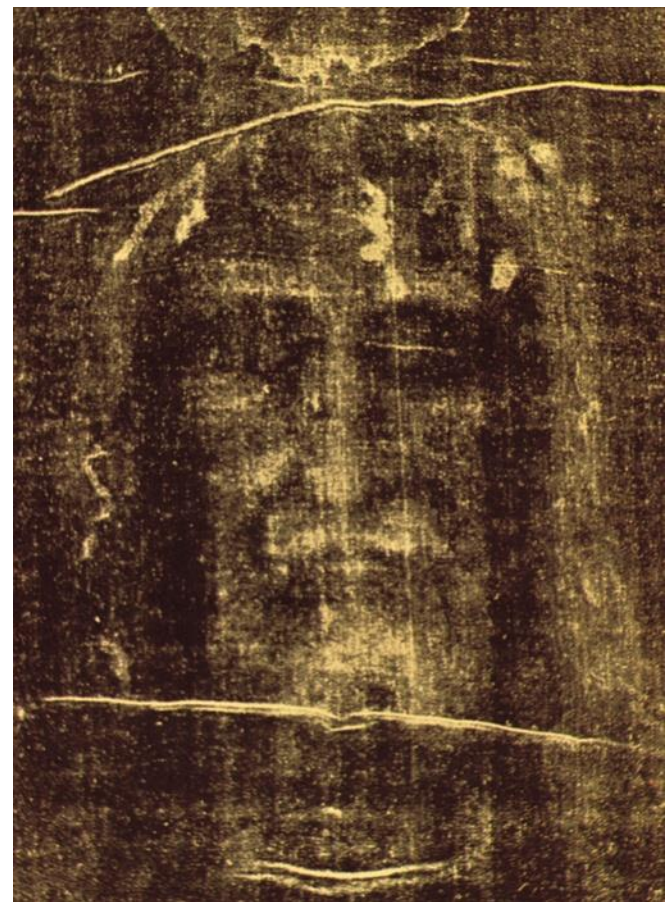


Chemical Kinetics

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).



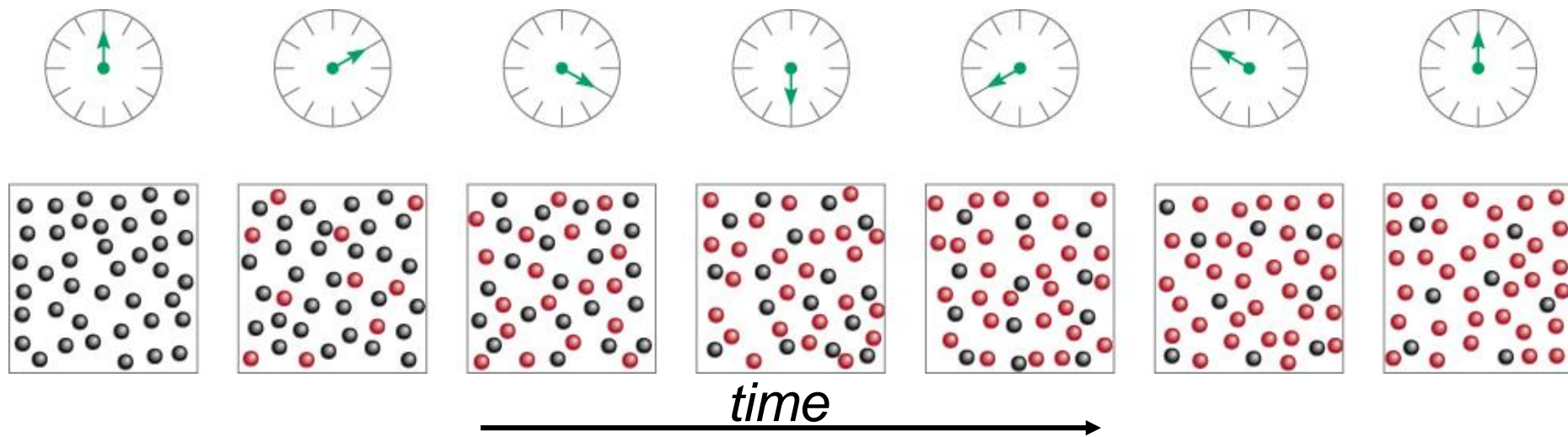
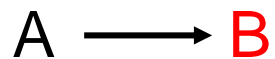
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

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

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

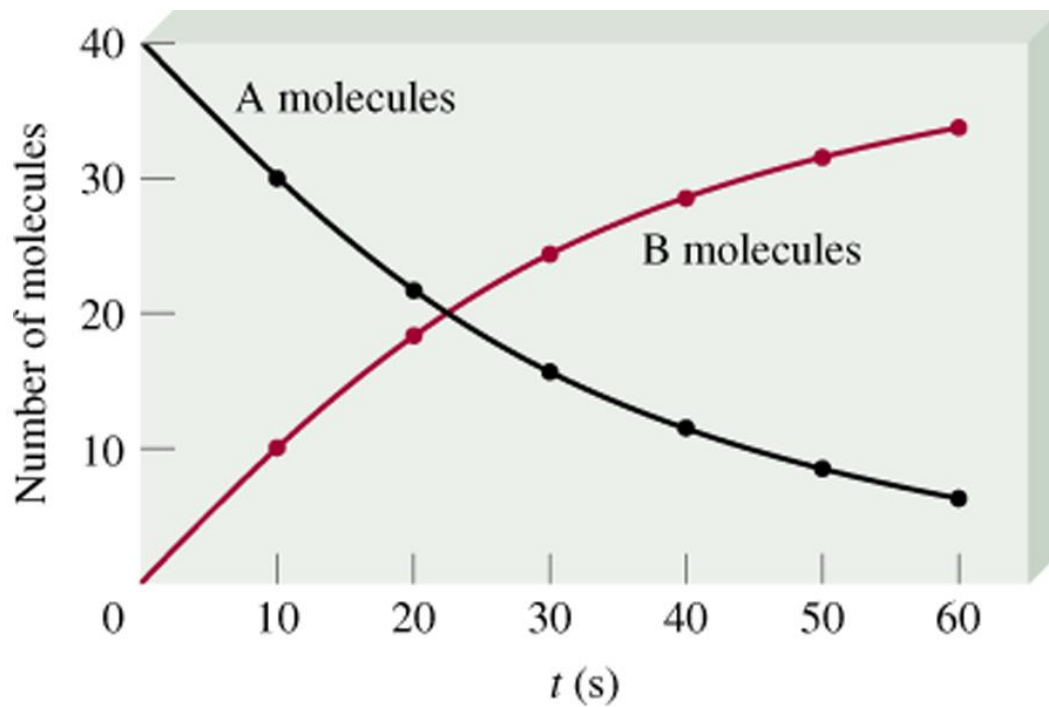
$\Delta[B]$ = change in concentration of **B** over time period Δt

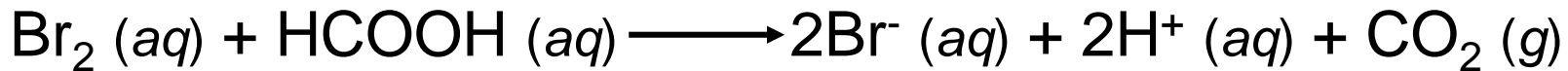
Because $[A]$ decreases with time, $\Delta[A]$ is negative.



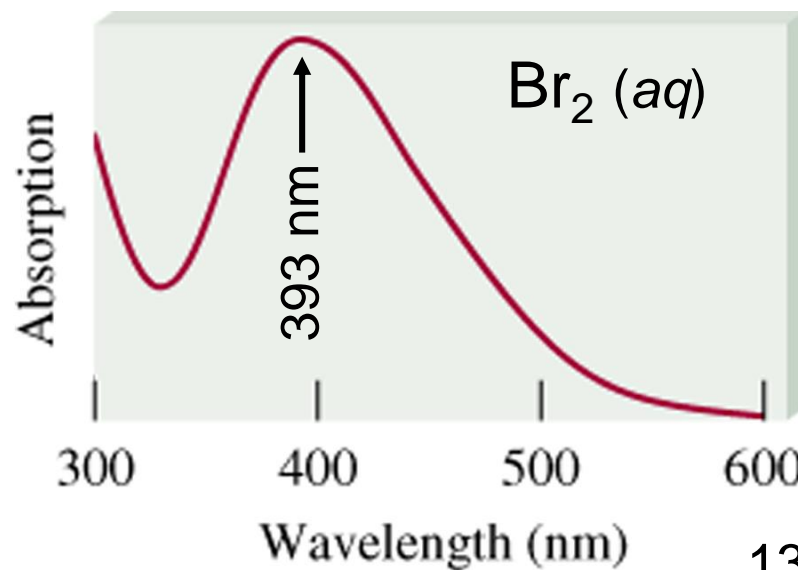
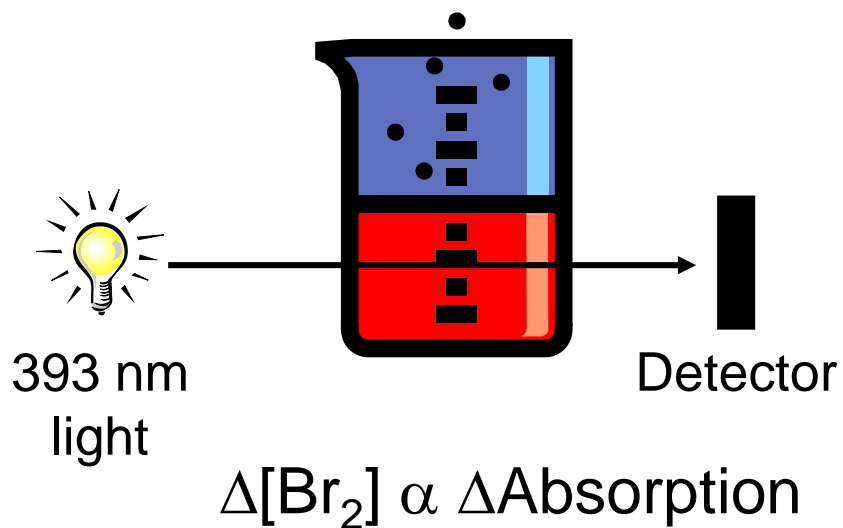
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

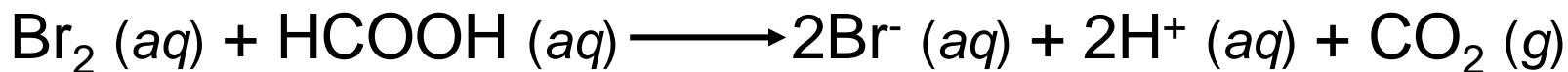
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



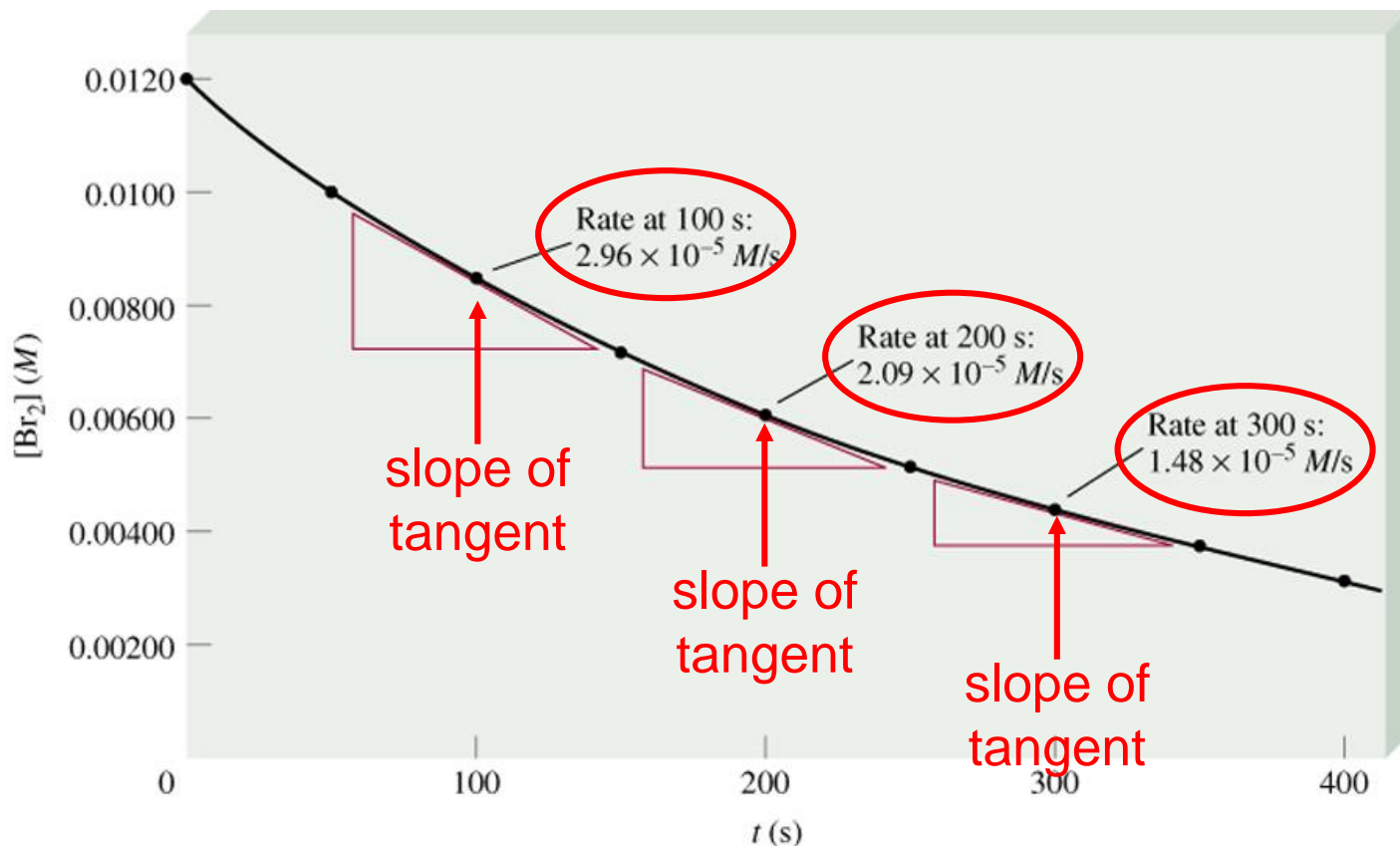


time





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

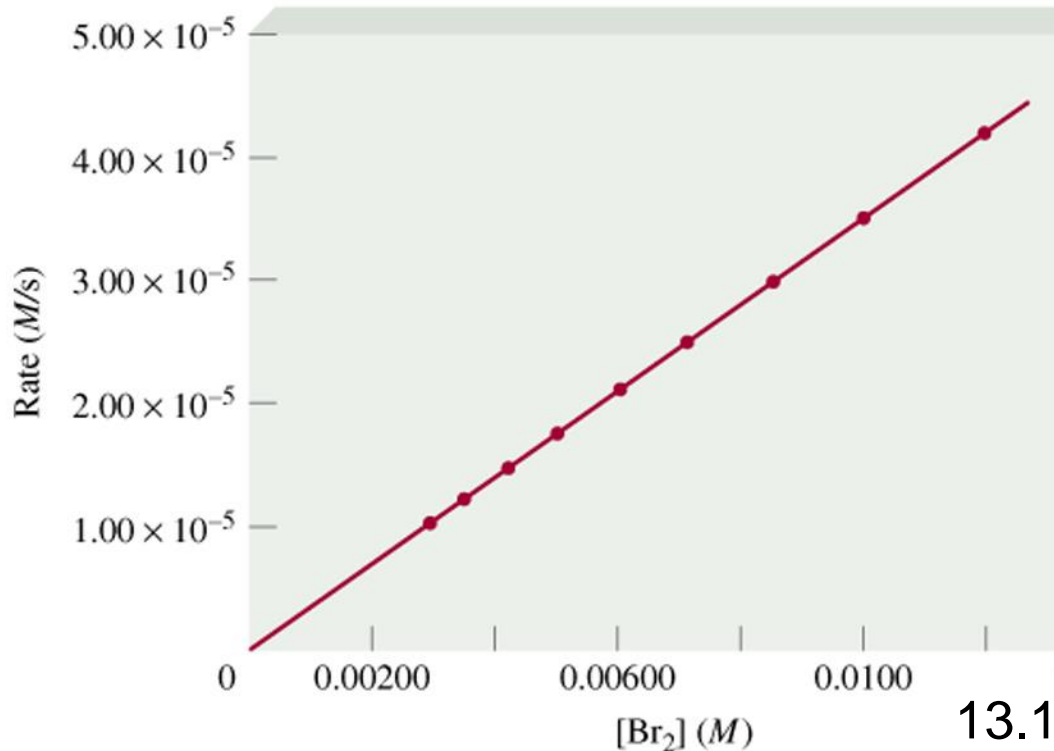
Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500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

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

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

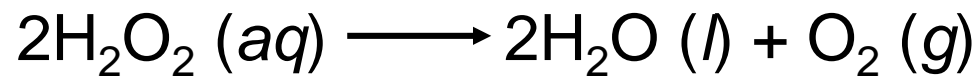
$$k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}$$

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





measure ΔP over time

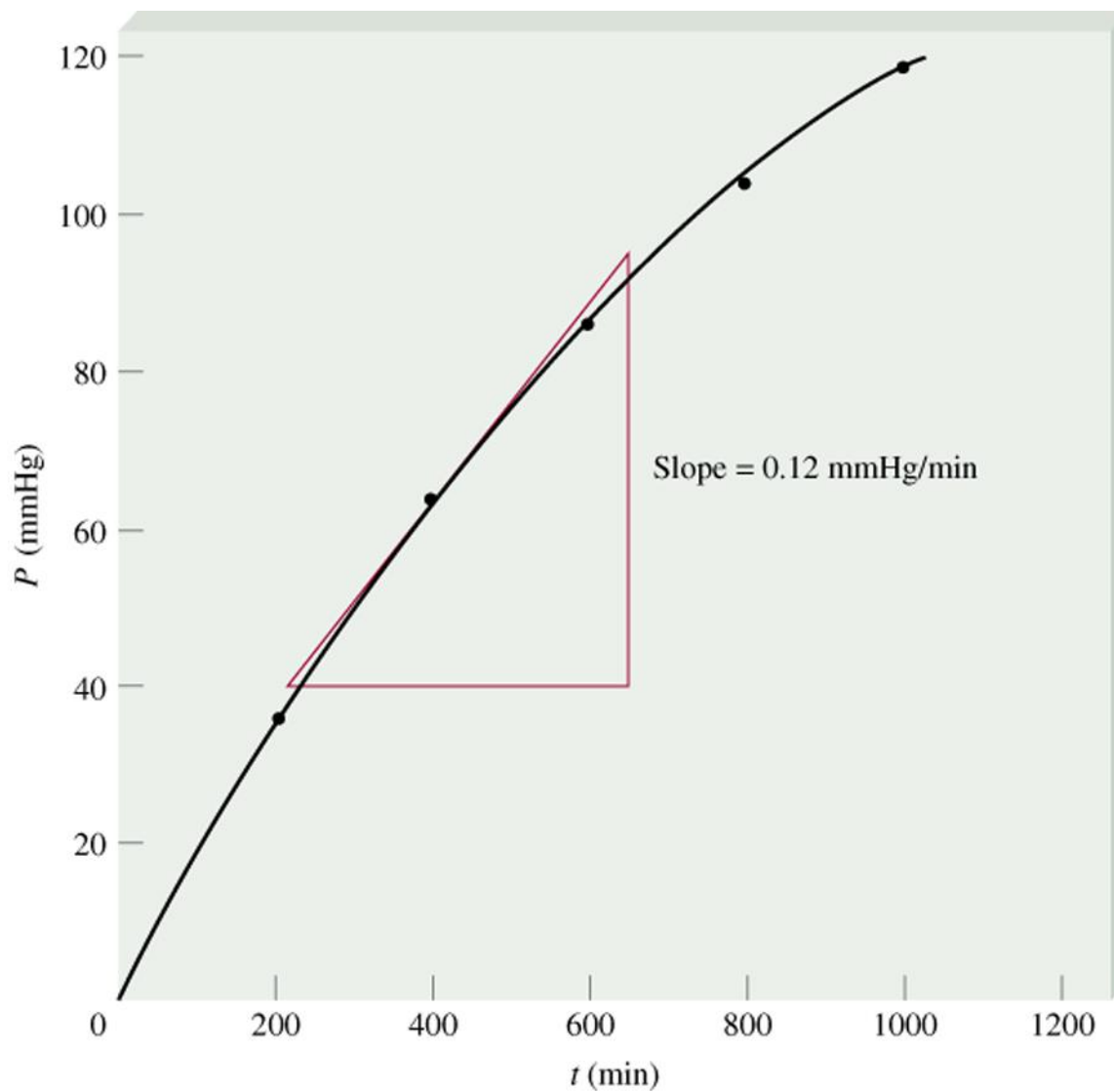
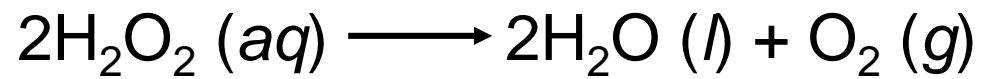


$$PV = nRT$$

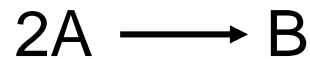
$$P = \frac{n}{V} RT = [\text{O}_2]RT$$

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

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



Reaction Rates and Stoichiometry



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

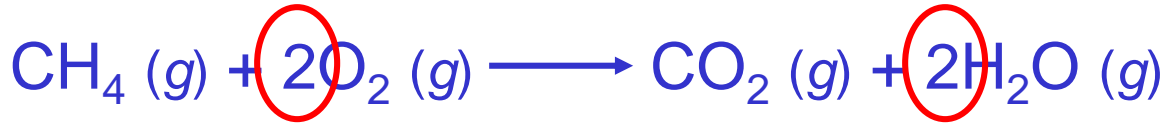
$$\text{rate} = - \frac{1}{2} \frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$



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



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**.



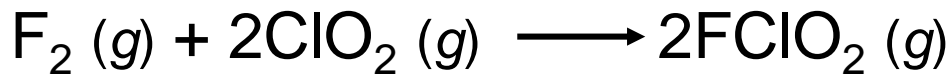
$$\text{Rate} = k [A]^x [B]^y$$



reaction is **xth order** in **A**

reaction is **yth order** in **B**

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



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

$$\underline{2.4 \times 10^{-3}} = \underline{k [0.2]^x [0.01]^y}$$

$$\underline{1.2 \times 10^{-3}} = \underline{k [0.1]^x [0.01]^y}$$

$$2 = 2^x \quad \mathbf{x = 1}$$

$$\underline{4.8 \times 10^{-3}} = \underline{k [0.1]^x [0.04]^y}$$

$$\underline{1.2 \times 10^{-3}} = \underline{k [0.1]^x [0.01]^y}$$

$$4 = 4^y \quad \mathbf{y = 1}$$

Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

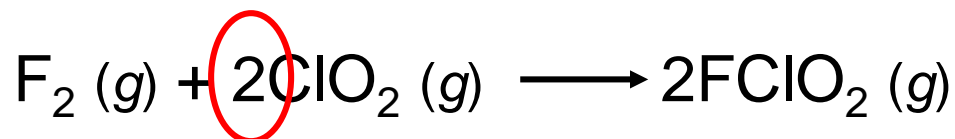
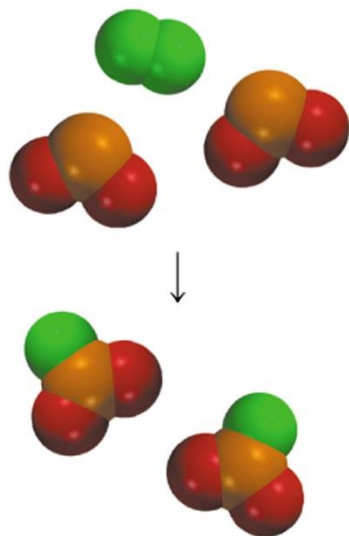
	$[\text{F}_2](M)$	$[\text{ClO}_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

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

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

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.



$$\text{rate} = k [F_2][ClO_2]^1$$



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}

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

$$y = 1$$

$$x = 1$$

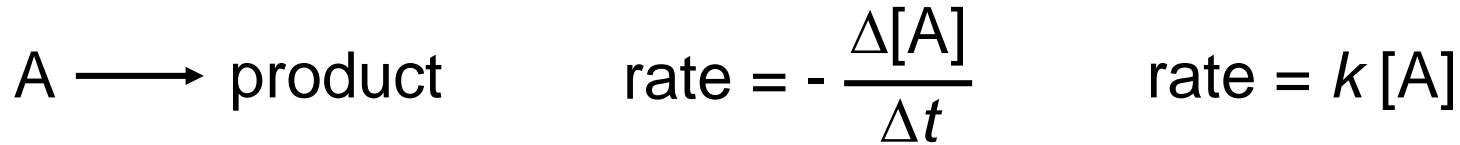
$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

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

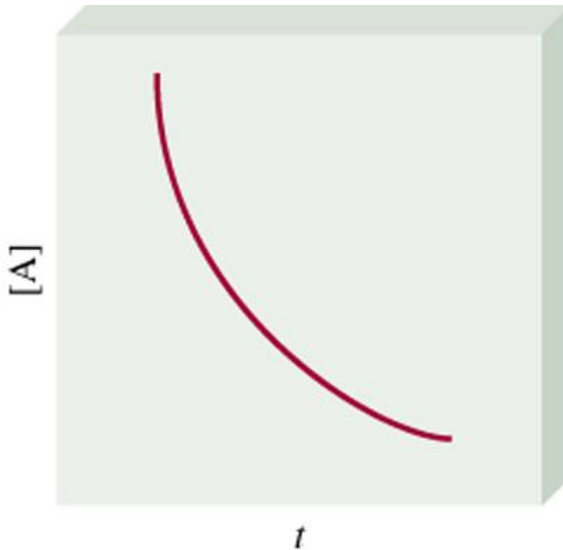


$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

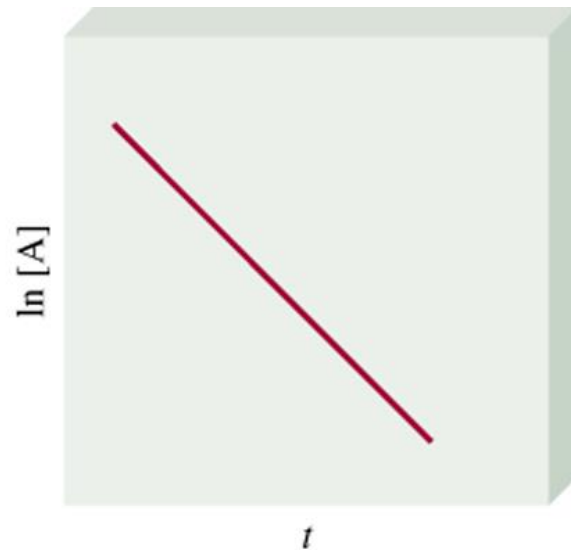
$$- \frac{\Delta[A]}{\Delta t} = k [A]$$

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

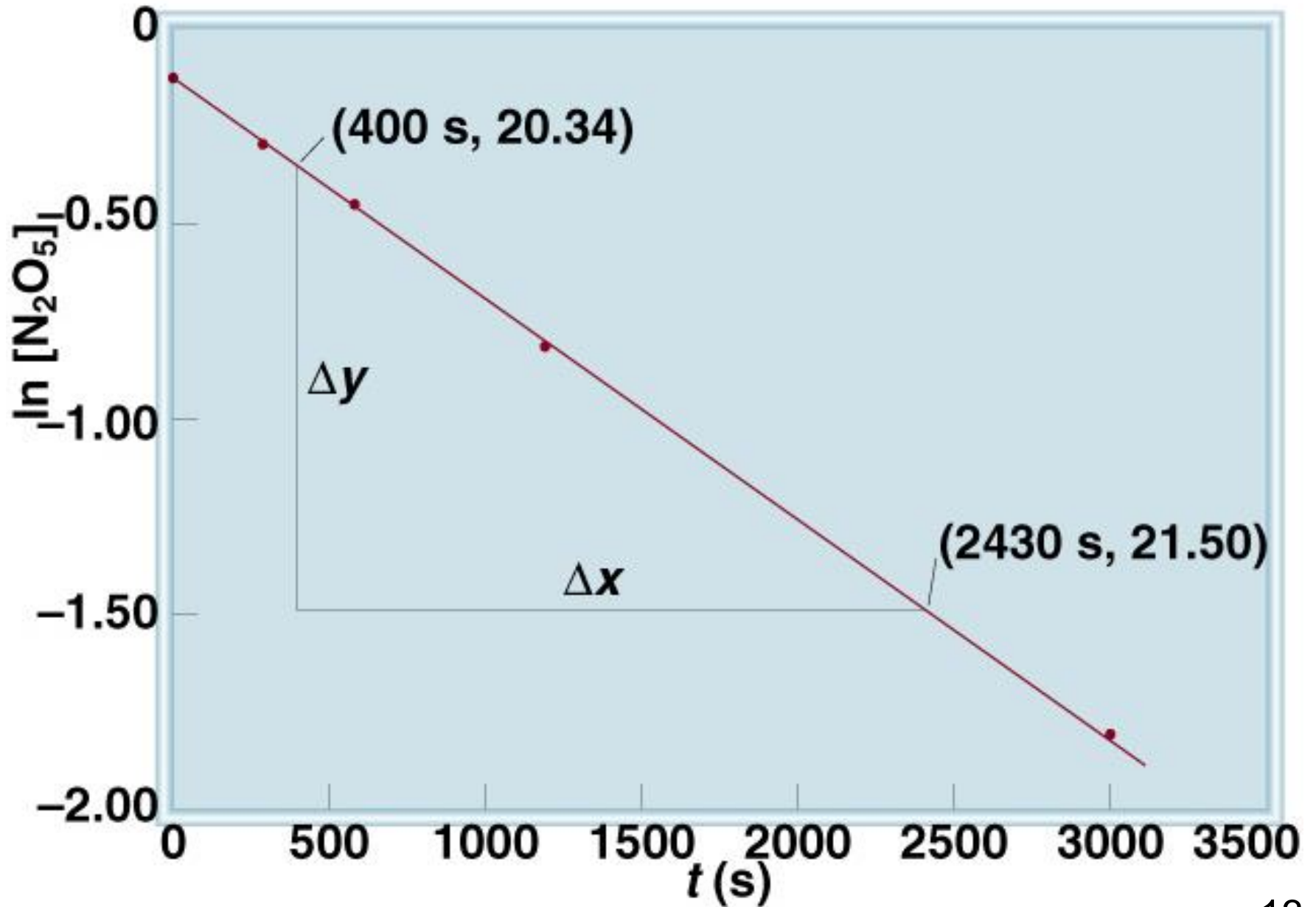
$$[A] = [A]_0 \exp(-kt)$$



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



Decomposition of N_2O_5





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**.

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

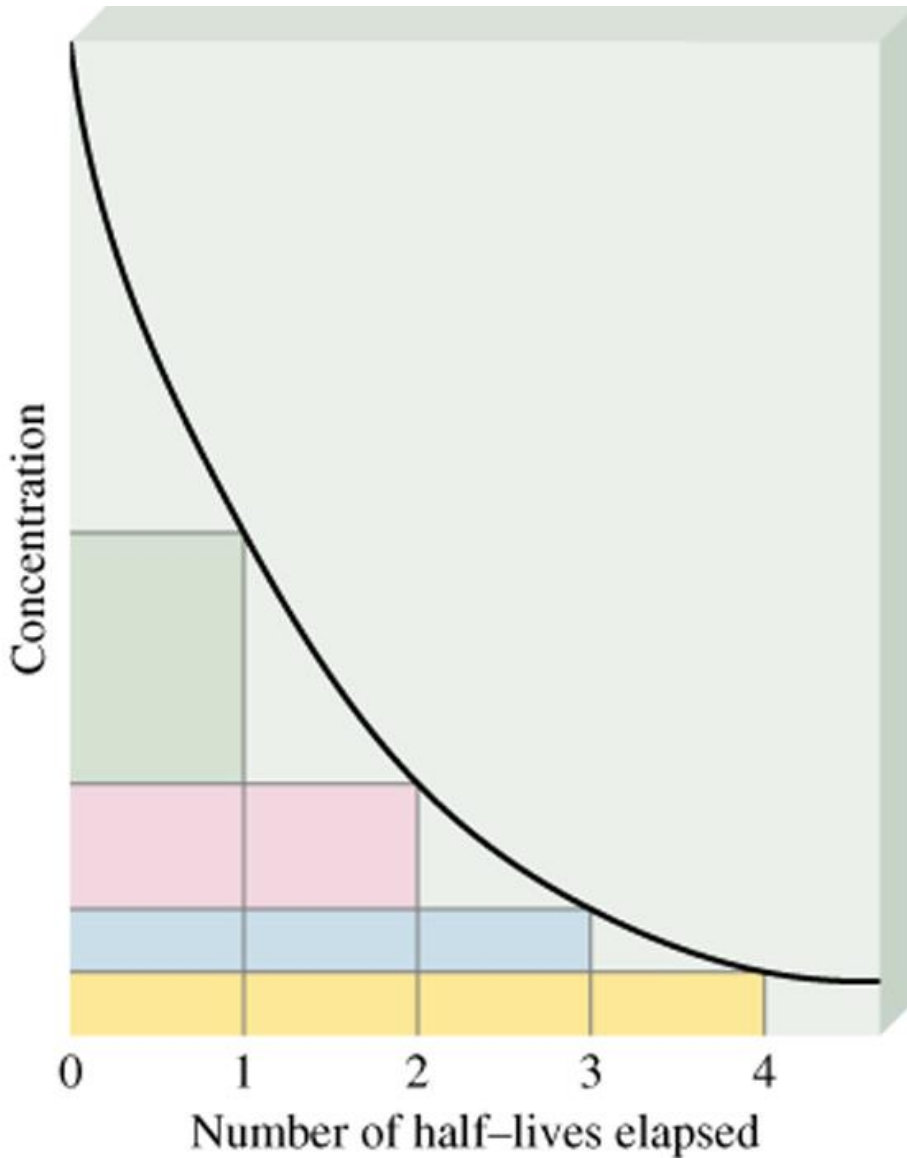
$$t_{1/2} = \frac{\ln \frac{\cancel{[A]}_0}{\cancel{[A]}_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$



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

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

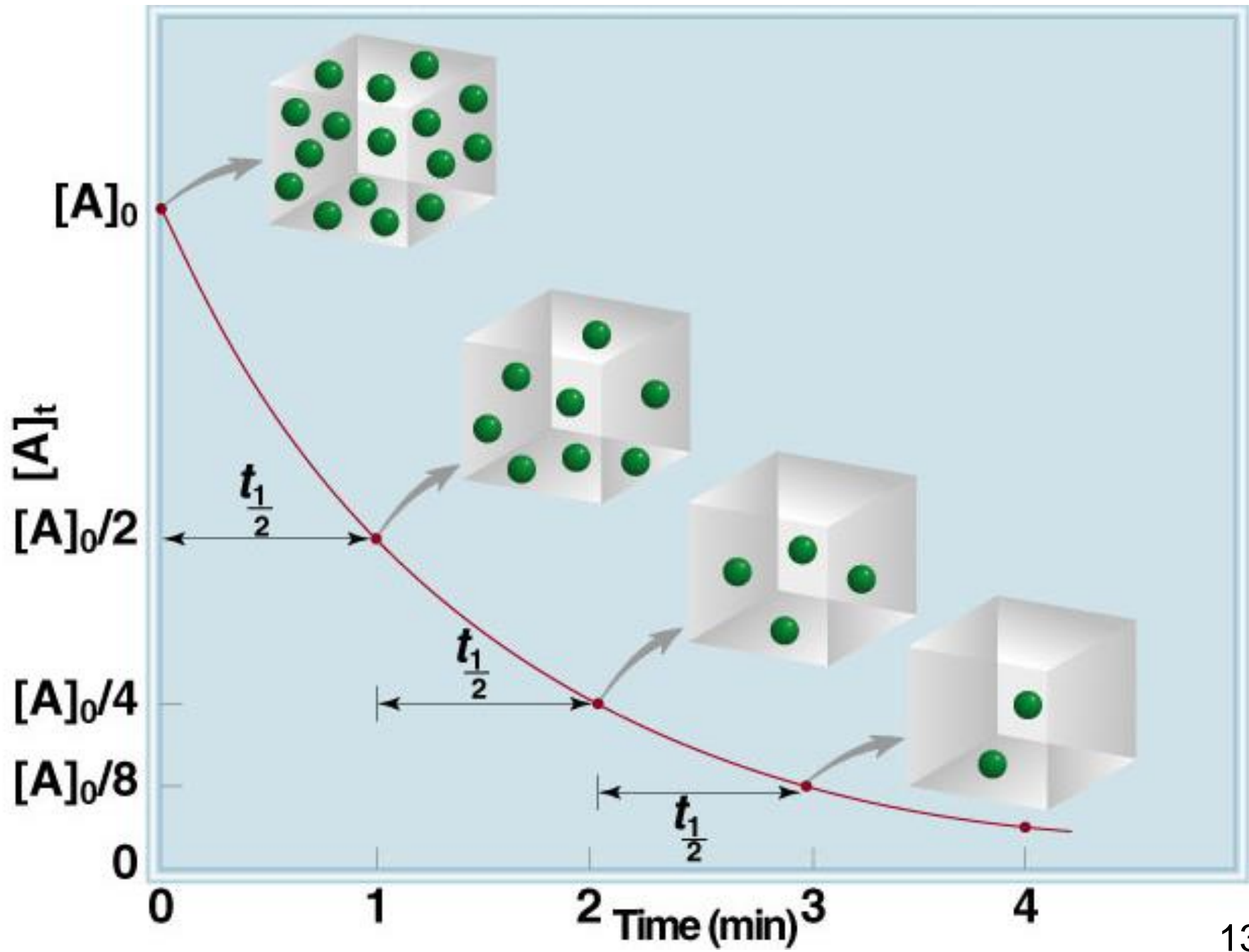
How do you know decomposition is first order?



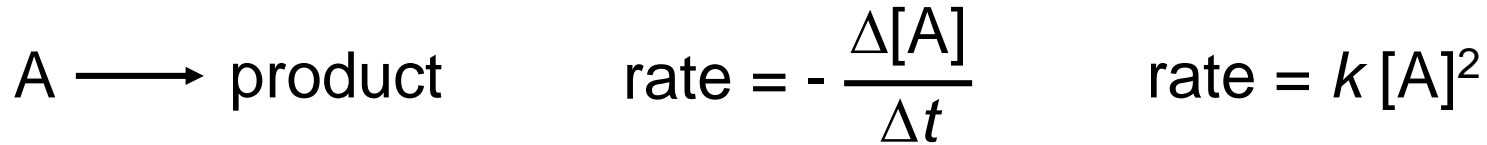
First-order reaction



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



Second-Order Reactions



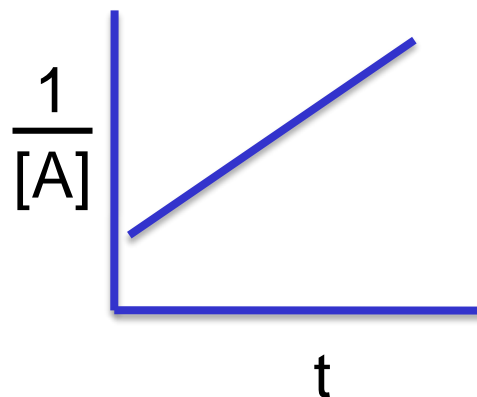
$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M \cdot s \quad - \frac{\Delta[A]}{\Delta t} = k [A]^2$$

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

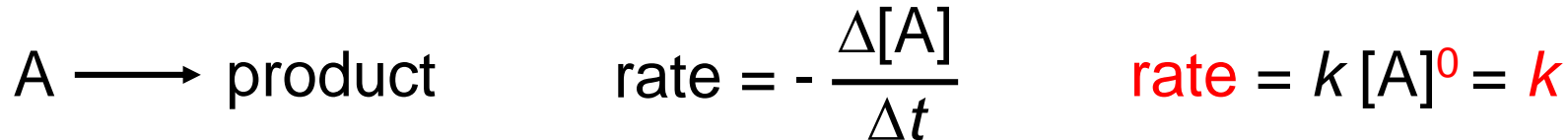
[A] is the concentration of A at any time t
[A]₀ is the concentration of A at time $t = 0$

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

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



Zero-Order Reactions



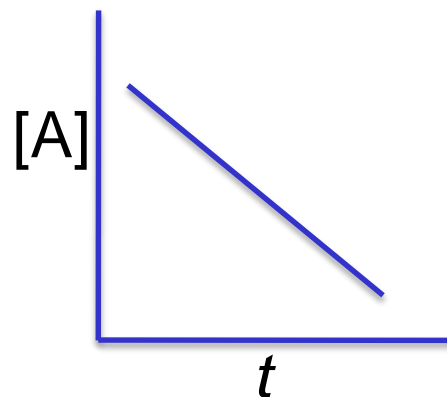
$$k = \frac{\text{rate}}{[A]^0} = M/s \quad - \frac{\Delta[A]}{\Delta t} = k$$

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

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

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

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

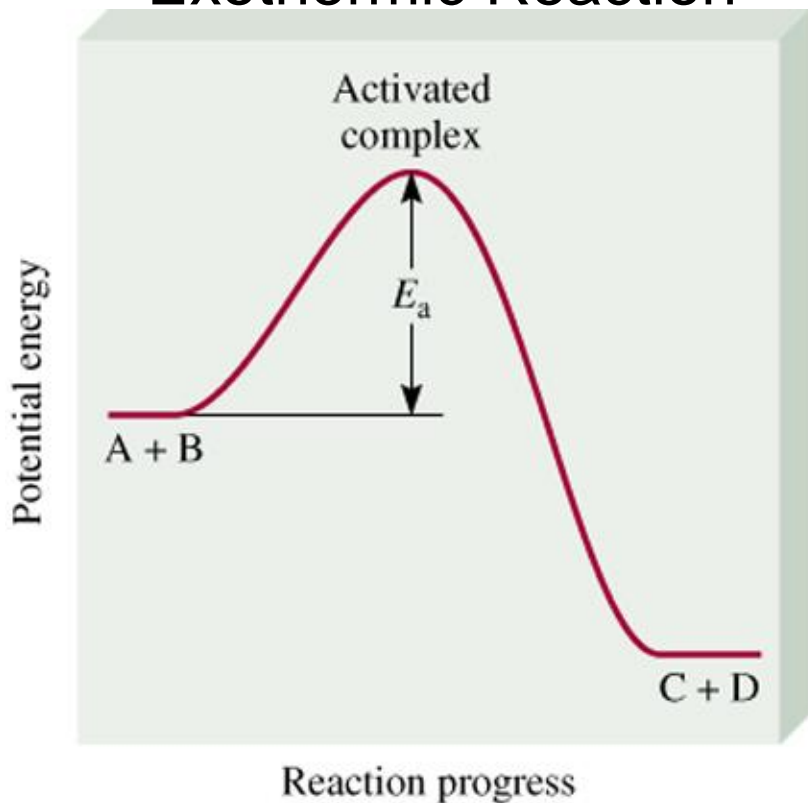


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

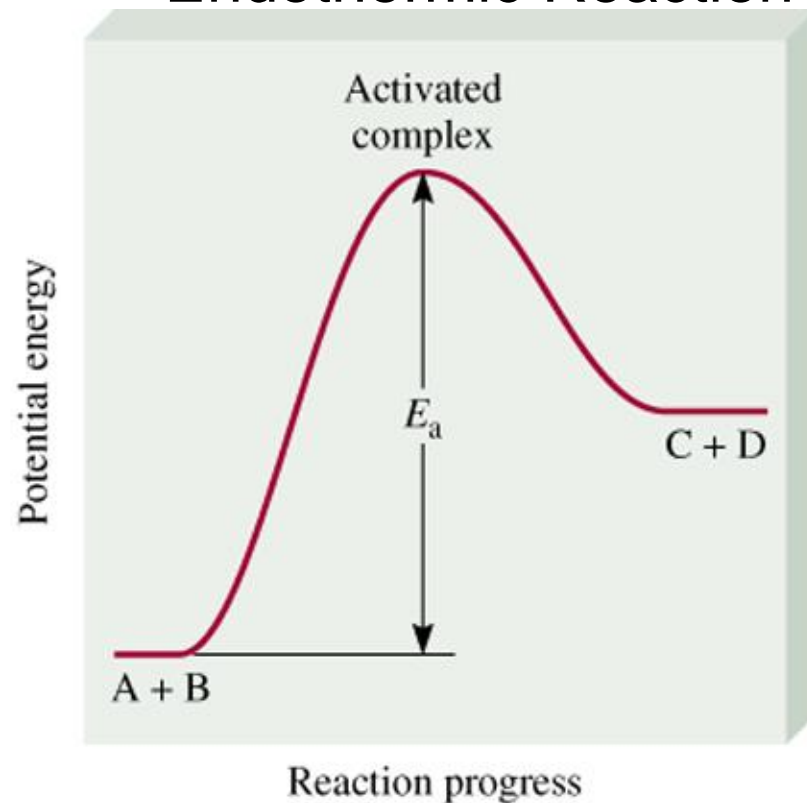
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$



Exothermic Reaction

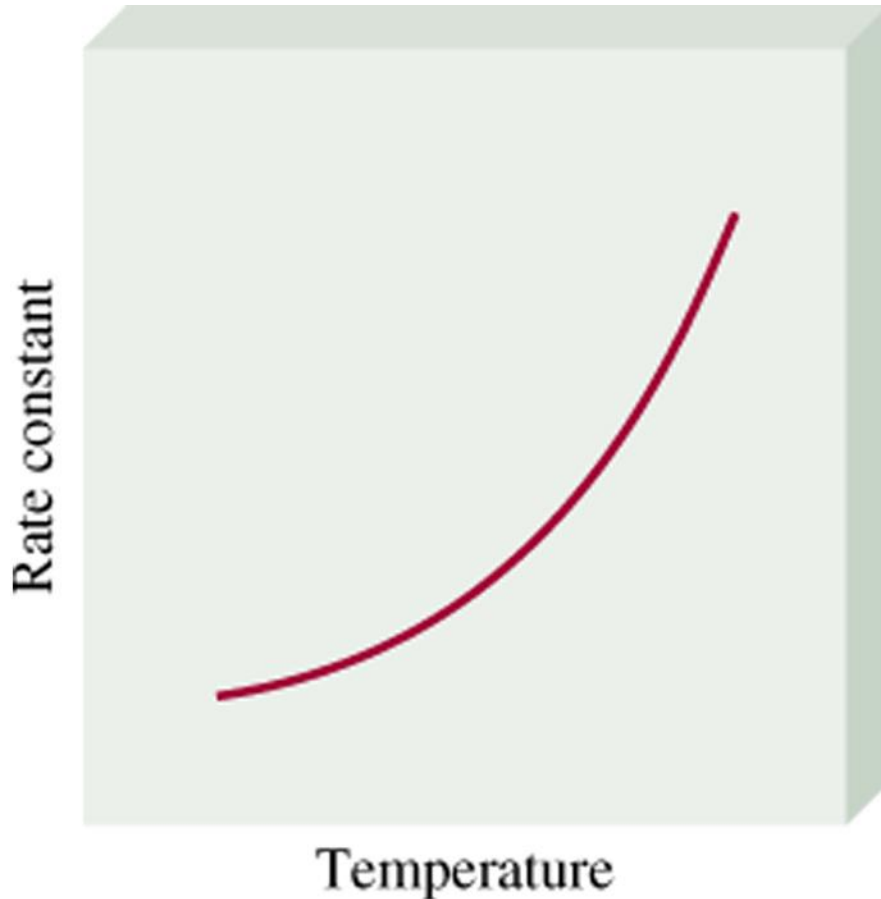


Endothermic Reaction



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

Temperature Dependence of the Rate Constant



$$k = A \cdot \exp(-E_a/RT)$$

(Arrhenius equation)

E_a is the activation energy (J/mol)

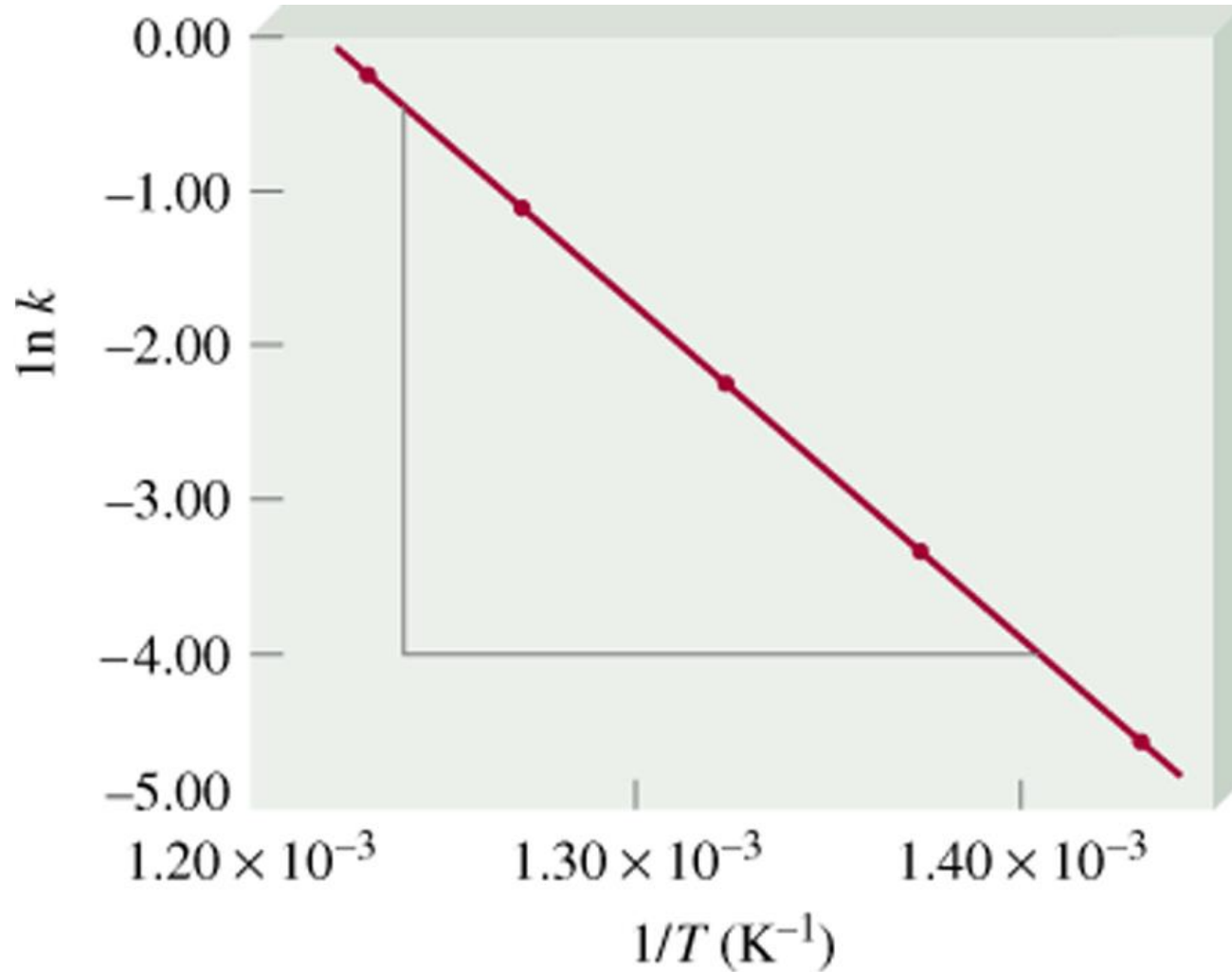
R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

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

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



2-Arrhenius Equation

$$\ln (k_2/k_1) = E_a / R [(T_2 - T_1) / T_2 T_1]$$

Ex:

❖ The activation energy of a certain reaction is 76.7 KJ/mol How many times faster will the reaction occur at 50°C than at 0°C ?

Solution

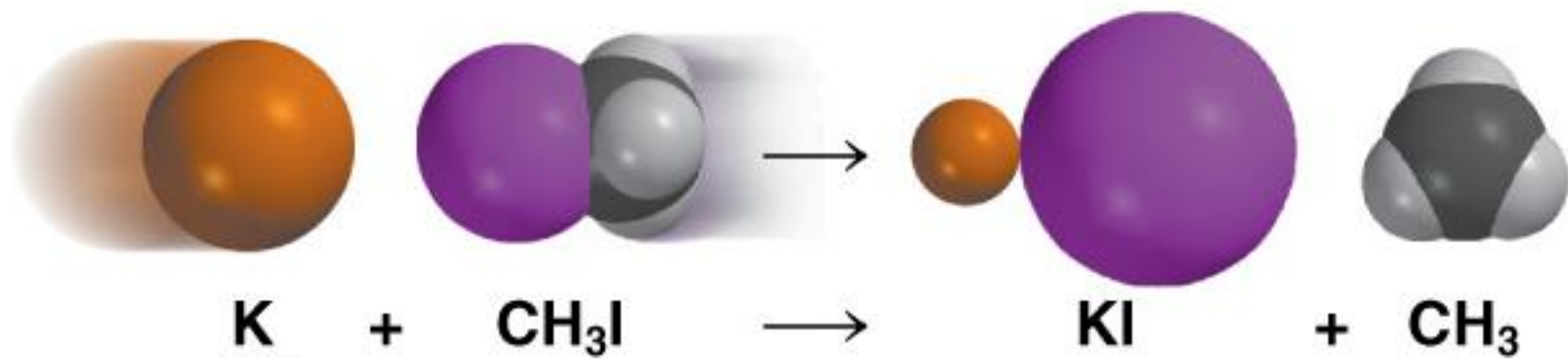
$$\ln (k_2/k_1) = (E_a / R) [(T_2 - T_1) / T_2 T_1]$$

$$\ln (k_2 / k_1) = [(76.7 \times 1000) / 8.314] [(323 - 273) / 323 \times 273]$$

$$\ln k_2 / k_1 = 5.23$$

$$k_2 / k_1 = 187$$

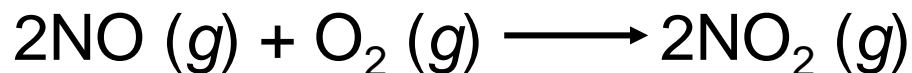
$$k_2 = 187 k_1$$



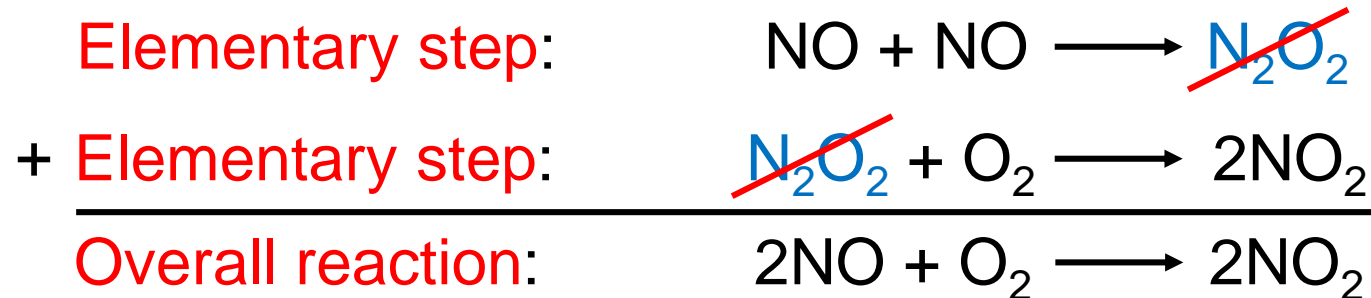
Reaction Mechanisms

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**.

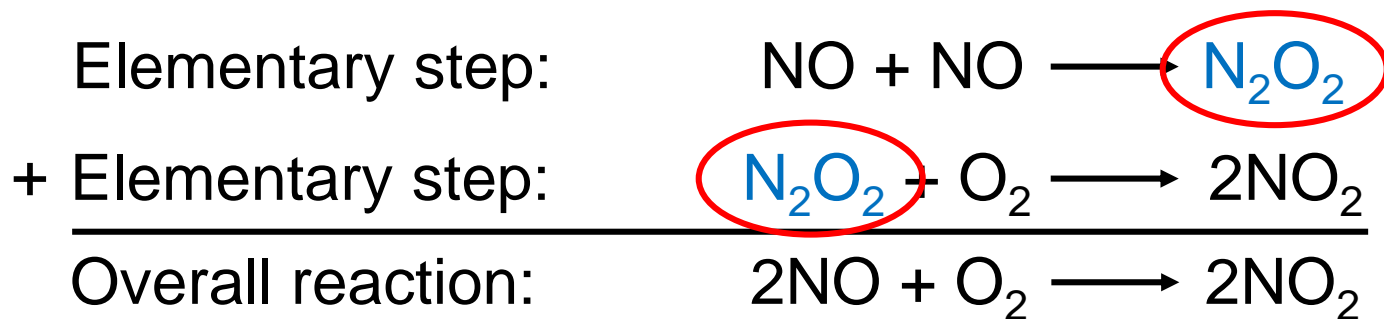


N_2O_2 is detected during the reaction!



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 $A \longrightarrow$ products rate = $k [A]$

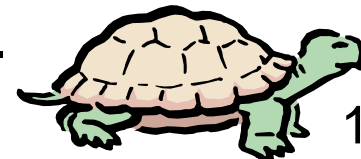
Bimolecular reaction $A + B \longrightarrow$ products rate = $k [A][B]$

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

Writing plausible reaction mechanisms:

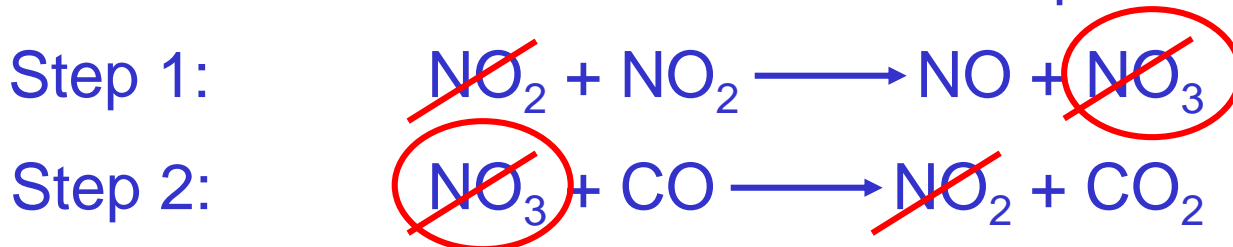
- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

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





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?

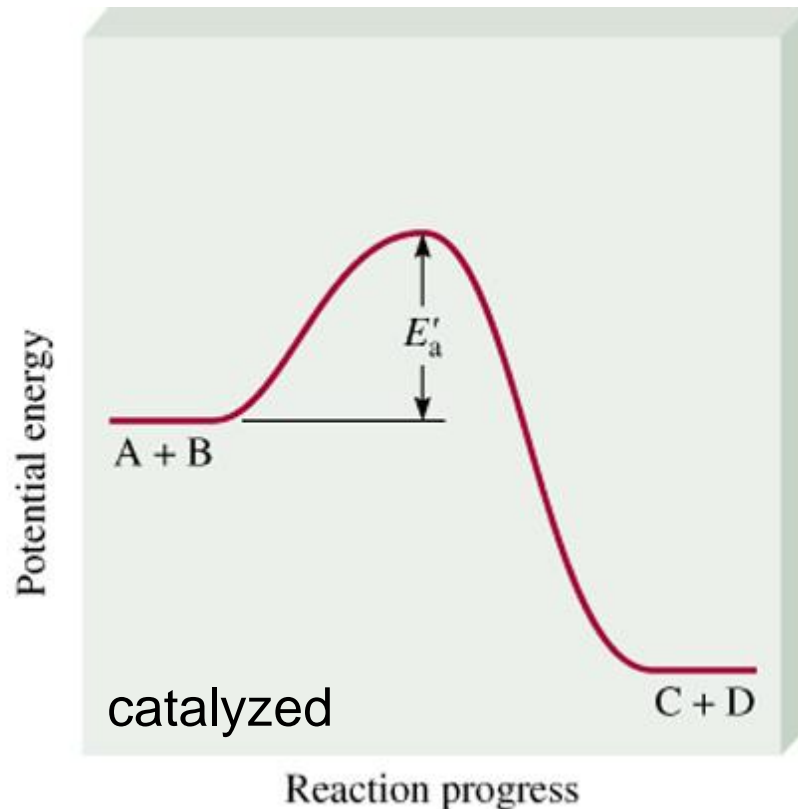
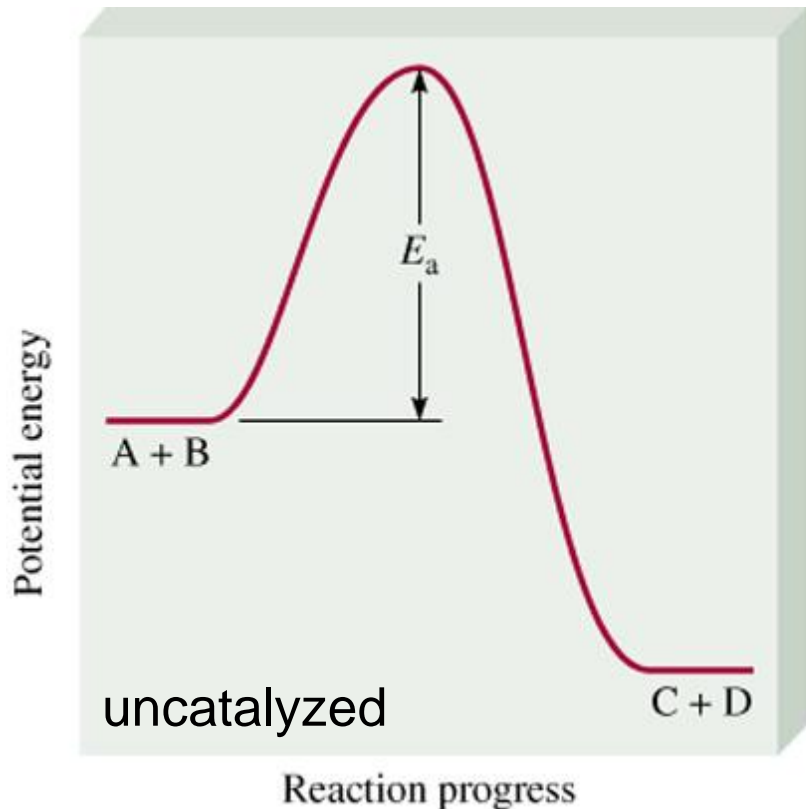


What can you say about the relative rates of steps 1 and 2?

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

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

$$k = A \cdot \exp(-E_a/RT) \quad E_a \downarrow \quad k \uparrow$$



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

$$E'_a < E_a$$

Catalysts

❖ **Catalyst – substance that increases the rate of a reaction without undergoing permanent chemical change itself .**

❖ **A catalyst lowers the activation energy for the reaction .**

❖ **Usually , by providing a completely different mechanism . (Alters the reaction mechanism)**

❖ **At equilibrium the catalyst speeds up the forward and backward reactions (does not affect the equilibrium position).**

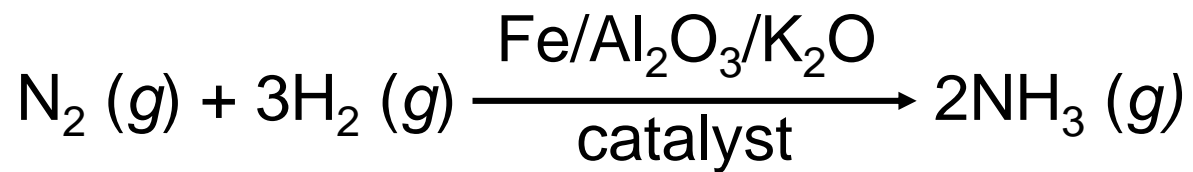
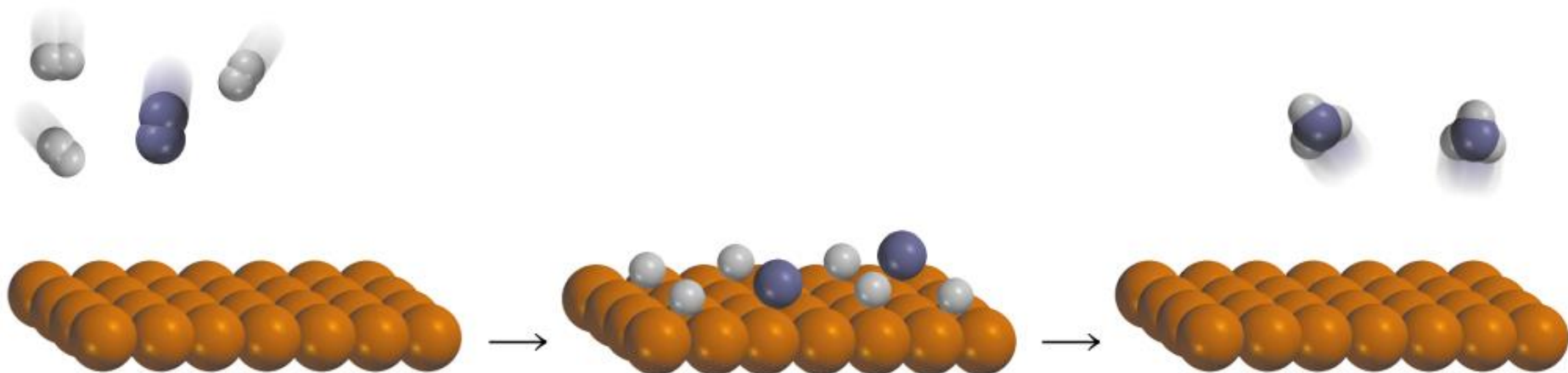
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

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

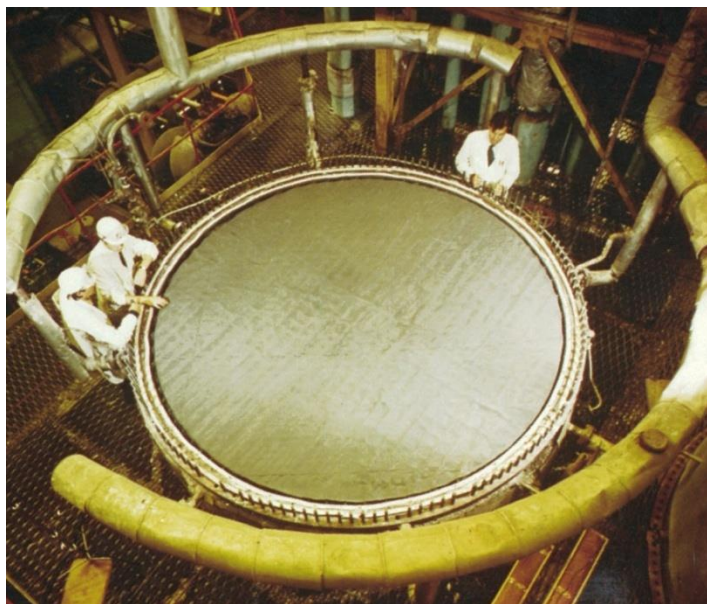
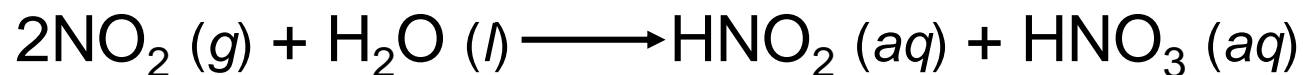
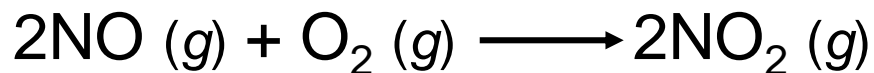
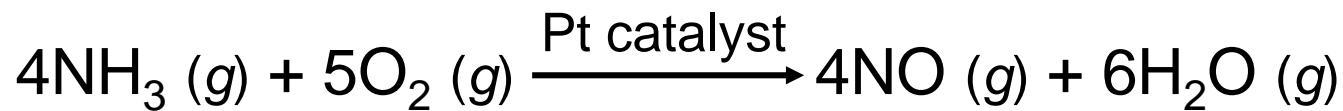
In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

Haber Process



Ostwald Process

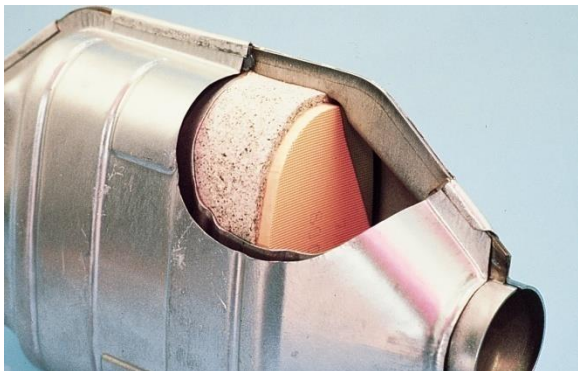
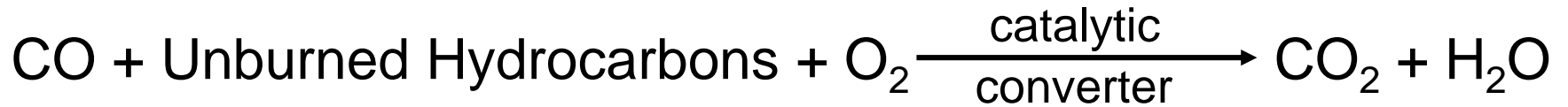
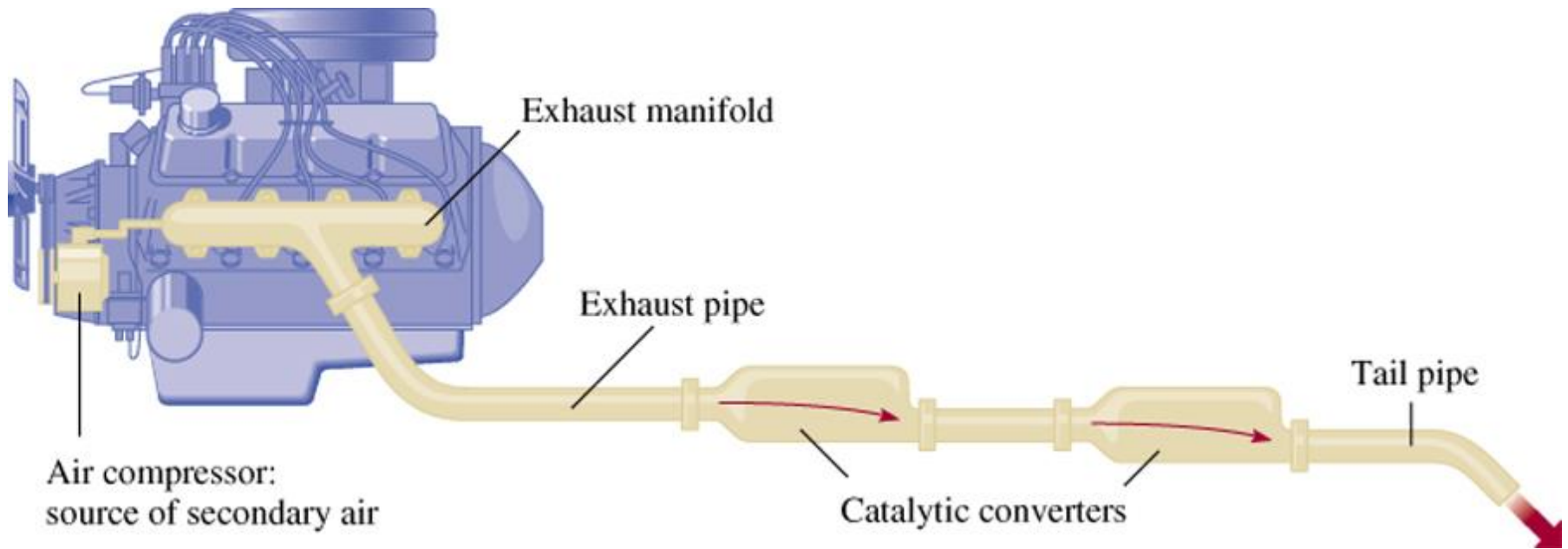


Pt-Rh catalysts used
in Ostwald process

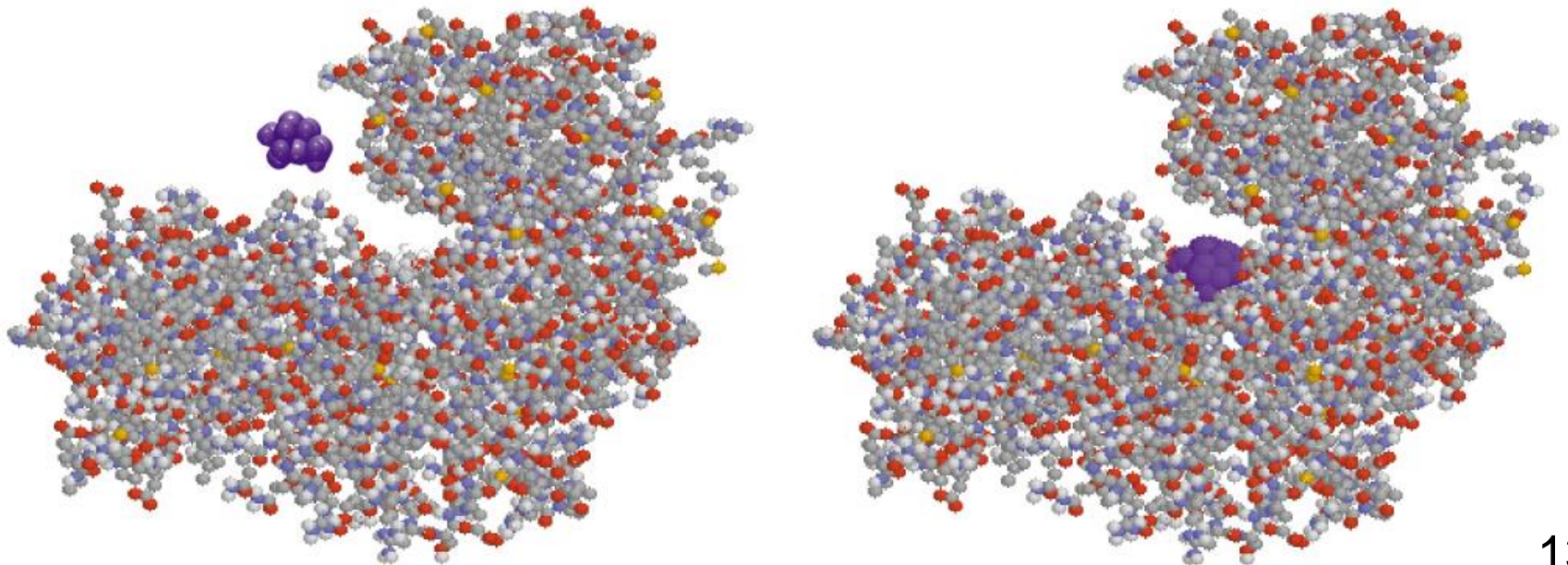
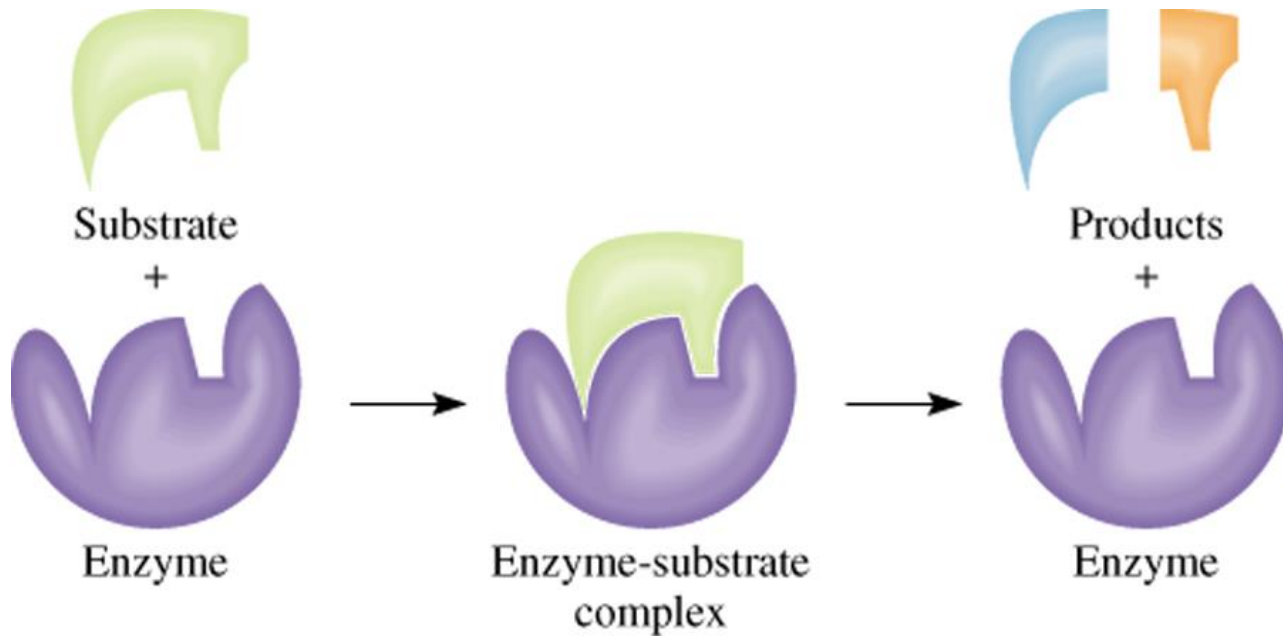


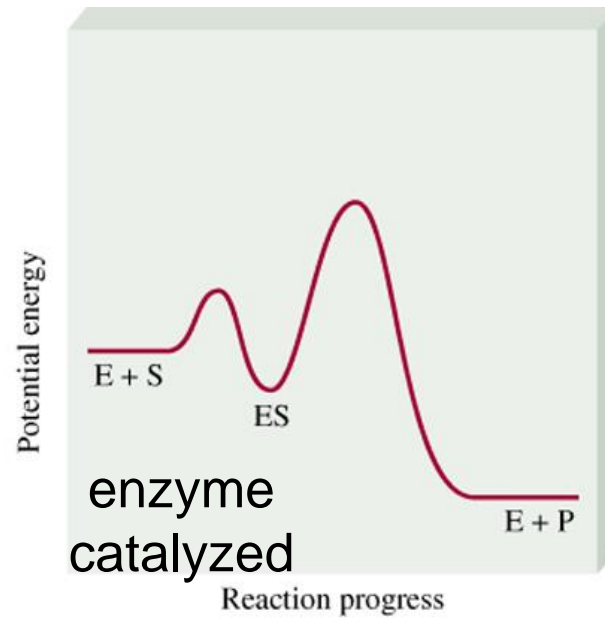
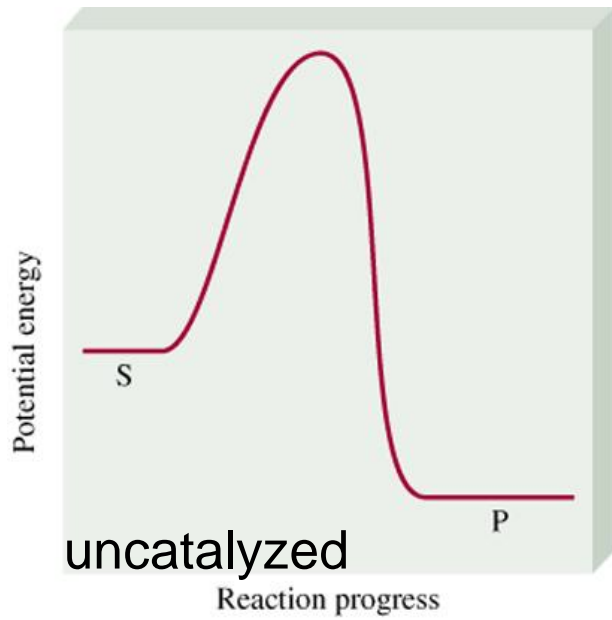
Hot Pt wire
over NH_3 solution

Catalytic Converters



Enzyme Catalysis





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

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

