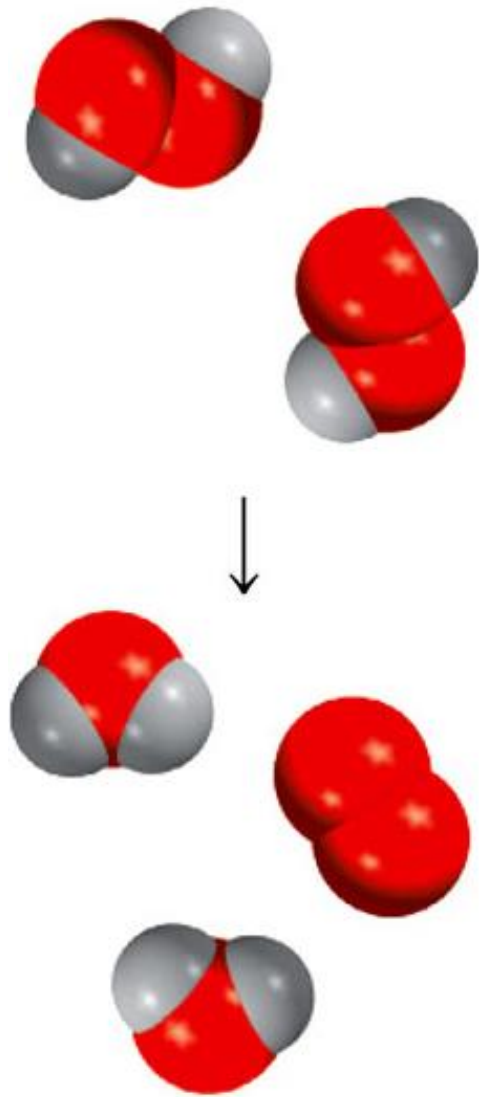
$$PV = nRT$$

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

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

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

measure ΔP over time



Reaction Rates and Stoichiometry



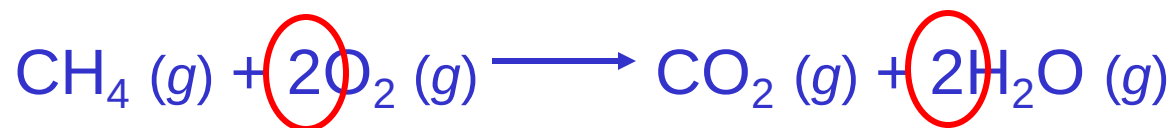
Two moles of A disappear for each mole of B that is formed.

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



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

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**

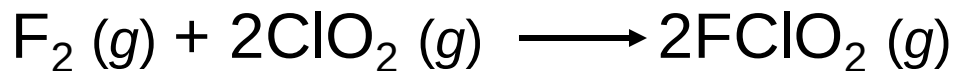


TABLE 13.2 Rate Data for the Reaction Between F_2 and ClO_2

$[\text{F}_2] \text{ (M)}$	$[\text{ClO}_2] \text{ (M)}$	Initial Rate (M/s)
1. 0.10	0.010	1.2×10^{-5}
2. 0.10	0.040	4.8×10^{-5}
3. 0.20	0.010	2.4×10^{-5}

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

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

Rate doubles

$$x = 1$$

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

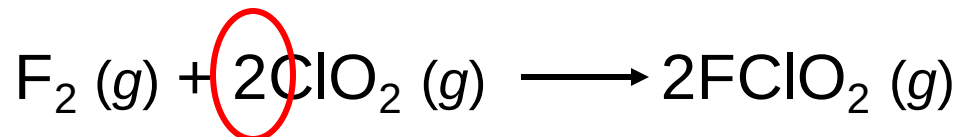
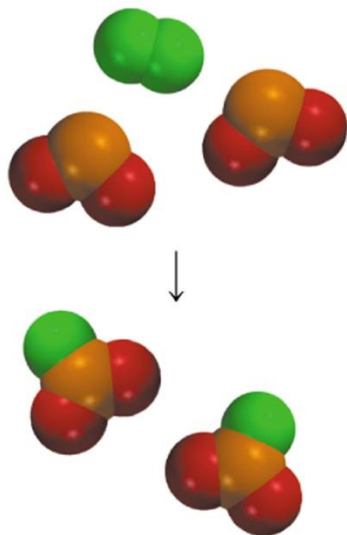
Rate quadruples

$$y = 1$$

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

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}

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

$$y = 1$$

$$x = 1$$

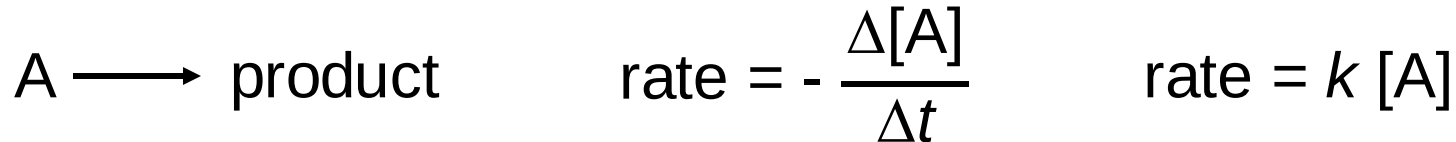
$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

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

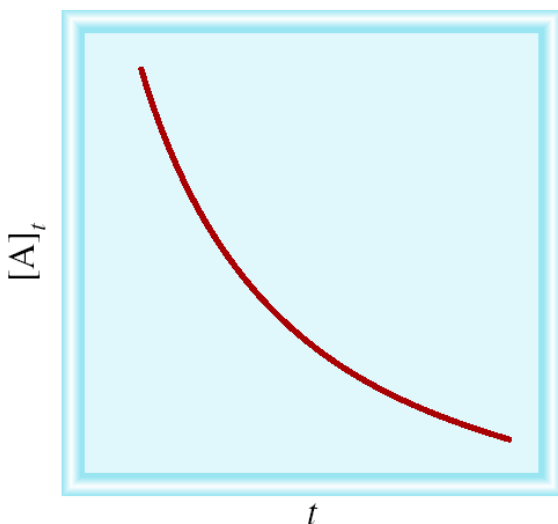


$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1} \quad - \frac{\Delta[A]}{\Delta t} = k [A]$$

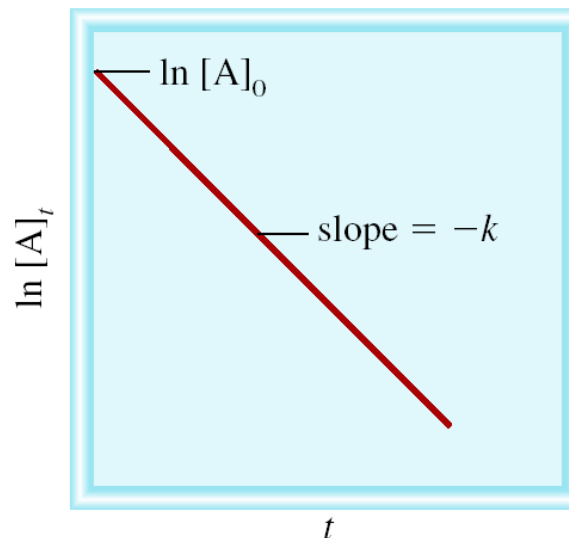
$[A]$ is the concentration of A at any time t

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

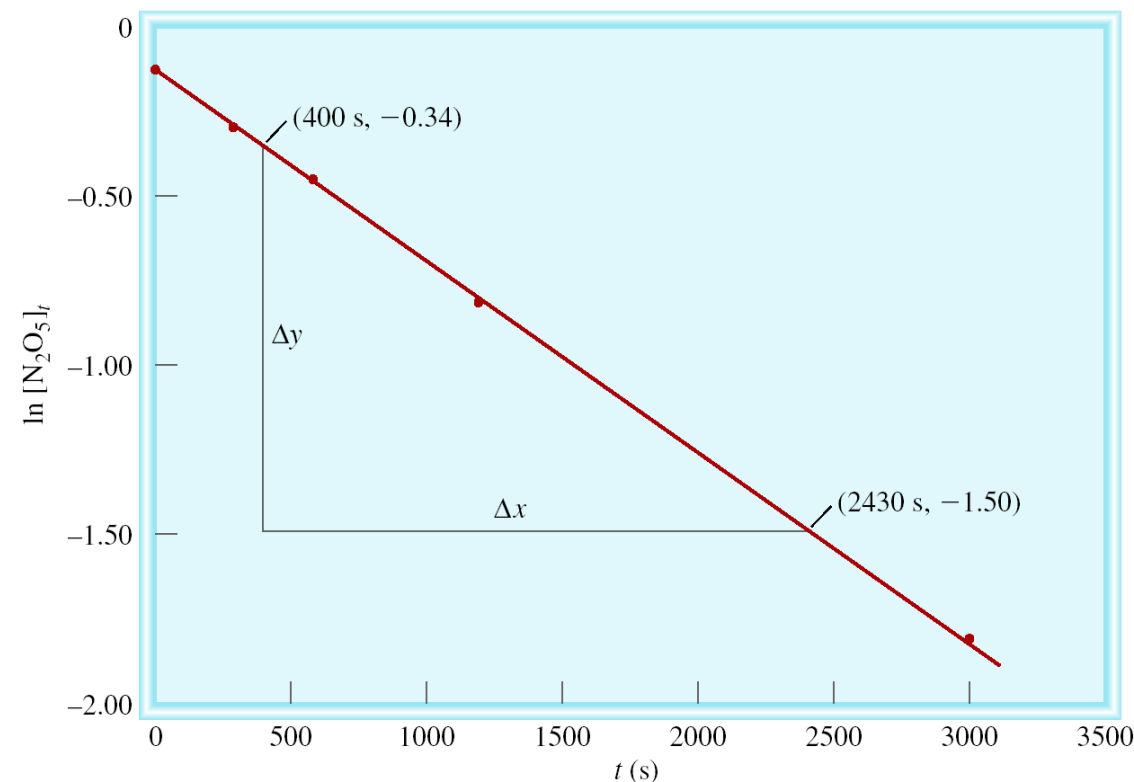
$$[A] = [A]_0 e^{-kt}$$



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



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.

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

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

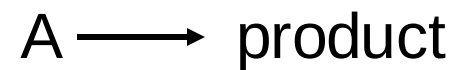
What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

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

How do you know decomposition is first order?

units of k (s^{-1}) ¹⁸

First-order reaction



of
half-lives $[A] = [A]_0/n$

1

2

2

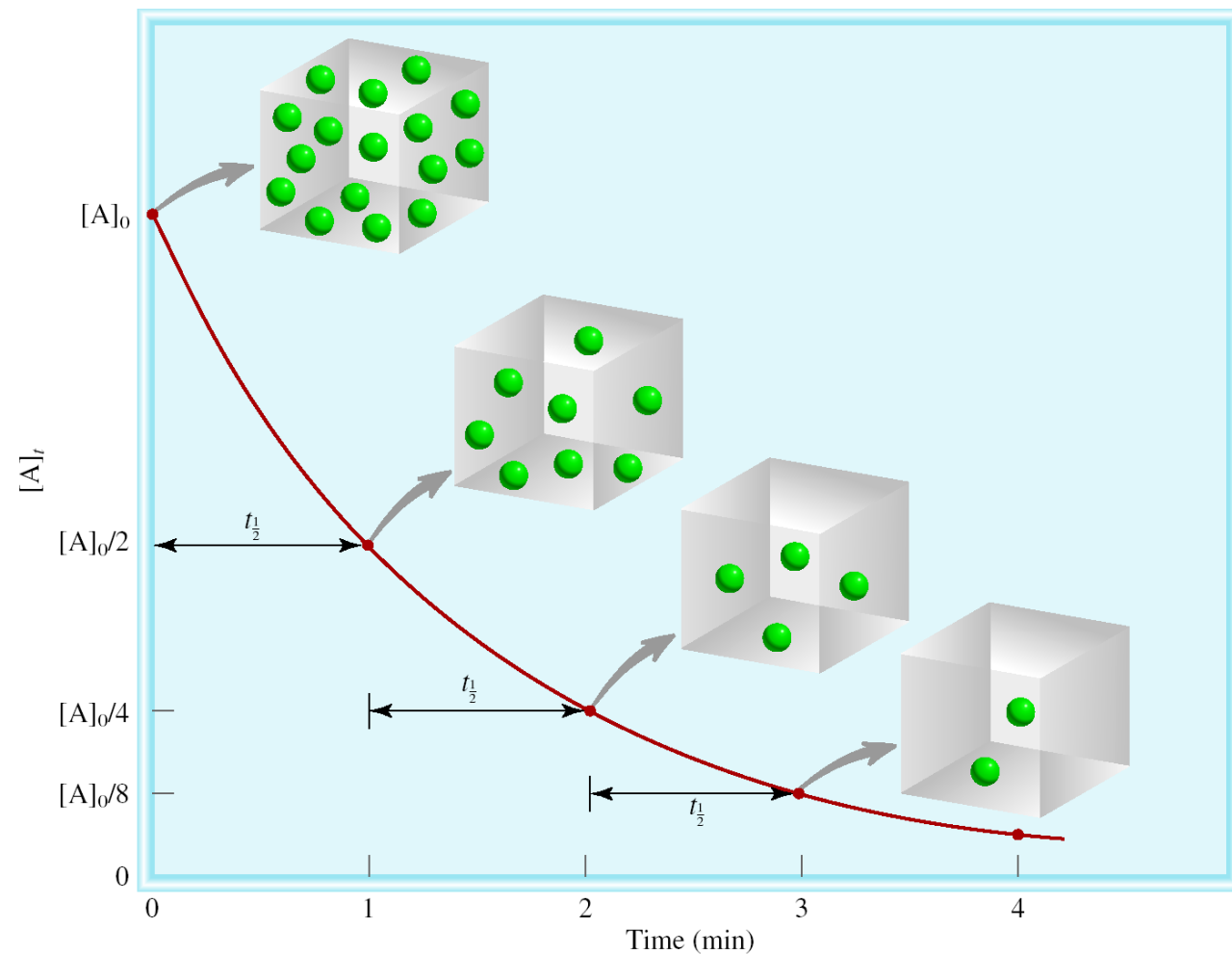
4

3

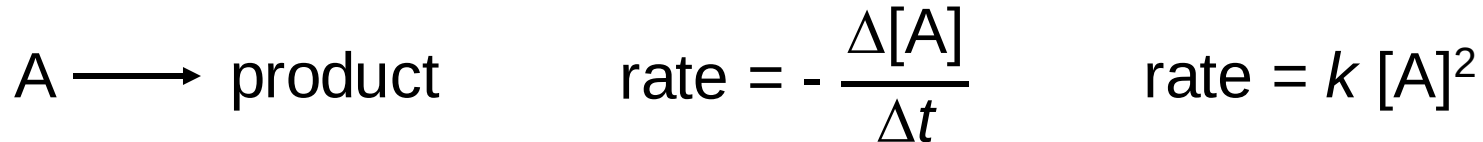
8

4

16



Second-Order Reactions



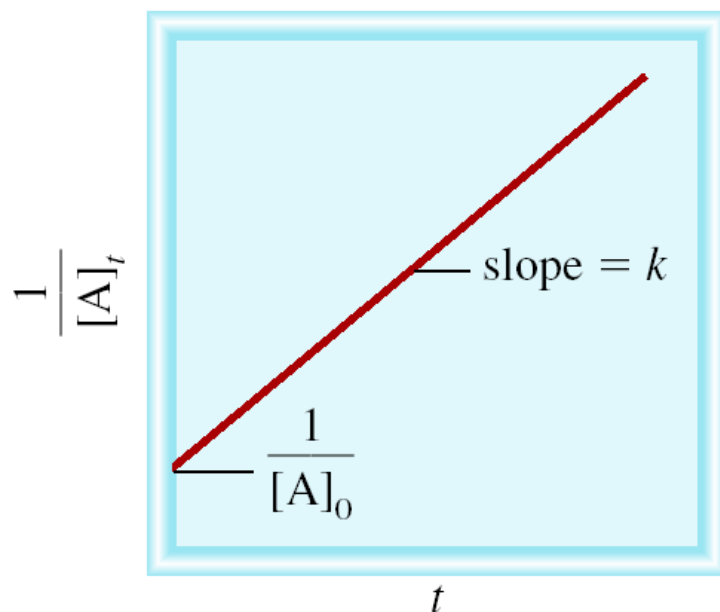
$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M \cdot s \quad - \frac{\Delta[A]}{\Delta t} = k [A]^2$$

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

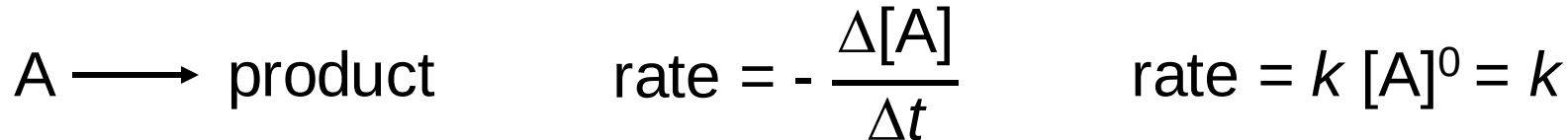
$[A]$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t=0$

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

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



Zero-Order Reactions



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

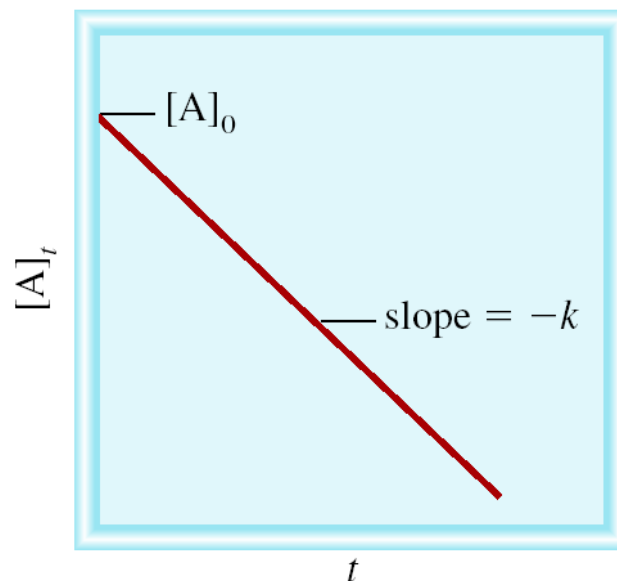
$$- \frac{\Delta[A]}{\Delta t} = k$$

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

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

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

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

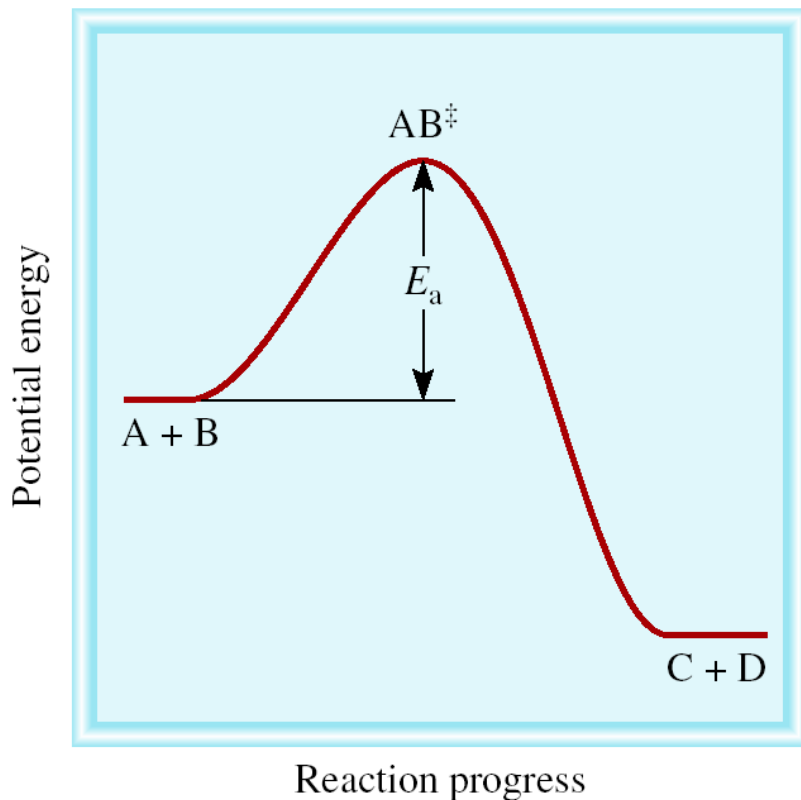


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

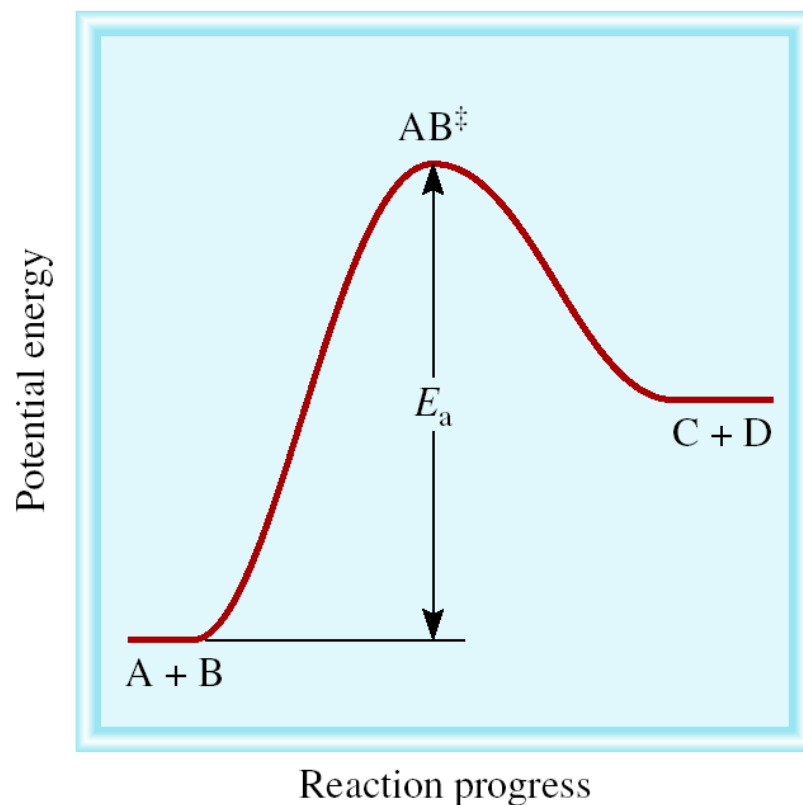
Order	Rate Law	Concentration-Time	
		Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k [A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$



Exothermic Reaction

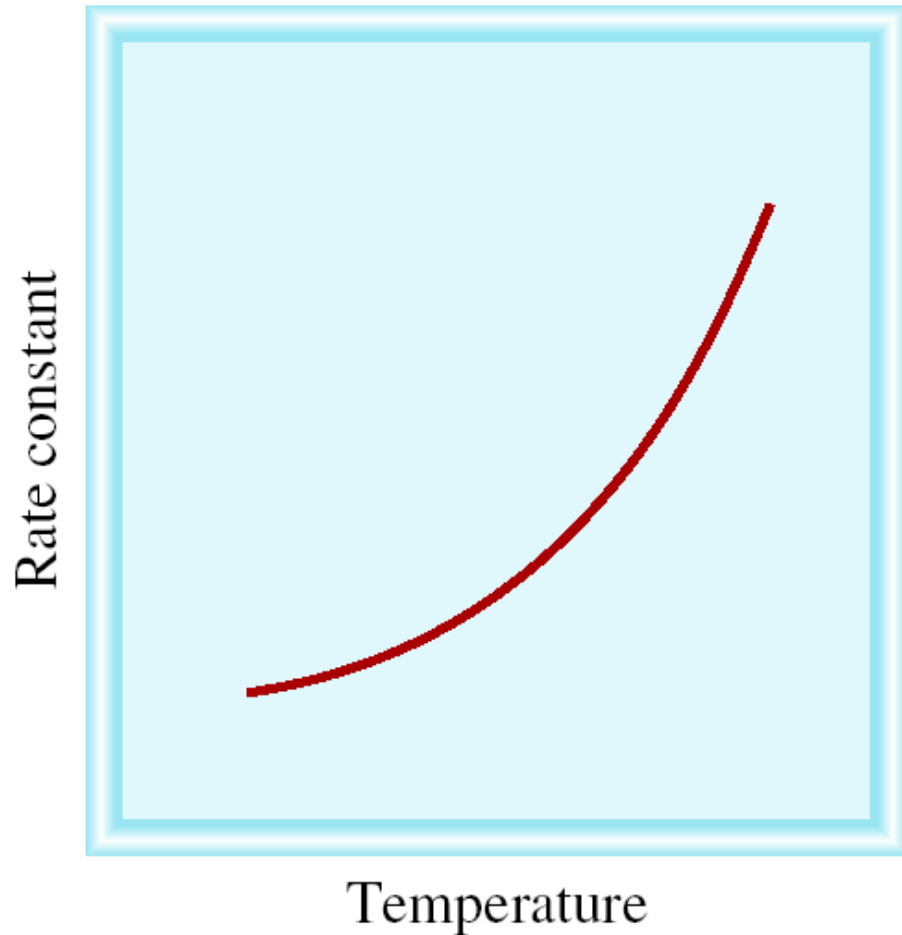


Endothermic Reaction



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

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:

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

Alternate Form of the Arrhenius Equation

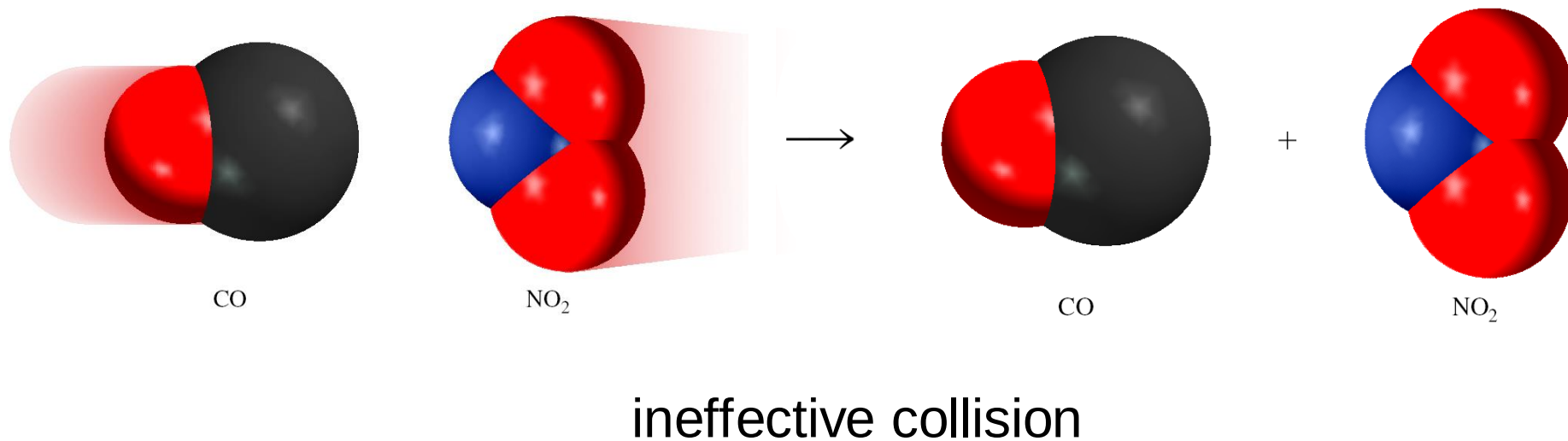
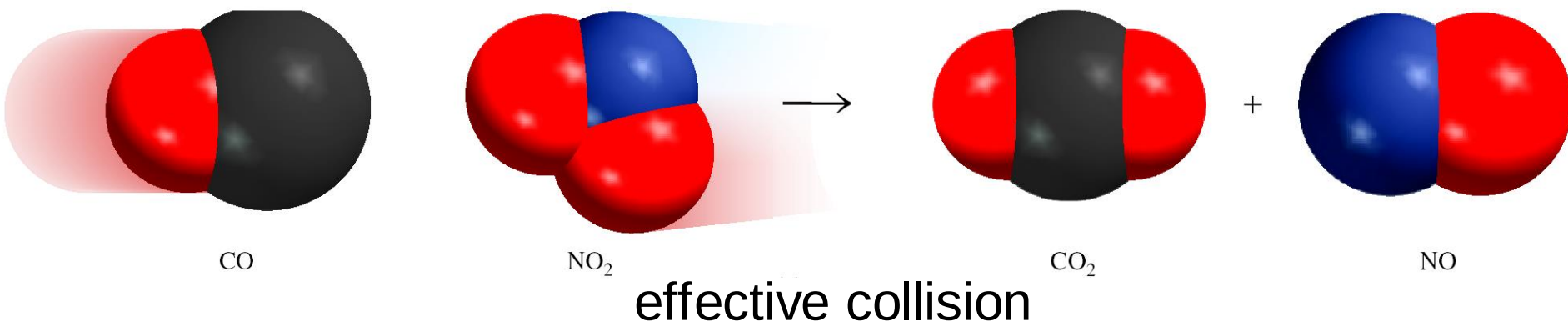
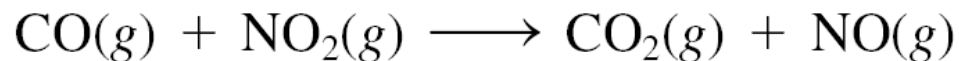
At two temperatures, T_1 and T_2

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

or

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

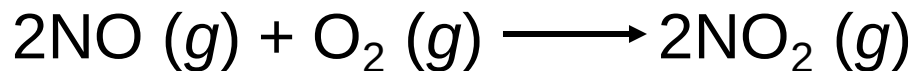
Importance of Molecular Orientation



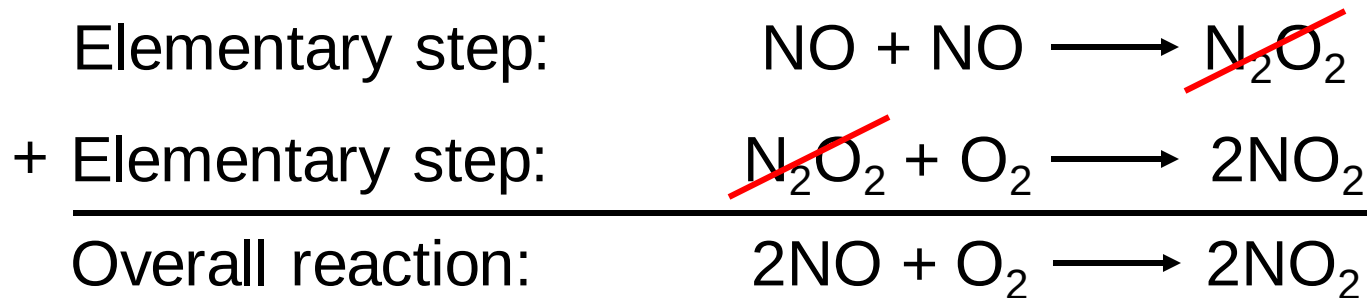
Reaction Mechanisms

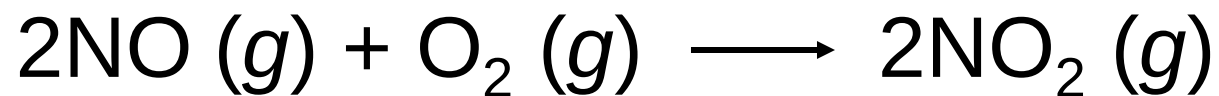
The overall progress of a chemical reaction can be represented at the molecular level by a series of simple ***elementary steps*** or ***elementary reactions***.

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

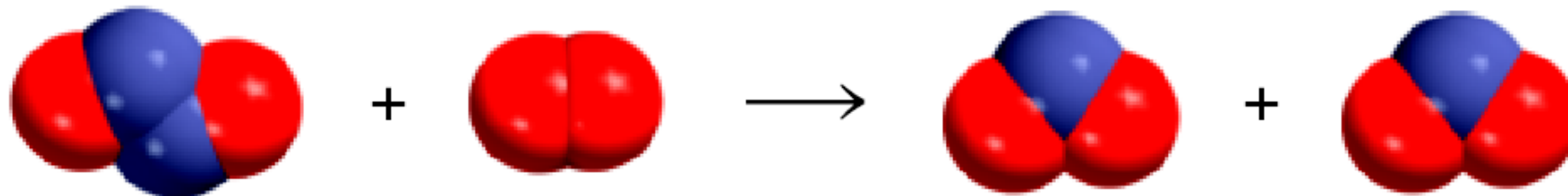
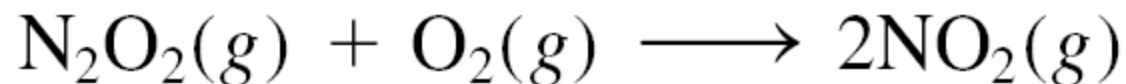
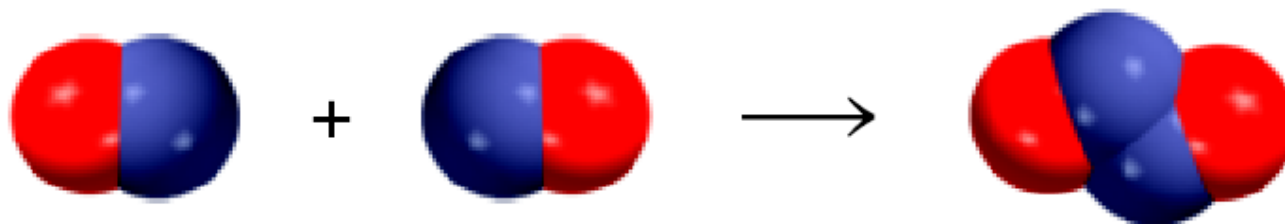
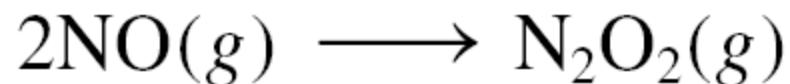


N_2O_2 is detected during the reaction!



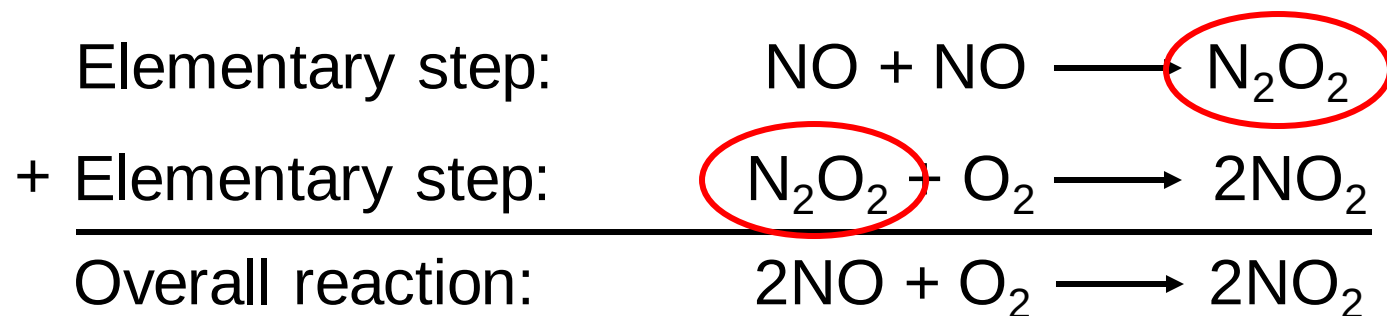


Mechanism:



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.

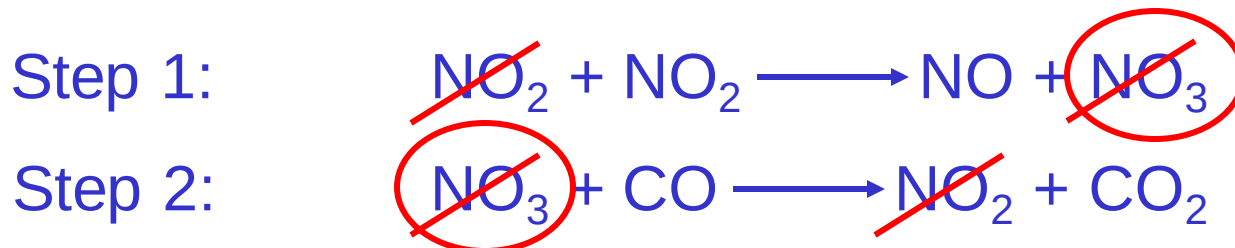
Sequence of Steps in Studying a Reaction Mechanism

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?



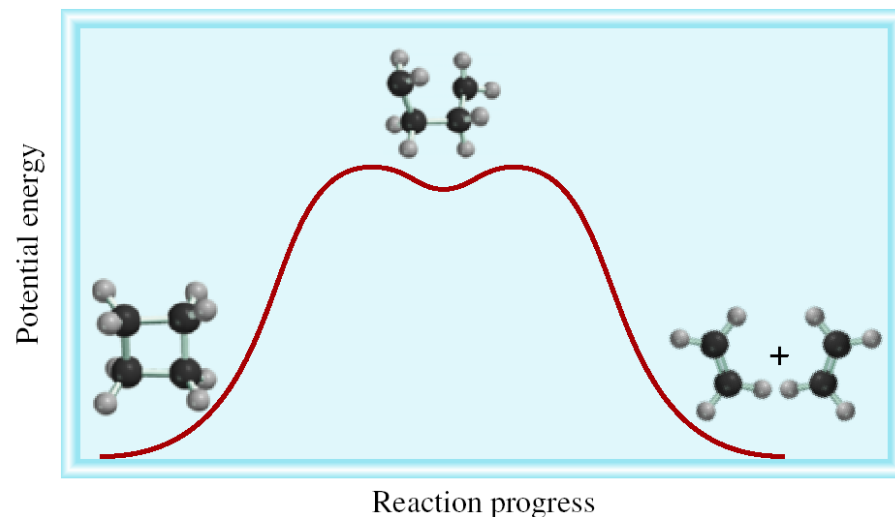
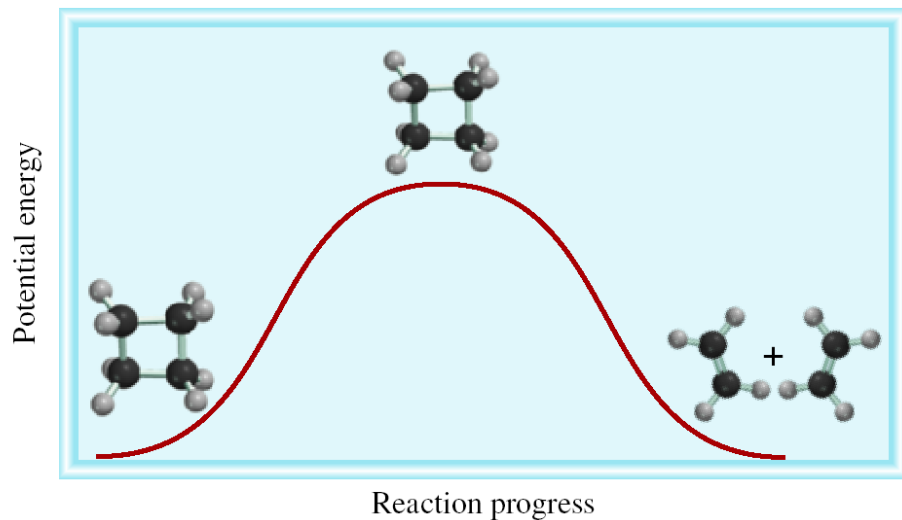
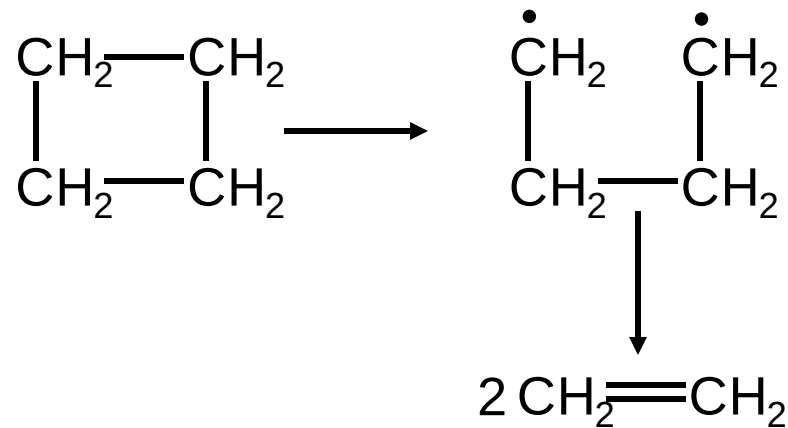
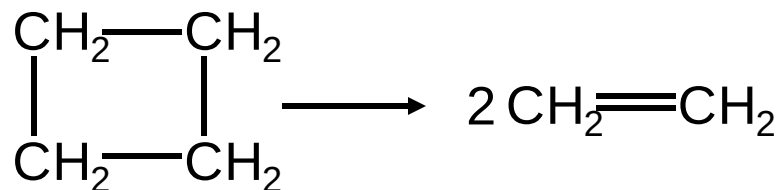
What is the intermediate?



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



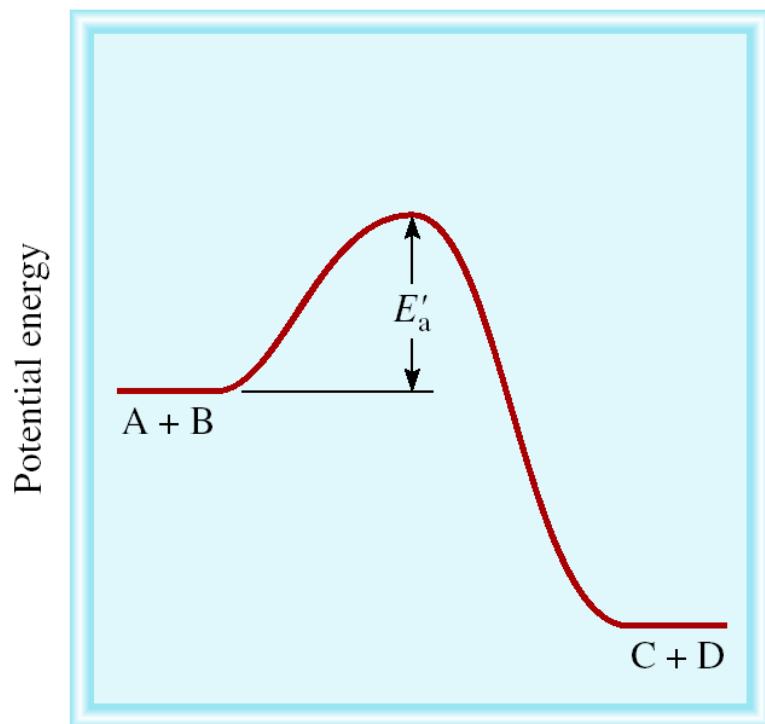
A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

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

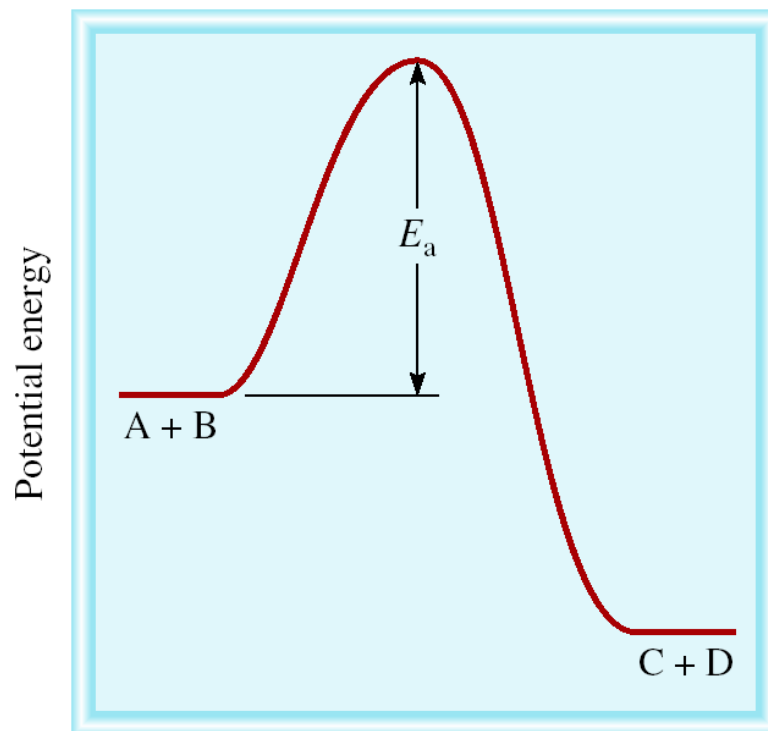
Uncatalyzed

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

Catalyzed



Reaction progress



Reaction progress

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

$$E'_a < E_a$$

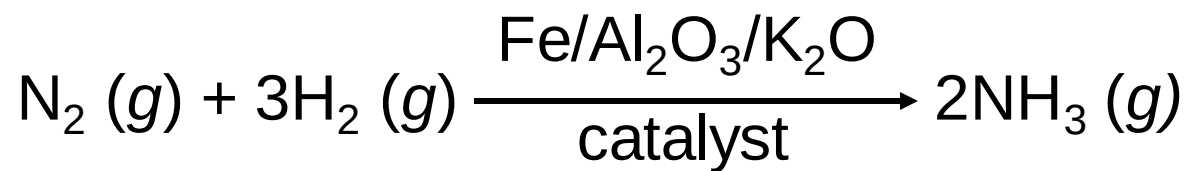
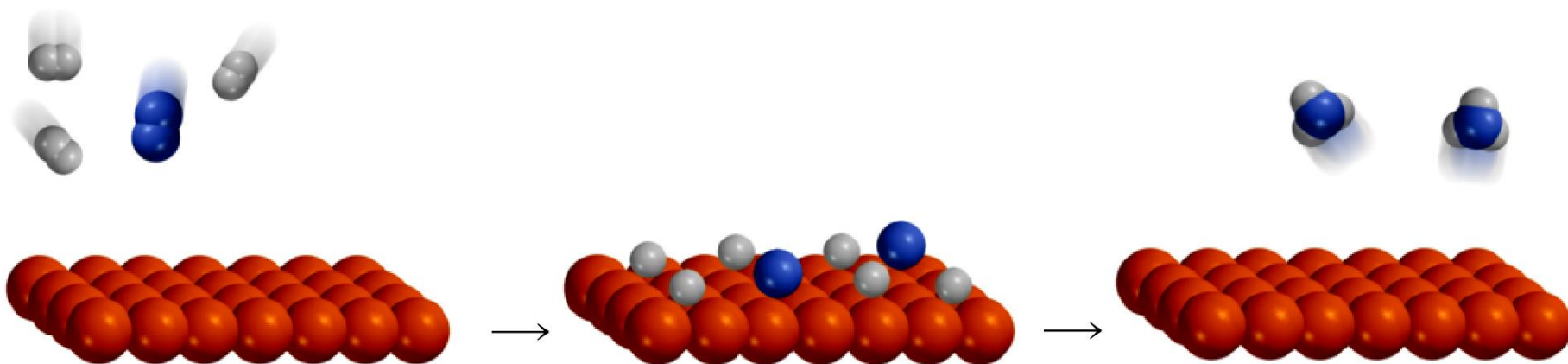
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

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

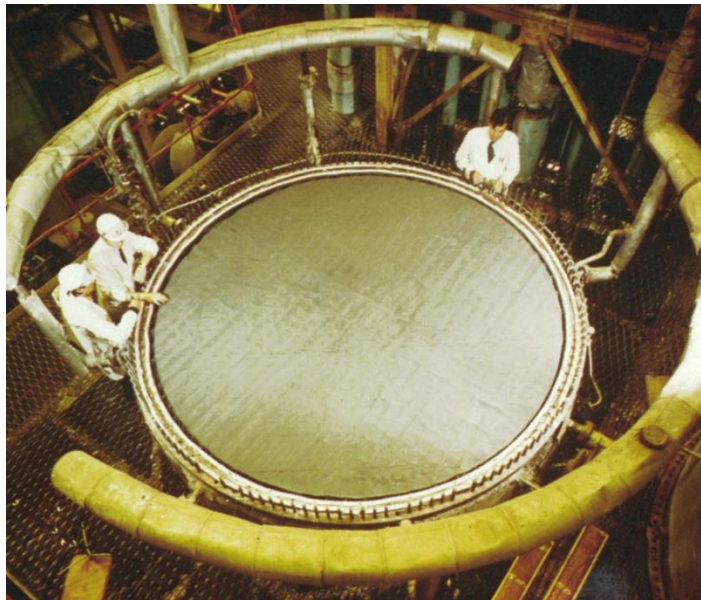
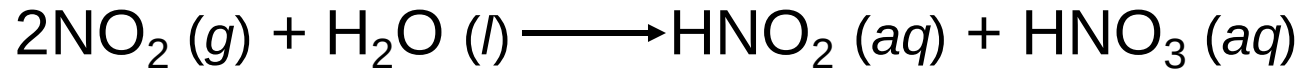
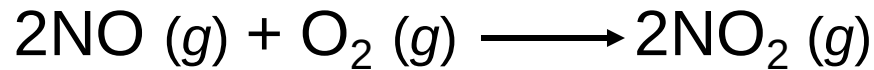
In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

Haber Process

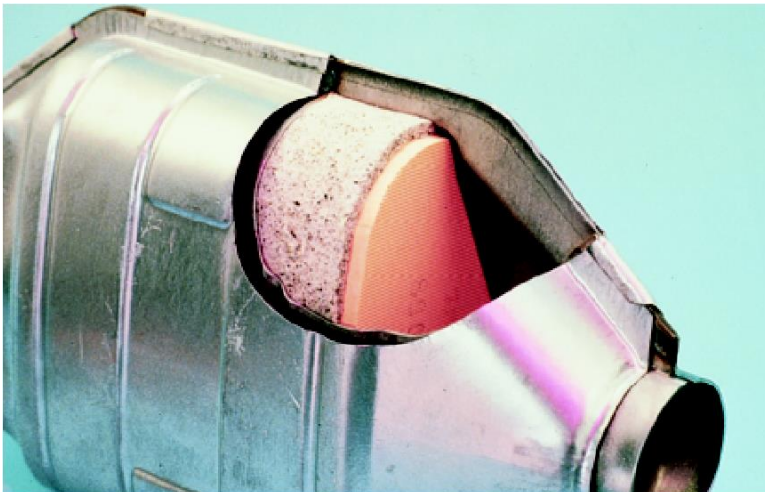
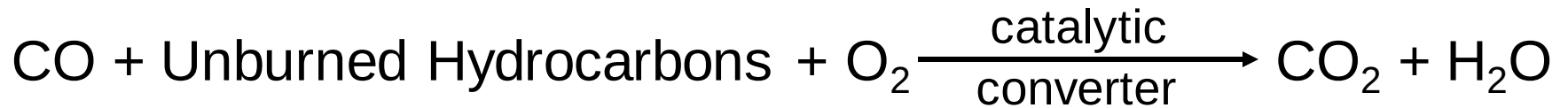
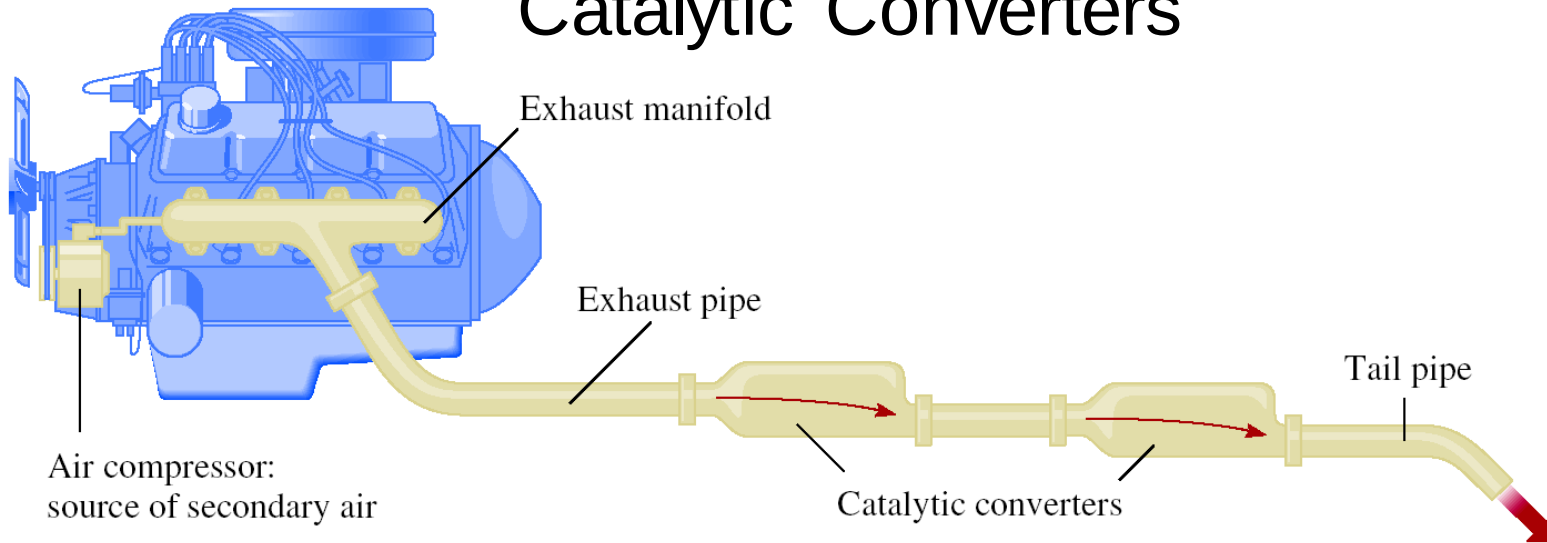


Ostwald Process

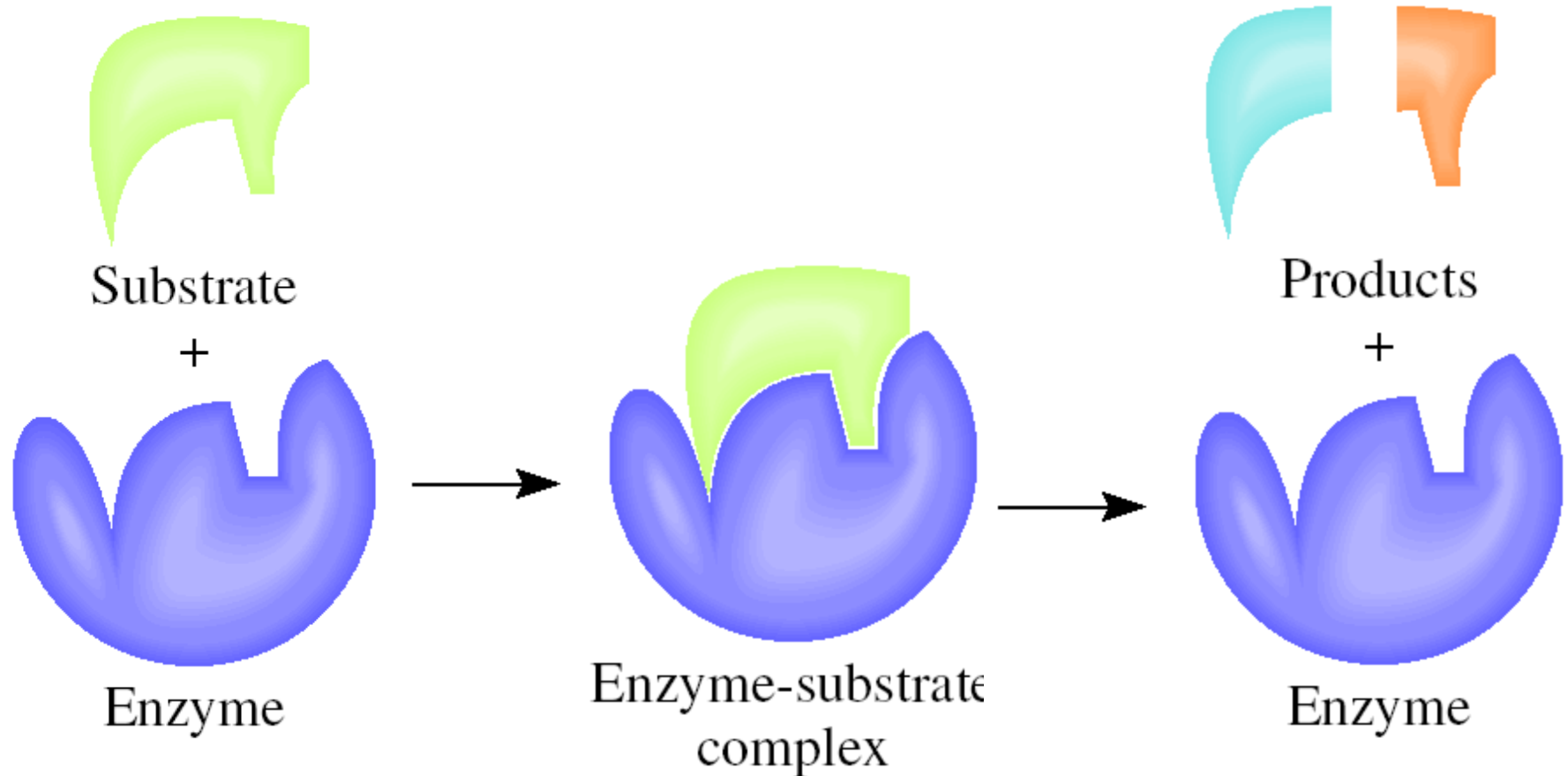


Pt-Rh catalysts used
in Ostwald process

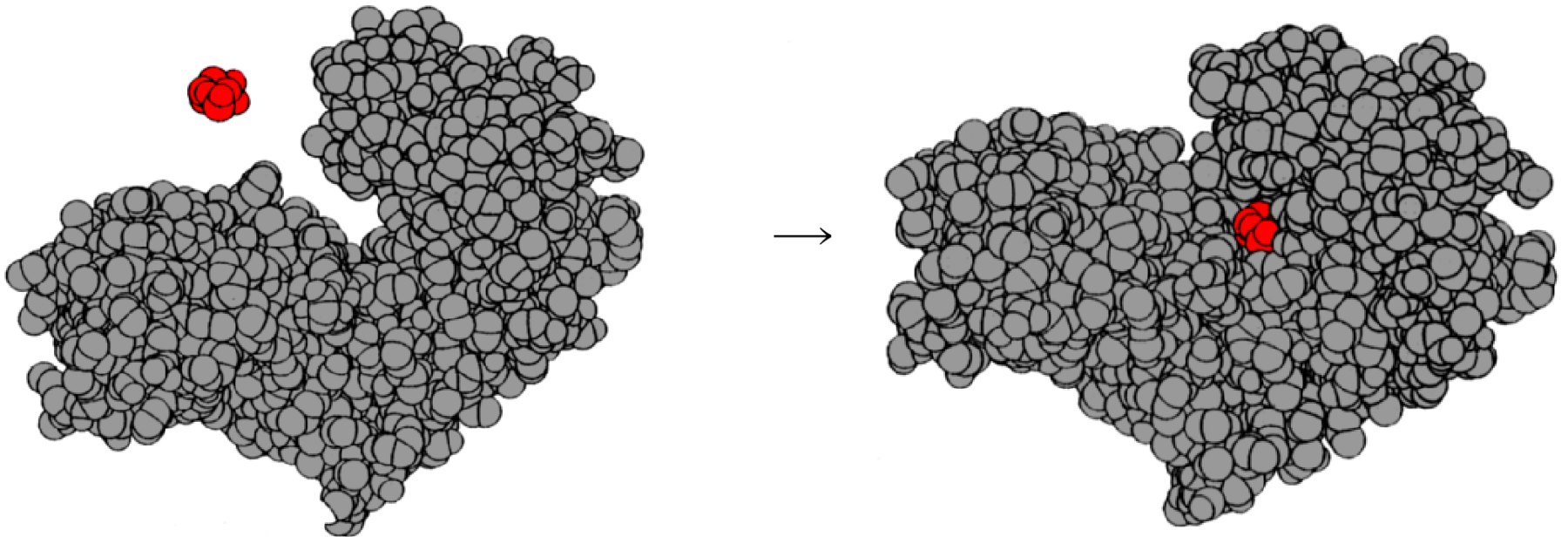
Catalytic Converters



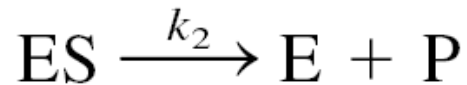
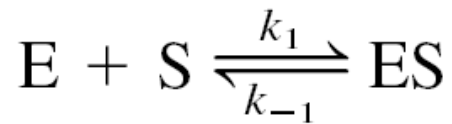
Enzyme Catalysis



Binding of Glucose to Hexokinase



Enzyme Kinetics



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

$$\text{rate} = k [ES]$$

