Chemical Kinetics and Equilibrium

Part 1: Kinetics

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Chemical Kinetics

- The study of the rates of chemical reactions and how they occur.
- The conditions that affect the rate or speed at which reactions occur.
- The **reaction mechanism** (*how* the reaction occurs at the atomic-molecular level).

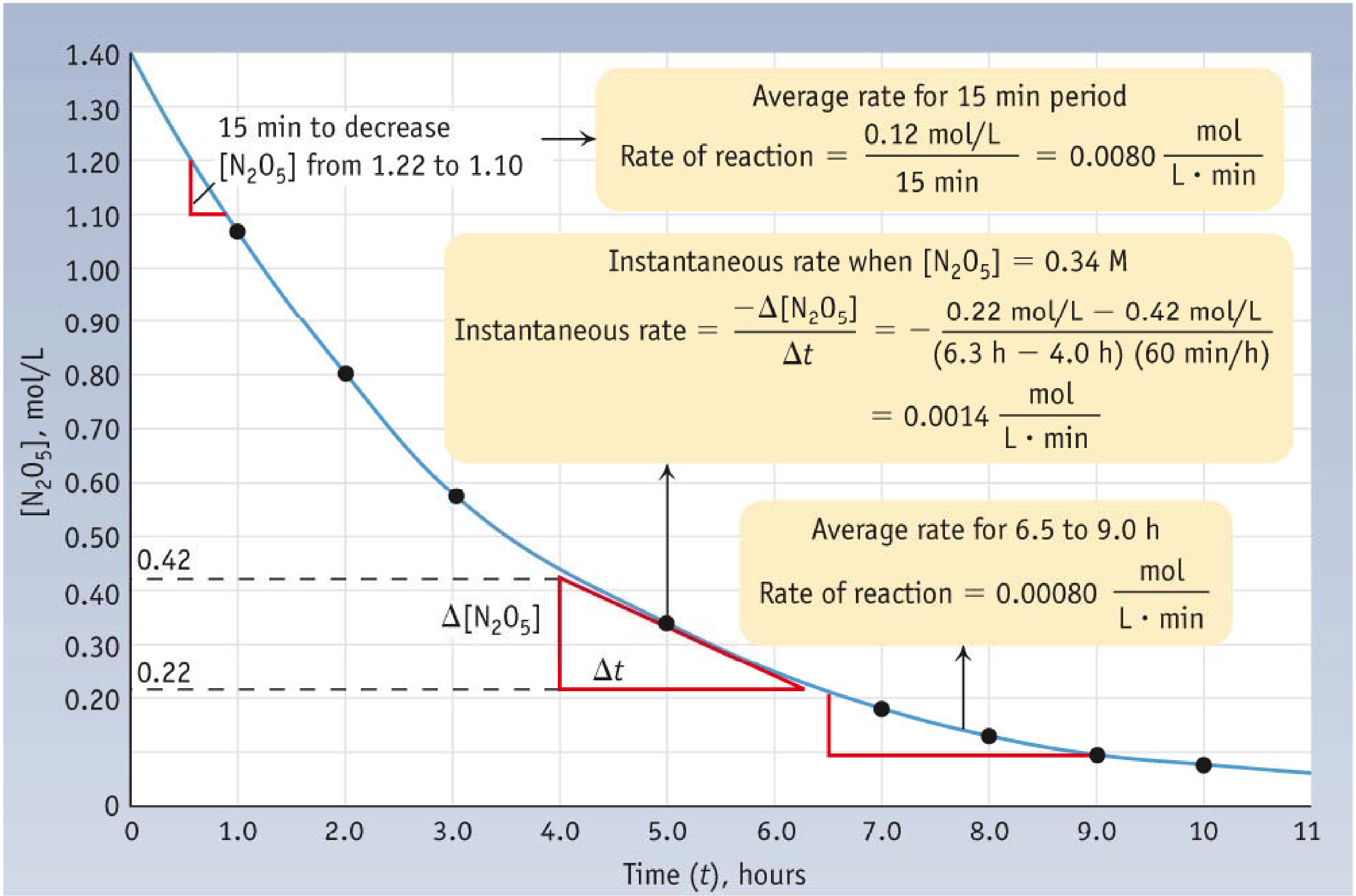
Reaction Rates

- **Reaction rate = change in concentration of a reactant or product with time.**

$$\text{Rate} = \frac{\Delta\text{concentration}}{\Delta\text{time}}$$

- **Rate can be expressed as**
  - **initial rate**
  - **average rate**
  - **instantaneous rate**

Determining a Reaction Rate



15 min to decrease $[N_2O_5]$ from 1.22 to 1.10

Average rate for 15 min period

$$\text{Rate of reaction} = \frac{0.12 \text{ mol/L}}{15 \text{ min}} = 0.0080 \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Instantaneous rate when $[N_2O_5] = 0.34$ M

$$\text{Instantaneous rate} = \frac{-\Delta[N_2O_5]}{\Delta t} = -\frac{0.22 \text{ mol/L} - 0.42 \text{ mol/L}}{(6.3 \text{ h} - 4.0 \text{ h})\ (60 \text{ min/h})}$$

$$= 0.0014 \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Average rate for 6.5 to 9.0 h

$$\text{Rate of reaction} = 0.00080 \frac{\text{mol}}{\text{L} \cdot \text{min}}$$

Factors Affecting Reaction Rates

- Physical State of the Reactants
  - ➢ In order to react, molecules must come in contact with each other.
  - ➢ The more homogeneous the mixture of reactants, the faster the molecules can react.
    - Gaseous reactions are preferred
    - Solutions are most convenient

Factors Affecting Reaction Rates

- Concentration of Reactants
  - ➢ As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

Burning an iron nail

Burning iron in air

Burning iron in oxygen

Lycopodium powder burning:

a) In an evaporating dish
b) In air

(a)

(b)

Factors Affecting Reaction Rates

- Temperature
    - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

Factors Affecting Reaction Rates

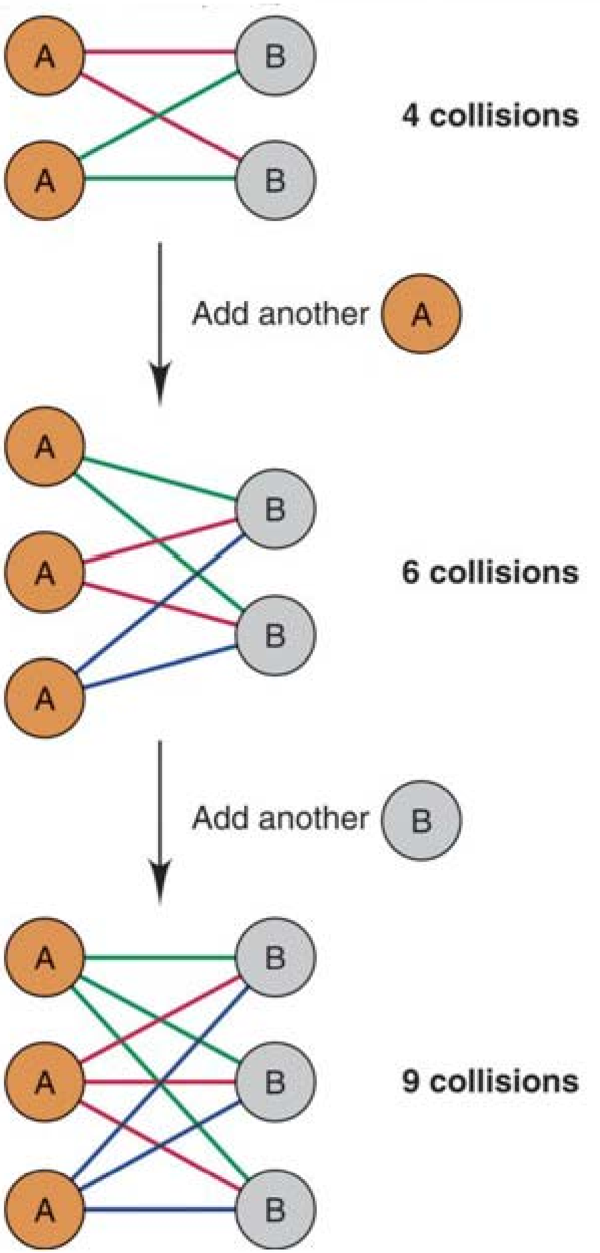
- Catalysis
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.
  - Negative catalysts (inhibitors) can be used to slow down the rate of a reaction.

Collision Theory of Reaction Rates

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

Collision Theory of Reaction Rates

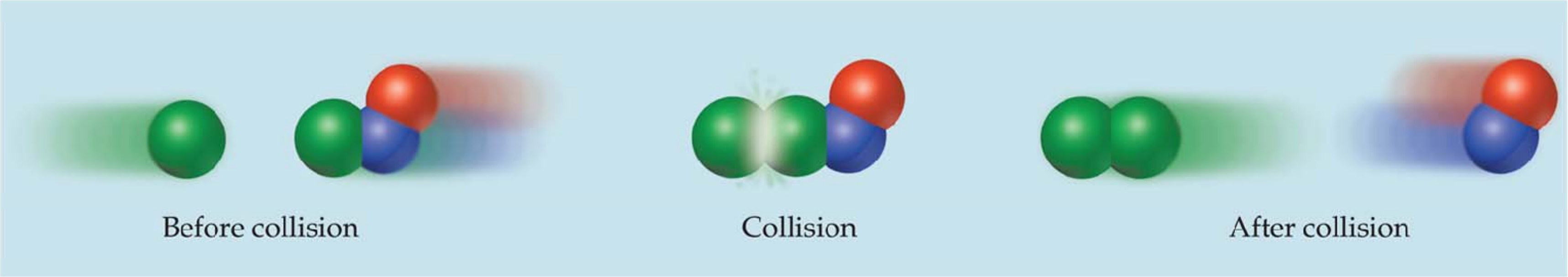
The possible collisions for three sets of molecules that would result in a possible reaction



Collision Theory of Reaction Rates

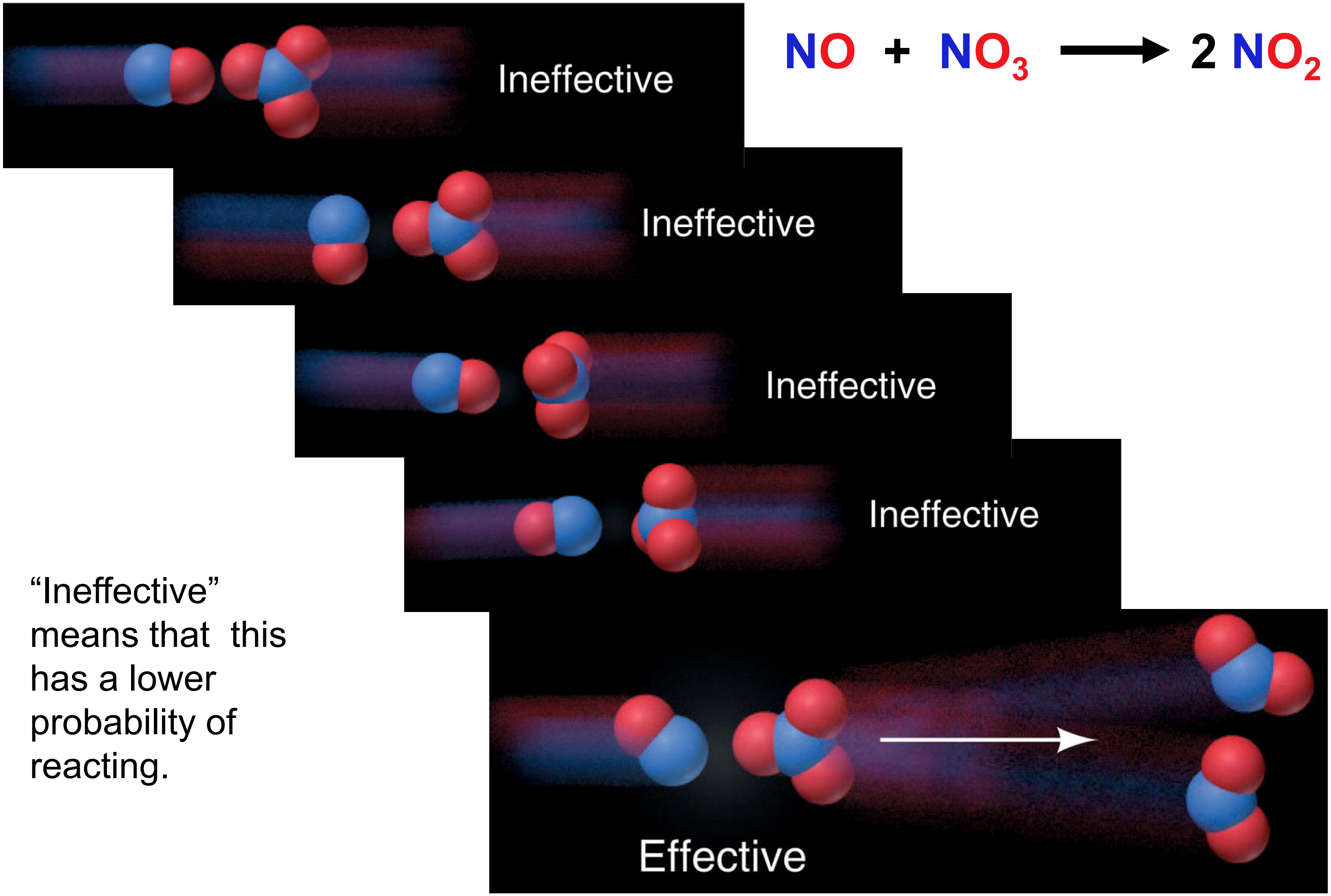
For a collision to be effective (i.e., result in a reaction):

- Molecules must collide with the correct orientation (or alignment)
- There must be enough energy to overcome repulsions so molecules do not rebound
- Bonds must break and new bonds formed.



Collision Theory of Reaction Rates

$NO + NO_3 \longrightarrow 2\,NO_2$



"Ineffective" means that this has a lower probability of reacting.

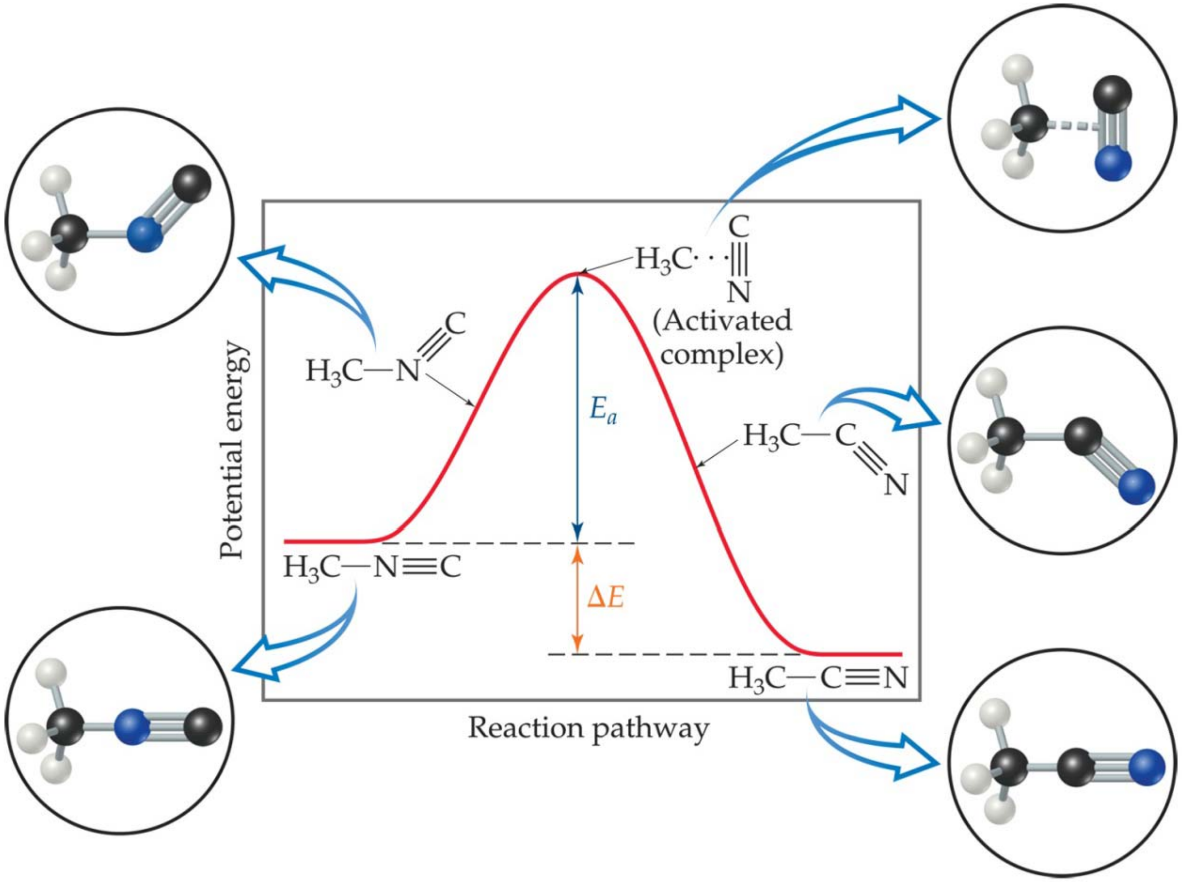
Activation Energy

- There is a minimum amount of energy required for reaction: the **activation energy**, E_a.
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

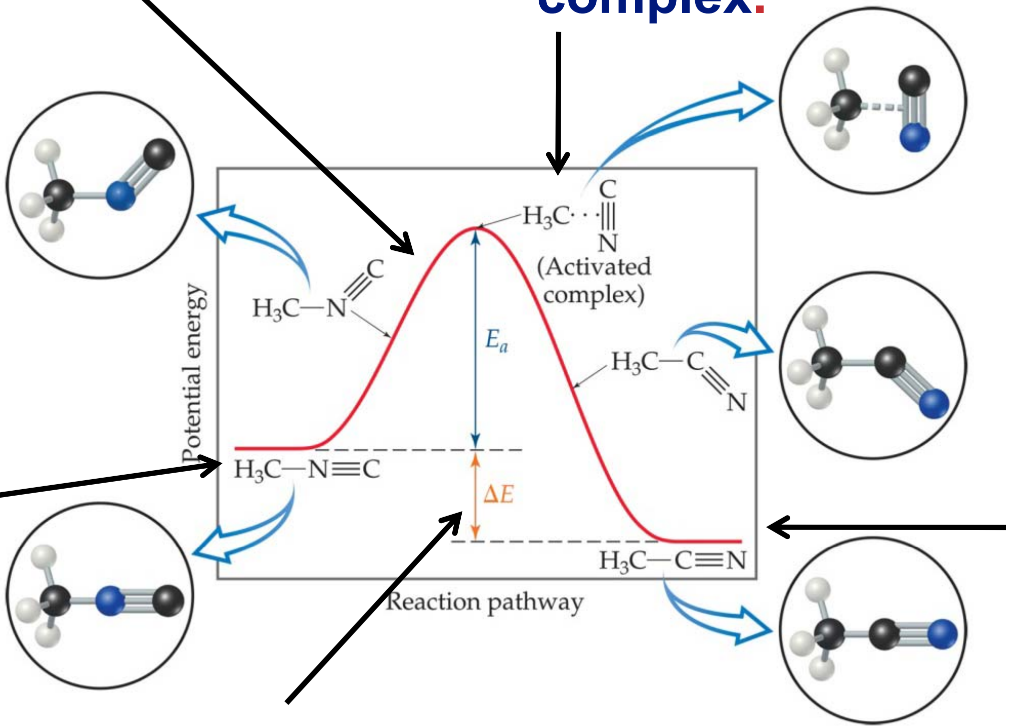
Reaction Energy Diagrams

This diagram relates the energy for the rearrangement of methyl isonitrile.

To visualize the energy changes throughout a process we use a reaction energy or a reaction coordinate diagram



Reaction Energy Diagrams



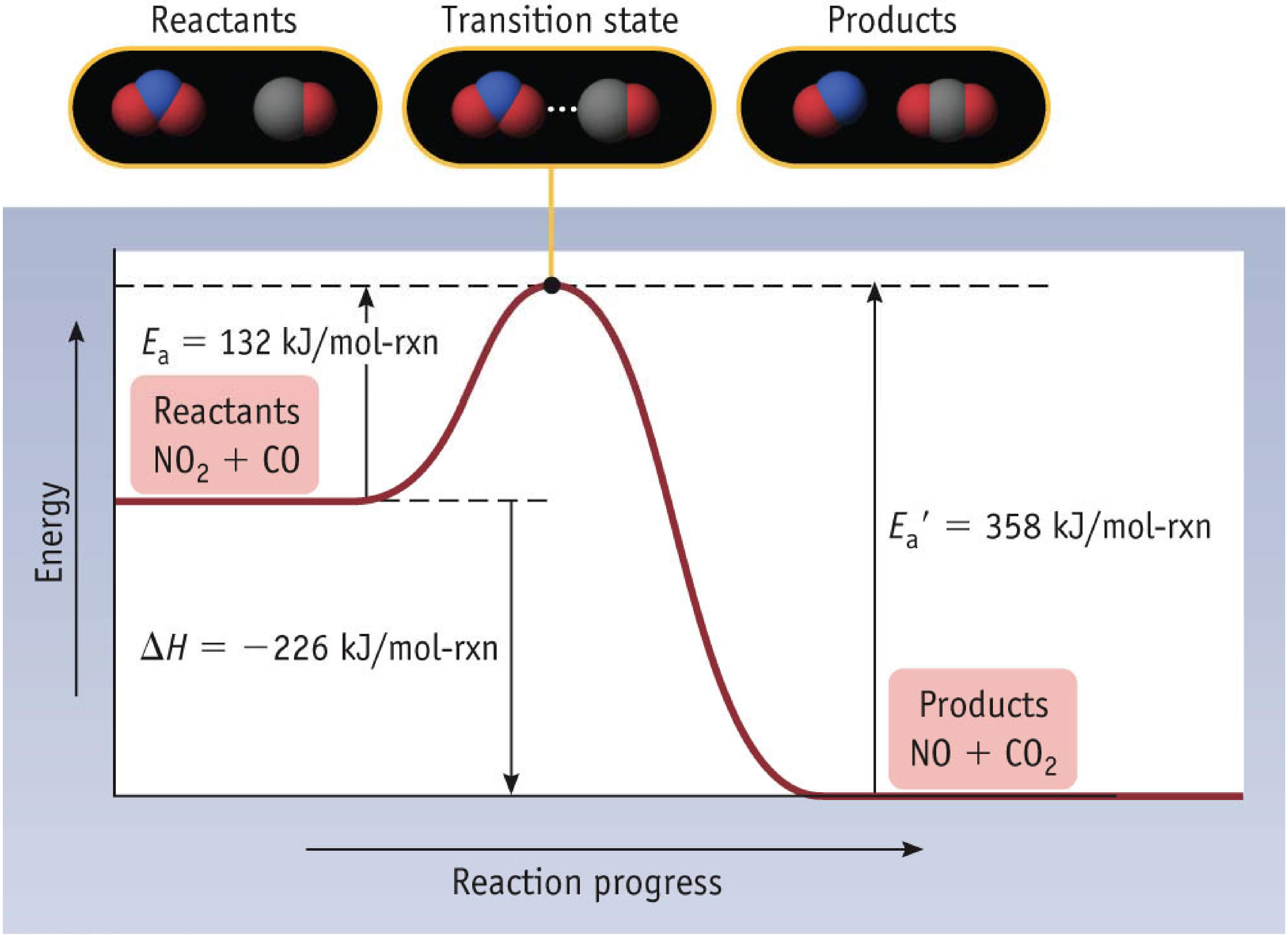
The height of the “hill” is called the activation energy, E_a

The species present at the transition state is called the **activated complex**.

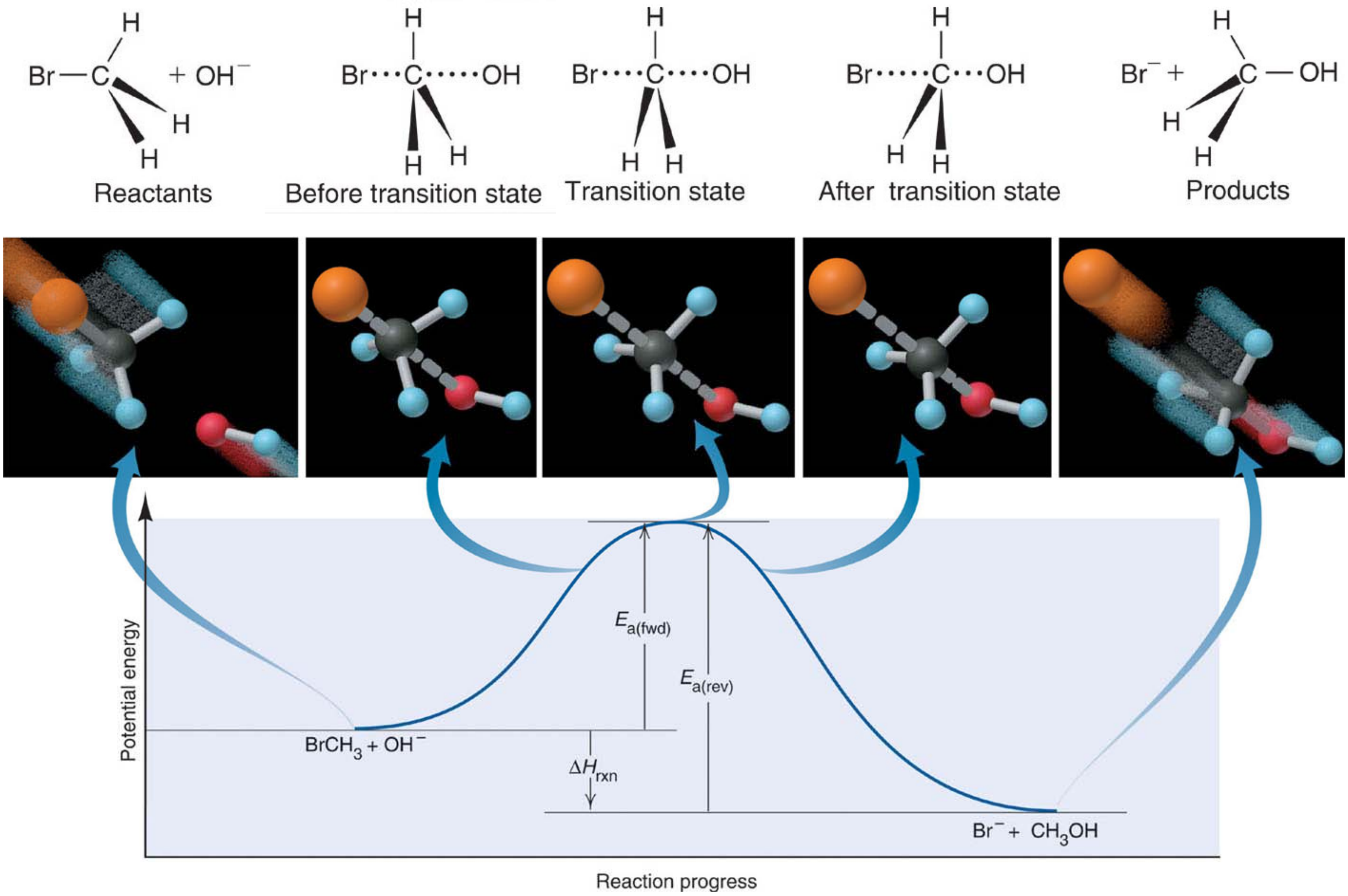
This is the energy of the reactants, E_{react}

This is the energy of the products, E_{prod}

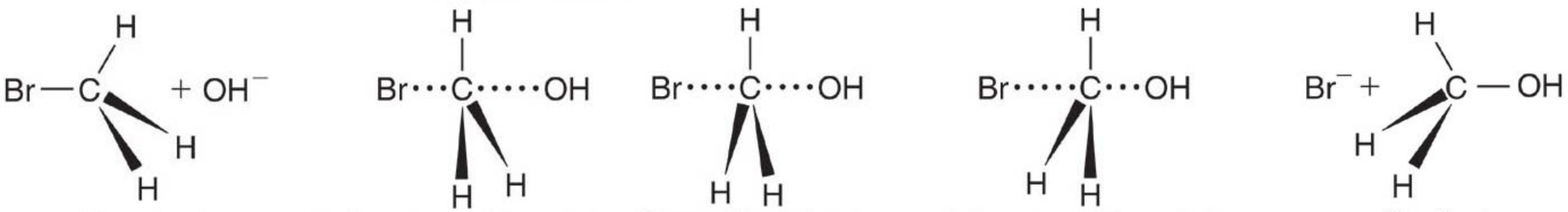
This is the net energy for the reaction, ΔE


Reactants
Transition state
Products
E_a = 132 kJ/mol-rxn
Reactants
$NO_2 + CO$
Energy
E_a' = 358 kJ/mol-rxn
ΔH = −226 kJ/mol-rxn
Products
$NO + CO_2$
Reaction progress

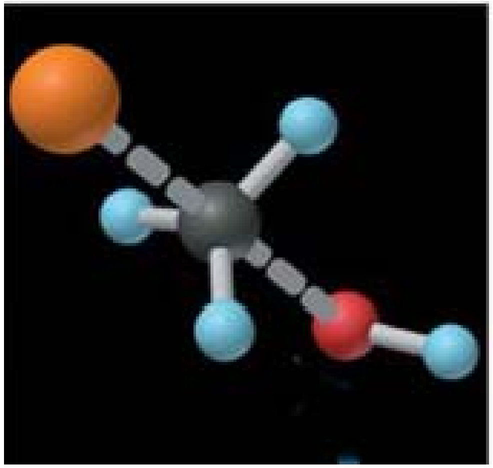
Reaction energy diagram for $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$



Reaction energy diagram for $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$



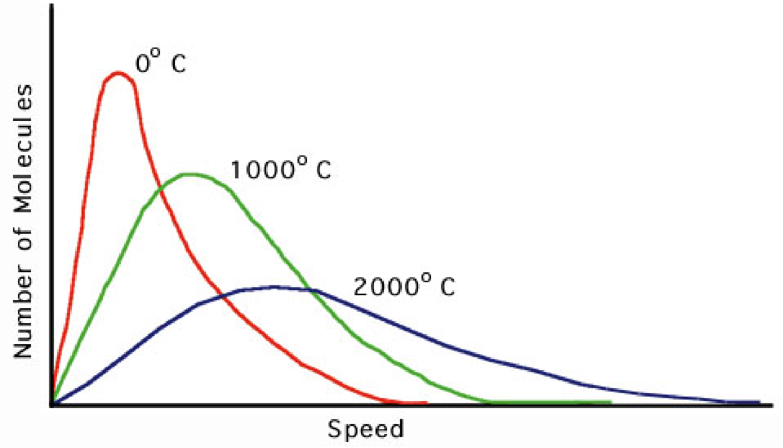
Reactants Before transition state Transition state After transition state Products



The transition state or activated complex has definite bond lengths and bond angles

Entropy on the Molecular Scale

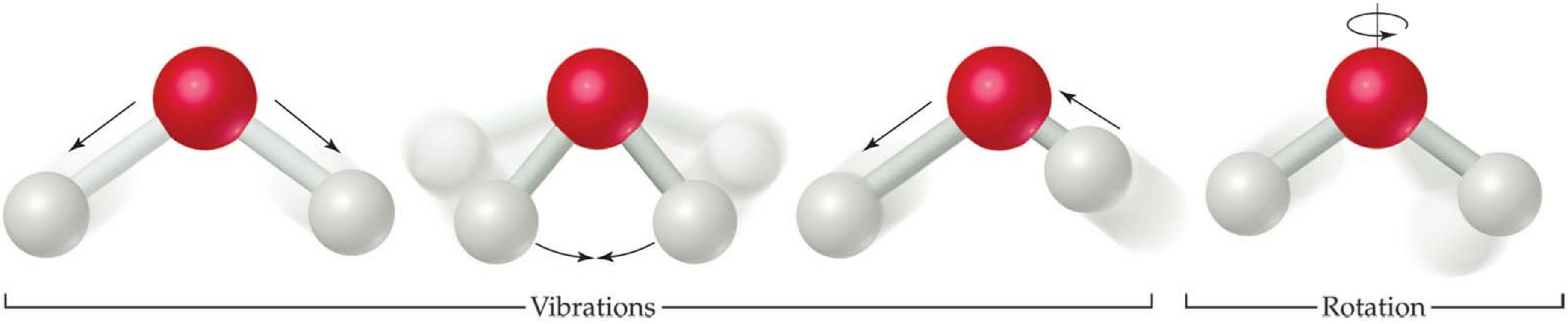
- Ludwig Boltzmann (1844-1906) described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



An animation of the Maxwell-Boltzman distribution for molecular speeds in a gas can be found at http://www.chm.davidson.edu/chemistryapplets/KineticMolecularTheory/Maxwell.html

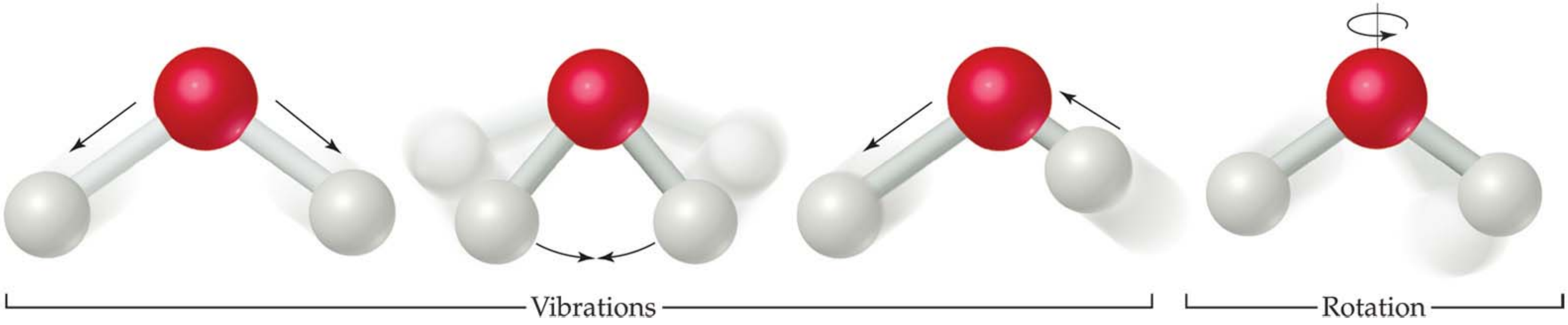
Entropy on the Molecular Scale

- Molecules exhibit several types of motion:
  - Vibrational: Periodic motion of atoms within a molecule. (This is the lowest energy state)
    - Vibrations occur at absolute zero. Called zero-point energy.
  - Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.
  - Translational: Movement of the entire molecule from one place to another. (This is the highest energy state)

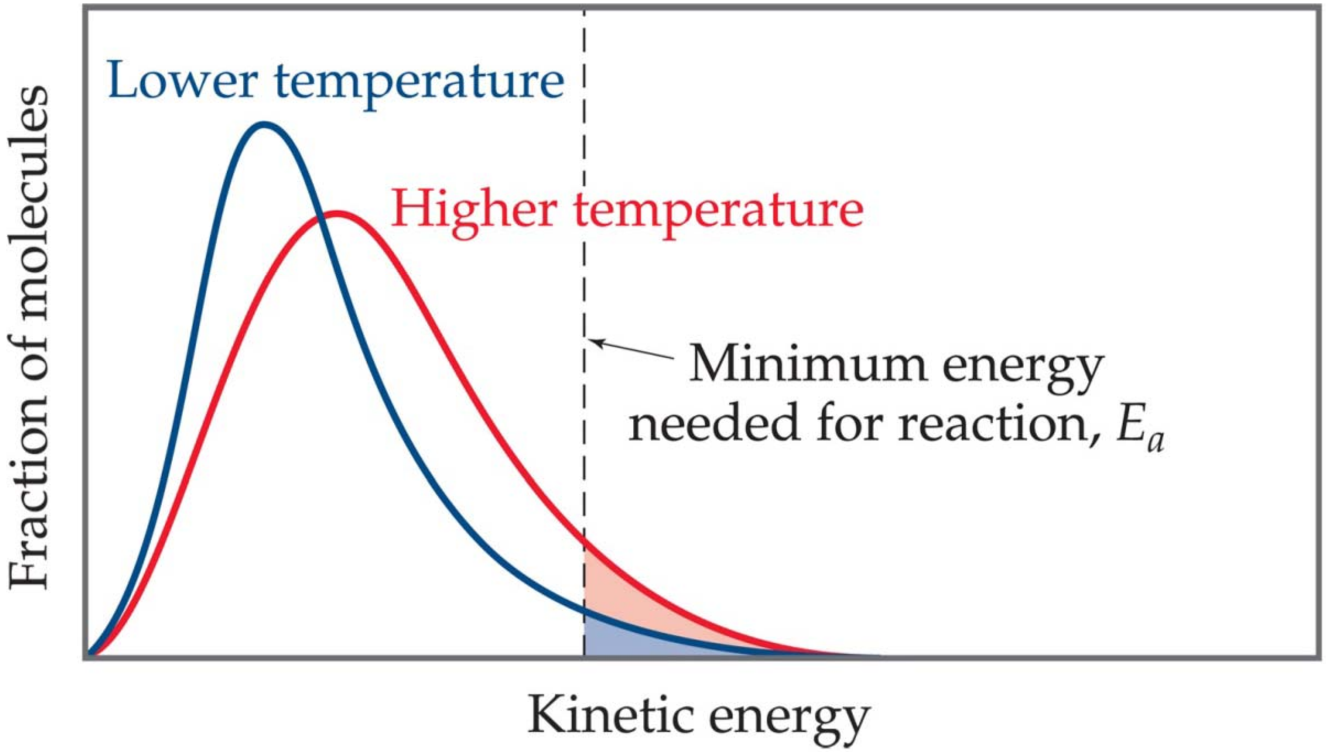


Entropy on the Molecular Scale

- **Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.**
  - **This would be akin to taking a snapshot of all the molecules.**
- **He referred to this sampling as a microstate of the thermodynamic system.**



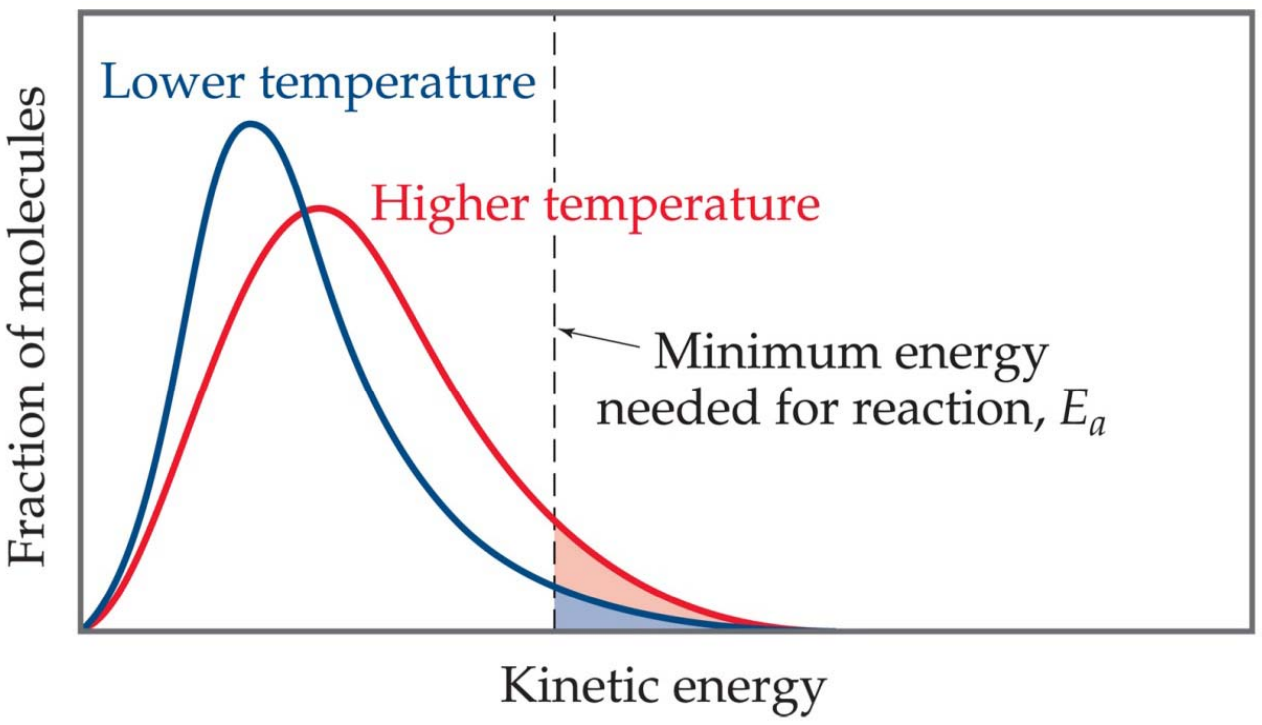
Maxwell–Boltzmann Distributions



Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.

Maxwell–Boltzmann Distributions

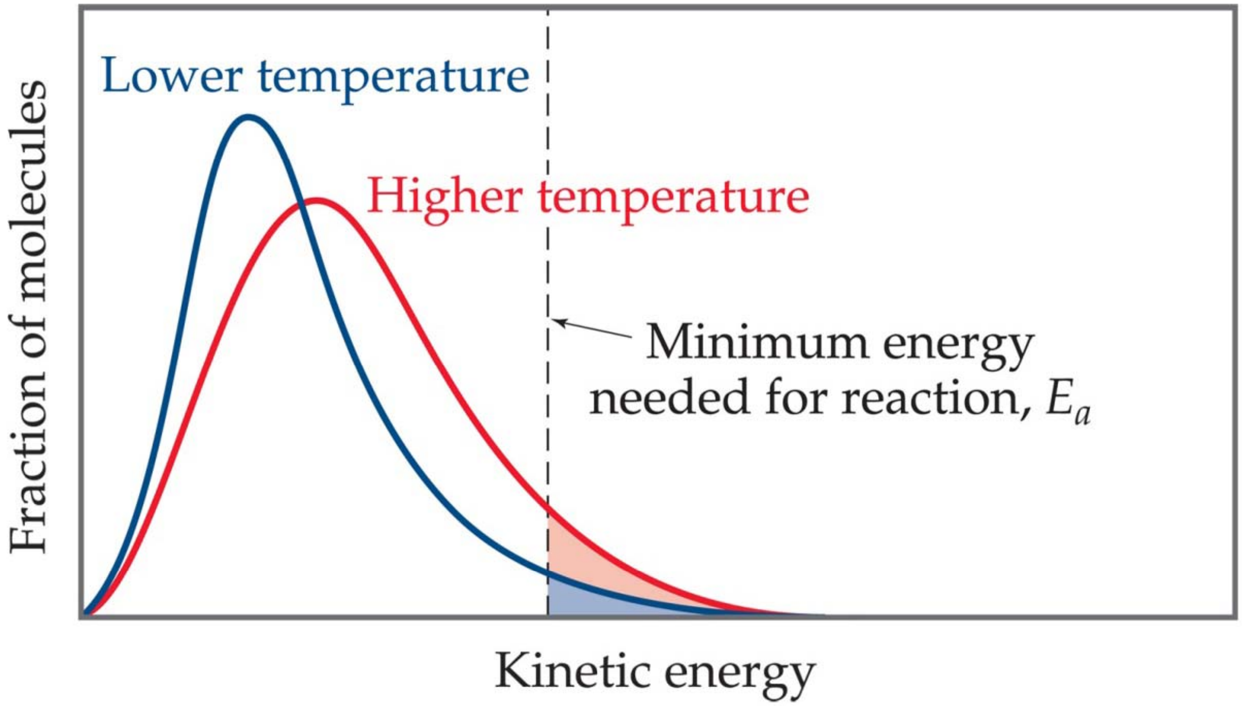


As the temperature increases, the curve flattens and broadens.

Thus, at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

- **If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.**



As a result, the reaction rate increases.

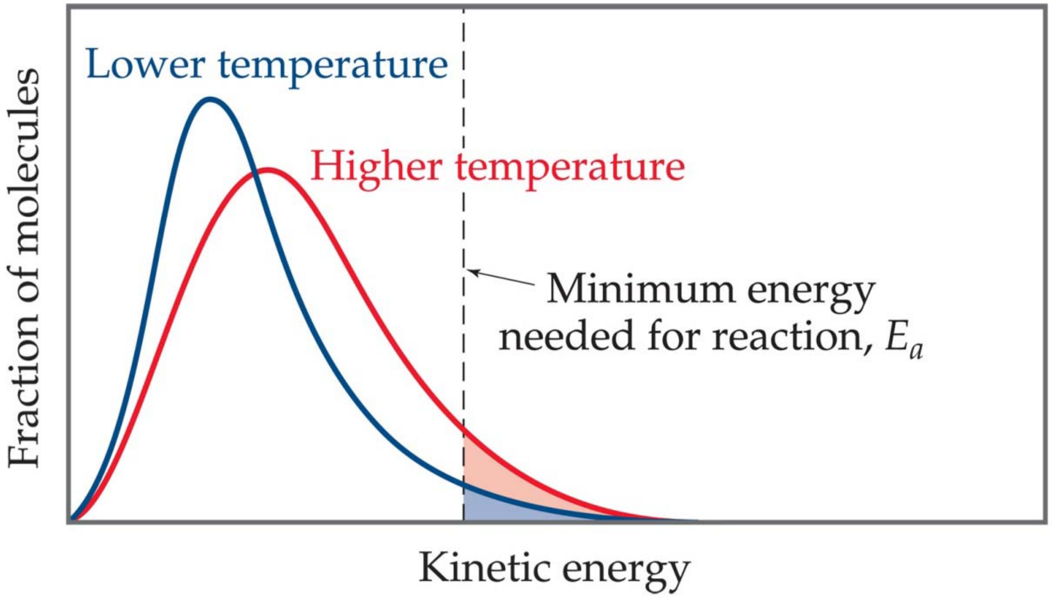
Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{-E_a/RT}$$

where R = the ideal gas constant (8.31 x 10^{-3} kJ/K•mol)

T = the absolute temperature in K



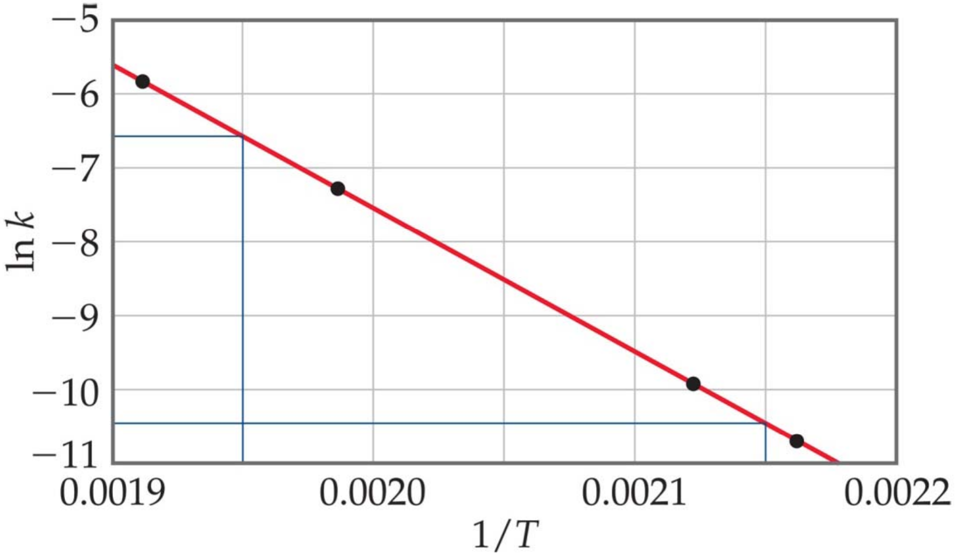
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

$$k = A\, e^{-E_a/RT}$$

where A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



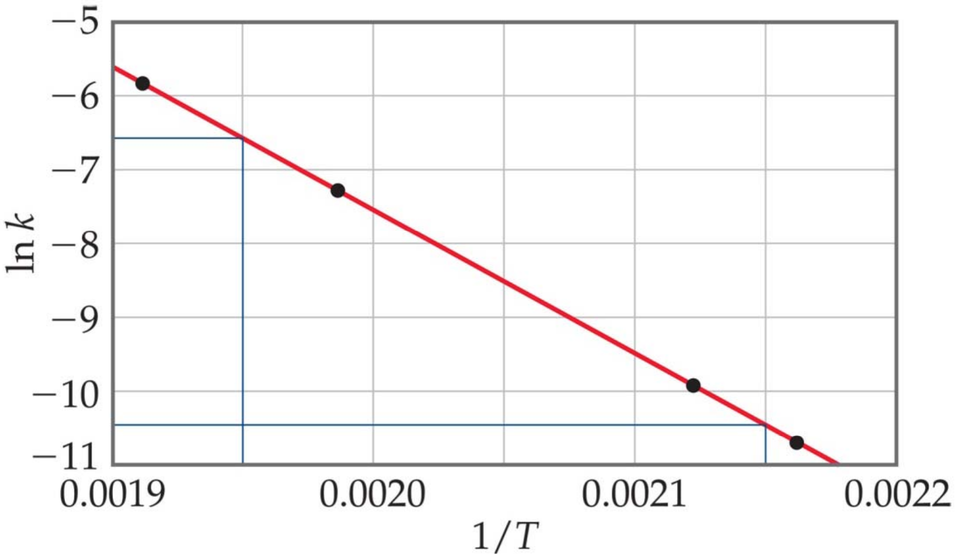
Taking the natural logarithm of both sides, the equation becomes

$$\ln k = -E_a \left(\frac{1}{RT}\right) + \ln A$$

A graph of ln k vs. 1/T is a straight line

$$y = mx + b$$

Arrhenius Equation



Therefore, if *k* is determined experimentally at several temperatures, *E_a* can be calculated from the slope of a plot of ln *k* vs. 1/*T*

$$\text{slope} = -\frac{E_a}{R}$$

R = gas constant = 8.31 J/mol K

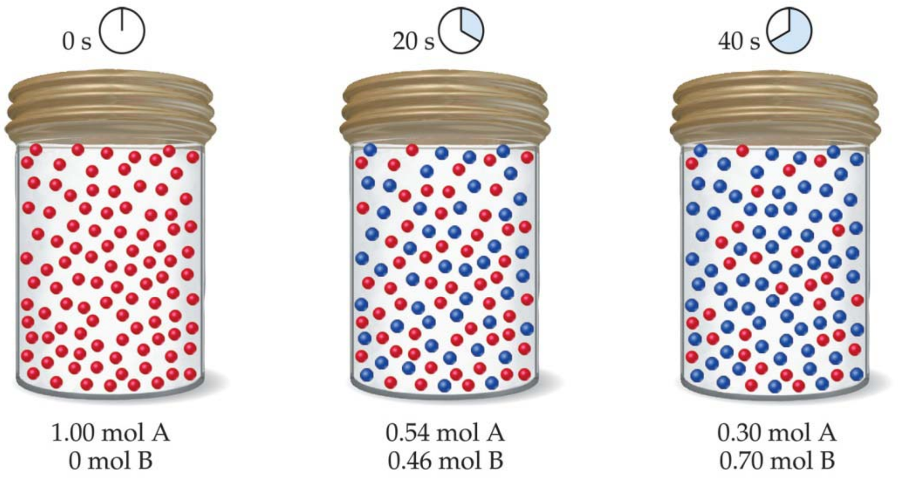
Arrhenius Equation

If *k* is determined experimentally at two or more temperatures, you can select two points from your data or graph, and E_a can be calculated from the equation:

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

R = gas constant = 8.31 J/mol K
T = temperature in K

Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, C_4H_9Cl, was measured at various times.

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{Average rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t}$$

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

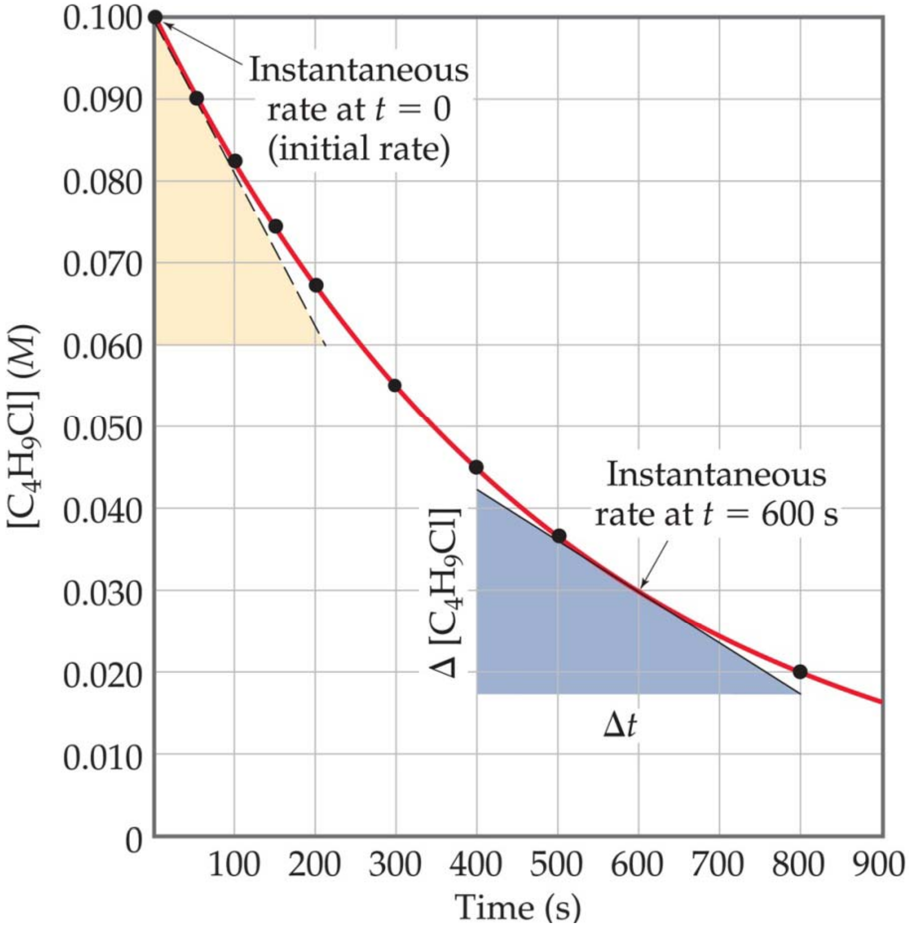
Note that the average rate decreases as the reaction proceeds.

This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

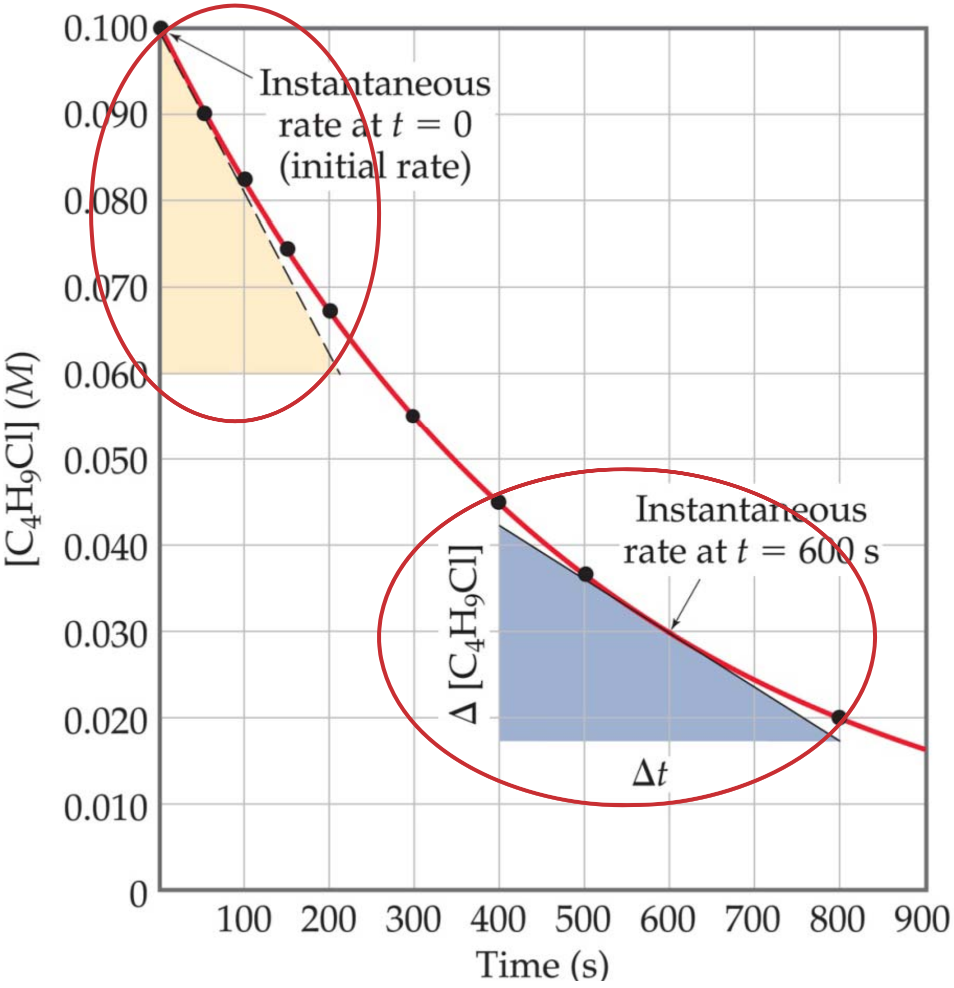
- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.



Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

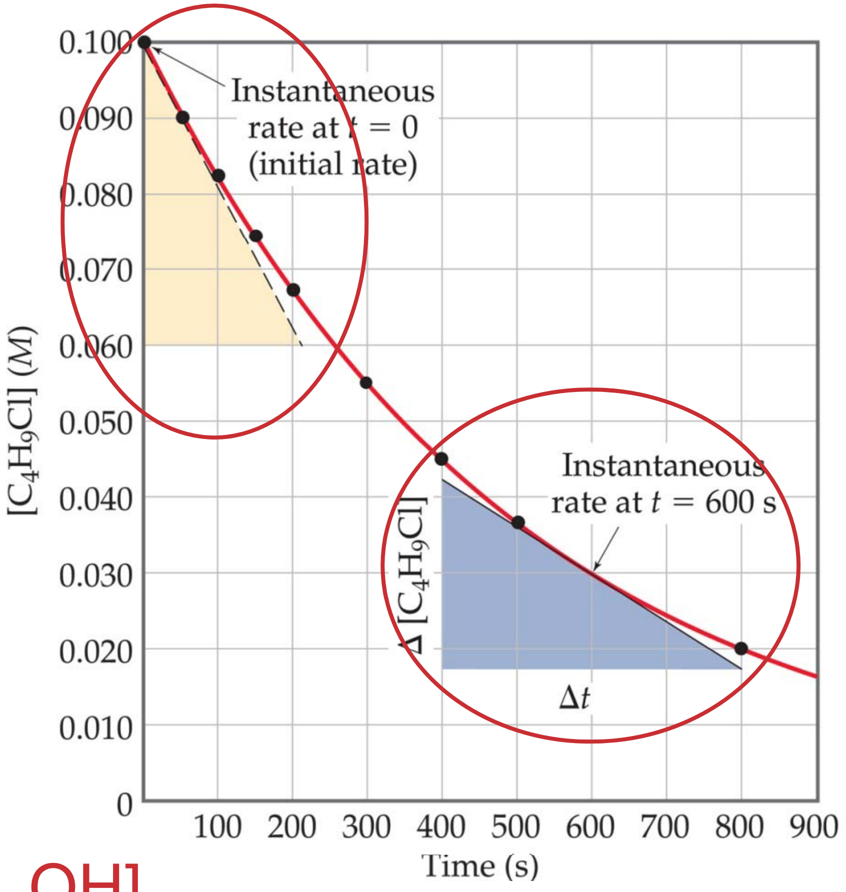
- All reactions slow down over time.
- Therefore, the rate of a reaction is generally stated as the **instantaneous rate** near the beginning.



Reaction Rates and Stoichiometry

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?

$$2\ \mathrm{HI}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

- Then:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\mathrm{HI}]}{\Delta t} = \frac{\Delta[\mathrm{I_2}]}{\Delta t}$$

The ½ represents the stoichiometery of the reaction

Reaction Rates and Stoichiometry

- To generalize, for the reaction

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

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

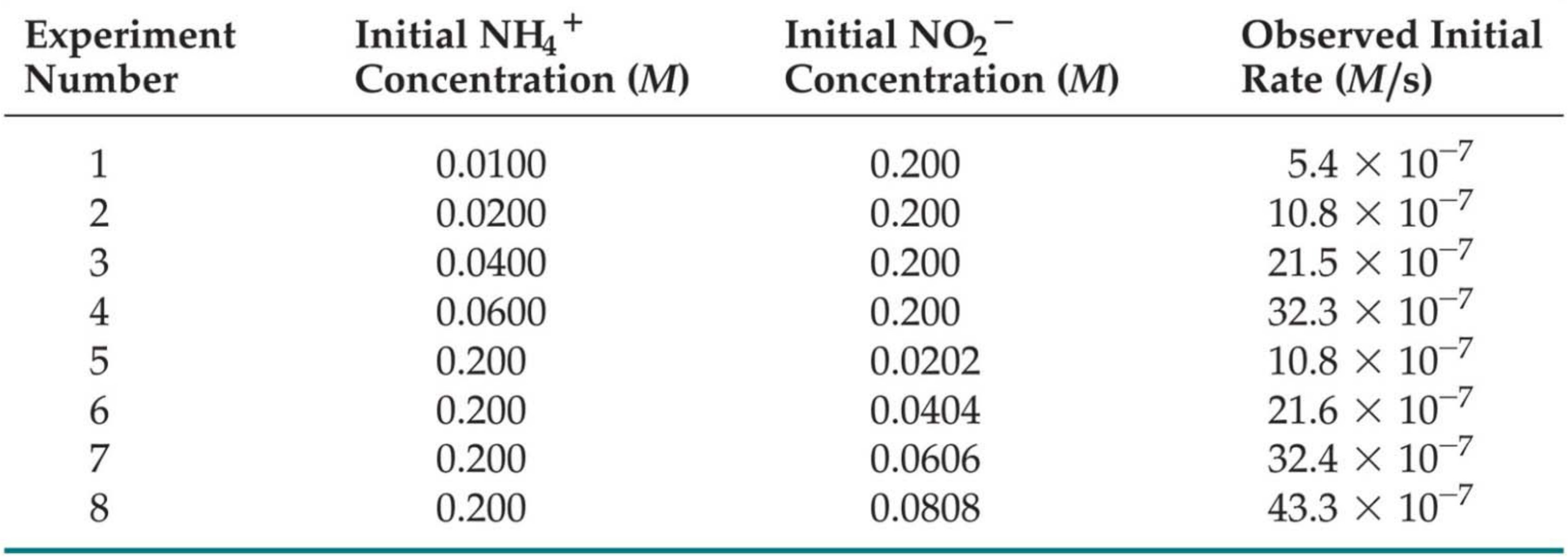
One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration

Concentration and Rate

For the reaction

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

Data is collected for several experiments:

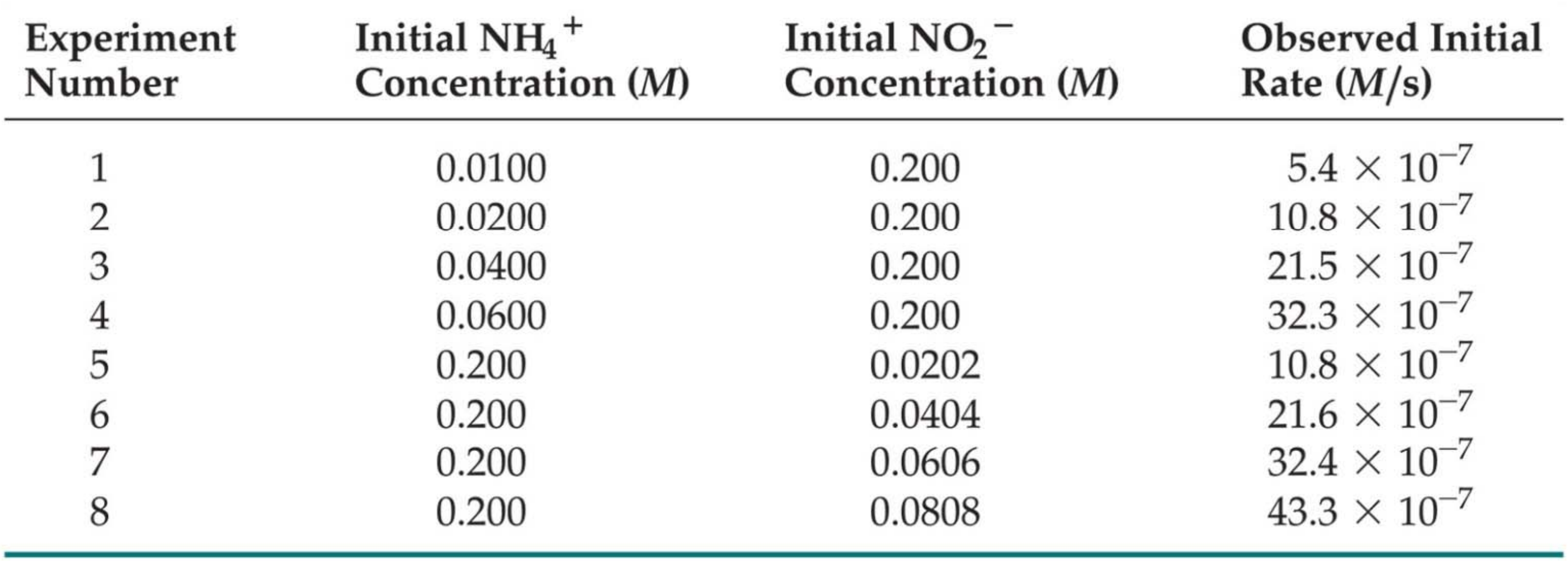


Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

Note that the concentrations are always changed, one at a time, in a systematic manner.

Concentration and Rate

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\,H_2O(l)$$



Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

- Comparing Experiments 1 and 2, when $[NH_4^+]$ doubles, the initial rate doubles. Note: $[NO_2^-]$ is constant.
- Also, comparing Experiments 2 and 3, when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

- Compare Experiments 1 and 2:

$$\frac{rate\,2}{rate\,1} = \frac{k[NH_4^+]_2^m[NO_2^-]_2^n}{k[NH_4^+]_1^m[NO_2^-]_1^n}$$

- Substitute data from the table:

$$\frac{10.8 \times 10^{-7}}{5.4 \times 10^{-7}} = \frac{k[0.0200]_2^m[0.200]_2^n}{k[0.0100]_1^m[0.200]_1^n}$$

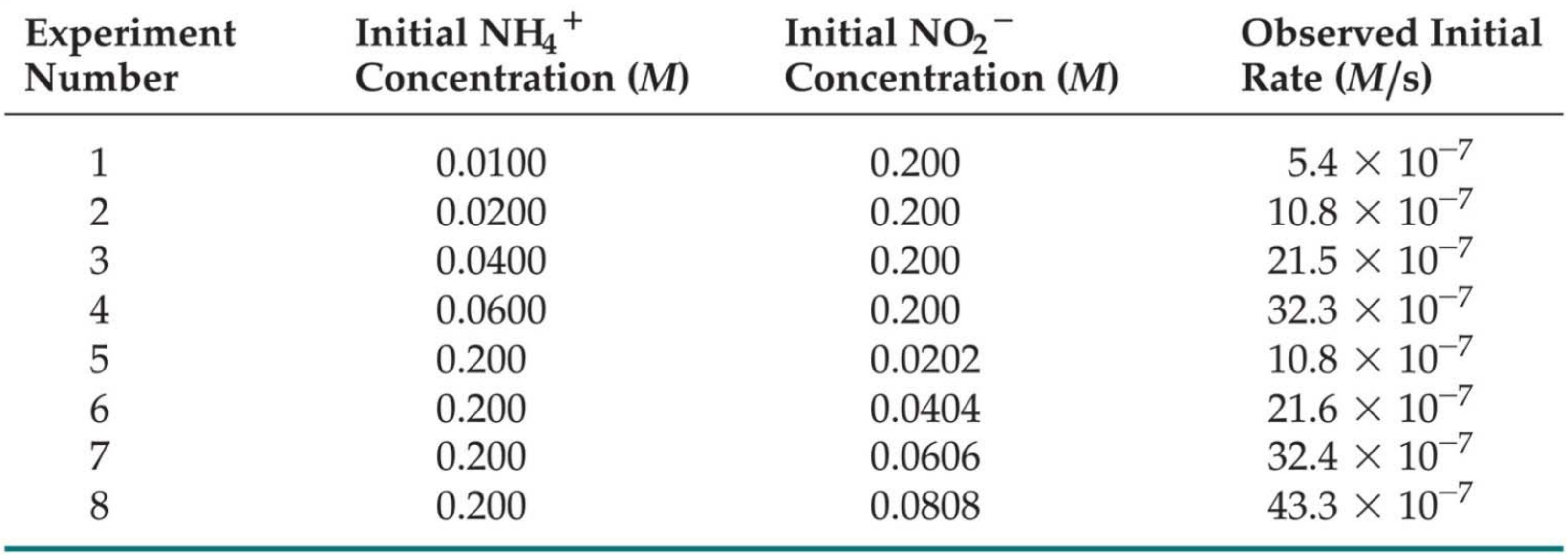
- Cancel terms to get:

$$2 = 2^m \Rightarrow m = 1$$

- This tells us that the reaction is first order with respect to $[NH_4^+]$ (i.e., only one molecule of NH_4^+ is involved in the reaction mechanism)

Concentration and Rate

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$



Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

- Comparing Experiments 5 and 6, when $[NO_2^-]$ doubles, the initial rate doubles. Note: $[NH_4^+]$ is constant.
- Also, comparing Experiments 6 and 8, when $[NO_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

$$\mathrm{NH_4^+}(aq) + \mathrm{NO_2^-}(aq) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2O}(l)$$

- Compare Experiments 5 and 6:

$$\frac{rate\,6}{rate\,5} = \frac{k\,[NH_4{}^+]_6^m\,[NO_2{}^-]_6^n}{k\,[NH_4{}^+]_5^m\,[NO_2{}^-]_5^n}$$

- Substitute data from the table:

$$\frac{21.6\times10^{-7}}{10.8\times10^{-7}} = \frac{k\,[0.200]_6^m\,[0.0404]_6^n}{k\,[0.200]_5^m\,[0.0202]_5^n}$$

- Cancel terms to get:

$$2 = 2^n \;\Rightarrow\; n = 1$$

- This tells us that the reaction is first order with respect to $[NO_2^-]$ (i.e., only one molecule of NO_2^- is involved in the reaction mechanism)

Concentration and Rate

- This means

$$\text{Rate} \propto [NH_4^+]$$

$$\text{Rate} \propto [NO_2^-]$$

$$\text{Rate} \propto [NH^+]\,[NO_2^-]$$

or

$$\text{Rate} = k\,[NH_4^+]\,[NO_2^-]$$

- This equation is called the **rate law**, and *k, the constant of proportionality,* is called the **rate constant**.

Rate Laws

- A rate law equation shows the relationship between the reaction rate and the concentrations of reactants.

$$\text{Rate} = k\,[NH_4^+]\,[NO_2^-]$$

- The exponents of the concentration terms tell the **order** of the reaction with respect to each reactant.
- For a **zero order** reaction, the rate is independent of concentration of reactants
- For a **first order** reaction, the rate depends on the concentration of one reactant
- For a **second order** reaction, the rate depends on the concentration of two molecules of reactant(s)

Rate Laws

For the reaction

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

$$\textbf{Rate} = k\,[NH_4^+]\,[NO_2^-]$$

- **This reaction is**

  First-order in $[NH_4^+]$ **(recall: m =1)**

  First-order in $[NO_2^-]$ **(recall: n = 1)**
- **The overall reaction order can be found by adding the exponents on the reactants in the rate law.**
- **This reaction is second-order overall.**

Rate Laws

For the reaction

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

$$\text{Rate} = k\ [NH_4^+]\ [NO_2^-]$$

- **To calculate the value of k, substitute data from any experiment**
- **Using Exp. 1:**

$$5.4 \times 10^{-7}\ M/s = k\ [0.0100]\ [0.200]$$

- **Solve for k**

$$k = 2.7 \times 10^{-4}\ M^{-1}s^{-1}$$

- **All the k values should be approximately the same at the same temperature.**

Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process gives us

$$\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$$

Where:

$[\mathrm{A}]_0$ is the initial concentration of A.

$[\mathrm{A}]_t$ is the concentration of A at some time, *t*, during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces…

$$\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$$

$$\ln [\mathrm{A}]_t - \ln [\mathrm{A}]_0 = -kt$$

$$\ln [\mathrm{A}]_t = -kt + \ln [\mathrm{A}]_0$$

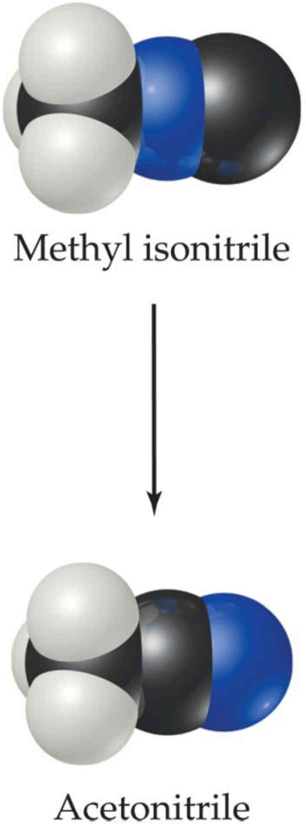
…which is in the form $y = mx + b$

First-Order Processes

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

Therefore, if a reaction is first-order, a plot of ln [A] vs. t will yield a straight line, and the slope of the line will be $-k$.

First-Order Processes



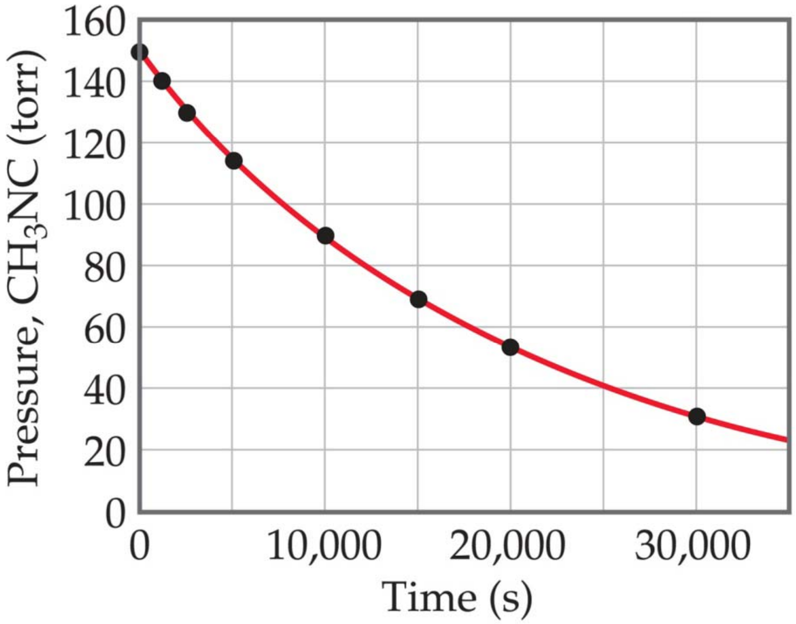
Consider the process in which methyl isonitrile is converted to acetonitrile.

$$CH_3NC \longrightarrow CH_3CN$$

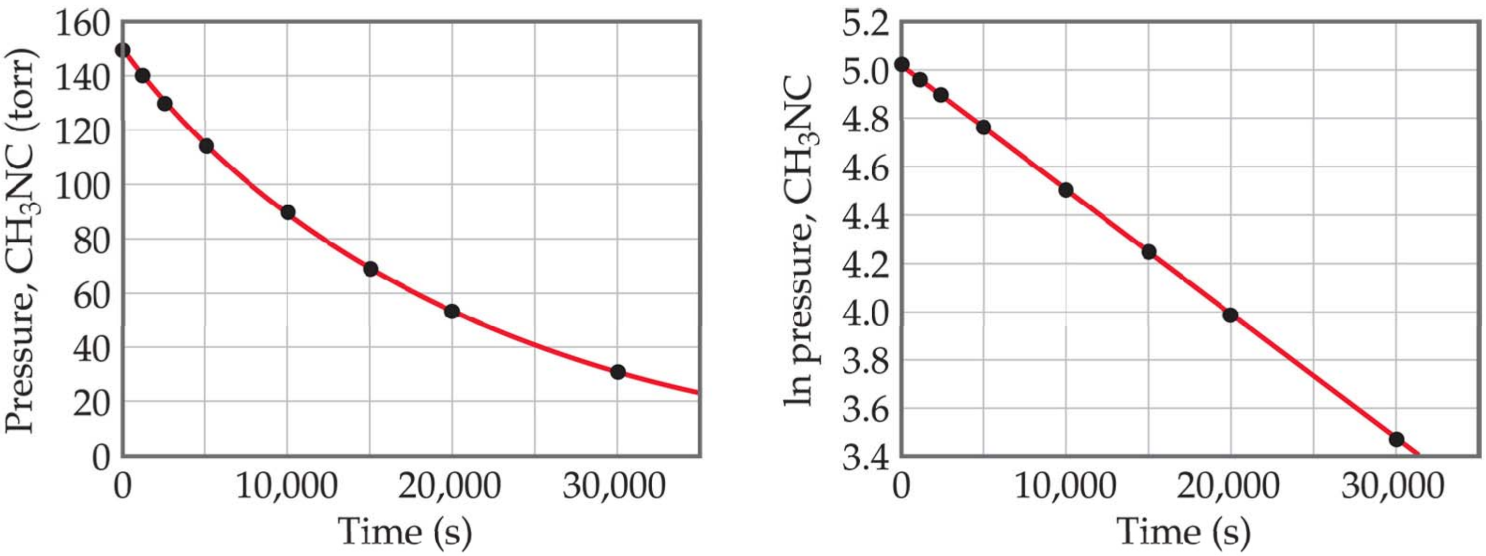
First-Order Processes

$$CH_3NC \longrightarrow CH_3CN$$

This data was collected for this reaction at 198.9° C.



First-Order Processes



- When ln *P* is plotted as a function of time, a straight line results.
- Therefore,
  - The process is first-order.
  - *k* is the negative slope: $5.1 \times 10^{-5}\ s^{-1}$.

Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A, we get

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

also in the form $y = \mathrm{m}\mathrm{x} + b$

Second-Order Processes

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

So if a process is second-order in A, a plot of 1/[A] vs. *t* will yield a straight line, and the slope of that line is *k*.

Second-Order Processes

The decomposition of NO_2 at 300° C is described by the equation

$$NO_2\,(g) \longrightarrow NO\,(g) + 1/2\ O_2\,(g)$$

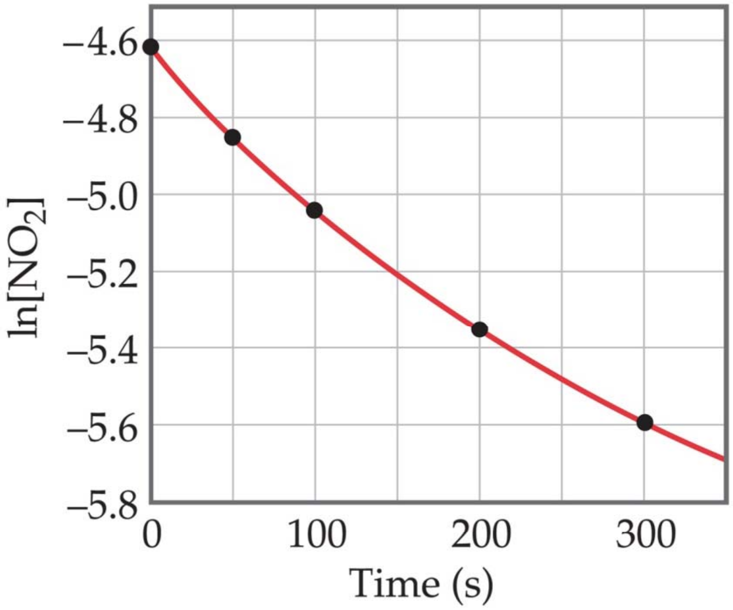
and yields data comparable to this:

Time (*s*)	$[NO_2]$, *M*
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

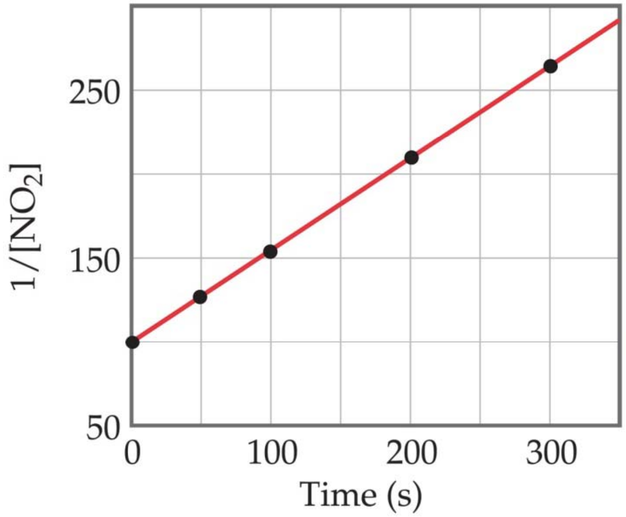
Second-Order Processes

- Graphing ln [NO_2] vs. *t* yields:
- The plot is *not* a straight line, so the process is *not* first-order in [A].

Time (*s*)	[NO_2], *M*	ln [NO_2]
0.0	0.01000	−4.610
50.0	0.00787	−4.845
100.0	0.00649	−5.038
200.0	0.00481	−5.337
300.0	0.00380	−5.573



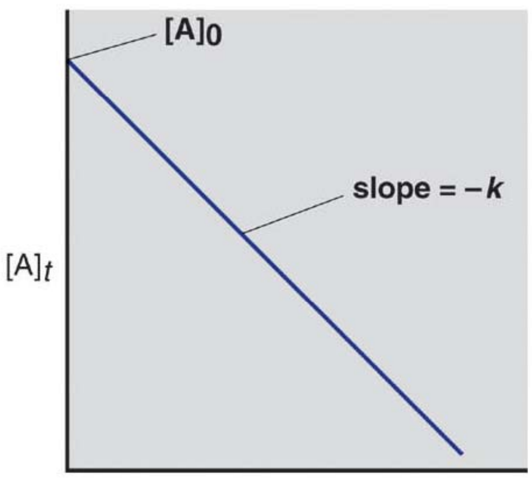
Second-Order Processes



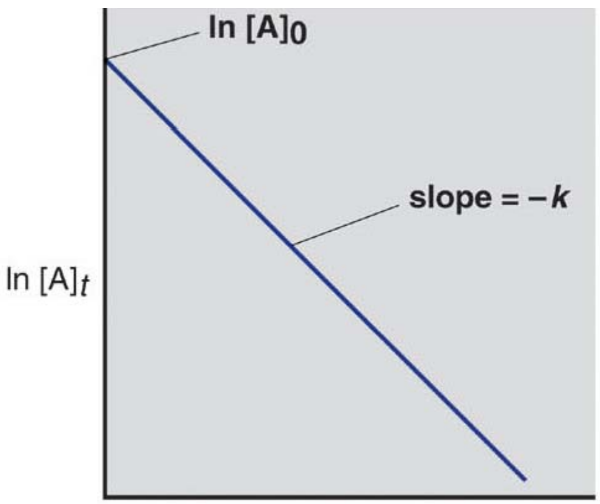
Time (s)	[NO_2], M	1/[NO_2]
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- Graphing ln 1/[NO_2] vs. t, however, gives this plot.
- Because this *is* a straight line, the process is second-order in [A].

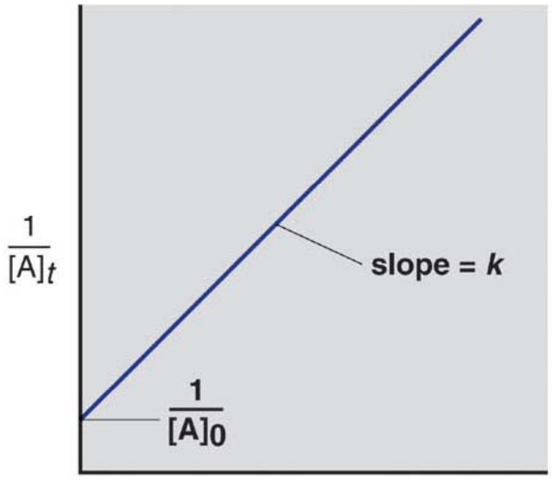
Summary of the Integrated Rate Law Graphs



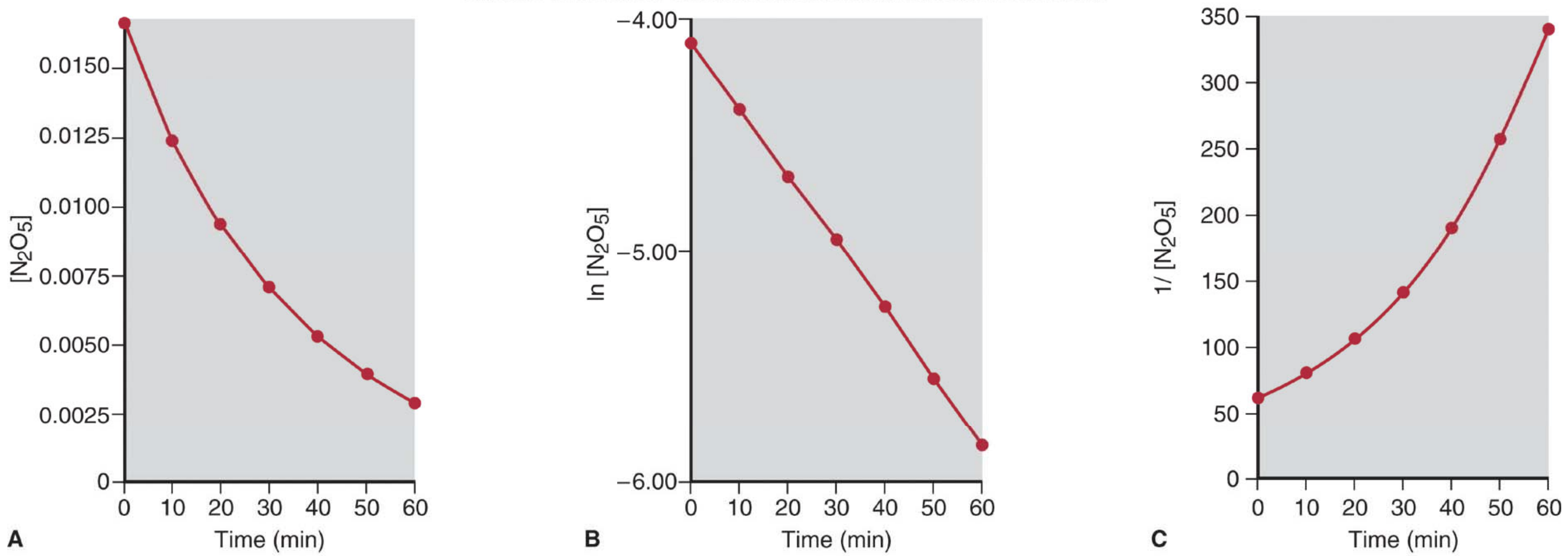
Zero order



A First order



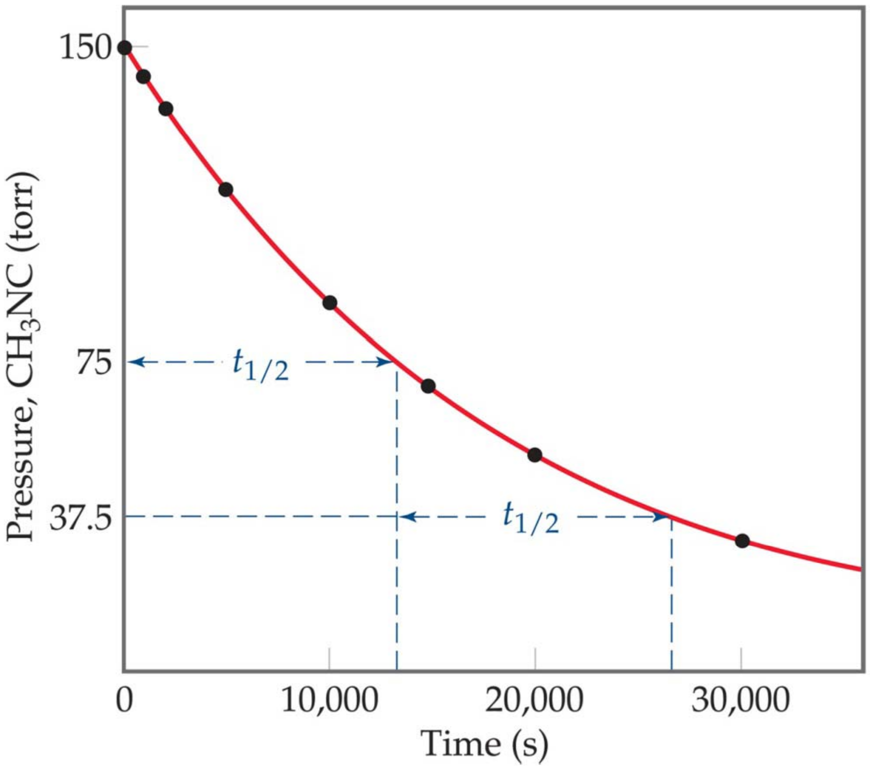
B Second order



Showing graphs for a 1st order reaction

Time (min)	[N_2O_5]	ln [N_2O_5]	1/[N_2O_5]
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

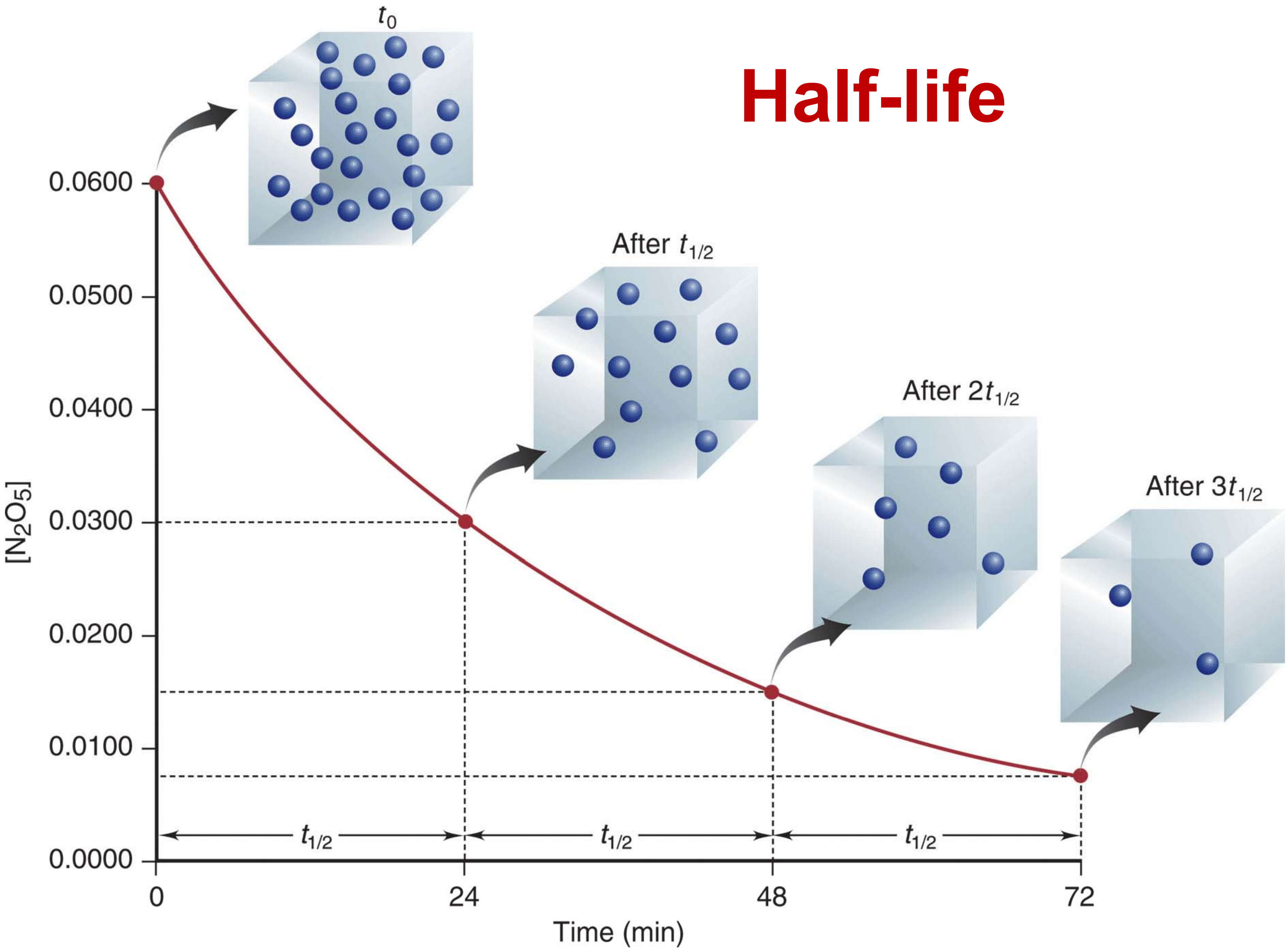
Half-Life



- Half-life is defined as the **time required for one-half of a reactant to react**.
- Because [A] at $t_{1/2}$ is one-half of the original [A],

$$[A]_t = 0.5\ [A]_0.$$

Half-life



t_0
After $t_{1/2}$
After $2t_{1/2}$
After $3t_{1/2}$
0.0600
0.0500
0.0400
0.0300
0.0200
0.0100
0.0000
$[N_2O_5]$
$t_{1/2}$
$t_{1/2}$
$t_{1/2}$
0
24
48
72
Time (min)

Half-Life: First Order Reaction

For a first-order process, the integrated rate law is

$$\ln \frac{0.5\,[A]_0}{[A]_0} = -kt_{1/2}$$

Which reduces to

$$\ln 0.5 = -kt_{1/2}$$

Calculate the value for ln 0.5

$$-0.693 = -kt_{1/2}$$

Solve for $t_{1/2}$

$$\frac{0.693}{k} = t_{1/2}$$

NOTE: For a first-order process, the half-life does not depend on $[A]_0$.

Half-Life: First Order Reaction

To calculate the concentration at time t, or the length of time needed for the concentration of reactant to reach a specific concentration, two equations may be needed:

The equation for half-life (to determine the value of k)

$$\frac{0.693}{k} = t_{1/2}$$

and the integrated rate equation

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

Half-Life: Second Order Reaction

For a second-order process, the integrated rate law is

$$\frac{1}{0.5\,[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

Divide the first term:

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

Subtract $1/[A]_0$ from both sides

$$\frac{2-1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

Solve for $t_{1/2}$

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

Half-Life: Second Order Reaction

To calculate the concentration at time t, or the length of time needed for the concentration of reactant to reach a specific concentration, two equations may be needed:

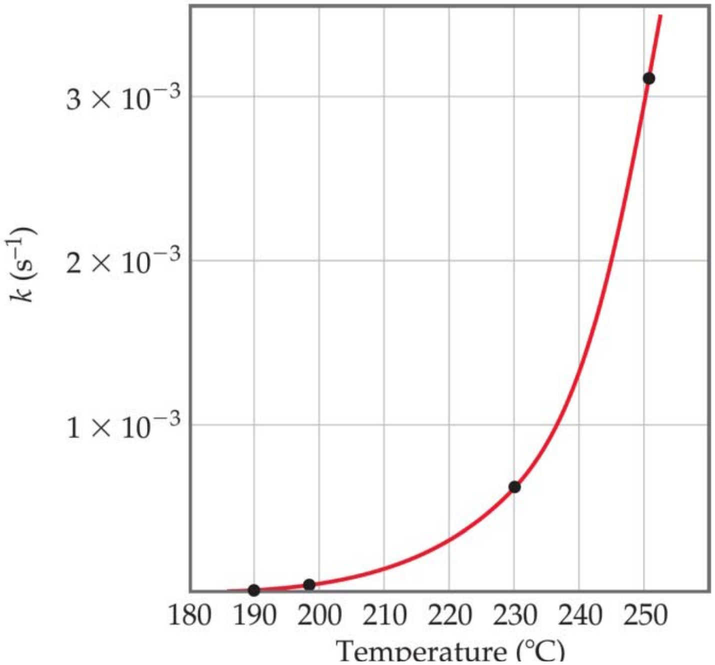
The equation for half-life (to determine the value of k)

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

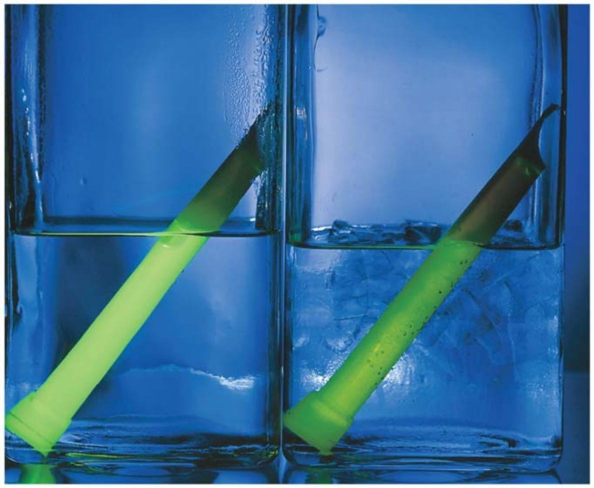
and the integrated rate equation

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

Temperature and Rate



- Generally, as temperature increases, so does the reaction rate.
- This is because *k* is temperature dependent.



Higher temperature Lower temperature

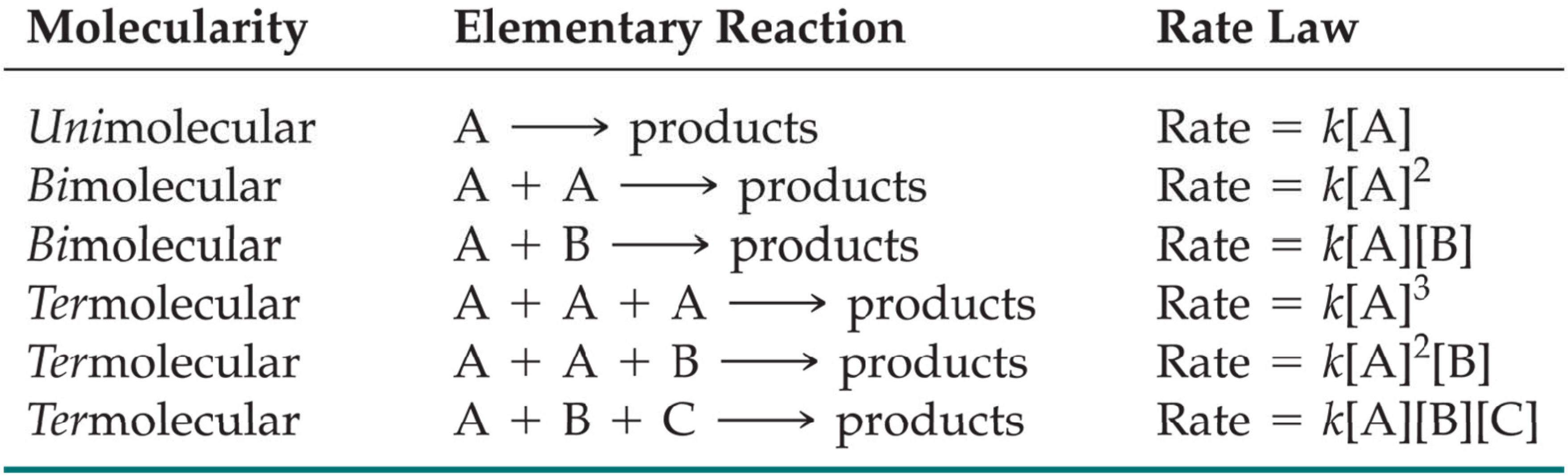
Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

Reaction Mechanisms

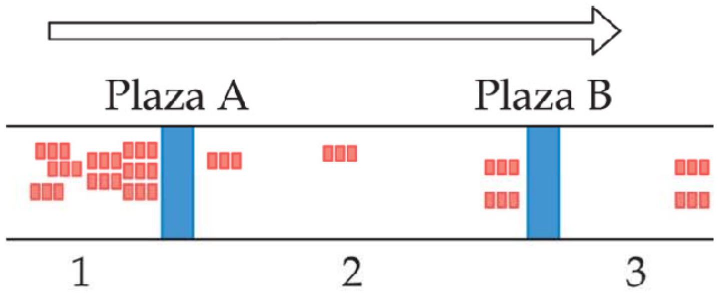


Molecularity	**Elementary Reaction**	**Rate Law**
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

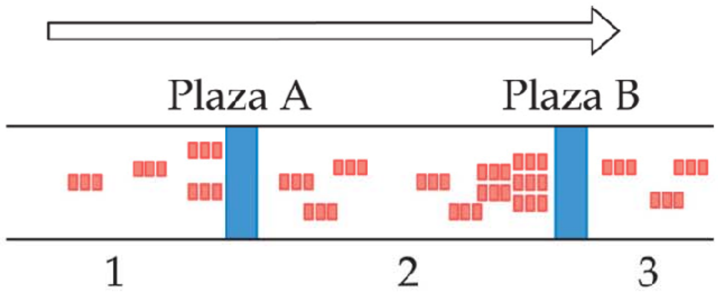
The molecularity of a process tells how many molecules are involved in the process.

Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.



Cars slowed at plaza A



Cars slowed at plaza B

Slow Initial Step

$$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)$$

- The rate law for this reaction is found experimentally to be

$$\text{Rate} = k\,[NO_2]^2$$

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

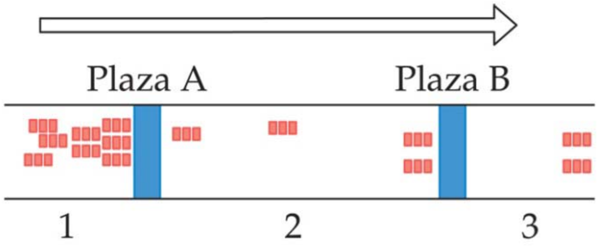
Slow Initial Step

- A proposed mechanism for this reaction is

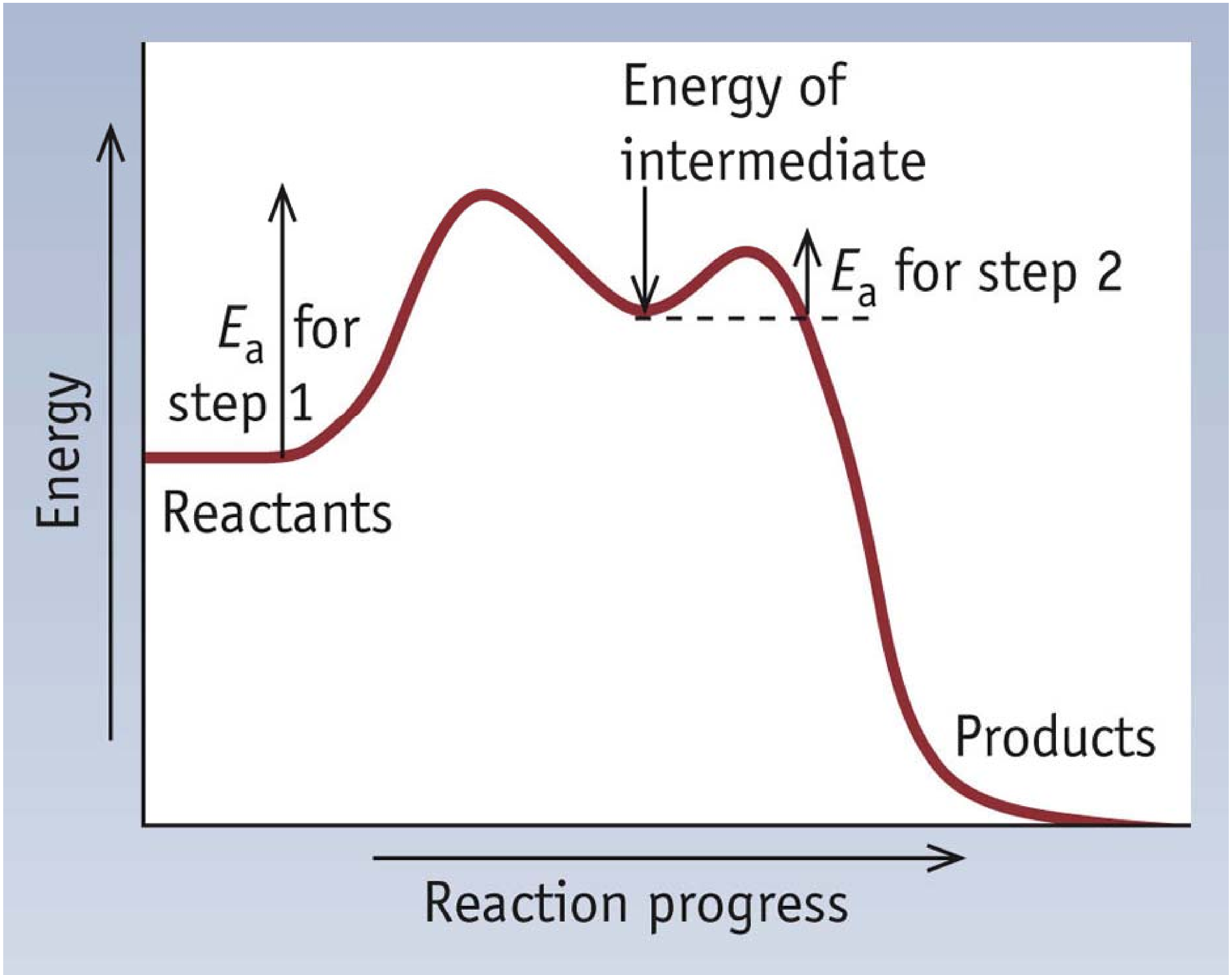
$$\text{Step 1: } NO_2 + NO_2 \longrightarrow NO_3 + NO \quad \text{(slow)}$$

$$\text{Step 2: } NO_3 + CO \longrightarrow NO_2 + CO_2 \quad \text{(fast)}$$

- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



Cars slowed at plaza A


Energy of intermediate
E_a for step 2
E_a for step 1
Energy
Reactants
Products
Reaction progress

Fast Initial Step

$$2\ \mathrm{NO}\ (g) + \mathrm{Br_2}\ (g) \longrightarrow 2\ \mathrm{NOBr}\ (g)$$

- The rate law for this reaction is found to be

$$\text{Rate} = k\ [\mathrm{NO}]^2\ [\mathrm{Br_2}]$$

- Because termolecular processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

- A proposed mechanism is

Step 1: $NO + Br_2 \leftrightarrows NOBr_2$ (fast)

Step 2: $NOBr_2 + NO \rightarrow 2\ NOBr$ (slow)

Note: Step 1 includes the forward *and* reverse reactions.

Fast Initial Step

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$\text{Rate} = k_2\,[\text{NOBr}_2]\,[\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?

Fast Initial Step

- $NOBr_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$\text{Rate}_f = \text{Rate}_r$$

Fast Initial Step

- Because $\text{Rate}_f = \text{Rate}_r$,

$$k_1 \, [\text{NO}] \, [\text{Br}_2] = k_{-1} \, [\text{NOBr}_2]$$

- Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] \, [\text{Br}_2] = [\text{NOBr}_2]$$

Fast Initial Step

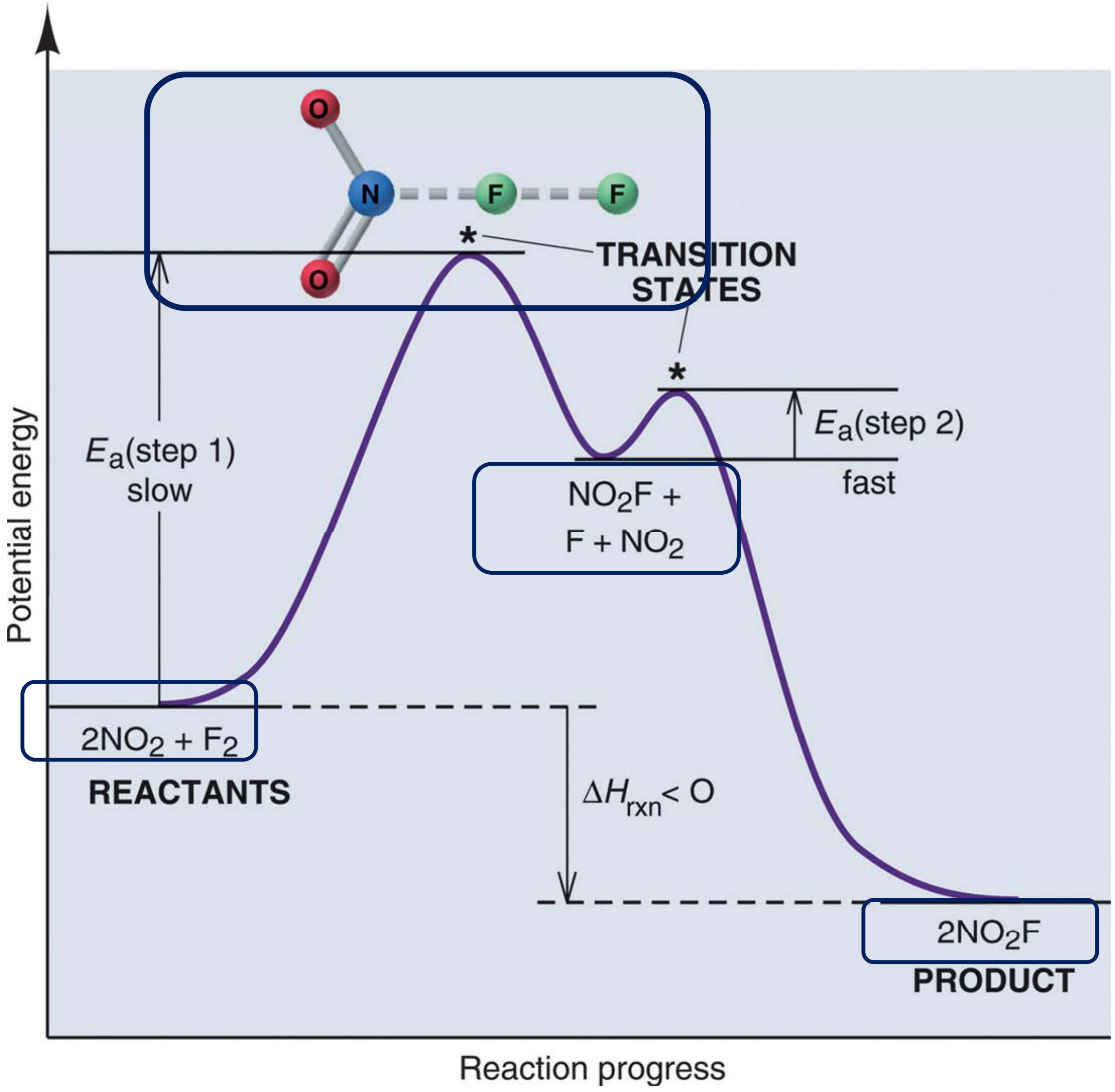
Substituting this expression for [NOBr$_2$] in the rate law for the rate-determining step gives

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] [\text{NO}]$$

Collecting terms and consolidating the constants into a single constant, the equation becomes

$$\text{Rate} = k\, [\text{NO}]^2 [\text{Br}_2]$$

Reaction energy diagram for the two-step NO_2-F_2 reaction



The Rate-Determining Step of a Reaction Mechanism

The overall rate of a reaction is related to the rate of the slowest, or rate-determining step.

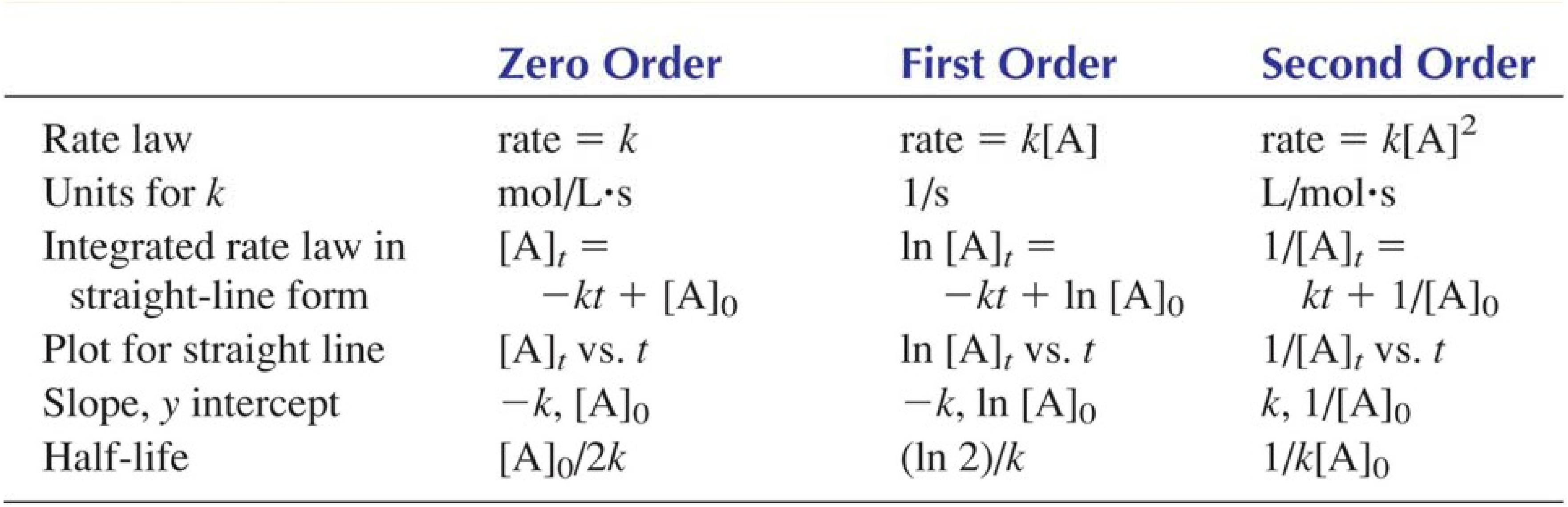
Correlating the Mechanism with the Rate Law

The elementary steps must add up to the overall equation.

The elementary steps must be physically reasonable.

The mechanism must correlated with the rate law.

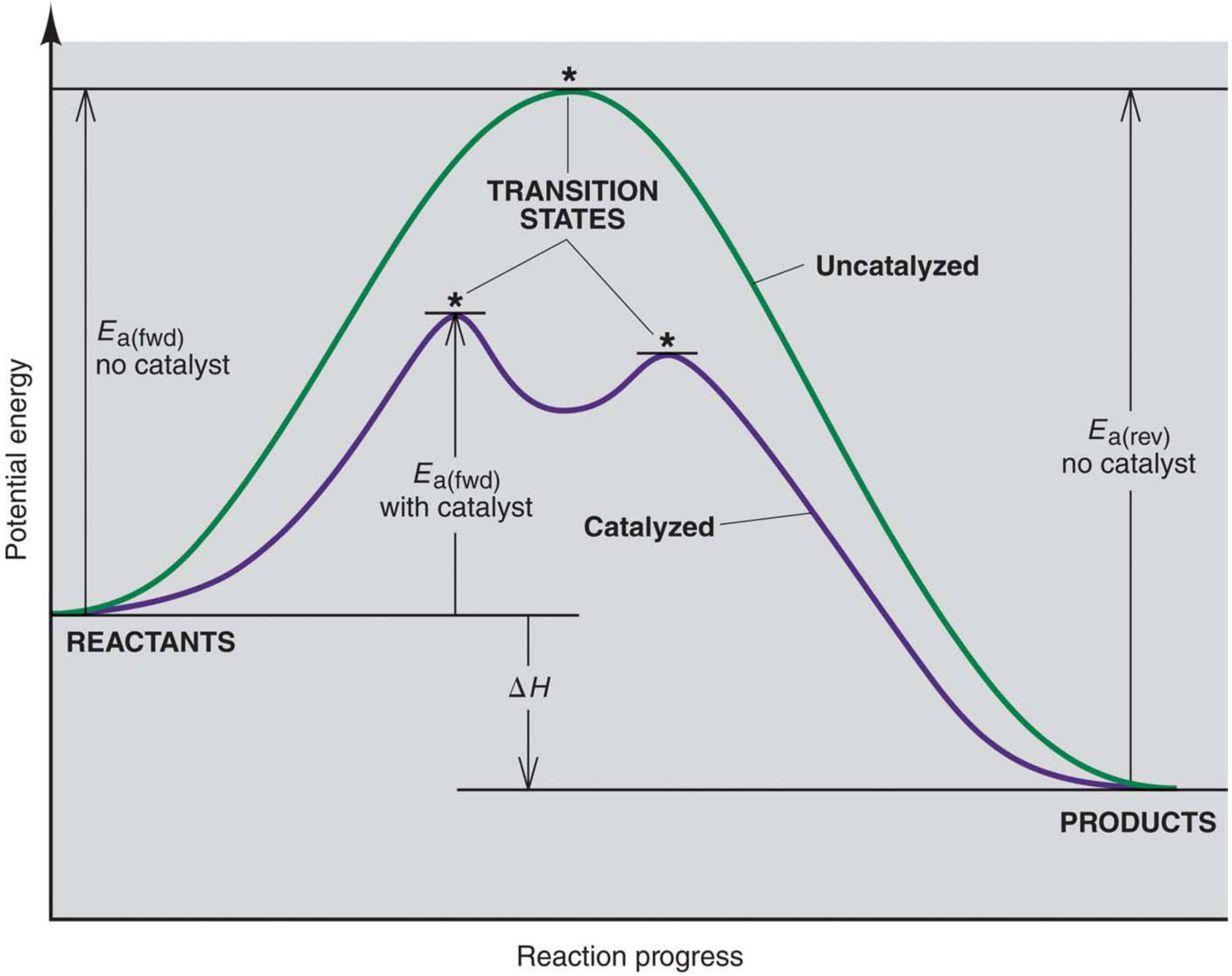
A summary of rate law information for zero order, first order, and second order reactions



	Zero Order	**First Order**	**Second Order**
Rate law	rate = k	rate = k[A]	rate = $k[A]^2$
Units for k	mol/L·s	1/s	L/mol·s
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$1/[A]_t = kt + 1/[A]_0$
Plot for straight line	$[A]_t$ vs. t	$\ln [A]_t$ vs. t	$1/[A]_t$ vs. t
Slope, y intercept	$-k$, $[A]_0$	$-k$, $\ln [A]_0$	k, $1/[A]_0$
Half-life	$[A]_0/2k$	$(\ln 2)/k$	$1/k[A]_0$

Catalysts

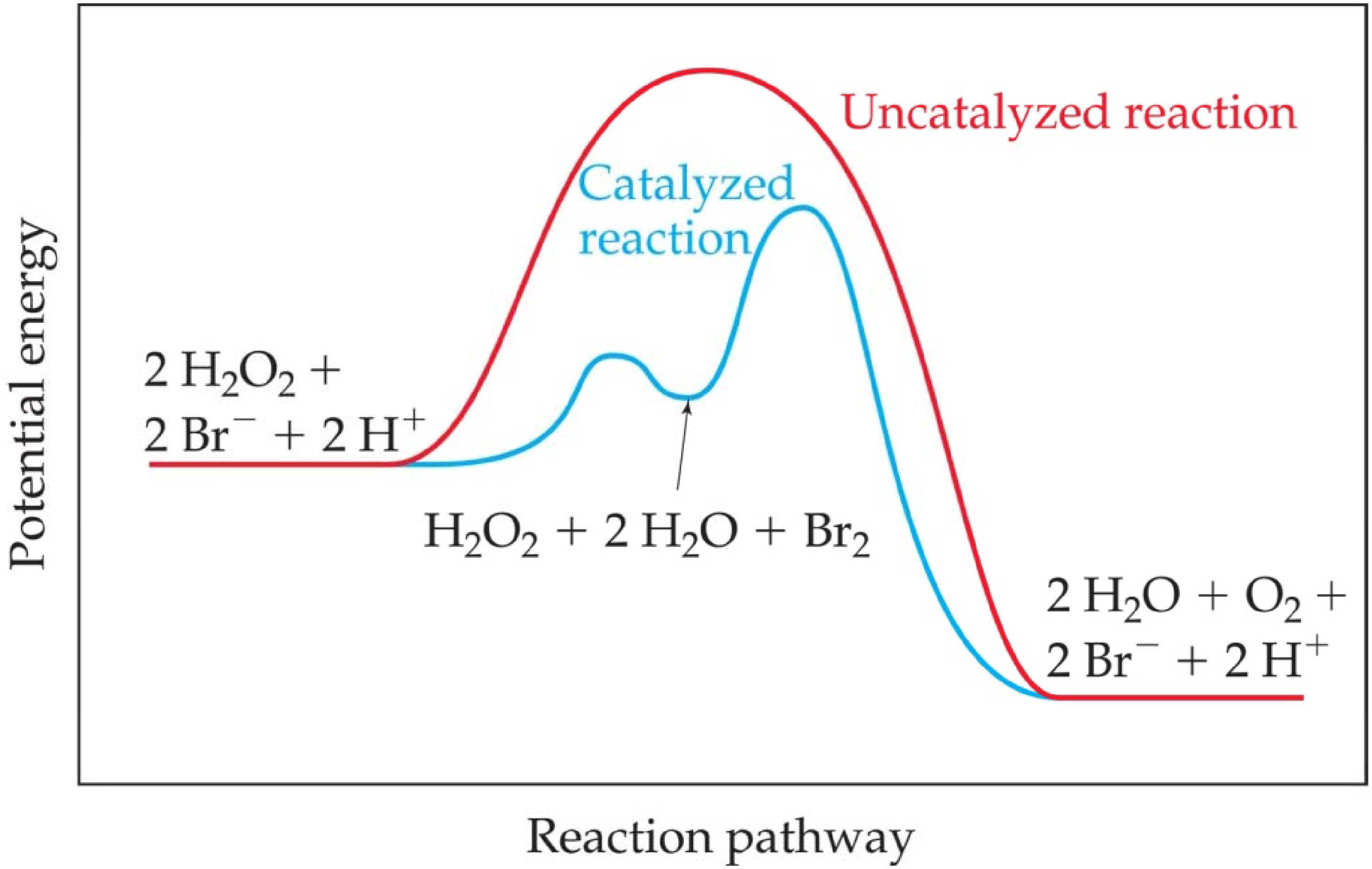
- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.



A Homogeneous Catalyst

Bromide ion catalyzes the reduction of hydrogen peroxide in acid solution

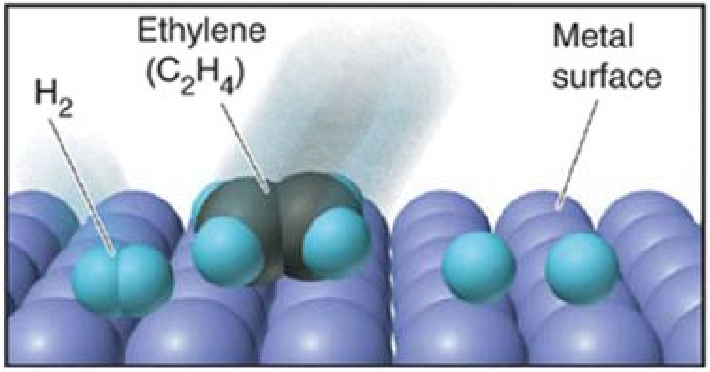
$2\ H_2O_2 + 2\ Br^- + 2\ H^+ \rightarrow H_2O_2 + 2\ H_2O + Br_2 \rightarrow 2\ H_2O + O_2 + 2\ Br^- + 2\ H^+$



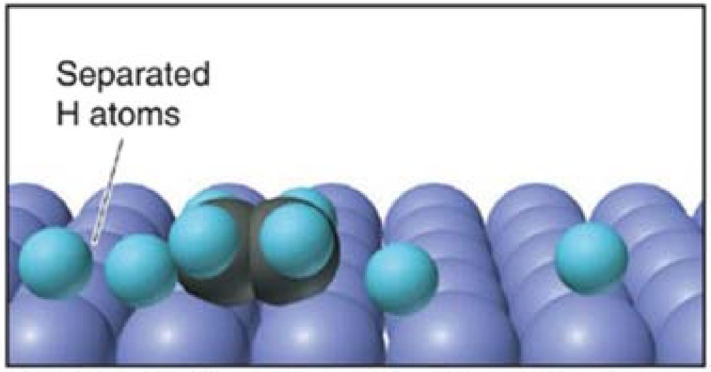
A Heterogeneous Catalyst

The hydrogenation of ethene (ethylene):

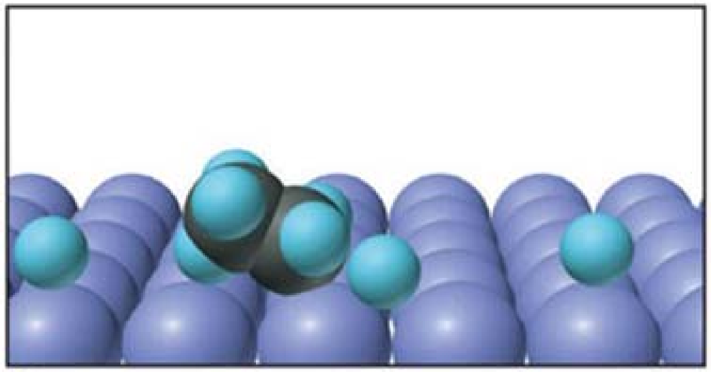
$$H_2C{=}CH_{2\,(g)} + H_{2\,(g)} \rightarrow CH_3\text{-}CH_{3\,(g)}$$



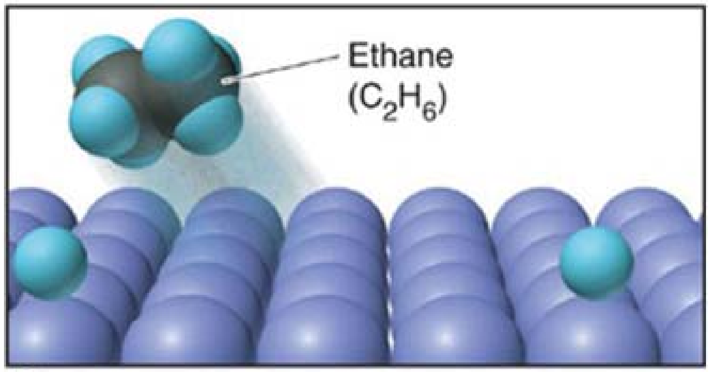
① *H_2 and C_2H_4 approach and adsorb to metal surface.*



② *Rate-limiting step is H—H bond breakage.*



③ *One H atom bonds to adsorbed C_2H_4.*

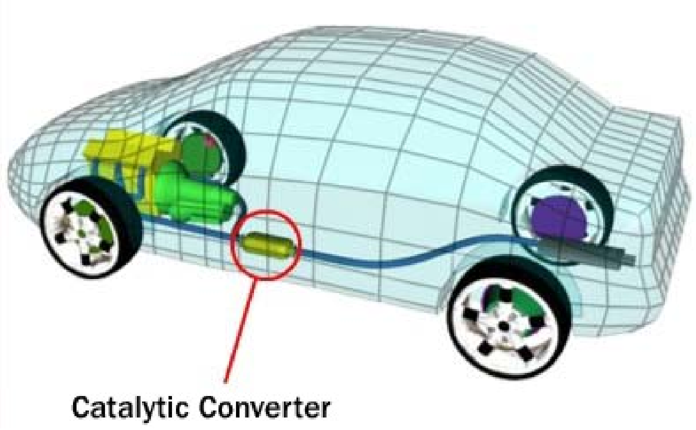


④ *Another C—H bond forms and C_2H_6 leaves the surface.*

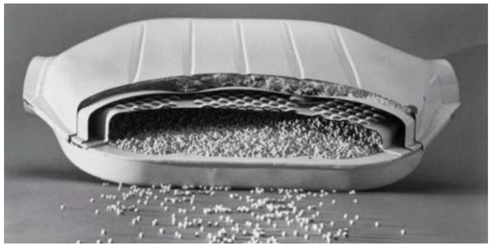
CATALYSIS

Catalytic converters in auto exhaust systems

The catalytic converter contains a ceramic surface that is coated with a thin later of platinum, palladium, and/or rhodium.



Older catalytic converters used ceramic beads.



Newer catalytic converters use a honeycomb structure.

Reduction of exhaust gases, mixed with air, takes place on the metal surface:

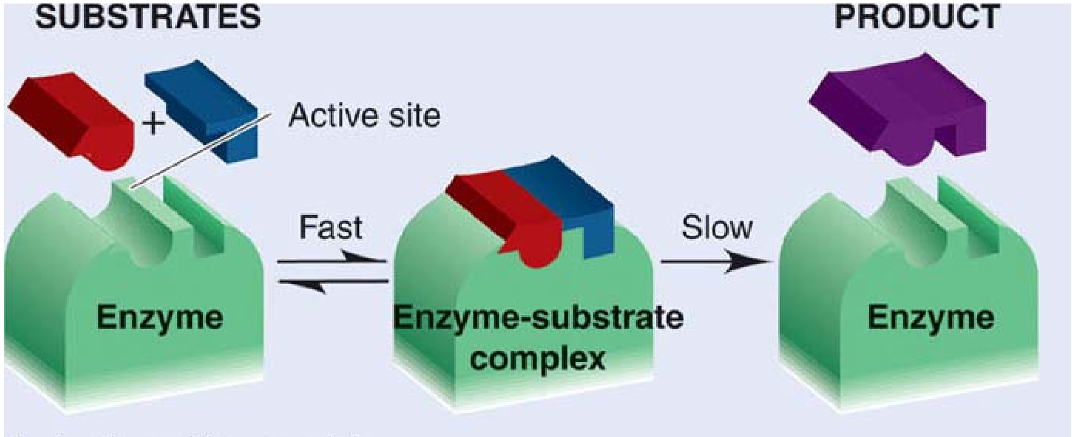
$$2\,CO + O_2 \rightarrow 2\,CO_2$$

$$2\,NO \rightarrow N_2 + O_2$$

Enzymes

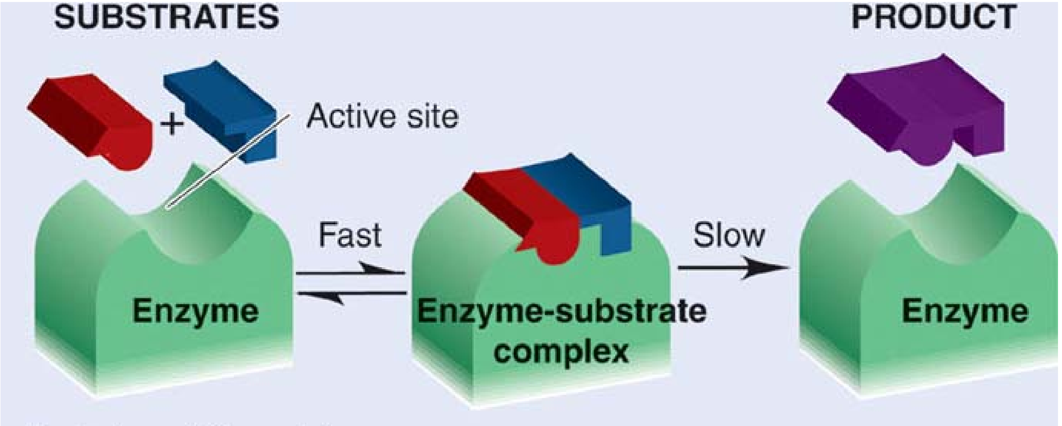
Enzymes are catalysts in biological systems.

In one type of reaction, the substrates fit into the active site of the enzyme much like a key fits into a lock.



A Lock-and-key model

In a second type of reaction the substrates fit into a more generalize active site of the enzyme



B Induced-fit model