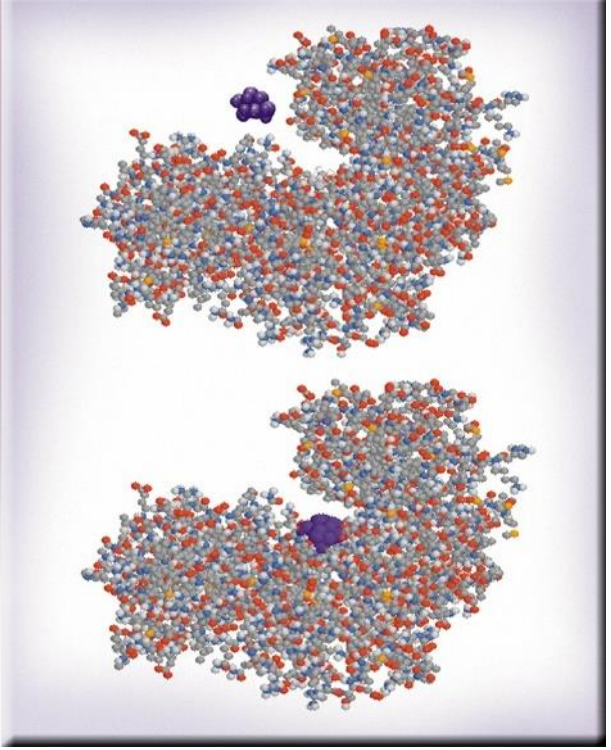

Chemical Kinetics

Chapter 13

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Chemical Kinetics

Chapter Four Contains:

4.1 The Rate of a Reaction
4.2 The Rate Law
4.3 The Relation Between Reactant Concentration and Time
4.4 Activation Energy and Temperature Dependence of Rate Constants
4.5 Reaction Mechanisms
4.6 Catalysis

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}.

$$A \longrightarrow B$$

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

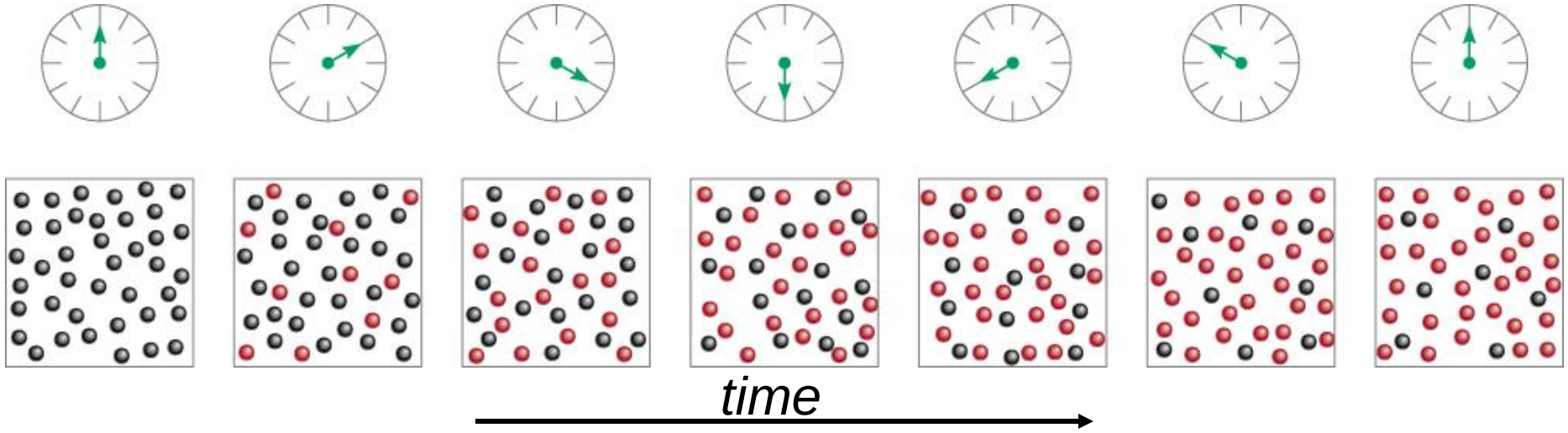
$\Delta[A]$ = change in concentration of A over time period Δt

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

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

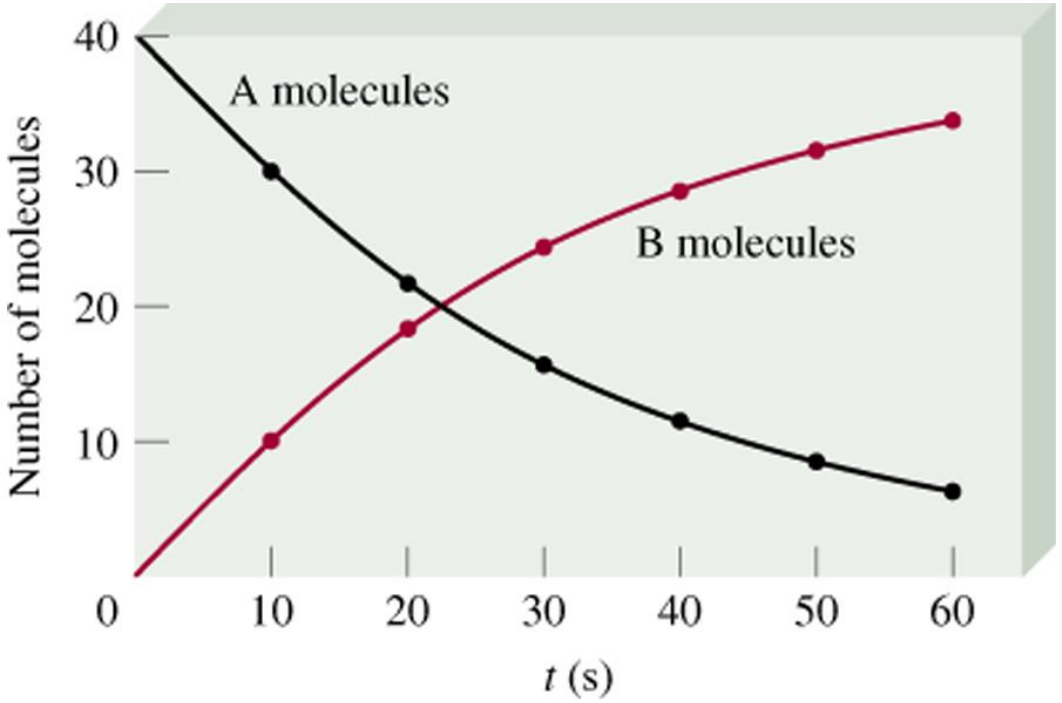
Because [A] decreases with time, $\Delta[A]$ is negative.

A ⟶ B



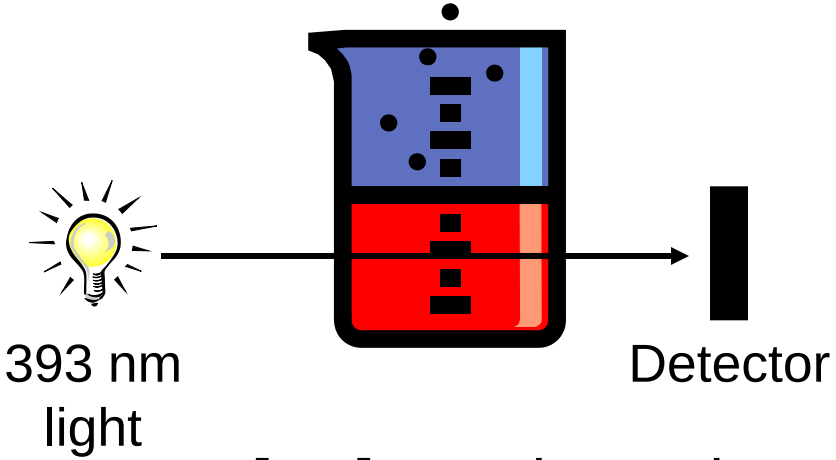
$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

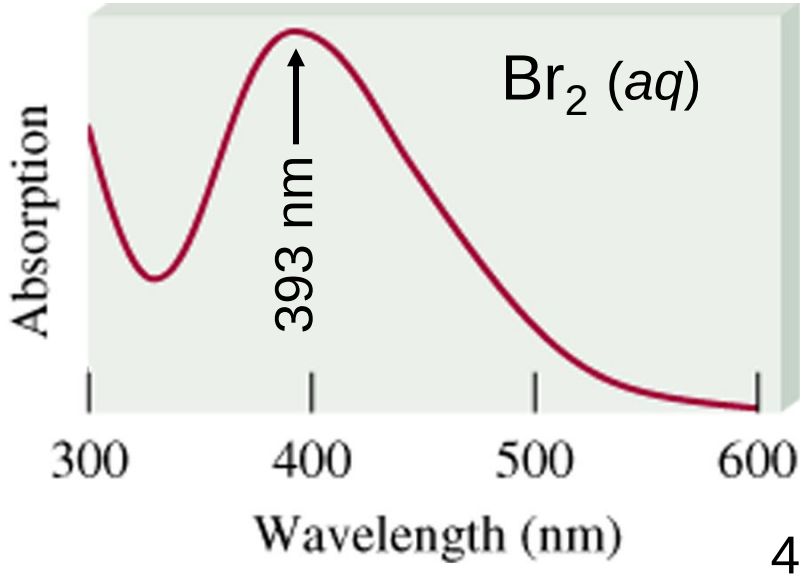


$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

time →

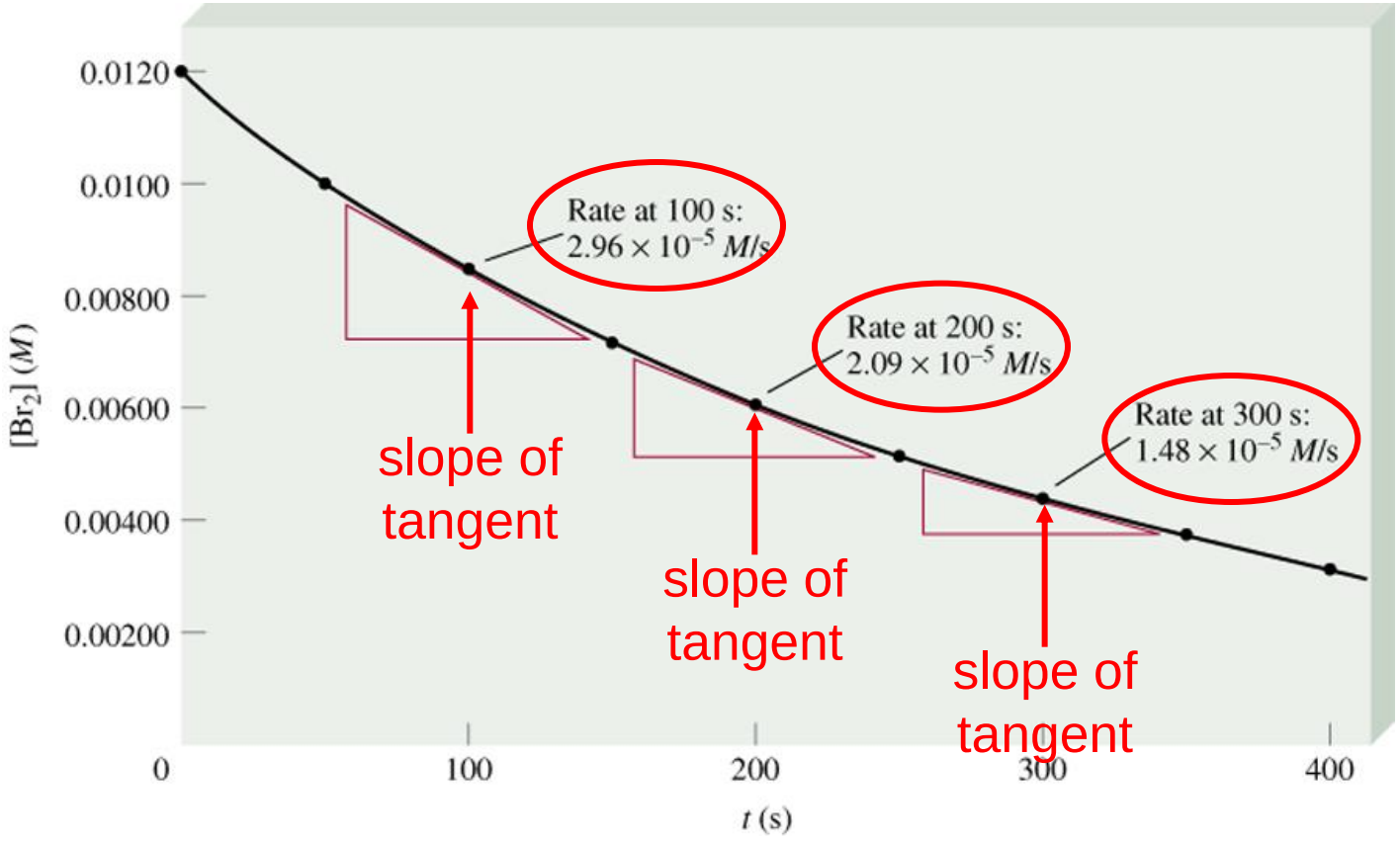


$\Delta[Br_2] \alpha \Delta Absorption$



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

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

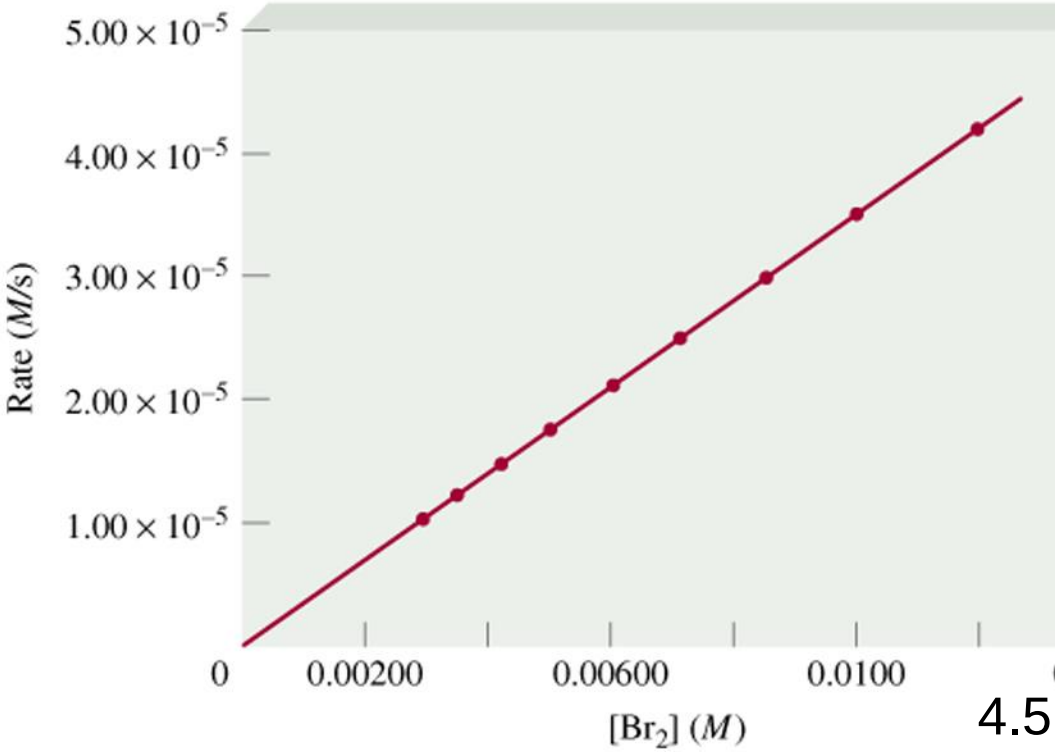
Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}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

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

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



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

$$PV = nRT$$

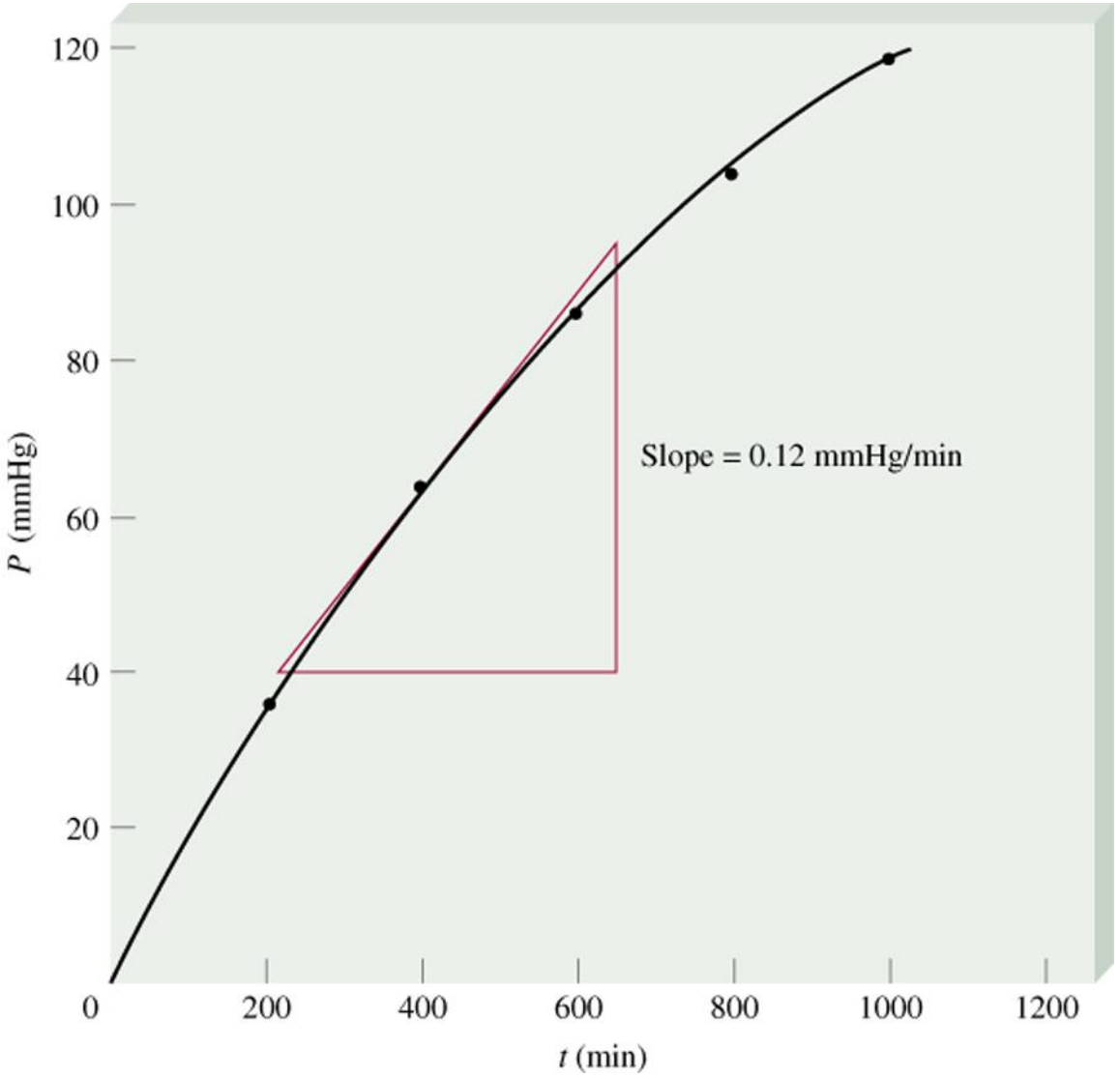
$$P = \frac{n}{V}RT = [O_2]RT$$

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

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

measure ΔP over time

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



Reaction Rates and Stoichiometry

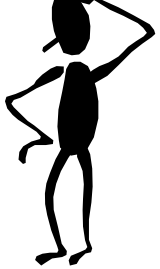
$$2A \longrightarrow B$$

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

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

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

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



Example 4.1Write the rate expression for the following reaction:

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

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

Example 4.2 : Consider the reaction

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s. (a) at what rate is N_2O_5 being formed? (b) at what rate is NO_2 reacting?

$$\text{rate} = -\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

$$\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = 0.024 \qquad -\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = 0.024$$

$$\frac{\Delta[N_2O_5]}{\Delta t} = 0.024 \times 2 = 0.048 \text{ M/s} \qquad \frac{\Delta[NO_2]}{\Delta t} = -0.024 \times 4 = -0.096 \text{ M/s}$$

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**

Example 4.3 $F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$

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 /$[F_2][ClO_2]$

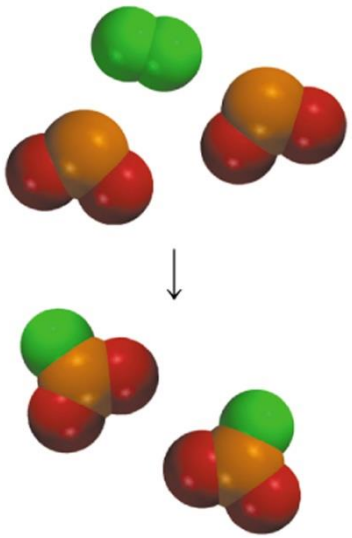
K = 1.2 $\times10^{-3}$ / 0.10 x 0.01

K = 4.8 x 10^{-3} / 0.10 x 0.040

K = 2.4 $\times10^{-3}$ / 0.20 x0.010

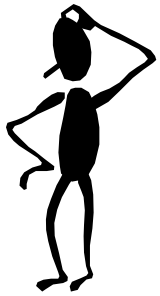
Rate Laws

- 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.



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

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



Example 4.4: 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)

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

Example 4.5: Drive rate Law and k for

$$CH_3\,CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$$

For experimental data for rate of disappearance of CH_3CHO

Exp	[CH3CHO]	R(mol / L .s)
1	0.1	0.02
2	0.2	0.081
3	0.3	0.81
4	0.4	0.318

rate = $k\,[CH_3CHO]^x$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{0.081}{0.02} = 4 = \frac{k\,(0.2)^x}{k\,(0.1)^x} \Rightarrow 4 = (2)^x \Rightarrow x = 2$$

rate = $k\,[CH_3CHO]^2$

$R_1 = 0.02 = k\,(0.1)^2 \Rightarrow 0.02 = 0.01\,k \Rightarrow k = 0.02 / 0.01 = 2.0\ L / mol\ .s$

First-Order Reactions

A $\longrightarrow$ product

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

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

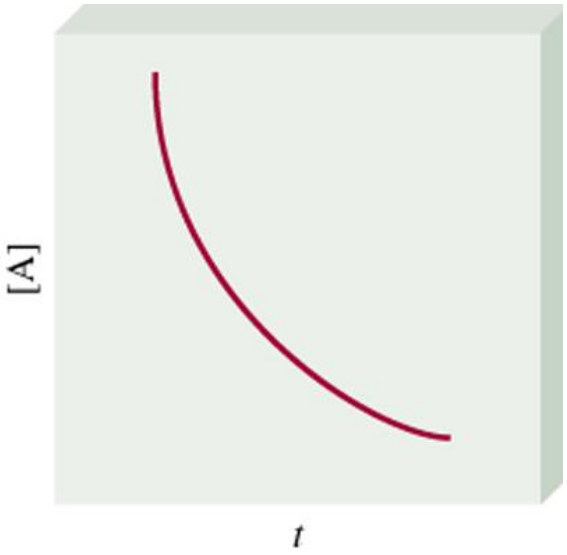
$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

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

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

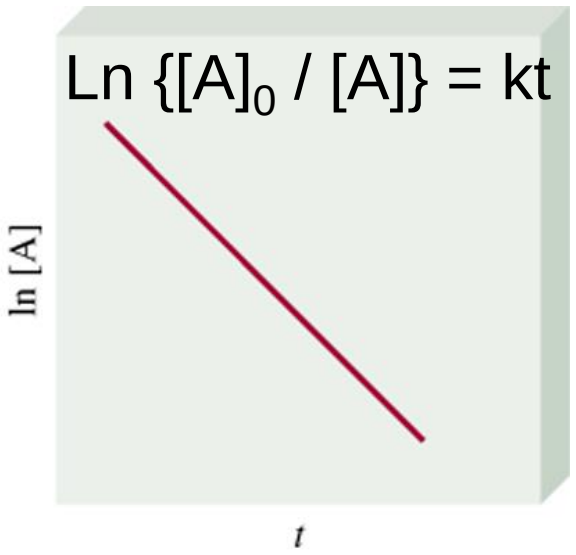
$[A]_0$ is the concentration of A at time *t*=0

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

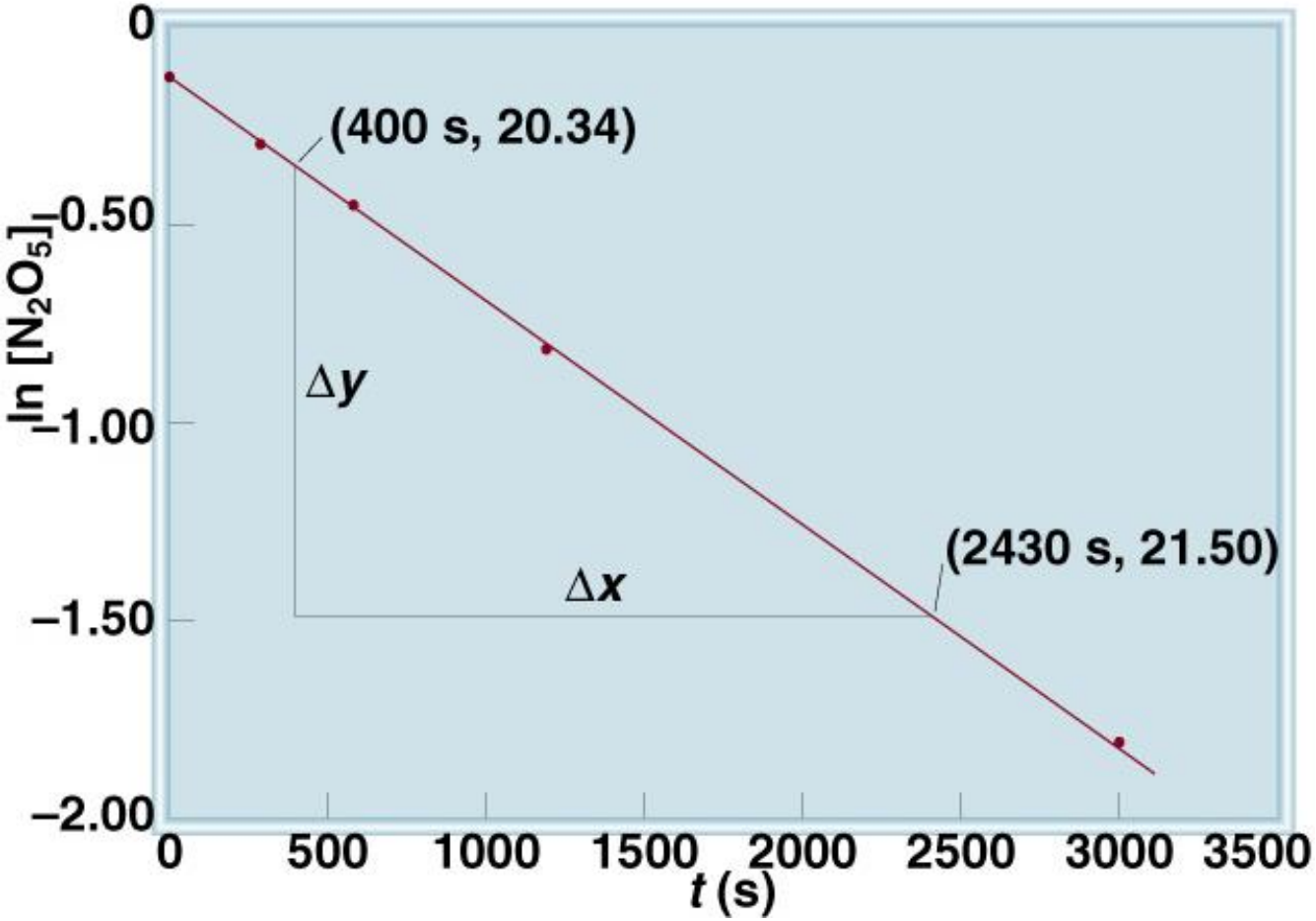


$$\ln[A] = \ln[A]_0 - kt$$

$$\text{Ln}\{[A]_0 / [A]\} = kt$$

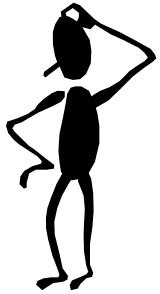


Decomposition of N_2O_5



For gas-phase reactions we can replace the concentration terms with the pressures of the gaseous reactant

$\ln[A] = \ln[A]_0 - kt$ ⟹ $\ln P = \ln P_0 - kt$



Example 4.6: 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* ?

$$\ln \{[A]_0 / [A]\} = kt$$

$$[A]_0 = 0.88\ M$$

$$[A] = 0.14\ M$$

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

Example 4.7: The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4}\ s^{-1}$ at 500°C.

(a) If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min?

(b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M?

(c) How long (in minutes) will it take to convert 74 percent of the starting material?

a) $[A]_0 = 0.25\ M$, t= 8.8 min = 8.8x60 = 528 s , $k = 6.7 \times 10^{-4}\ s^{-1}$, [A] = ?

$$\ln[A] = \ln[A]_0 - kt$$
$$= \ln(0.25) - ((6.7 \times 10^{-4}\ s^{-1})(528))$$
$$= -1.74$$
$$[A] = e^{-1.74} = 0.18M$$

b) $[A]_0 = 0.25\ M$, [A] = 15M , k= $6.7 \times 10^{-4}\ s^{-1}$, t= ?

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

$$t = \frac{\ln[A] - \ln[A]_0}{-k} = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.25}{0.15}}{6.7 \times 10^{-4}}$$

$= 7.6 \times 10^{2}$ s

$= (7.6 \times 10^{2}) / 60 = 13$ min

C) The converted concentration will be 0.25 x (74/100) = 0.185 M
The remaining concentration will be = 0.25 -0.185 = 0.065 M

$[A]_0 = 0.25\ M$, [A] = 0.065M , k= $6.7 \times 10^{-4}\ s^{-1}$, t= ?

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

$$t = \frac{\ln[A] - \ln[A]_0}{-k} = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.25}{0.065}}{6.7 \times 10^{-4}}$$

$= 2.0 \times 10^{3}$ s

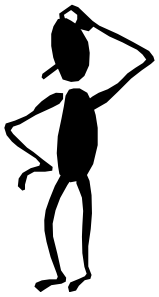
$= (2.0 \times 10^{2}) / 60 = 33$ min

First-Order Reactions

The ***half-life*, $t_{½}$,** is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{½} = t \text{ when } [A] = [A]_0/2$$

$$t_{½} = \frac{\ln \dfrac{\cancel{[A]_0}}{\cancel{[A]_0}/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

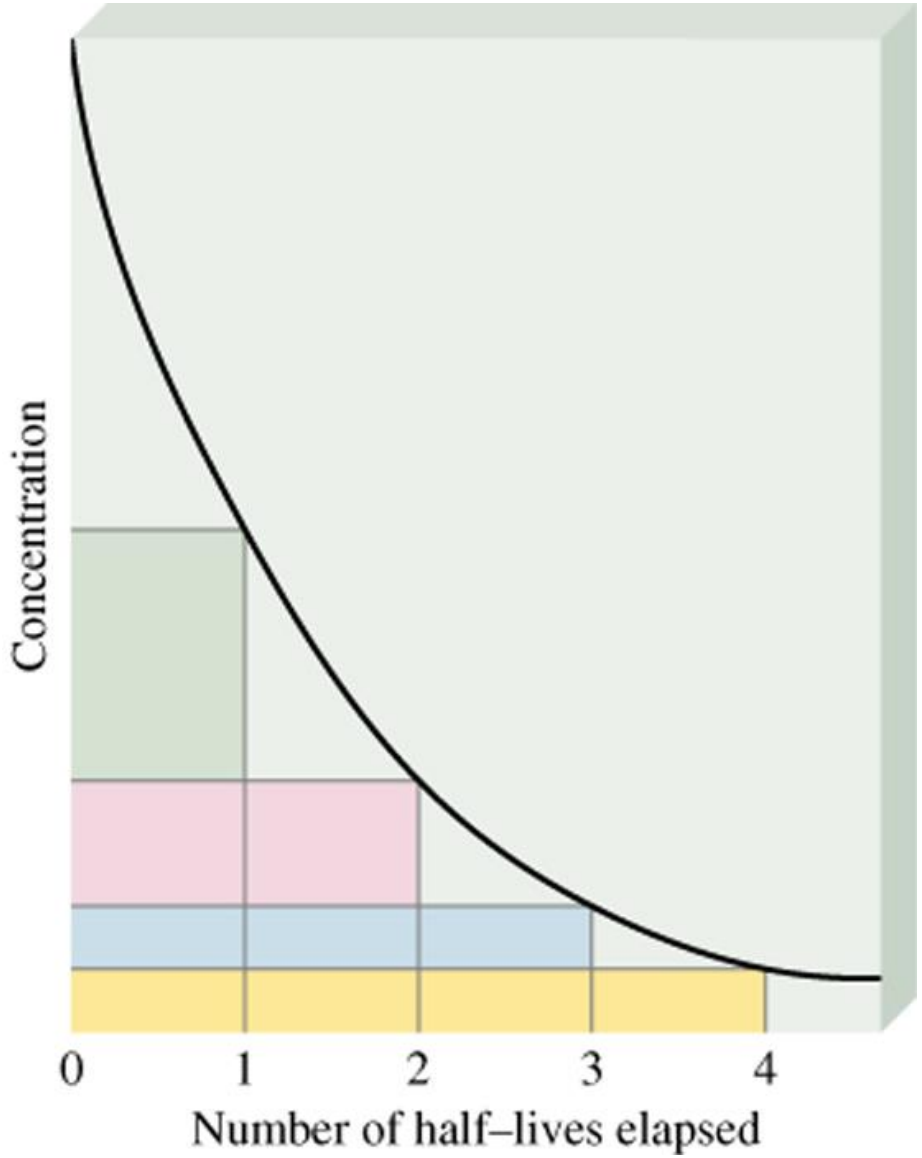


What is the half-life of N_2O_5 if it decomposes with a rate constant of 5.7×10^{-4} s^{-1}?

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4}\ s^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

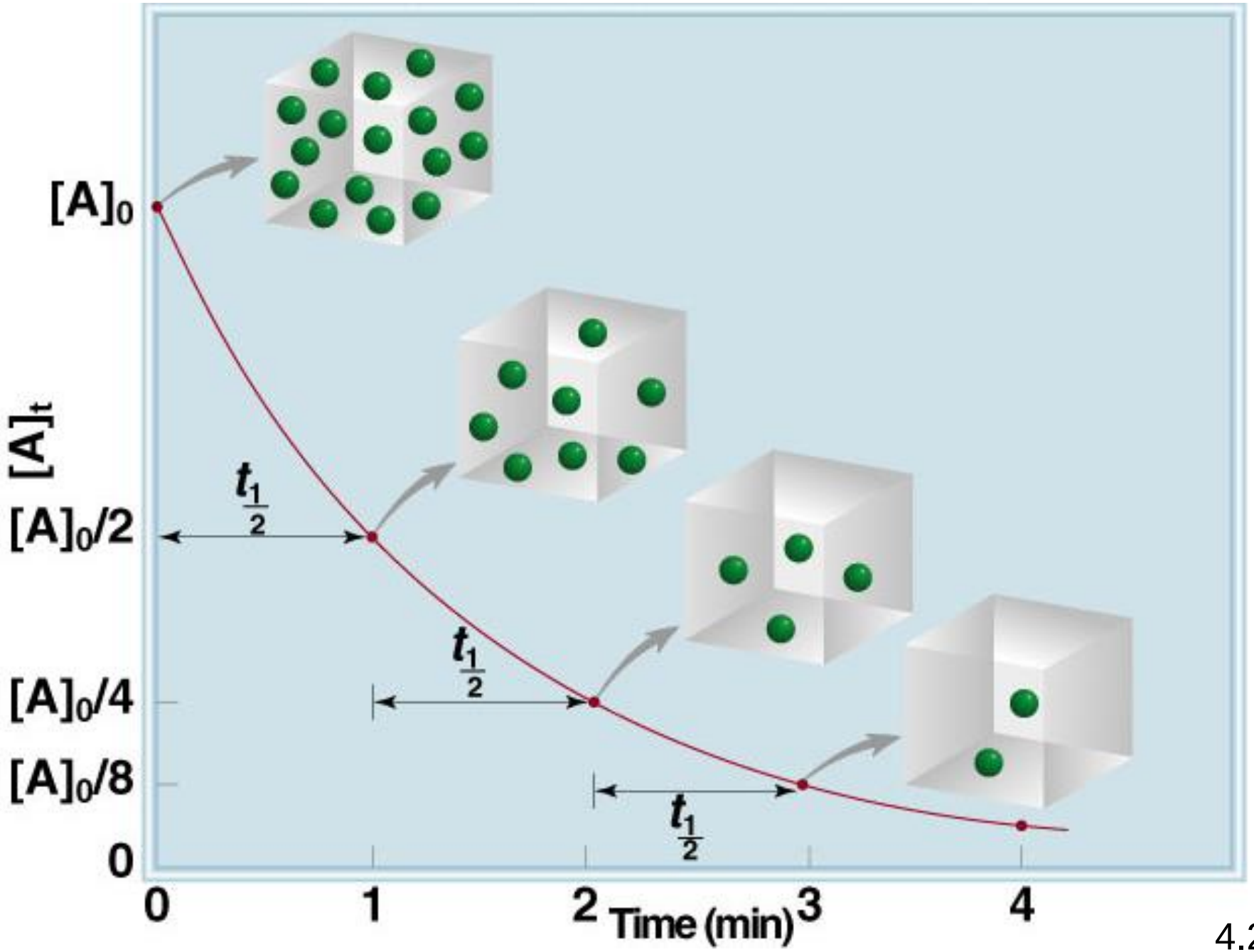
units of k (s^{-1})



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

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

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

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

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

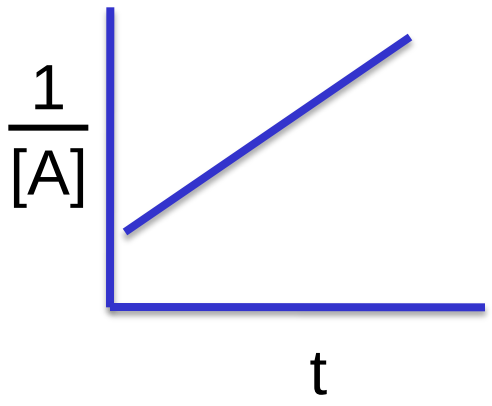
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

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

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

$t_{½} = t$ when $[A] = [A]_0/2$

$$t_{½} = \frac{1}{k[A]_0}$$



Example 4.8 :Iodine atoms combine to form molecular iodine in the gas phase

$I(g) + I(g) \longrightarrow I_2(g)$

This reaction follows second-order kinetics and has the high rate constant 7.0×10^9 /M.s at 23°C. (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M.

a) $[A]_0 = 0.086\ M$, $k = 7.0 \times 10^9$ /M.s , $t = 2\ \text{min} = 2 \times 60 = 120$ s, $[A] = ?$

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

$$\frac{1}{[A]} = \frac{1}{0.086} + (7.0 \times 10^9 \times 120)$$

$$[A] = 1.2 \times 10^{-12}\ M$$

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

$$t_{1/2} = \frac{1}{7.0 \times 10^9 \times 0.60} = 2.4 \times 10^{-10}\ s$$

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

$$t_{1/2} = \frac{1}{7.0 \times 10^9 \times 0.42} = 3.4 \times 10^{-10}\ s$$

Zero-Order Reactions

A $\longrightarrow$ product

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

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

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

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

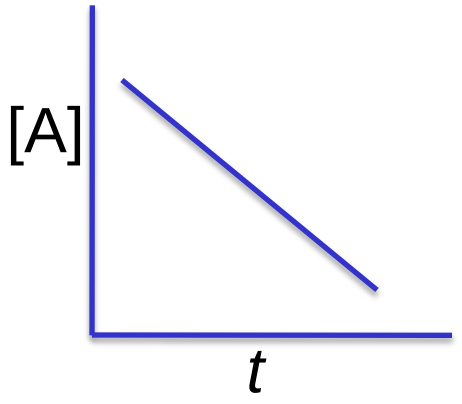
$$[A] = [A]_0 - kt$$

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

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

$t_{½} = t$ when $[A] = [A]_0/2$

$$t_{½} = \frac{[A]_0}{2k}$$

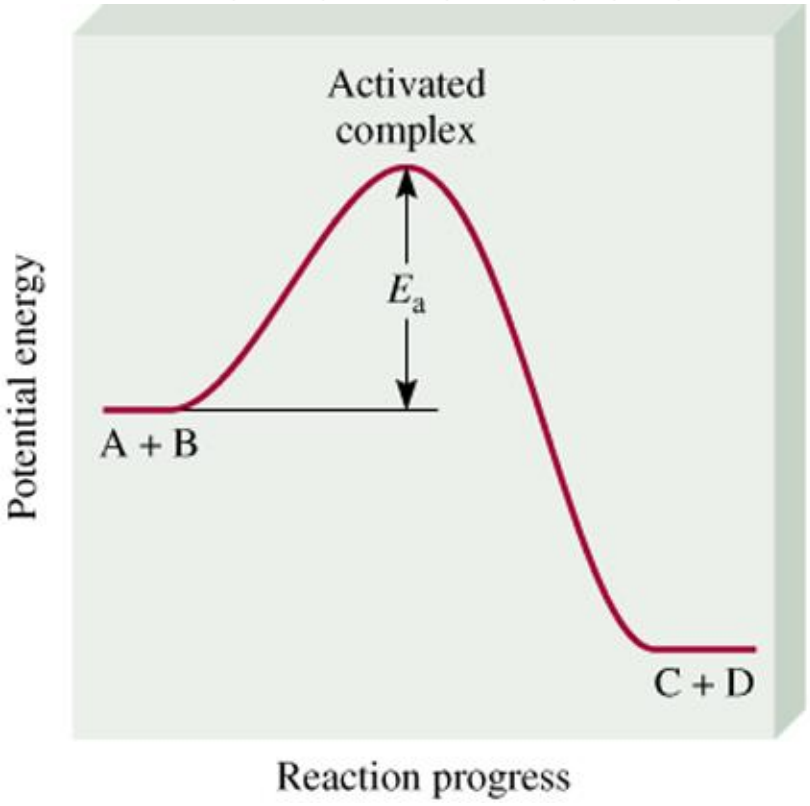


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

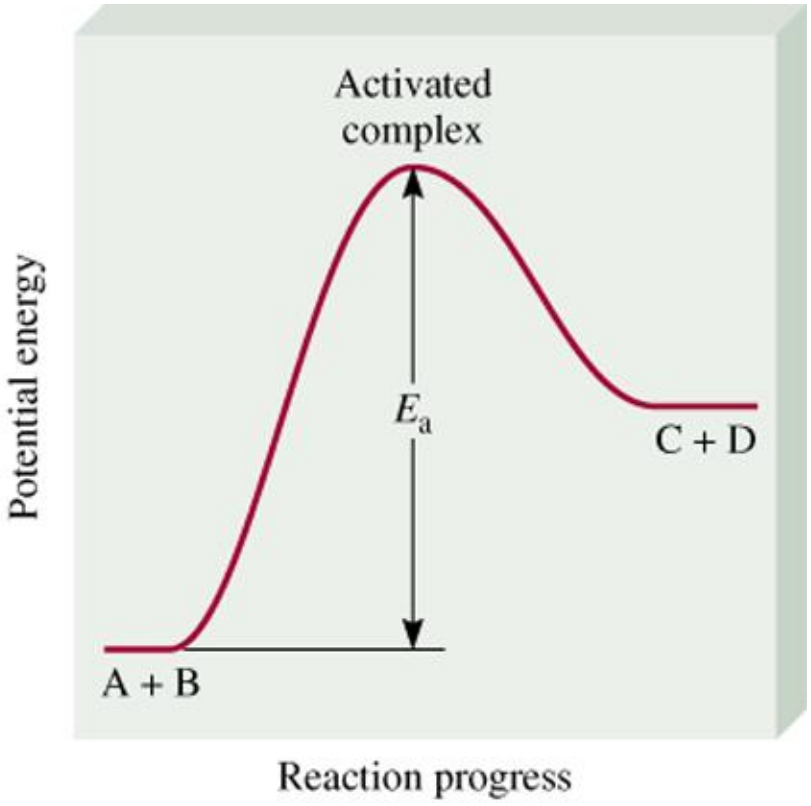
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = k [A]	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = k $[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

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

Exothermic Reaction



Endothermic Reaction



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

Collision Theory

✓Molecules must collide to react .

✓More collisions per unit time should lead to faster reaction

✓Colliding molecules must have a minimum amount of kinetic energy for a collision result in products (otherwise they just bounce off each other) .

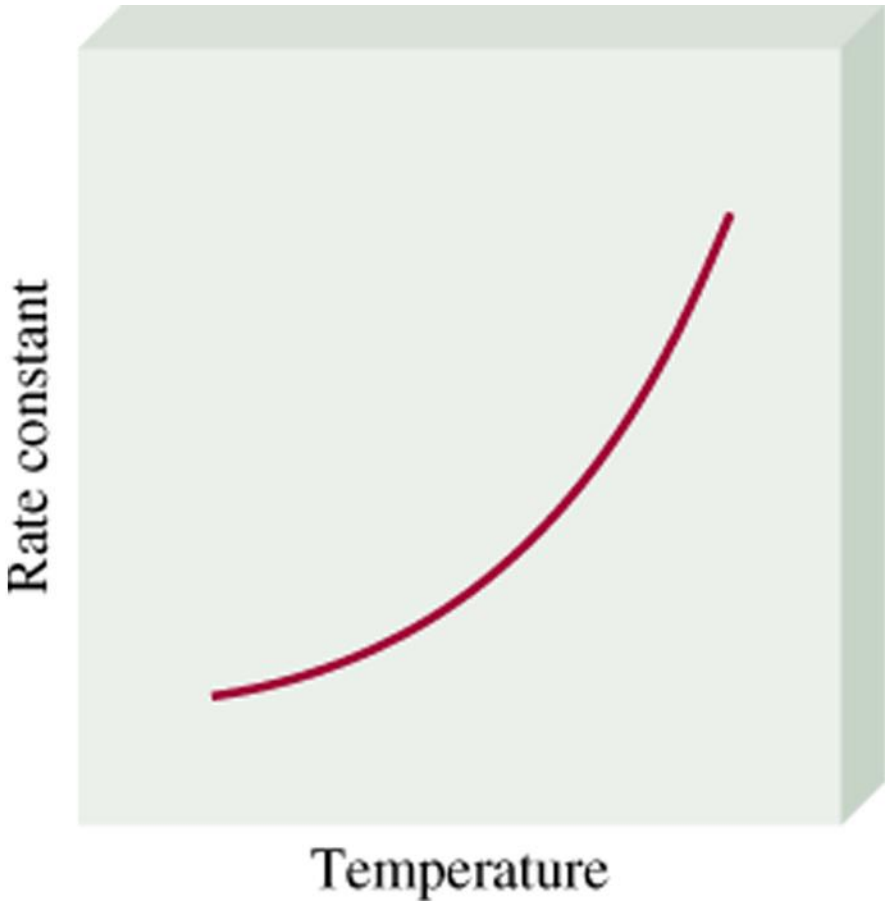
✓Minimum collision energy needed is called the activation energy , E_a

✓Raising the temperature of a reaction raises the kinetic energy of the reactants and increases the number of collisions per unit time .

✓Raising the temperature should lead to faster reactions .

✓At some point , when two molecules collide and react , there is a highest energy state called the transition state This barrier is the activation for the reaction to occur .

Temperature Dependence of the Rate Constant



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

(Arrhenius equation)

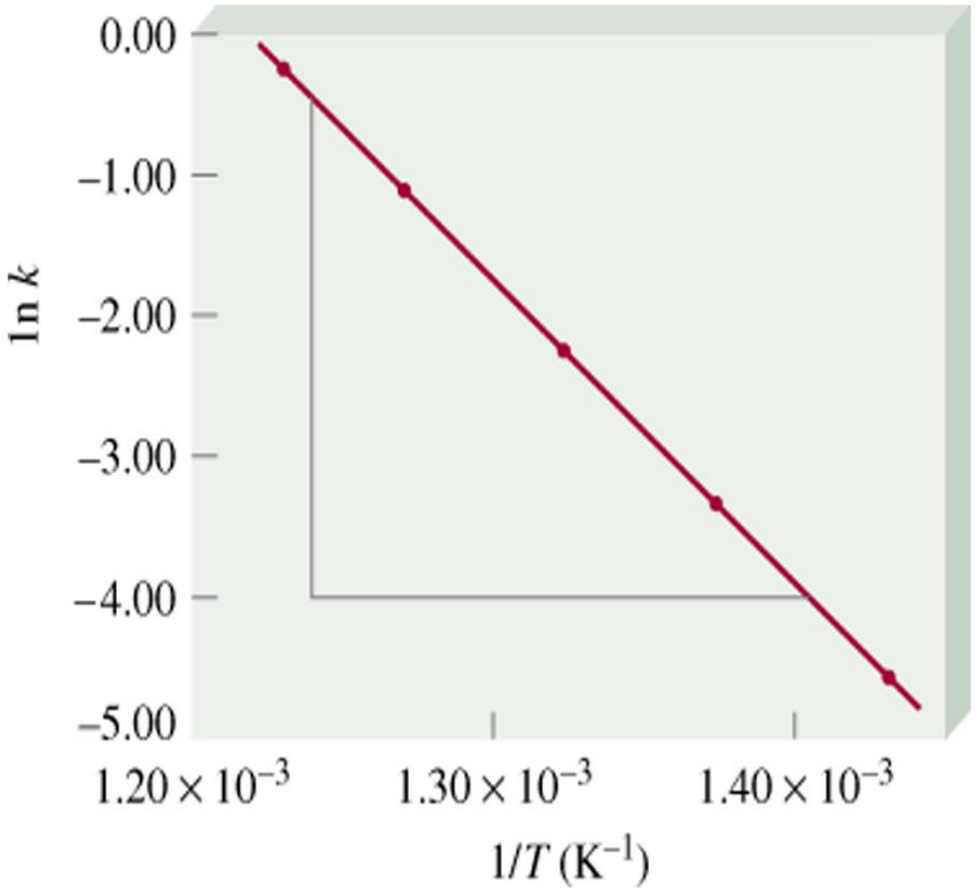
E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

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



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

$$\ln k_1 = -\frac{E_a}{R}\frac{1}{T_1} + \ln A$$

$$\ln k_2 = -\frac{E_a}{R}\frac{1}{T_2} + \ln A$$

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

Example 4.9 : The rate constant of a first-order reaction is $3.46 \times 10^{-2}\ s^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

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

$$\ln \frac{3.46 \times 10^{-2}}{k_2} = \frac{50.2 \times 10^{3}}{8.314}\left(\frac{298 - 350}{298 \times 350}\right)$$

$$\ln \frac{3.46 \times 10^{-2}}{k_2} = -3.01$$

$$\frac{3.46 \times 10^{-2}}{k_2} = e^{-3.01} = 0.0493$$

$$k_2 = 0.702\ s^{-1}$$

Example 4.10: 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 ?

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

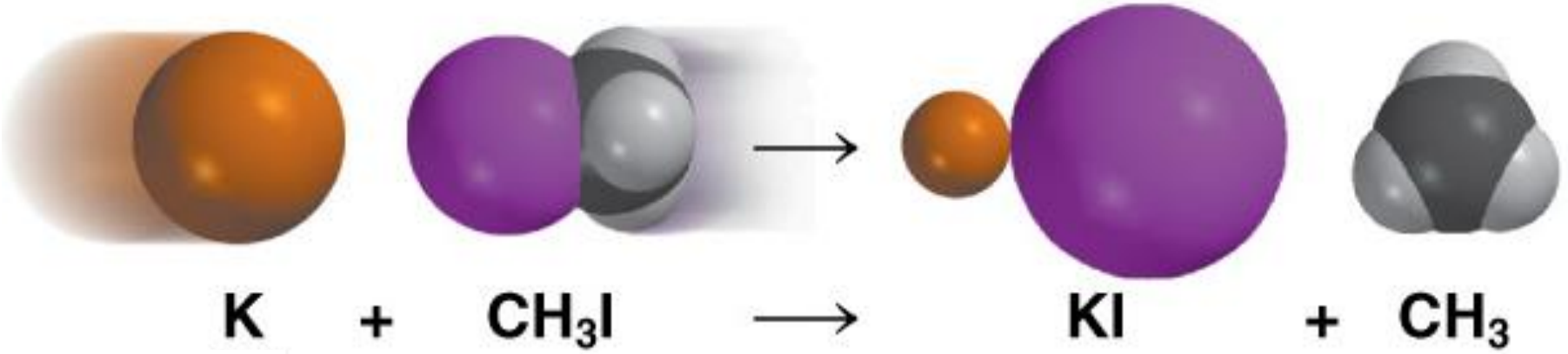
$$\ln \frac{k_1}{k_2} = \frac{76.7 \times 10^3}{8.314}\left(\frac{273 - 323}{273 \times 323}\right)$$

$$\ln \frac{k_1}{k_2} = -5.23$$

$$\frac{k_1}{k_2} = 0.00535$$

/0.00535

$k_1 = 0.00535\, k_2$ ⟹ $k_2 = 187\, k_1$



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***.

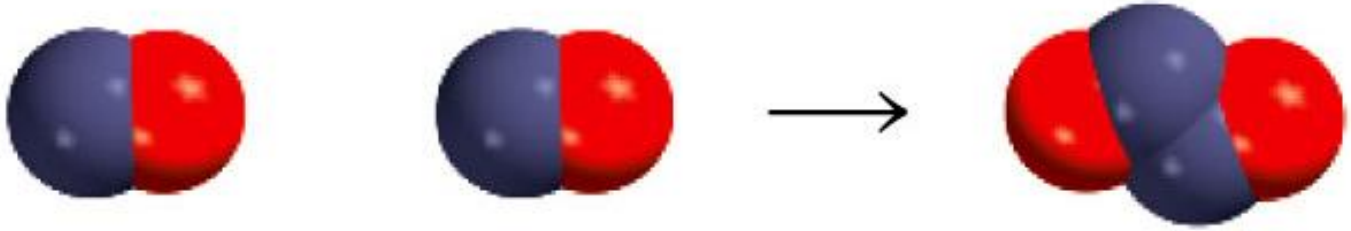
$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

N_2O_2 is detected during the reaction!

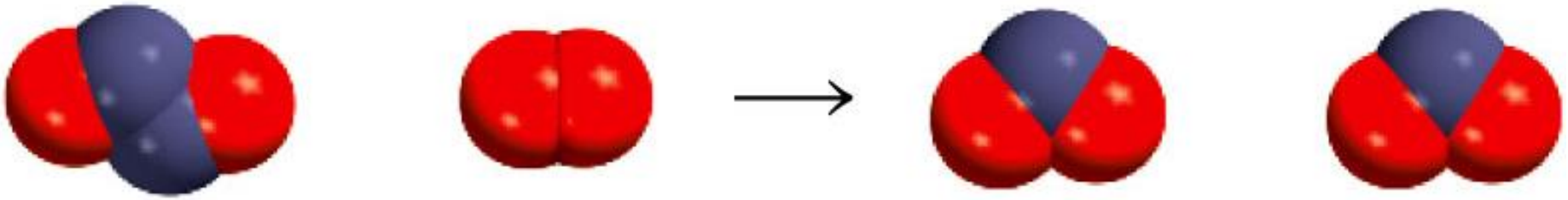
	Elementary step:	$NO + NO \longrightarrow \cancel{N_2O_2}$
+	Elementary step:	$\cancel{N_2O_2} + O_2 \longrightarrow 2NO_2$
	Overall reaction:	$2NO + O_2 \longrightarrow 2NO_2$

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

$$2NO(g) \longrightarrow N_2O_2(g)$$



$$N_2O_2(g) \quad O_2(g) \longrightarrow 2NO_2(g)$$



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

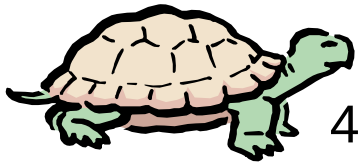
Rate Laws and Elementary Steps

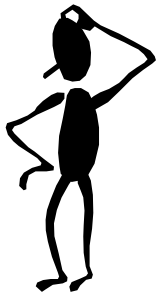
Unimolecular reaction	$A \longrightarrow$ products	rate = k [A]
Bimolecular reaction	$A + B \longrightarrow$ products	rate = k [A][B]
Bimolecular reaction	$A + A \longrightarrow$ products	rate = k [A]^2

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?

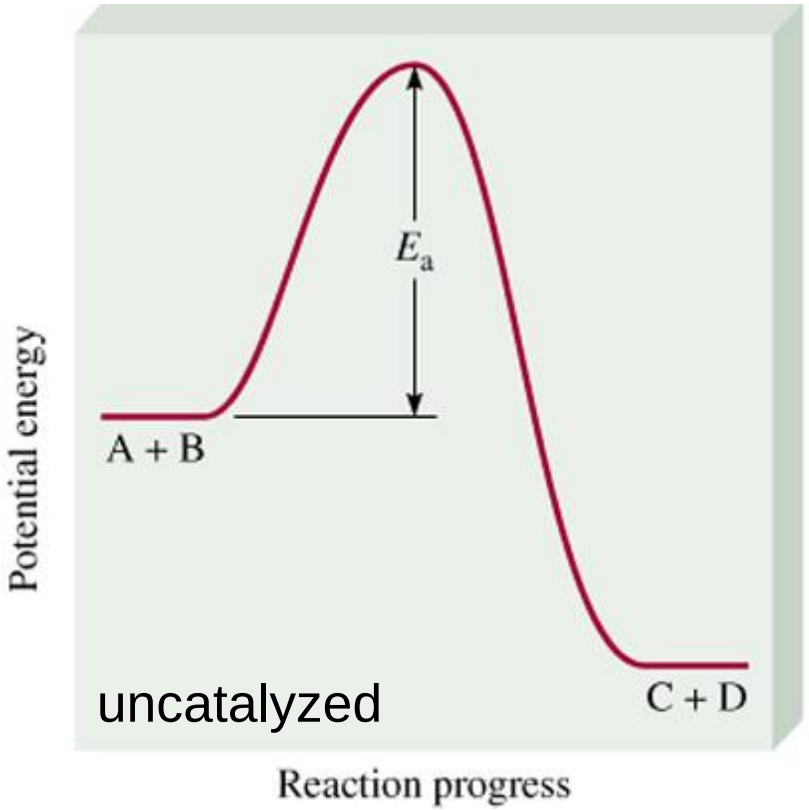
$$NO_3$$

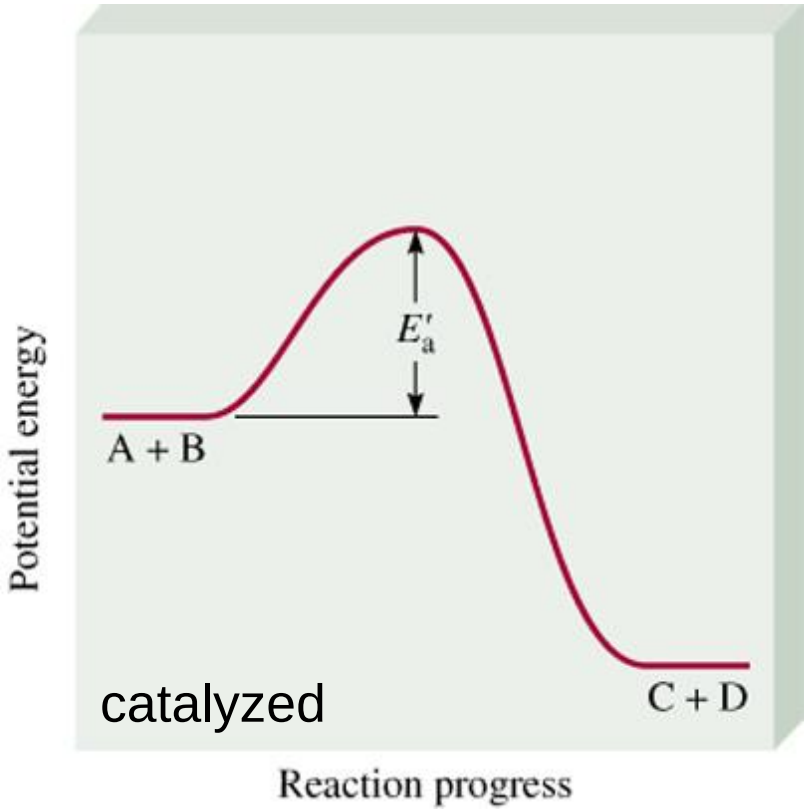
What can you say about the relative rates of steps 1 and 2?

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

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)

❖ A **catalyst** speeds up the forward and back reaction to the same extent. Because adding a **catalyst** doesn't affect the relative rates of the two reactions, it can't affect the **position** of **equilibrium**

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.

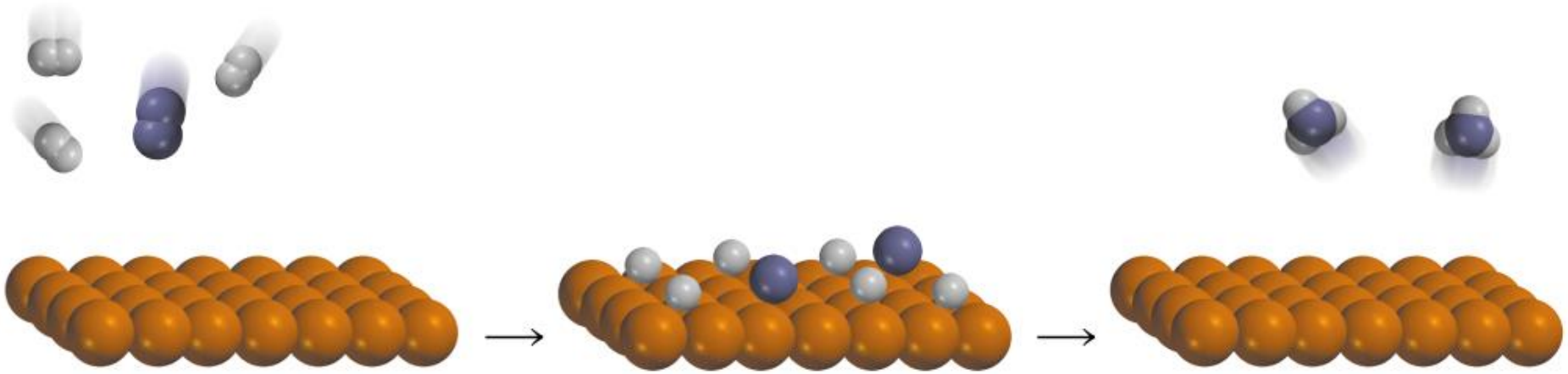
- Acid catalysis
- Base catalysis

$2N_2O(s) \rightarrow 2N_2(g) + O_2(g)$, Ea =245 KJ, No catalyst

$2N_2O(s) + \xrightarrow{Cl_2} 2N_2(g) + O_2(g) + CL_2$, Ea = 140 KJ ,
homogeneous catalyst.

$2N_2O \xrightarrow{Au} 2N_2(g) + O_2(g)$, Ea =120 KJ ,
heterogeneous.

Haber Process



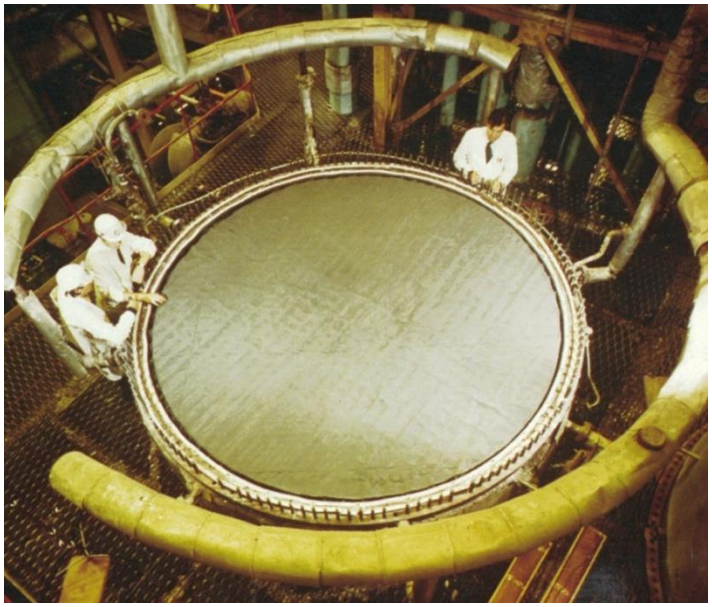
$$N_2\,(g) + 3H_2\,(g) \xrightarrow[\text{catalyst}]{Fe/Al_2O_3/K_2O} 2NH_3\,(g)$$

Ostwald Process

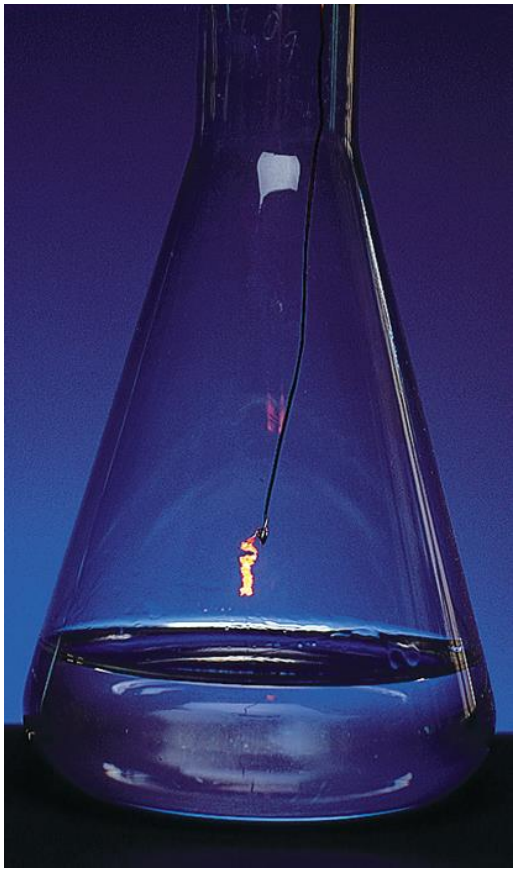
$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow{\text{Pt catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

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

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

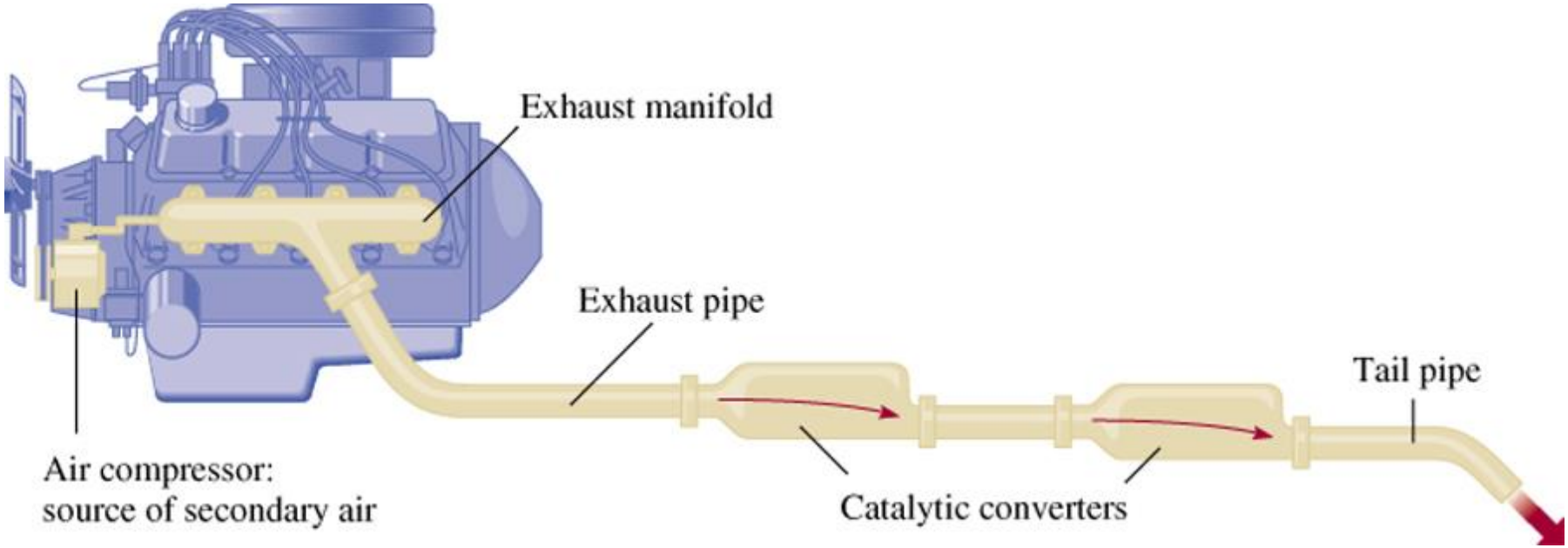


Pt-Rh catalysts used in Ostwald process

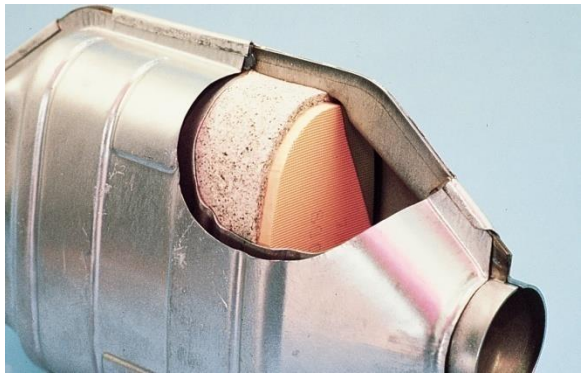


Hot Pt wire over NH_3 solution

Catalytic Converters

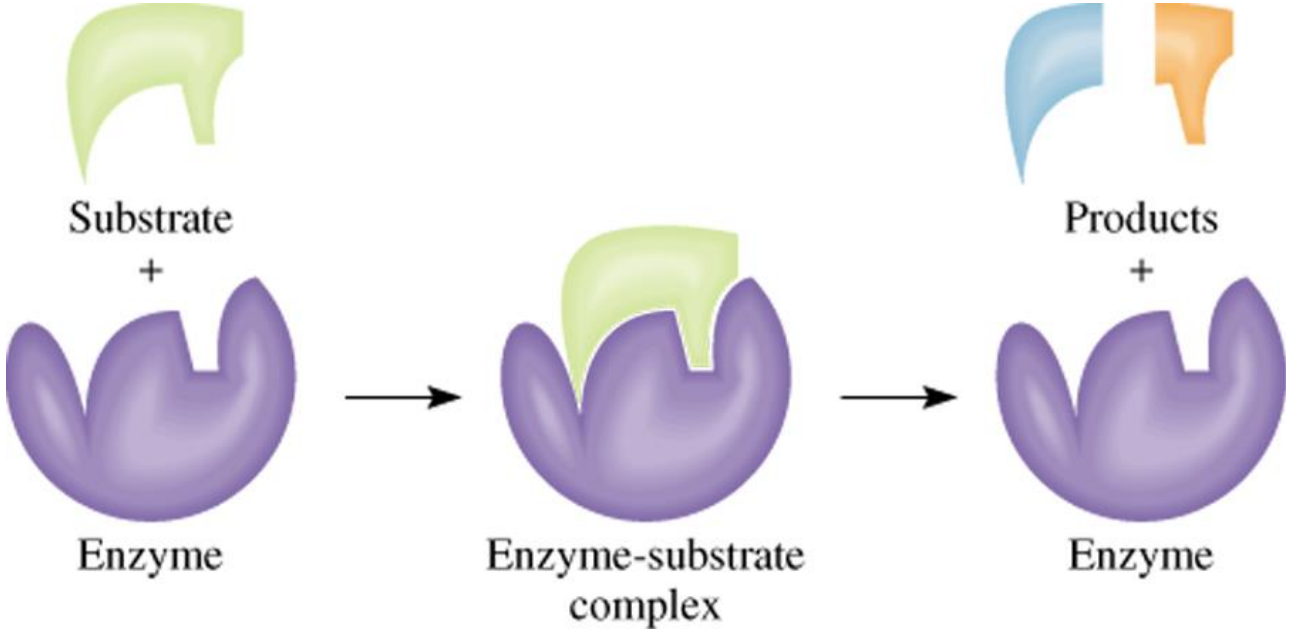


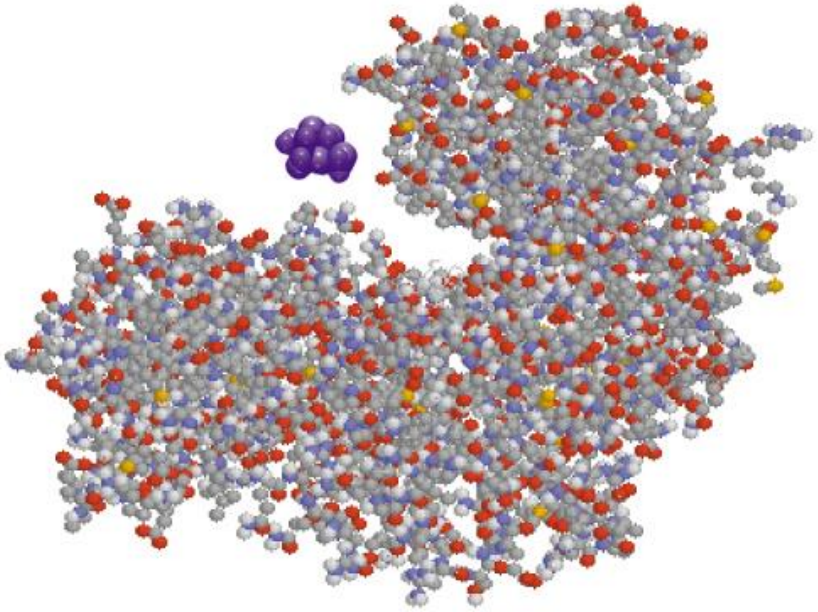
$$\text{CO + Unburned Hydrocarbons + } O_2 \xrightarrow[\text{converter}]{\text{catalytic}} CO_2 + H_2O$$

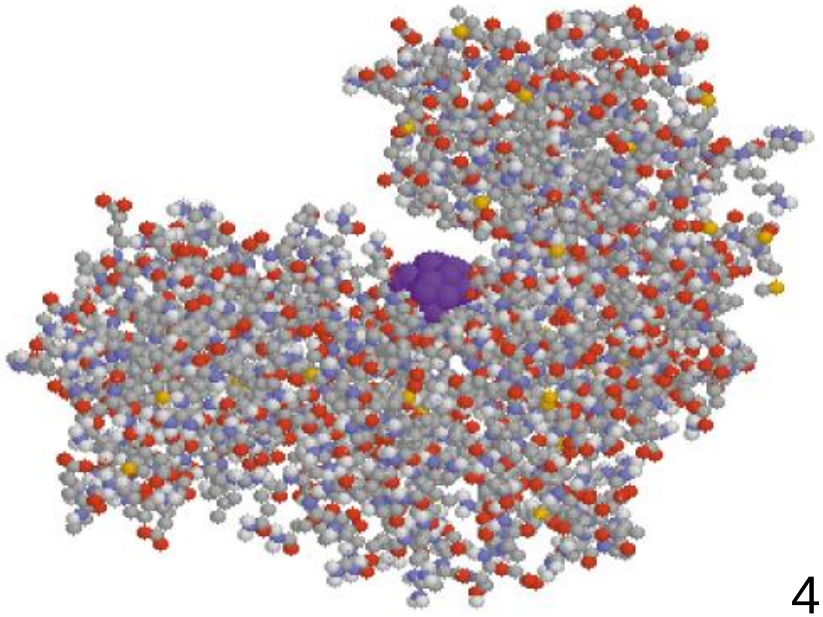


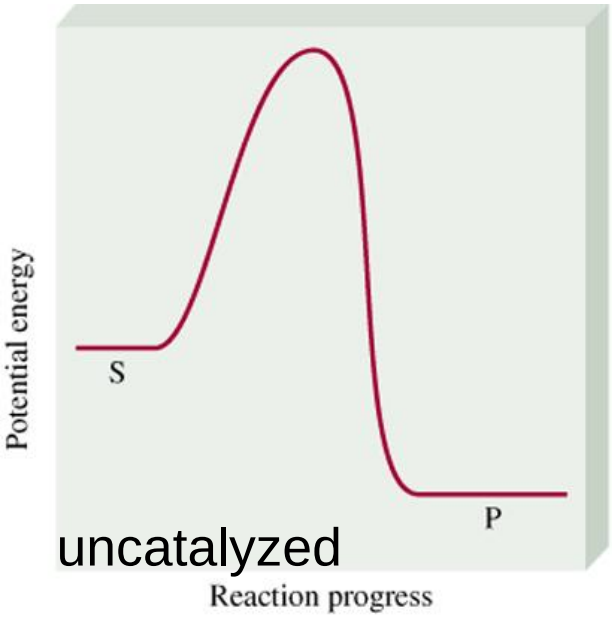
$$2NO + 2NO_2 \xrightarrow[\text{converter}]{\text{catalytic}} 2N_2 + 3O_2$$

Enzyme Catalysis

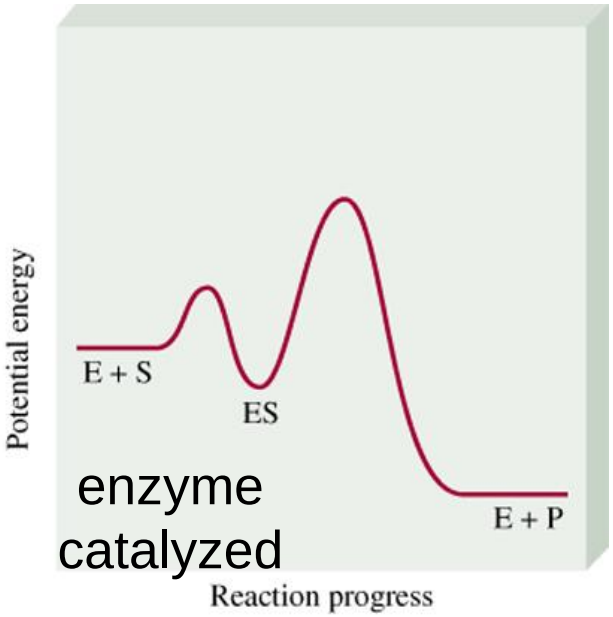




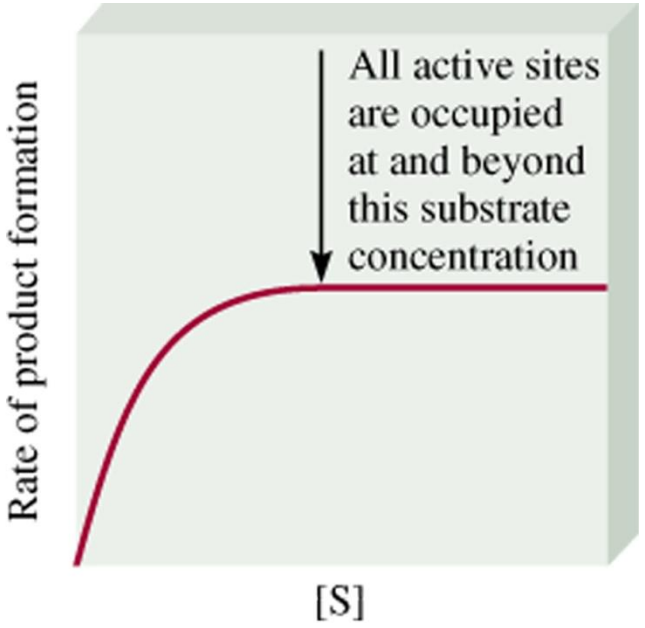




uncatalyzed



enzyme catalyzed

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

rate = k [ES]