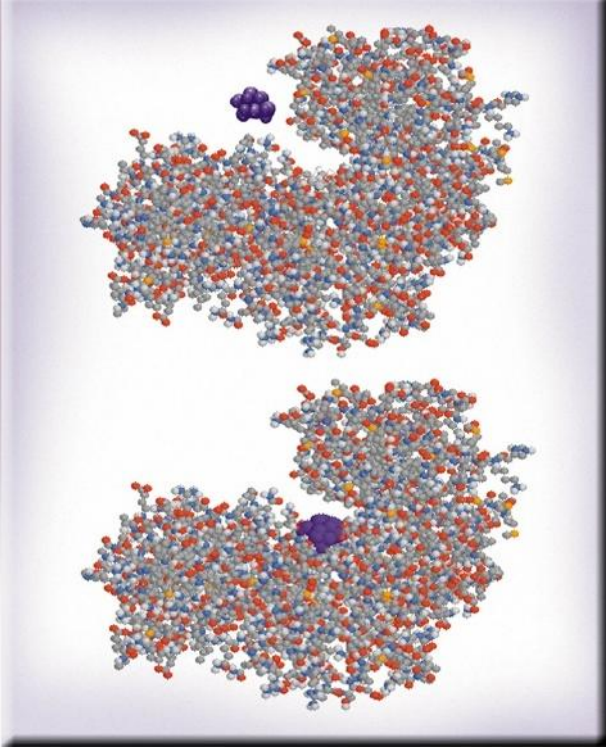

Chemical Kinetics

Chapter 13

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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) = mol. L^{-1} s^{-1}.

$$A \longrightarrow B$$

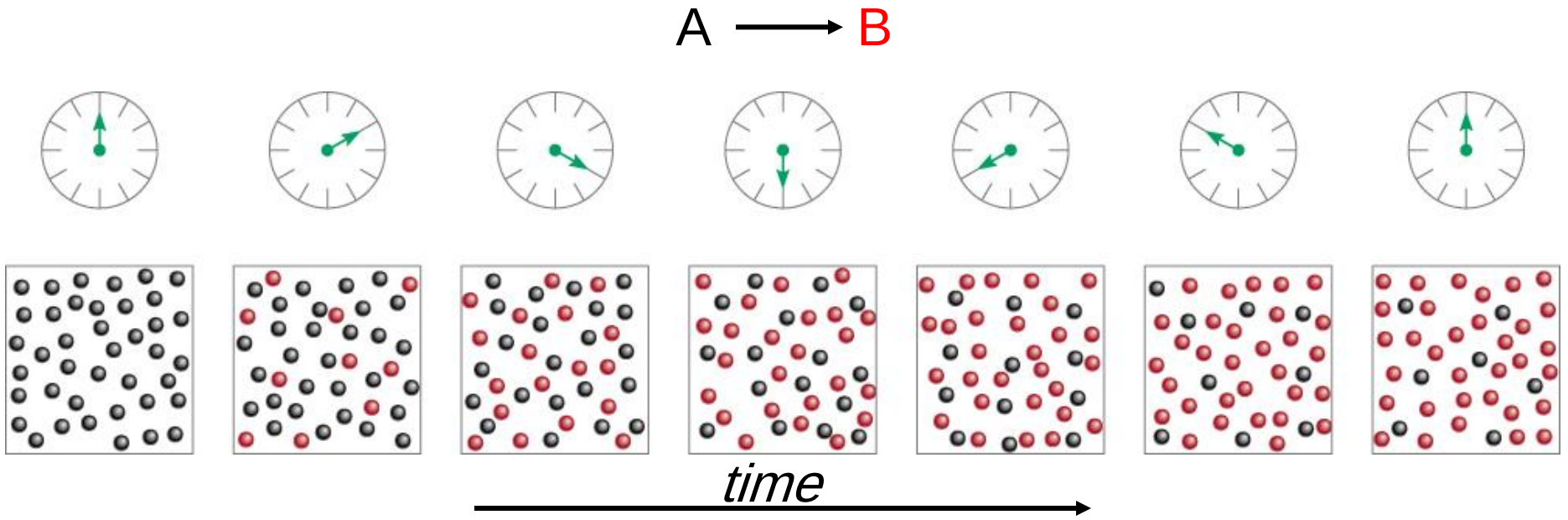
$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

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

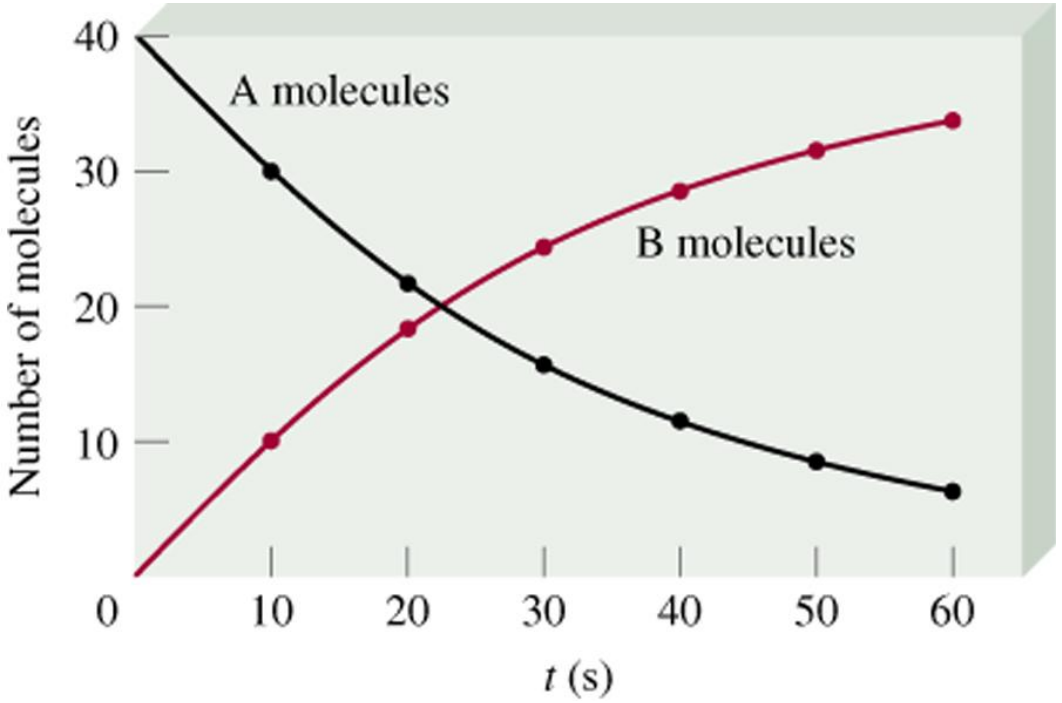
$\Delta[B]$ = change in concentration of B over time period Δt

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



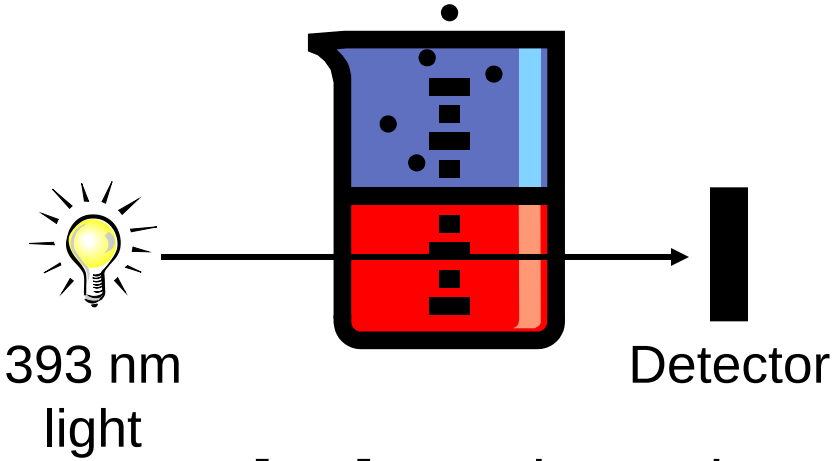
$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

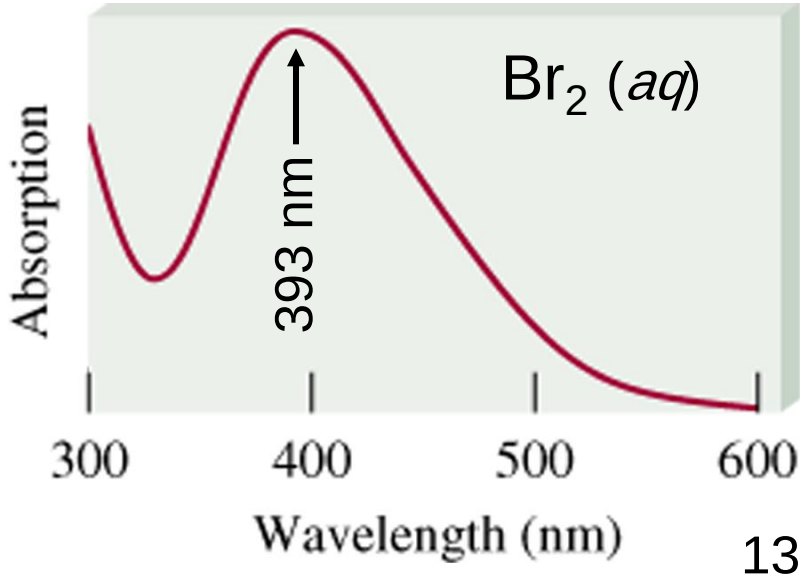


$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

time →

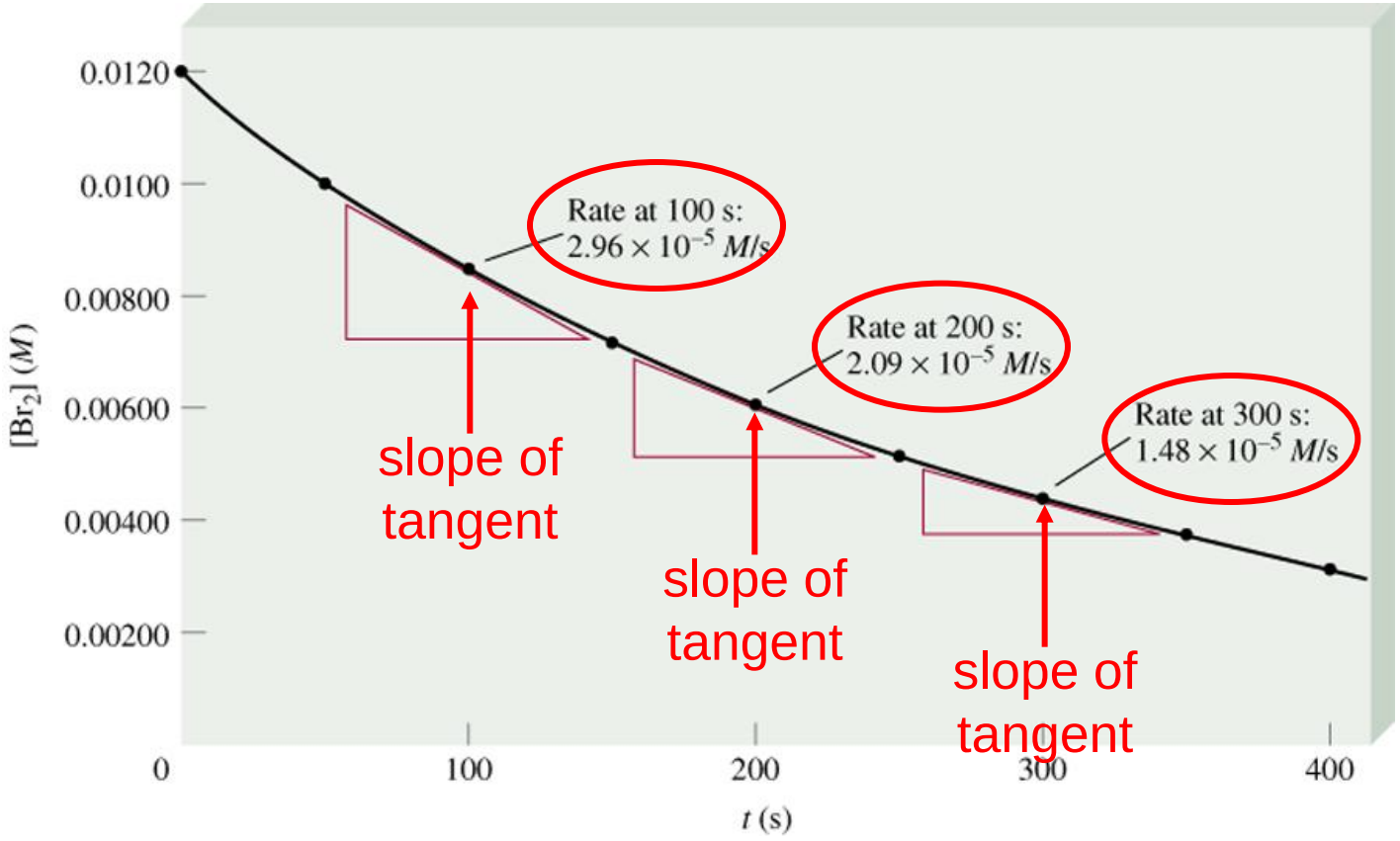


$\Delta[Br_2] \alpha \Delta Absorption$



$$Br_2\,(aq) + HCOOH\,(aq) \longrightarrow 2Br^-\,(aq) + 2H^+\,(aq) + CO_2\,(g)$$

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



$$\textbf{\textit{average rate}} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

instantaneous rate = rate for specific instance in time

TABLE 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

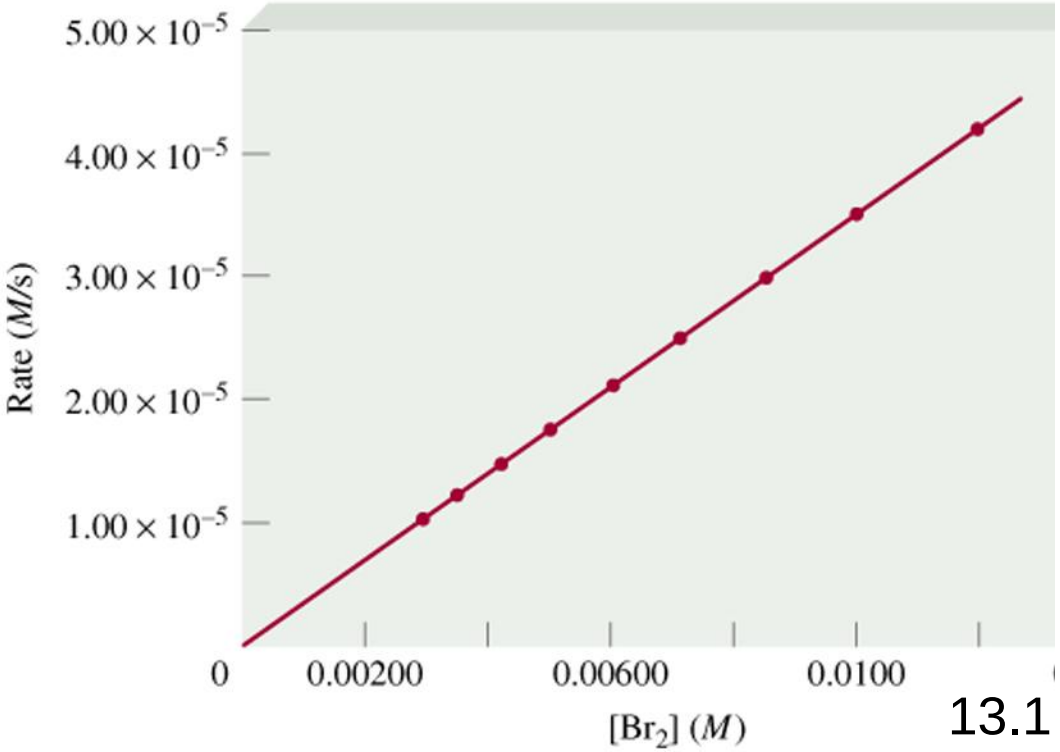
Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
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}

rate α $[Br_2]$

rate = $k[Br_2]$

$$k = \frac{\text{rate}}{[Br_2]} = \textbf{\textit{rate constant}}$$

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



$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$

$$PV = nRT$$

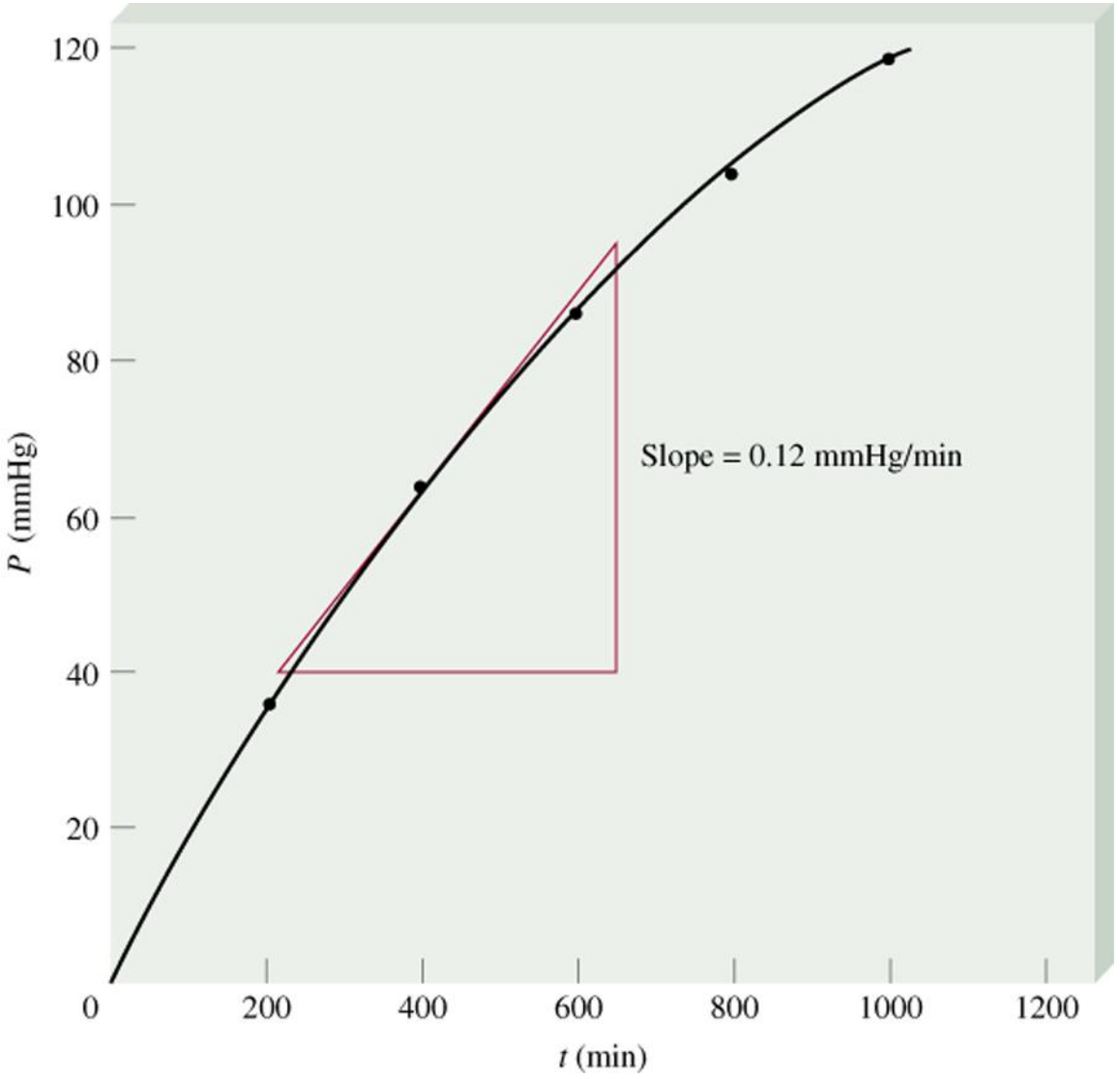
$$P = \frac{n}{V}RT = [O_2]RT$$

$$[O_2] = \frac{1}{RT}P$$

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P}{\Delta t}$$

measure ΔP over time

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$



Reaction Rates and Stoichiometry

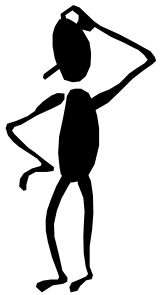
$$2A \longrightarrow B$$

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

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

$$aA + bB \longrightarrow cC + dD$$

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



Write the rate expression for the following reaction:

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g)$$

$$\text{rate} = -\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

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.

$$aA + bB \longrightarrow cC + dD$$

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

reaction is ***x*th order** in A

reaction is ***y*th order** in B

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

$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

rate = $k\,[F_2]^x[ClO_2]^y$

$2.4\times10^{-3} = k\,[0.2]^x[0.01]^y$

$1.2\times10^{-3} = k\,[0.1]^x[0.01]^y$

$2 = 2^x$ X =1

$4.8\times10^{-3} = k\,[0.1]^x[0.04]^y$

$1.2\times10^{-3} = k\,[0.1]^x[0.01]^y$

$4 = 4^y$ y =1

Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

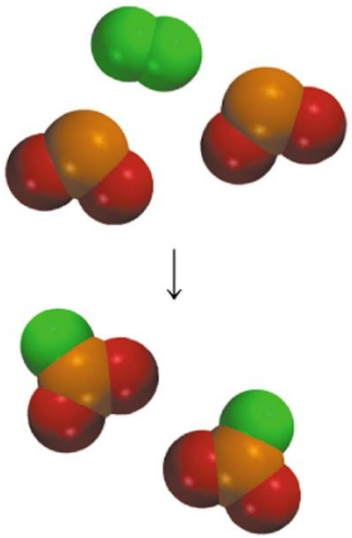
	$[F_2](M)$	$[ClO_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

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

K = rate /$[F_2][ClO_2]$

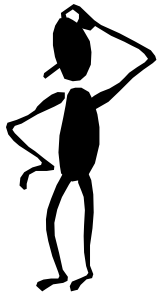
Rate Laws

- 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.



$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

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



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

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

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	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}

rate = $k[S_2O_8^{2-}]^x[I^-]^y$

$y = 1$

$x = 1$

rate = $k[S_2O_8^{2-}][I^-]$

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

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08/M\cdot\text{s}$$

First-Order Reactions

A $\longrightarrow$ product

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

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

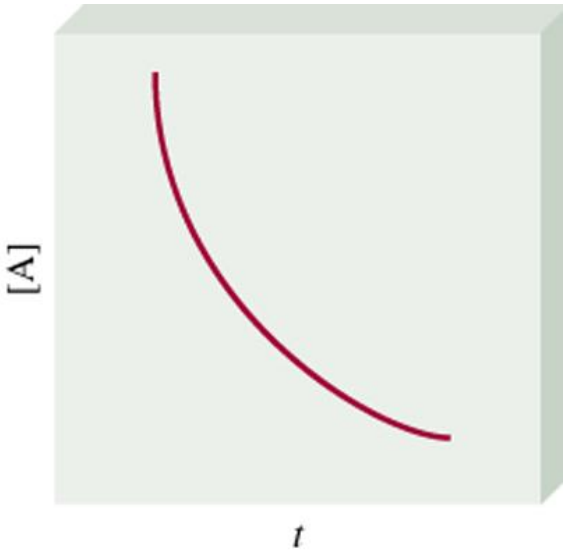
$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

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

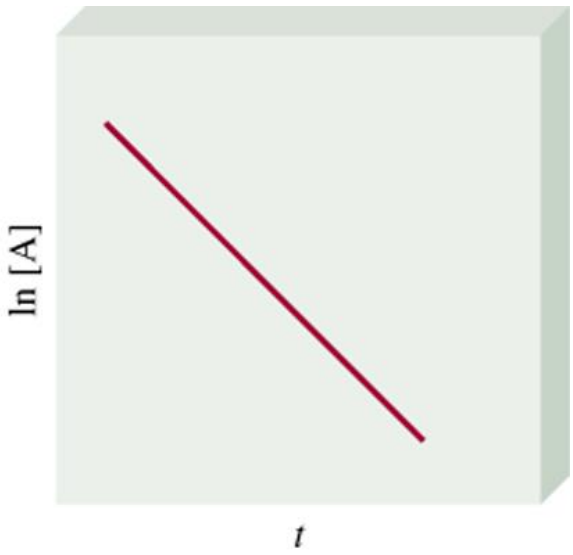
[A] is the concentration of A at any time t

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

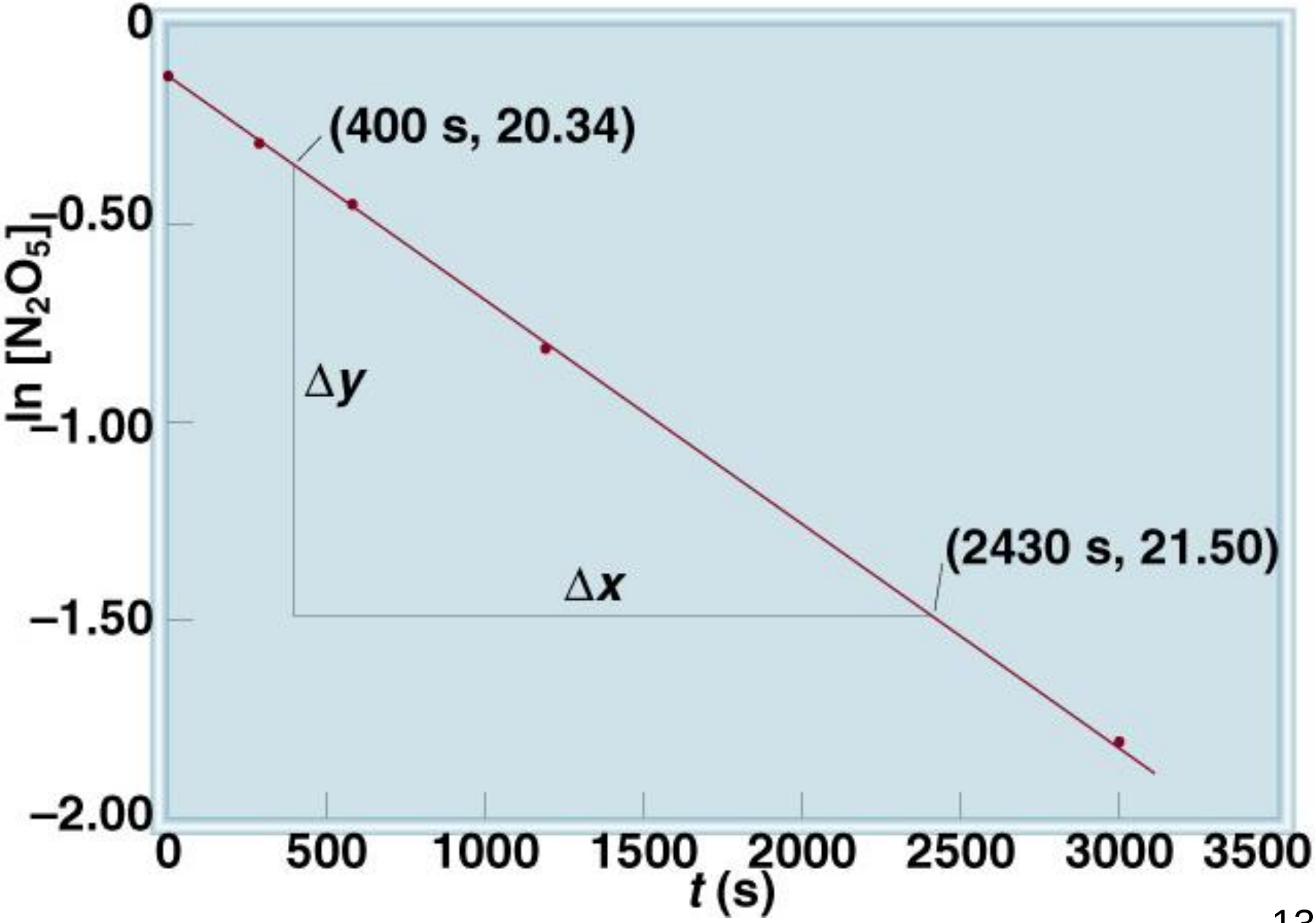
$$[A] = [A]_0 \exp(-kt)$$



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



Decomposition of N_2O_5



The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 80^0C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M*?

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

$[A]_0 = 0.88\ M$

$[A] = 0.14\ M$

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

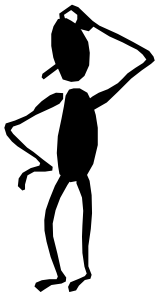
$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.88\ \cancel{M}}{0.14\ \cancel{M}}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ s$$

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.

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

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

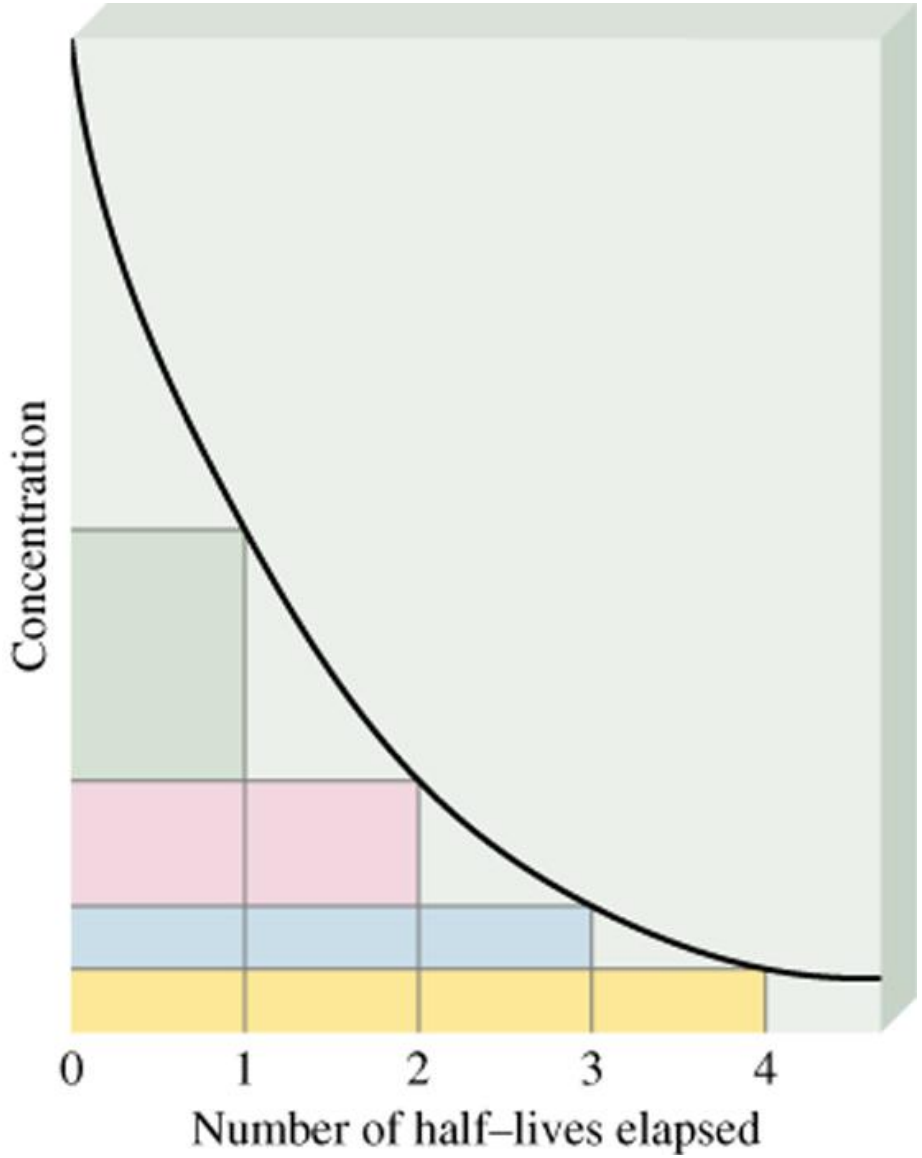


What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4}\ s^{-1}$?

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

How do you know decomposition is first order?

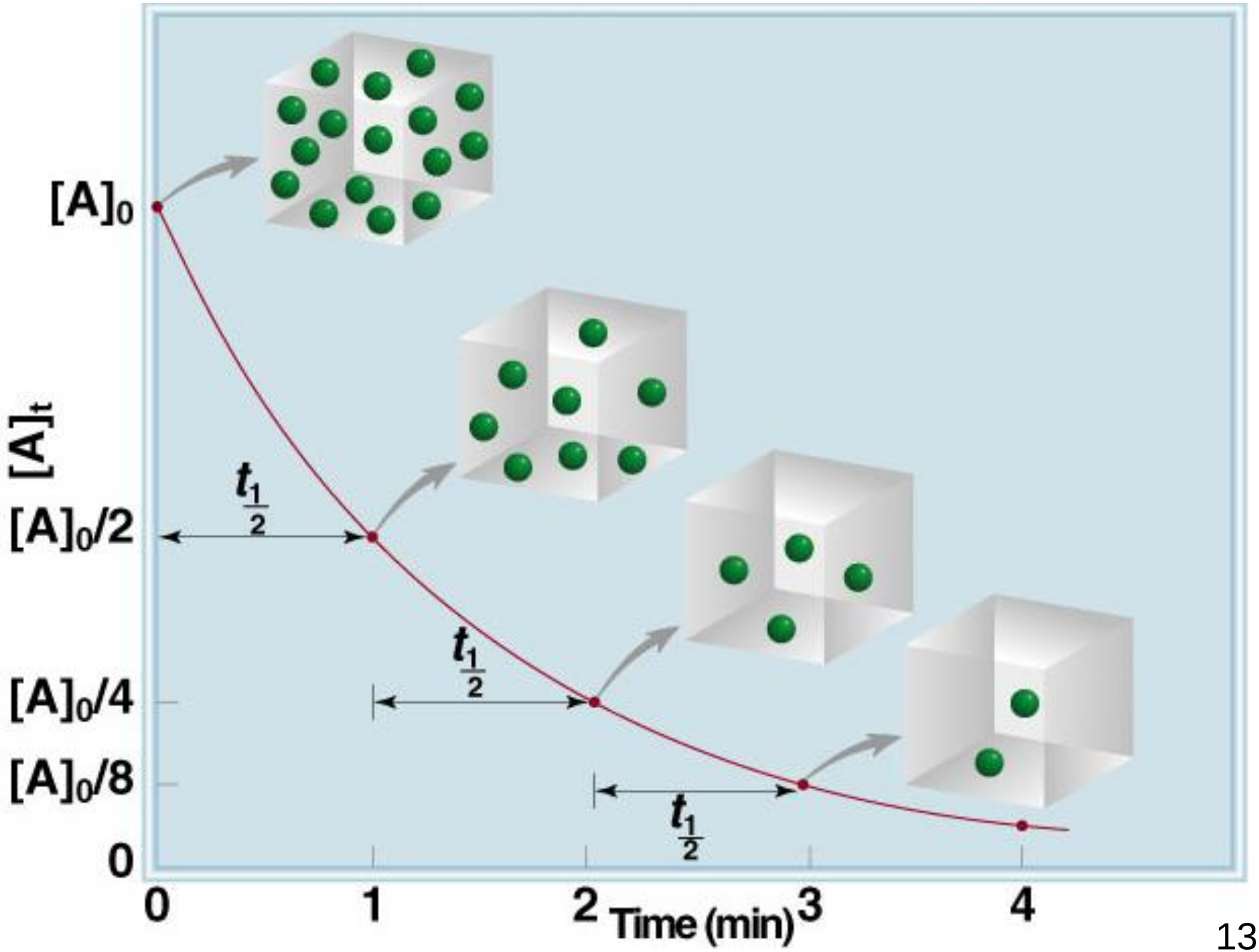
units of k (s^{-1})



First-order reaction

A ⟶ product

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


[A]0
[A]t
[A]0/2
[A]0/4
[A]0/8
0
t1/2
t1/2
t1/2
0
1
2
3
4
Time (min)

Second-Order Reactions

A $\longrightarrow$ product

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

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

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

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

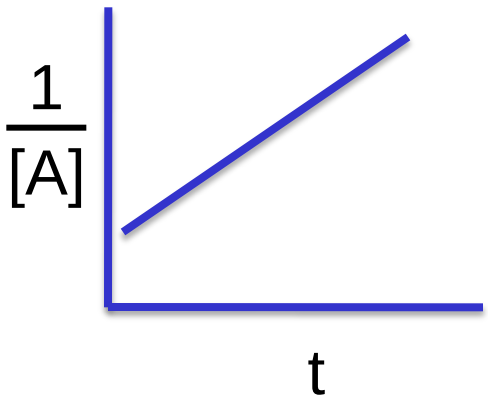
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

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

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

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

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



Zero-Order Reactions

$A \longrightarrow$ product

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

$$\text{rate} = k[A]^0 = k$$

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

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

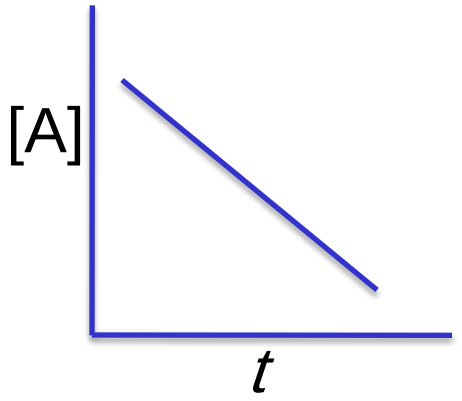
$$[A] = [A]_0 - kt$$

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

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

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

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

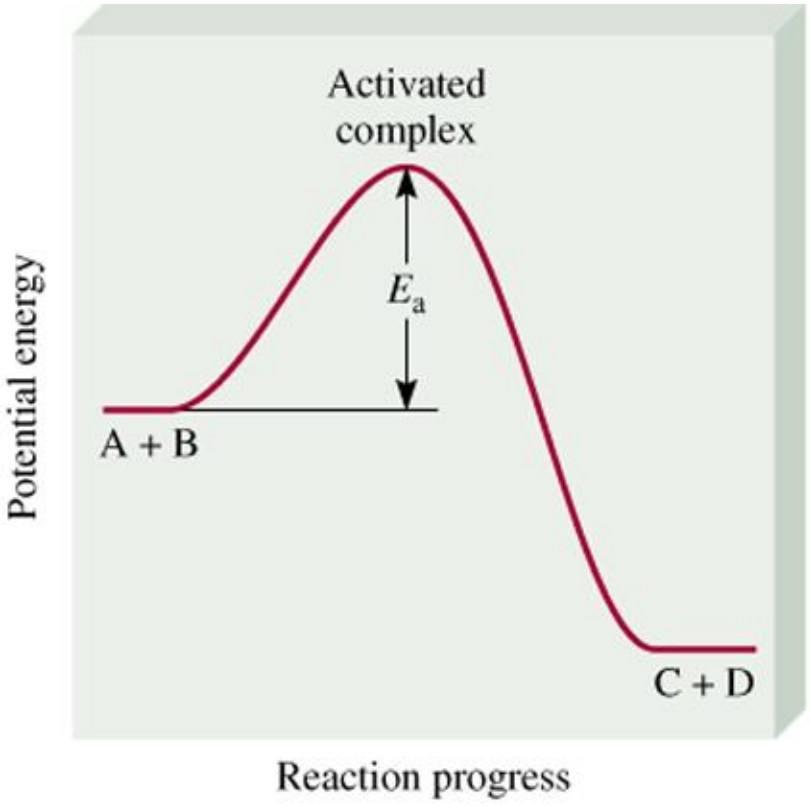


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

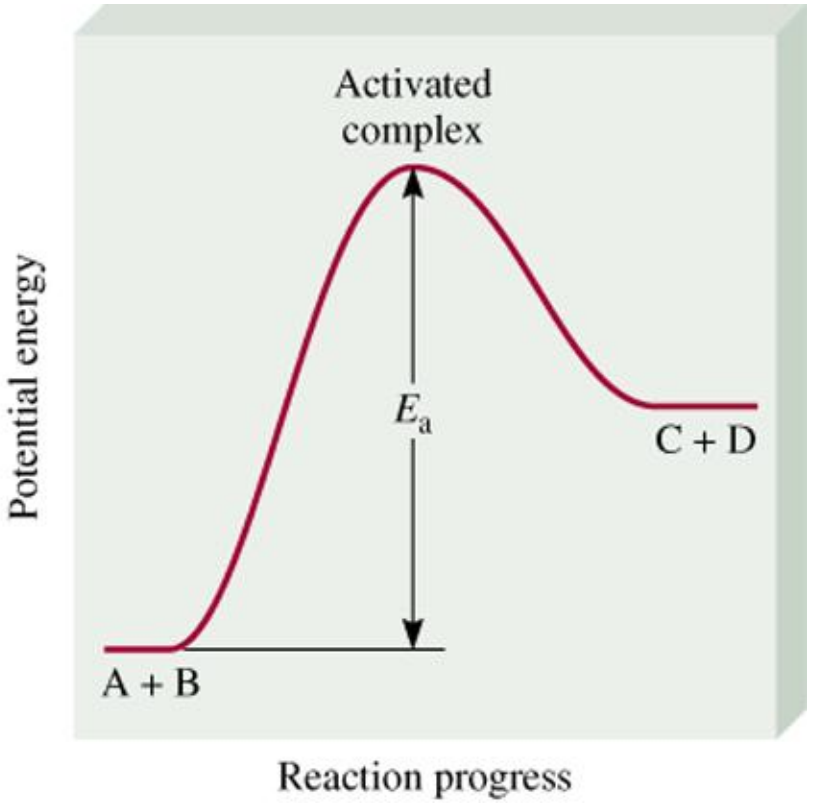
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

$$A + B \longrightarrow C + D$$

Exothermic Reaction

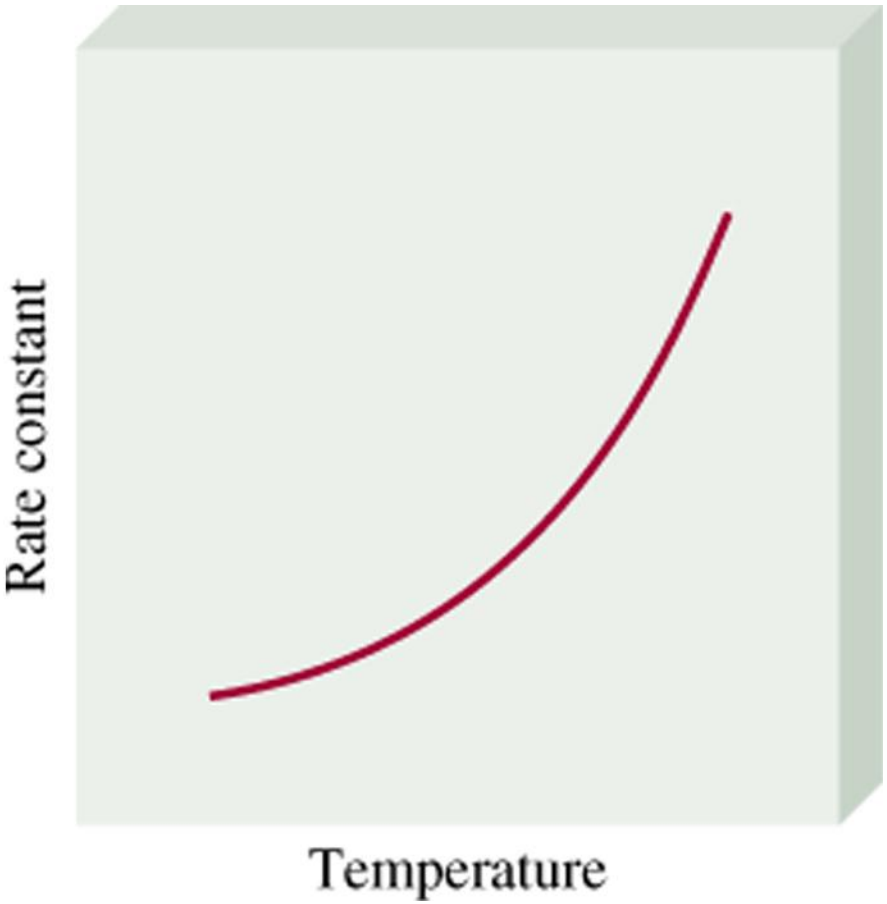


Endothermic Reaction



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)

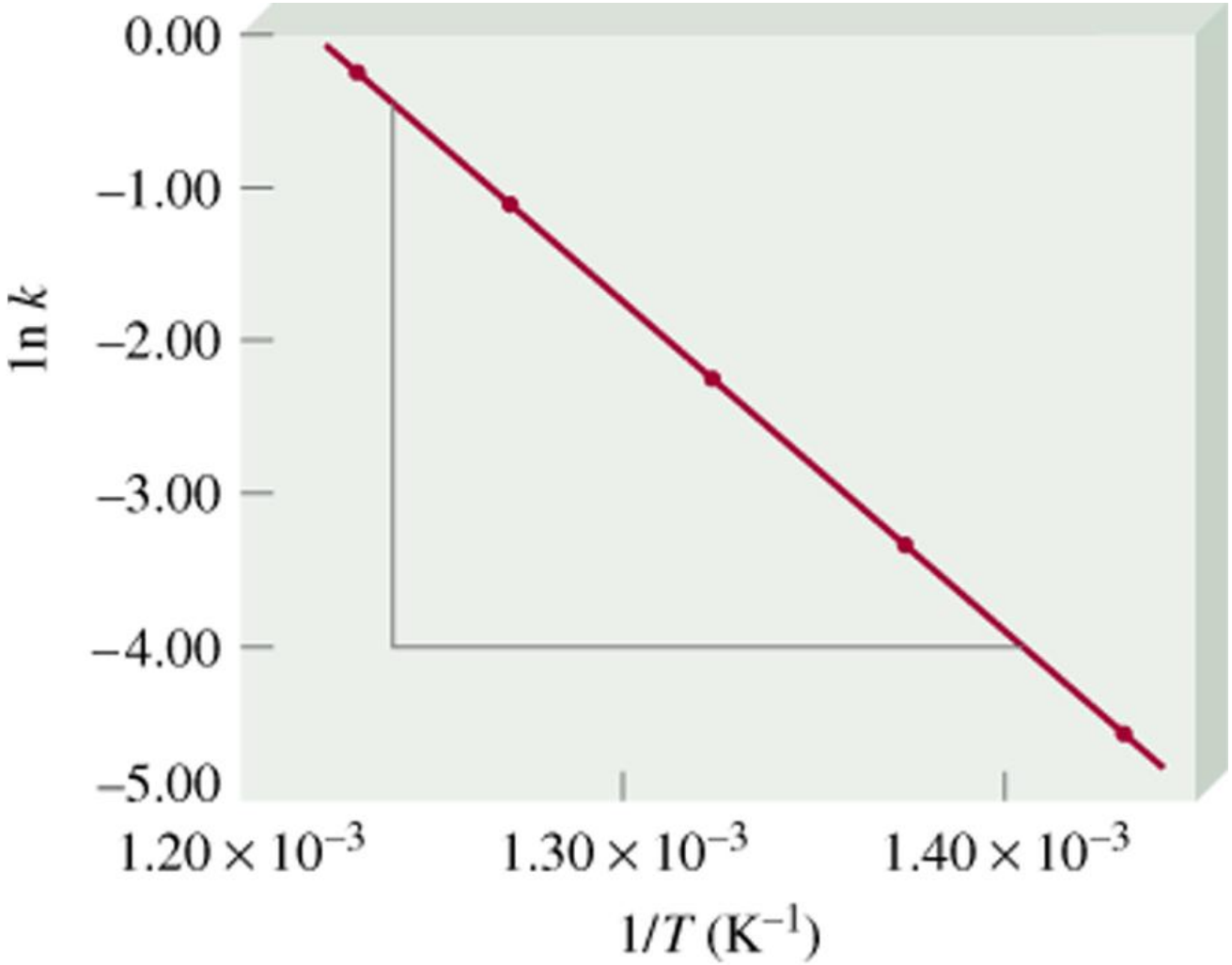
R is the gas constant (8.314 J/K•mol)

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

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

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

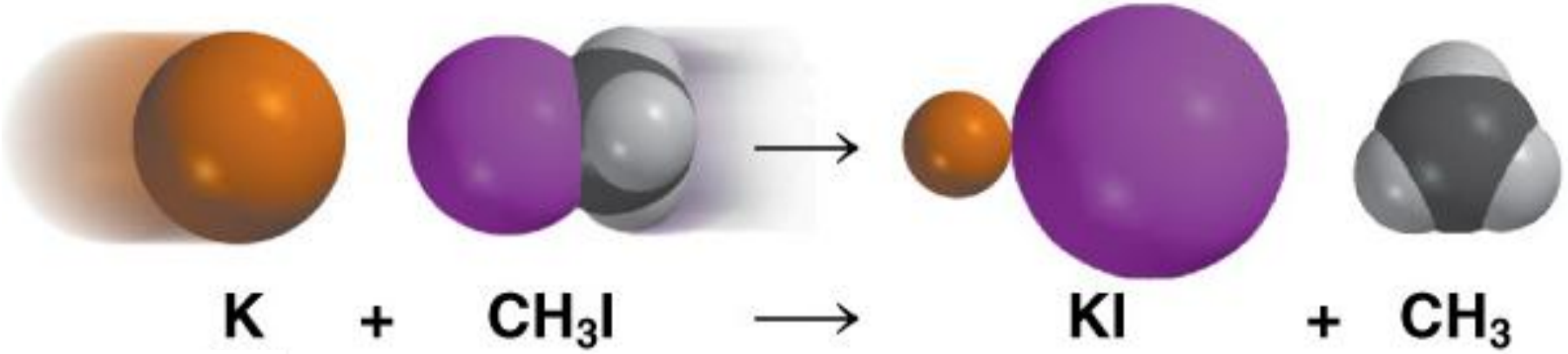
$$\ln (k_2/k_1) = (Ea / R) [(T_2 – T_1) / T_2T_1]$$

$$\ln (k_2 / k_1) = [(76.7 \times 1000) / 8.314] [(323- 273)/323x273]$$

$$\text{Ln } k_2 /k_1 = 5.23$$

$$k_2 / k_1 = 187$$

$$k_2 = 187\ k_1$$



No products formed

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***.

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

N_2O_2 is detected during the reaction!

	Elementary step:	$NO + NO \longrightarrow \cancel{N_2O_2}$
+	Elementary step:	$\cancel{N_2O_2} + O_2 \longrightarrow 2NO_2$
	Overall reaction:	$2NO + O_2 \longrightarrow 2NO_2$

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.

Elementary step: $NO + NO \longrightarrow N_2O_2$

\+ Elementary step: $N_2O_2 + O_2 \longrightarrow 2NO_2$

Overall reaction: $2NO + O_2 \longrightarrow 2NO_2$

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

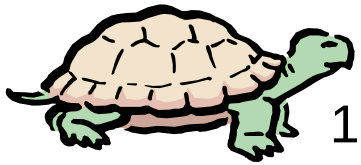
Rate Laws and Elementary Steps

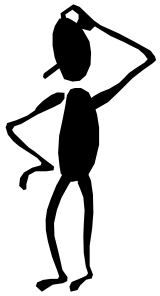
Unimolecular reaction	$A \longrightarrow$ products	rate = $k[A]$
Bimolecular reaction	$A + B \longrightarrow$ products	rate = $k[A][B]$
Bimolecular reaction	$A + A \longrightarrow$ products	rate = $k[A]^2$

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 rate = $k[NO_2]^2$. The reaction is believed to occur via two steps:

Step 1: $NO_2 + NO_2 \longrightarrow NO + NO_3$

Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$

What is the equation for the overall reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

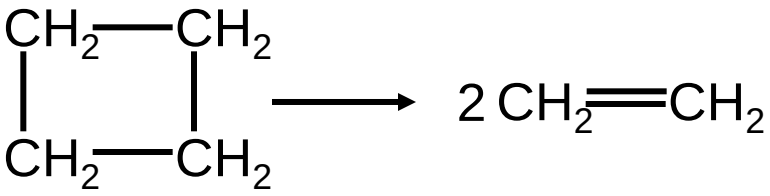
What is the intermediate?

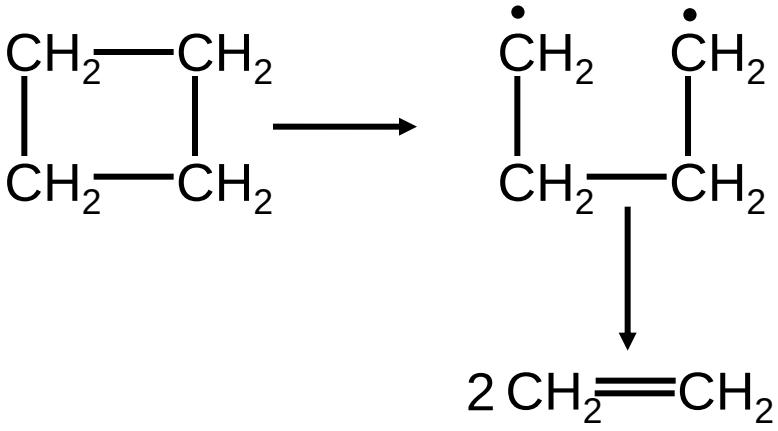
$$NO_3$$

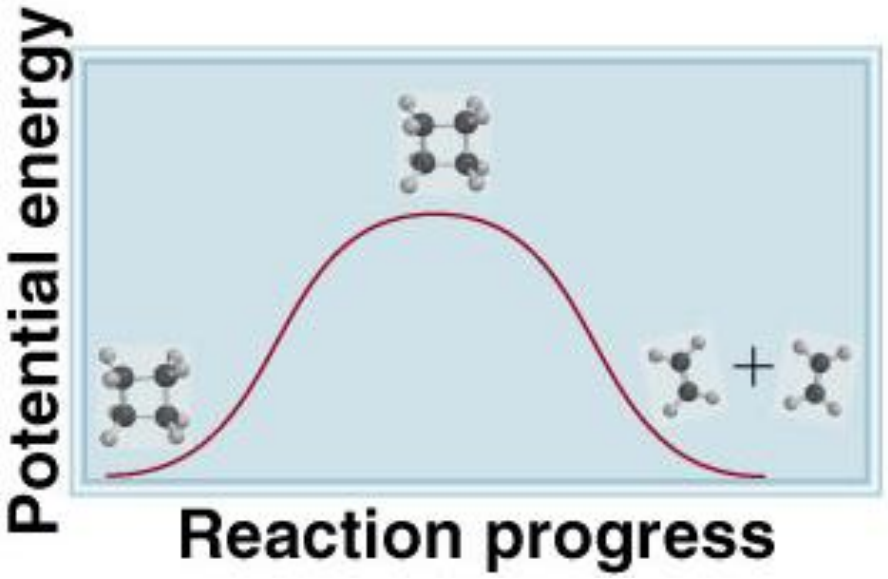
What can you say about the relative rates of steps 1 and 2?

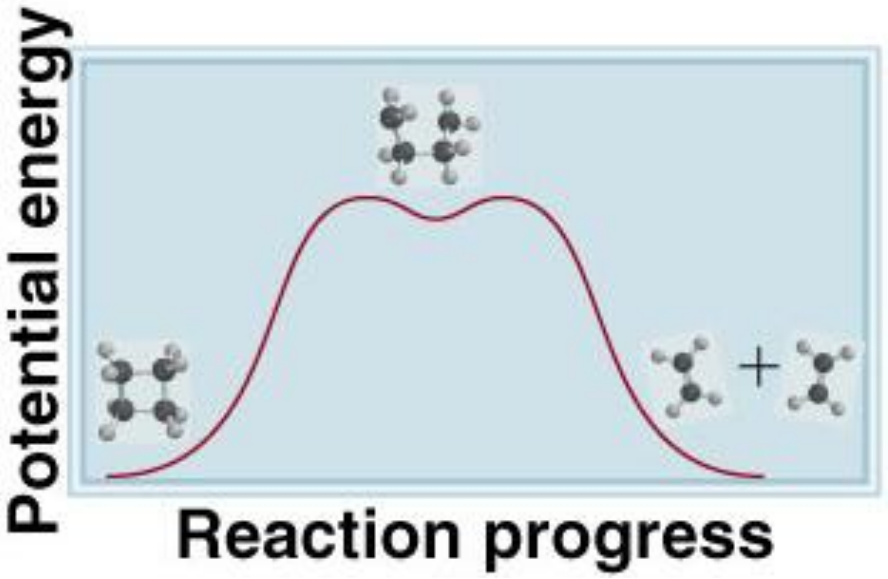
rate = $k[NO_2]^2$ is the rate law for step 1 so step 1 must be slower than step 2

Chemistry In Action: Femtochemistry



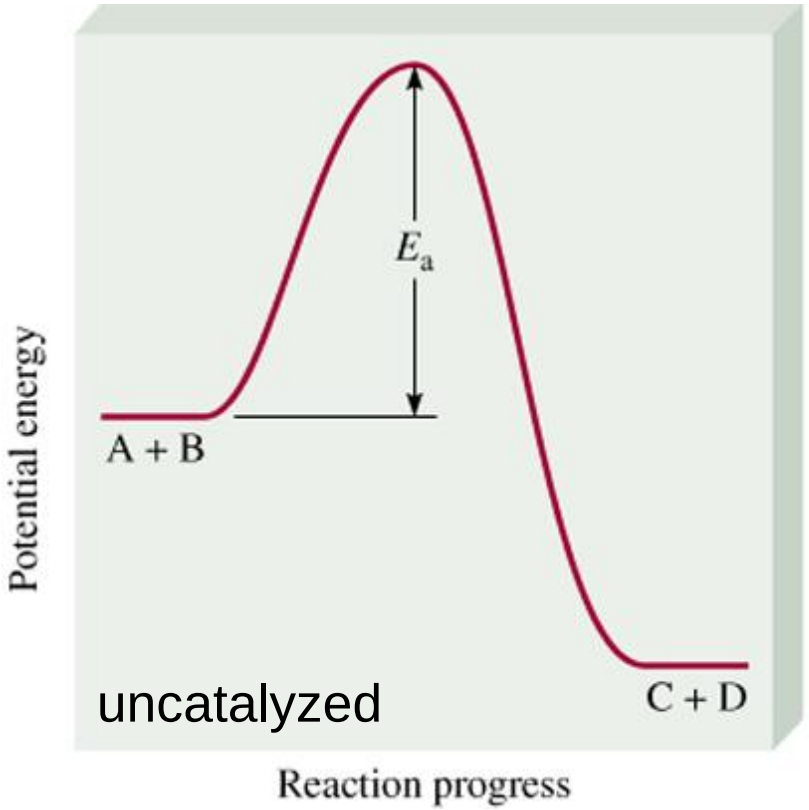


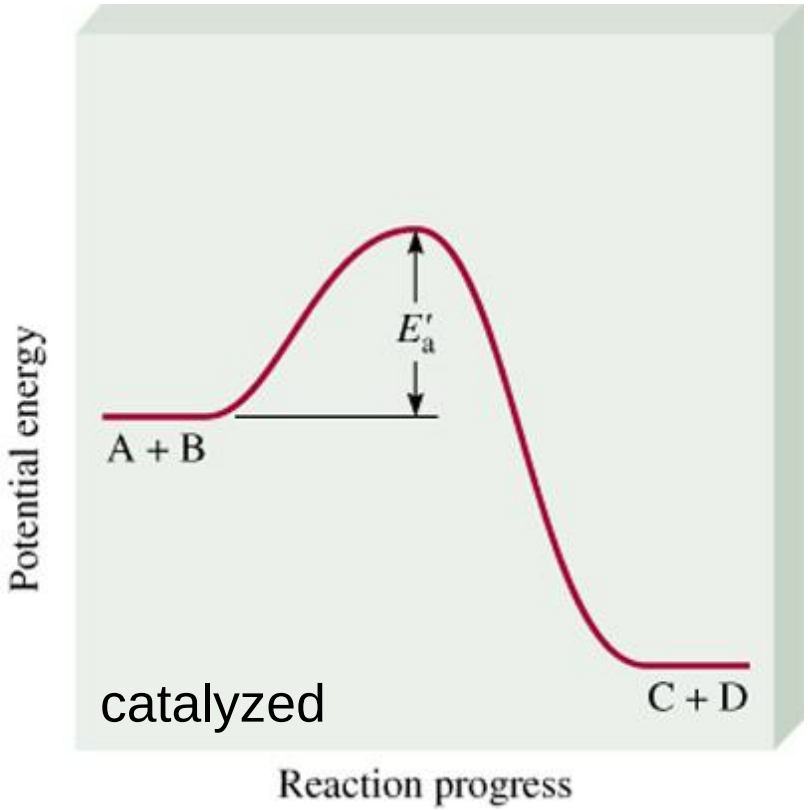




A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being consumed.

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





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

$$E_a' < E_a$$

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).

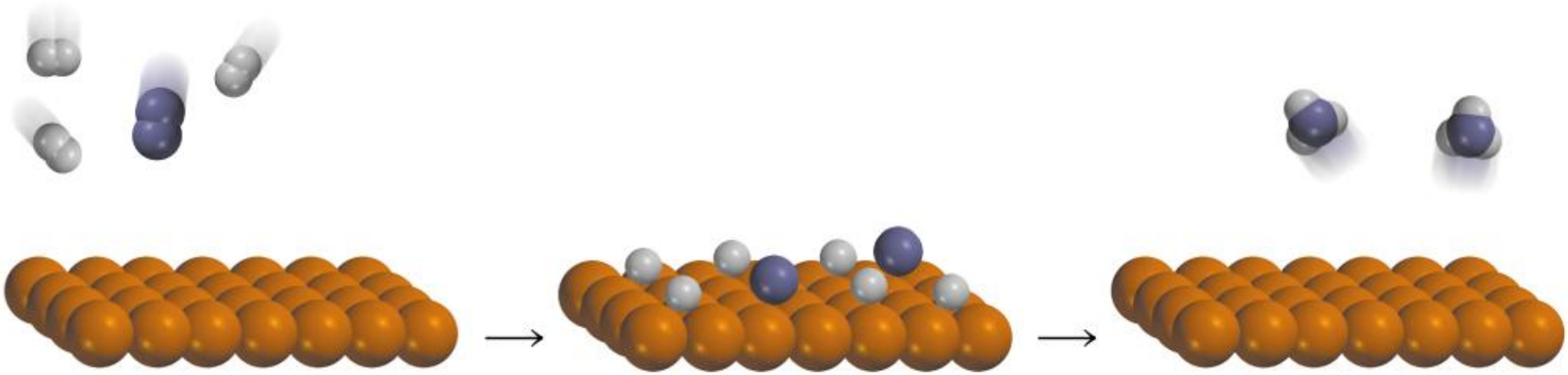
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

- 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



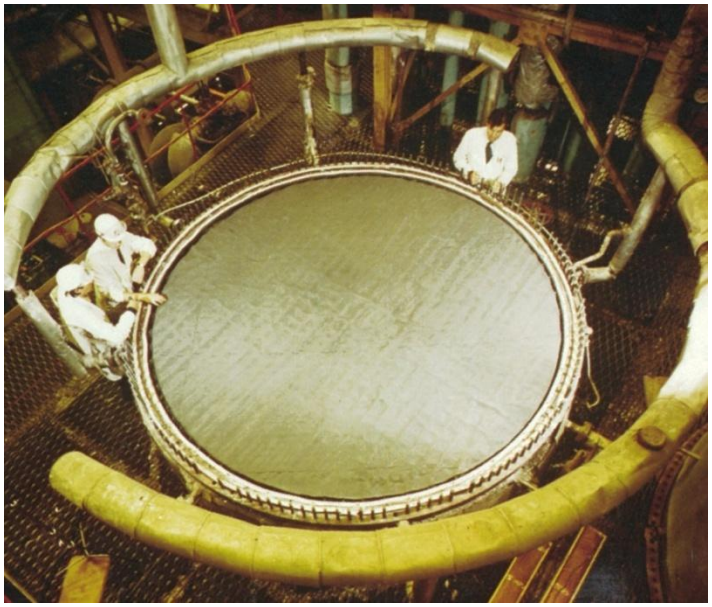
$$N_2\,(g) + 3H_2\,(g) \xrightarrow[\text{catalyst}]{Fe/Al_2O_3/K_2O} 2NH_3\,(g)$$

Ostwald Process

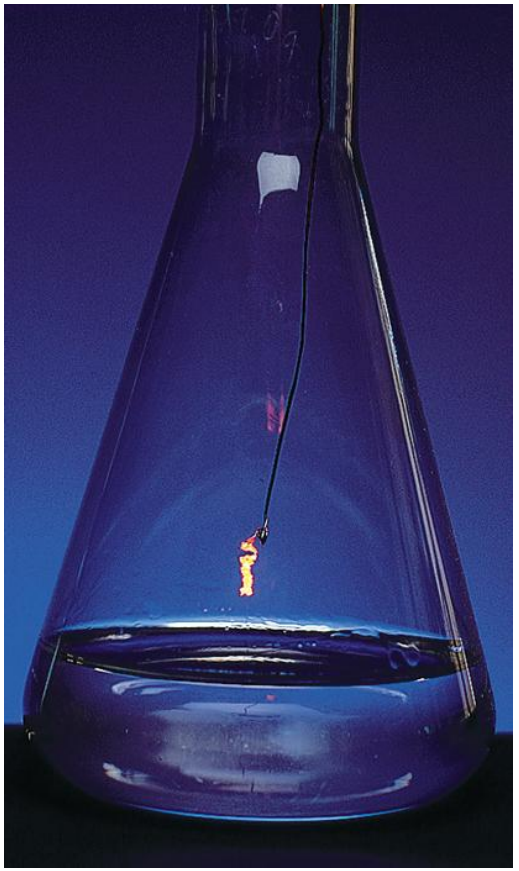
$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow{\text{Pt catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

$$2NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_2\,(aq) + HNO_3\,(aq)$$

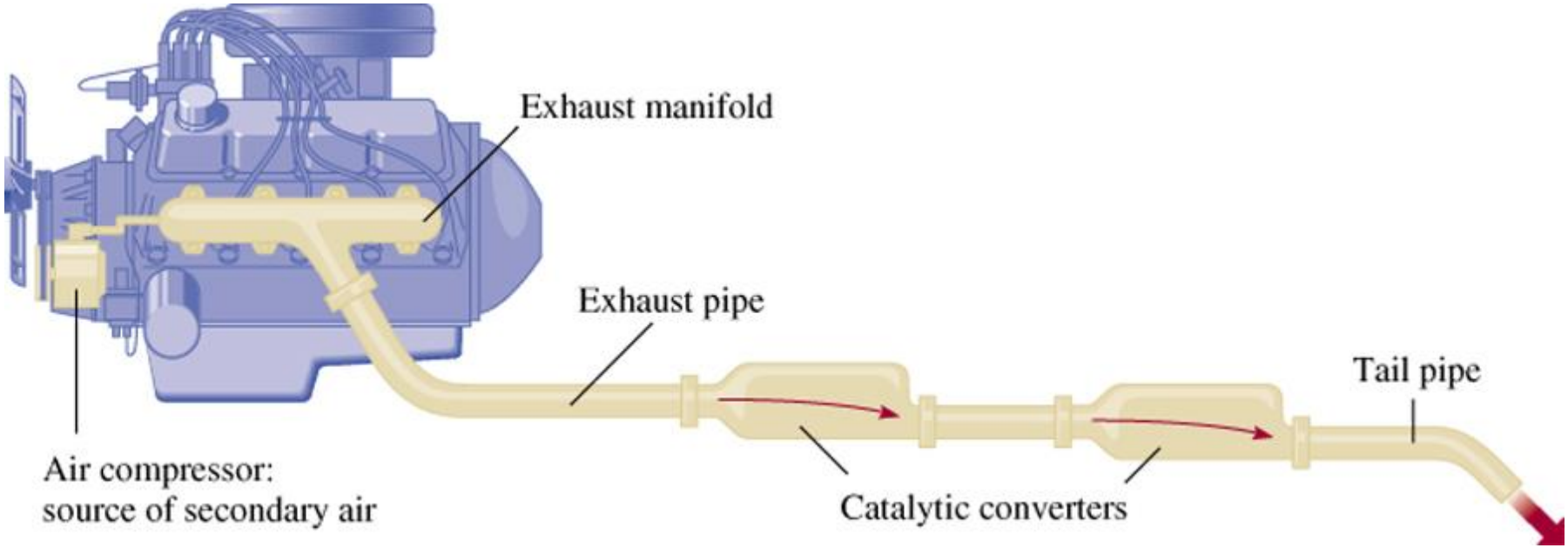


Pt-Rh catalysts used in Ostwald process

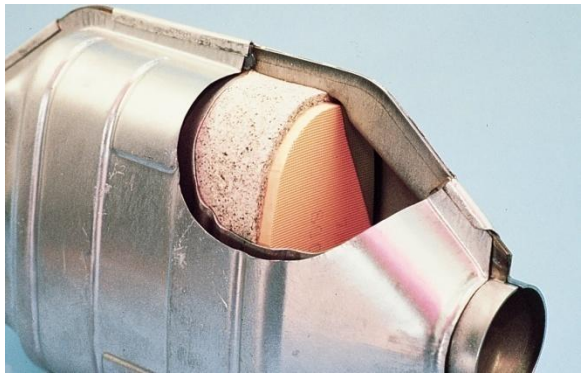


Hot Pt wire over NH_3 solution

Catalytic Converters

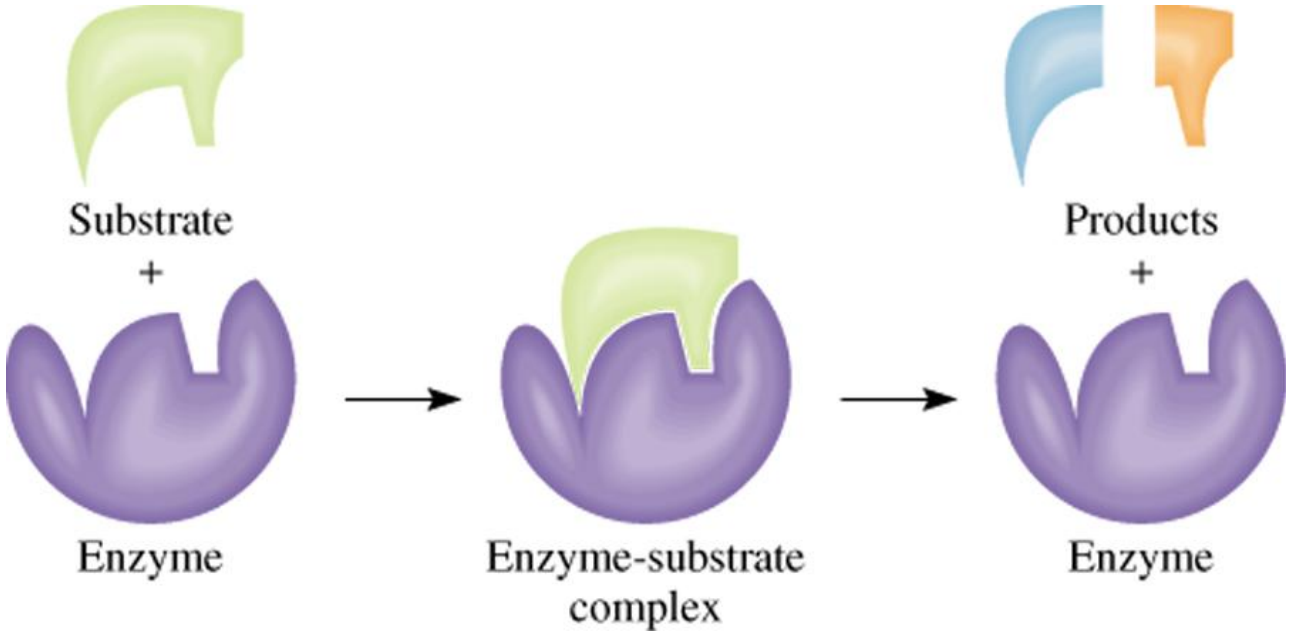


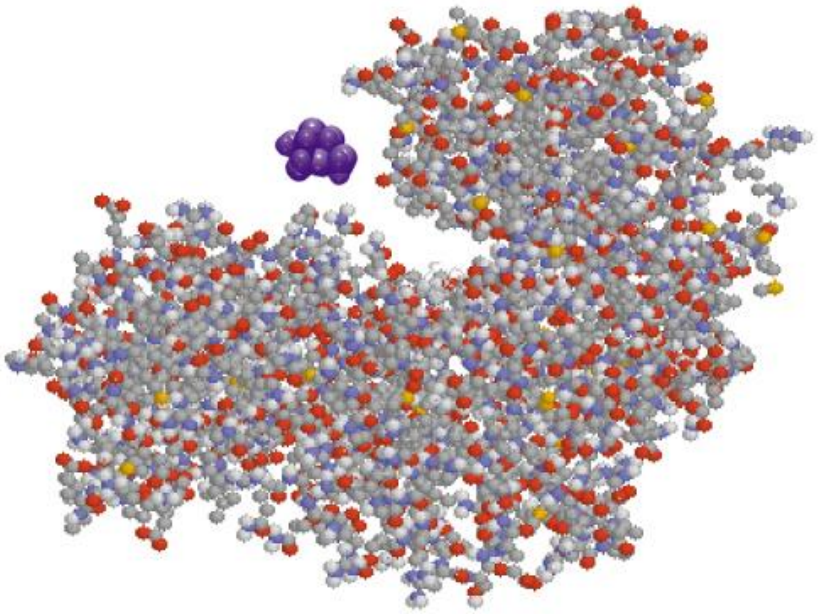
$$\text{CO + Unburned Hydrocarbons + } O_2 \xrightarrow[\text{converter}]{\text{catalytic}} CO_2 + H_2O$$

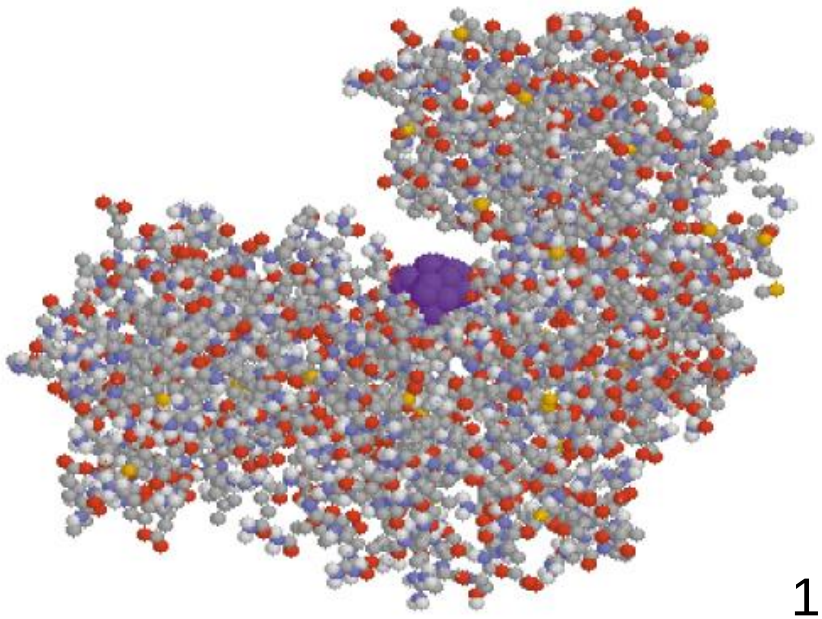


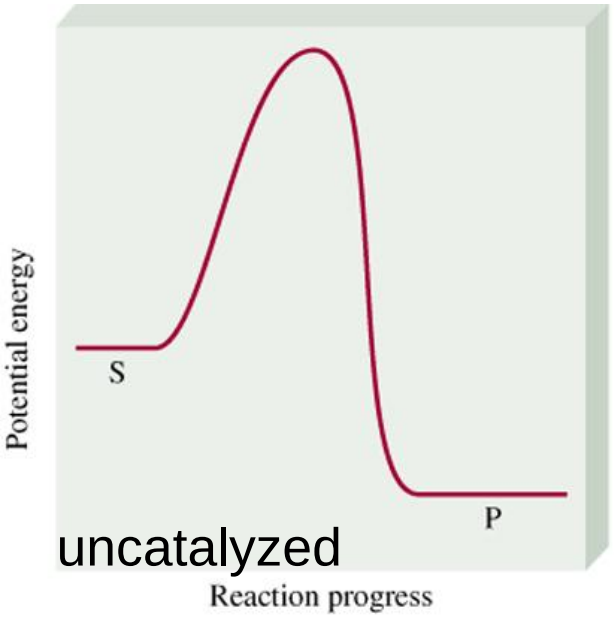
$$2NO + 2NO_2 \xrightarrow[\text{converter}]{\text{catalytic}} 2N_2 + 3O_2$$

Enzyme Catalysis

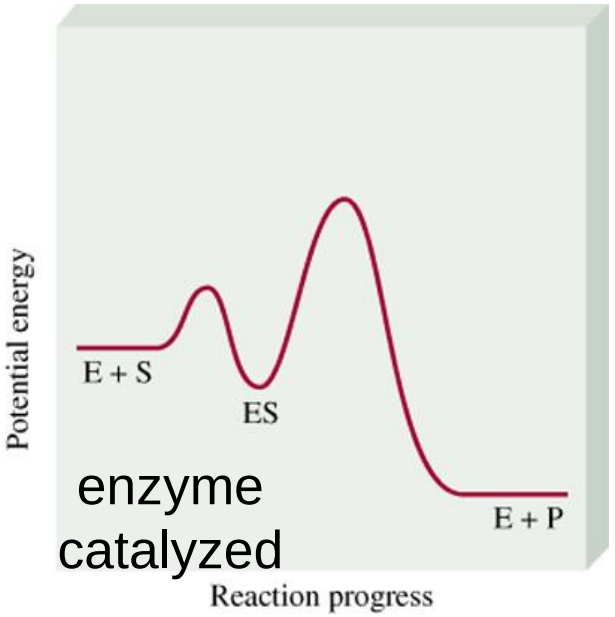




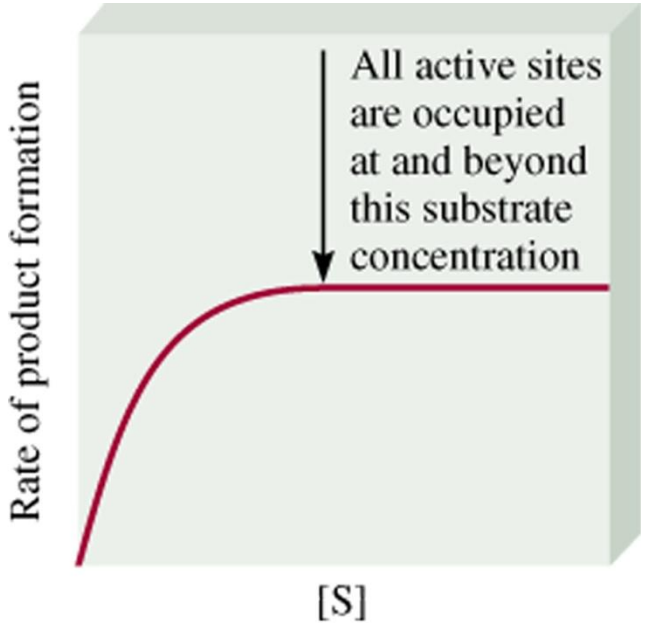




uncatalyzed



enzyme catalyzed

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

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