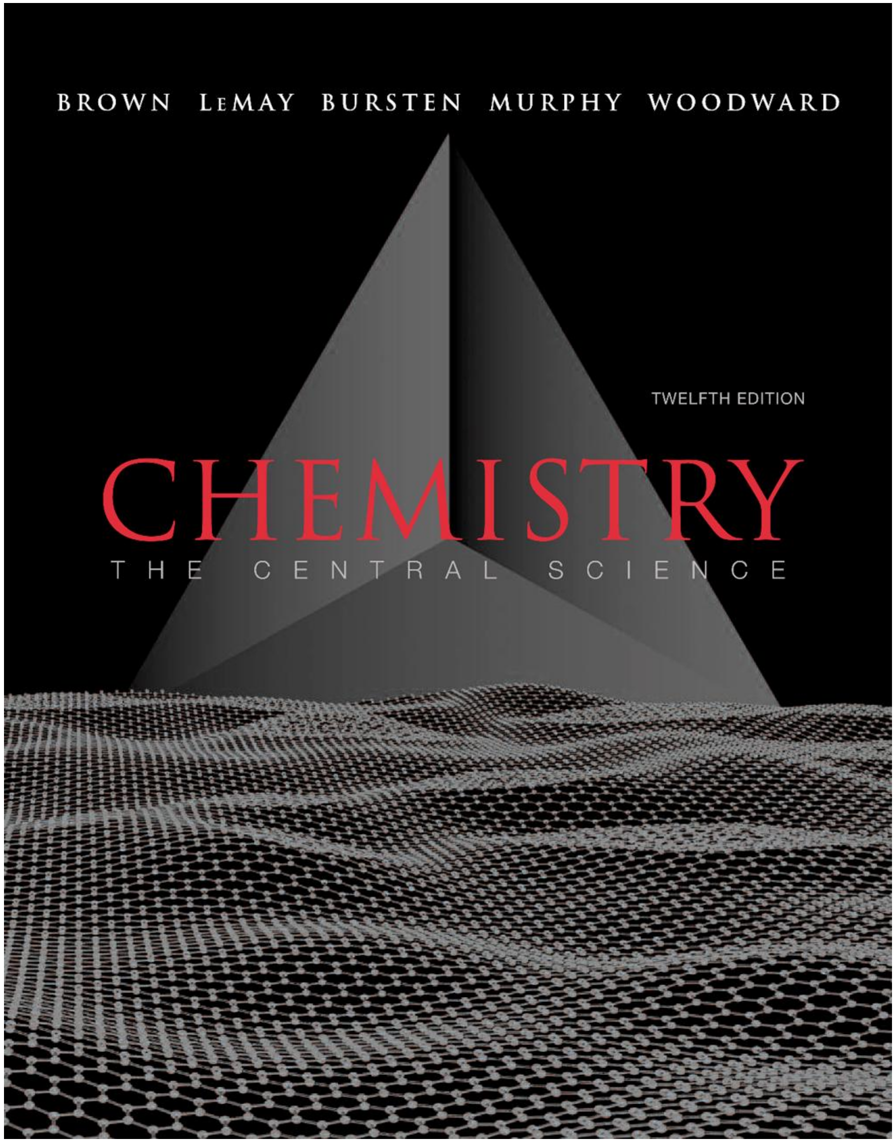

Lecture Presentation

Chapter 14

Chemical Kinetics

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St. Charles Community College
Cottleville, MO

Kinetics

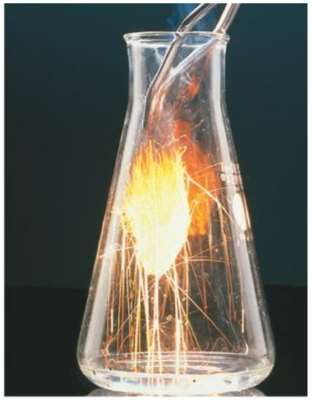
- In kinetics we study the rate at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

Factors That Affect 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.

Factors That Affect Reaction Rates

Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly



Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

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

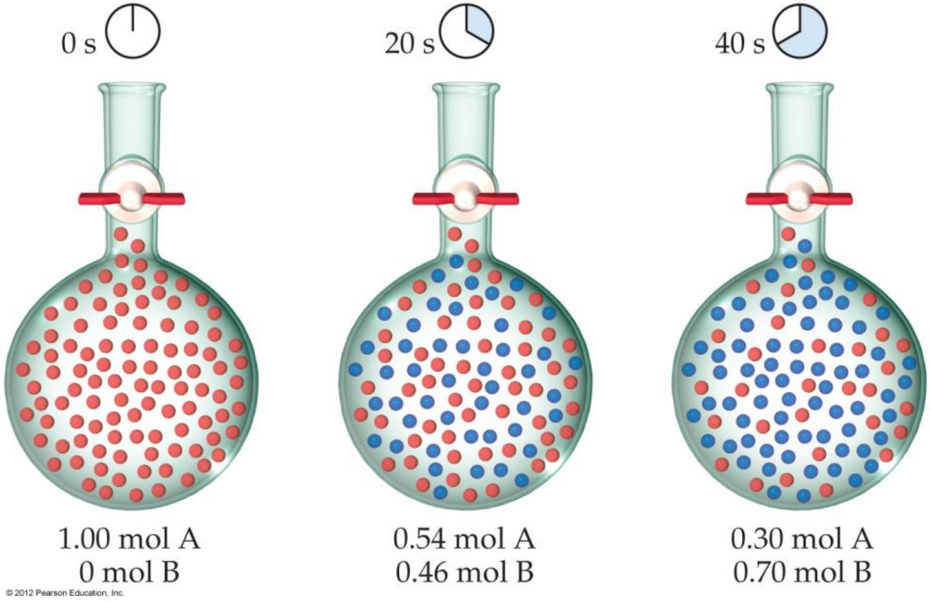
Factors That Affect Reaction Rates

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

Factors That Affect Reaction Rates

- Presence of a catalyst.
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.

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

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

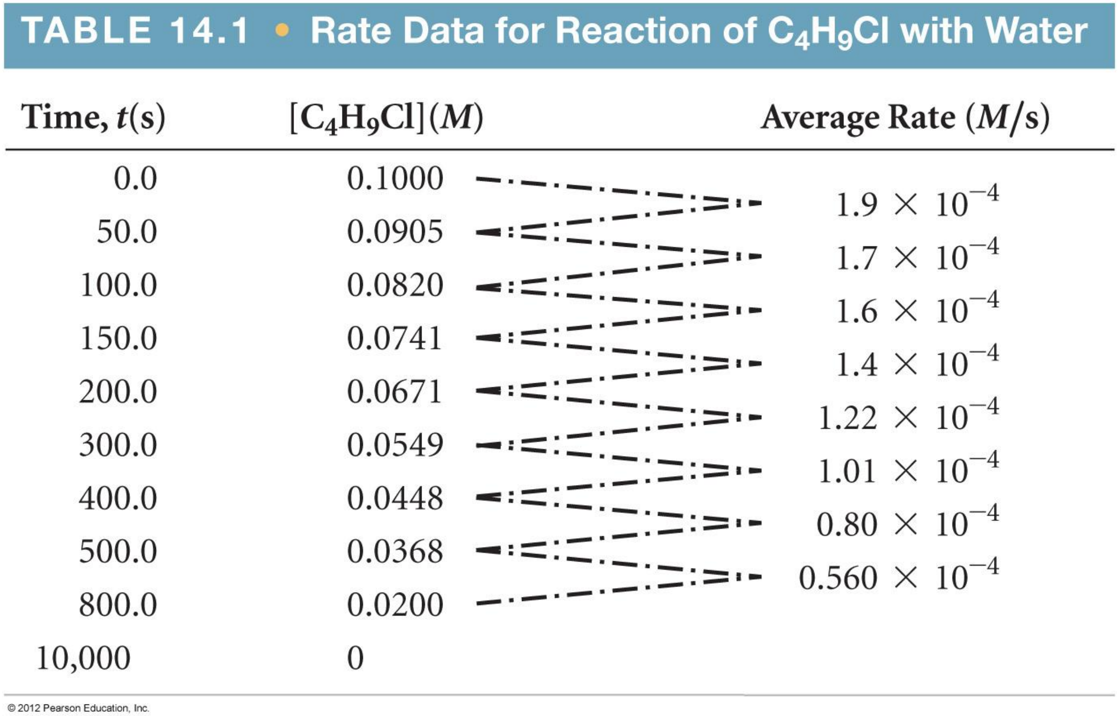


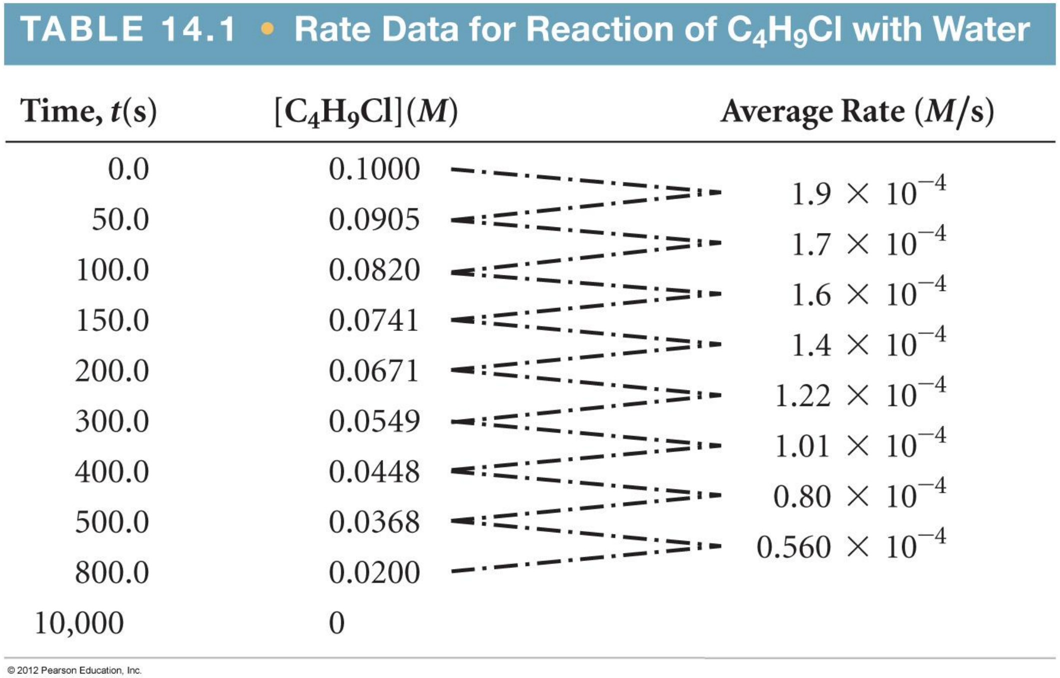
TABLE 14.1 • Rate Data for Reaction of C_4H_9Cl with Water

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	

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

Reaction Rates

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



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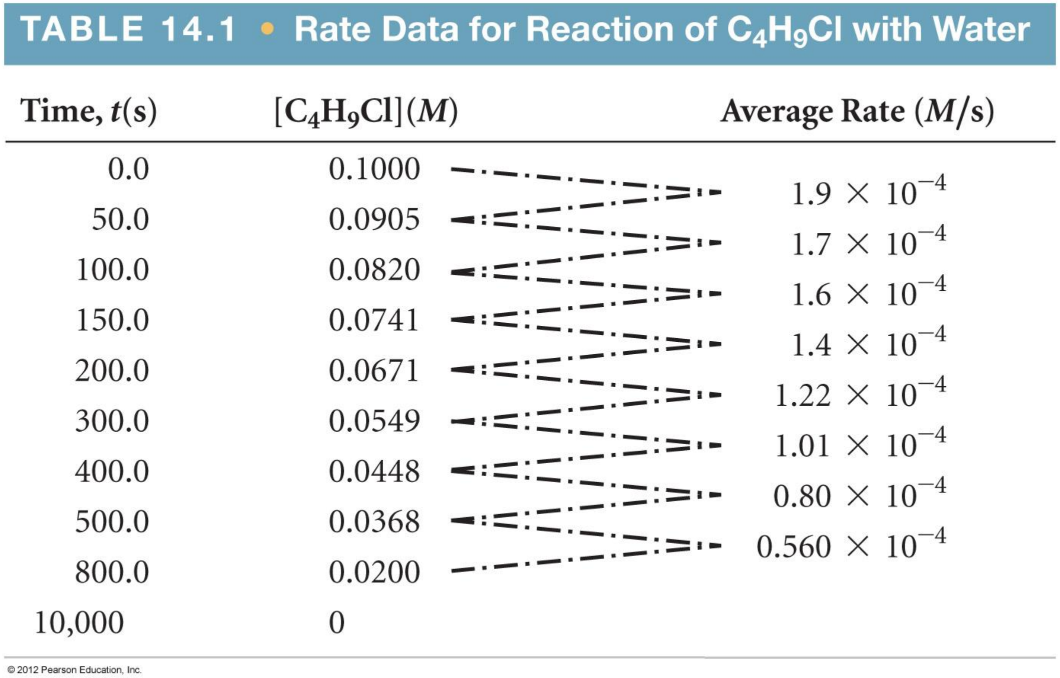
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

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

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



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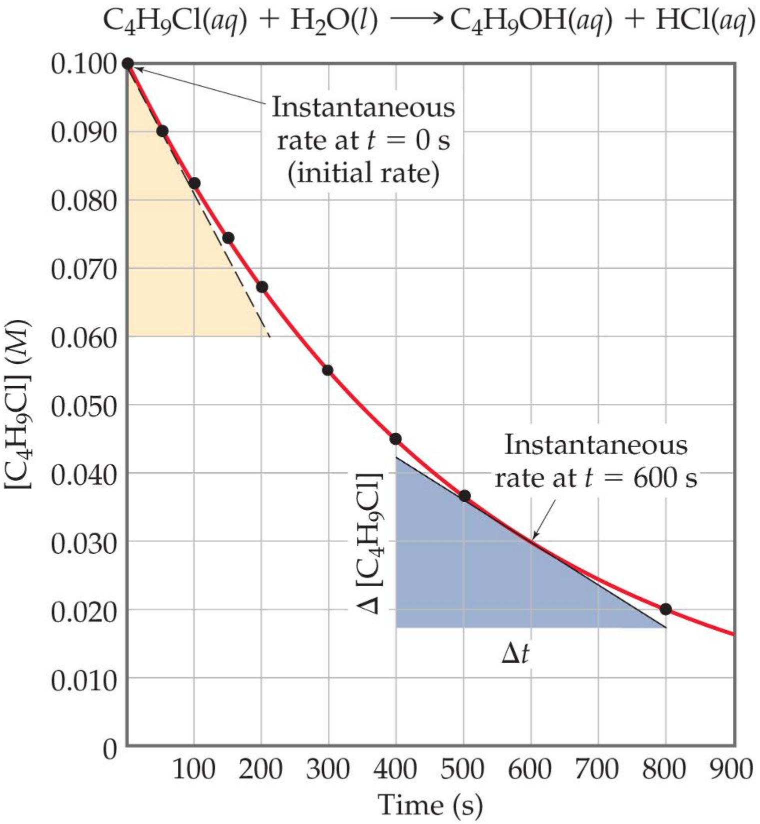
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

- 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

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

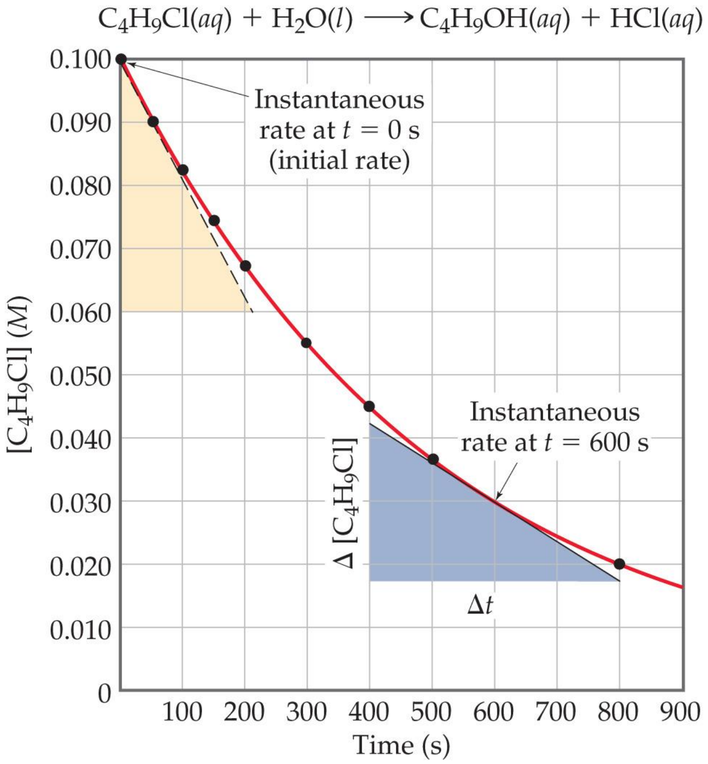
- A plot of [C_4H_9Cl] versus time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.



Reaction Rates

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

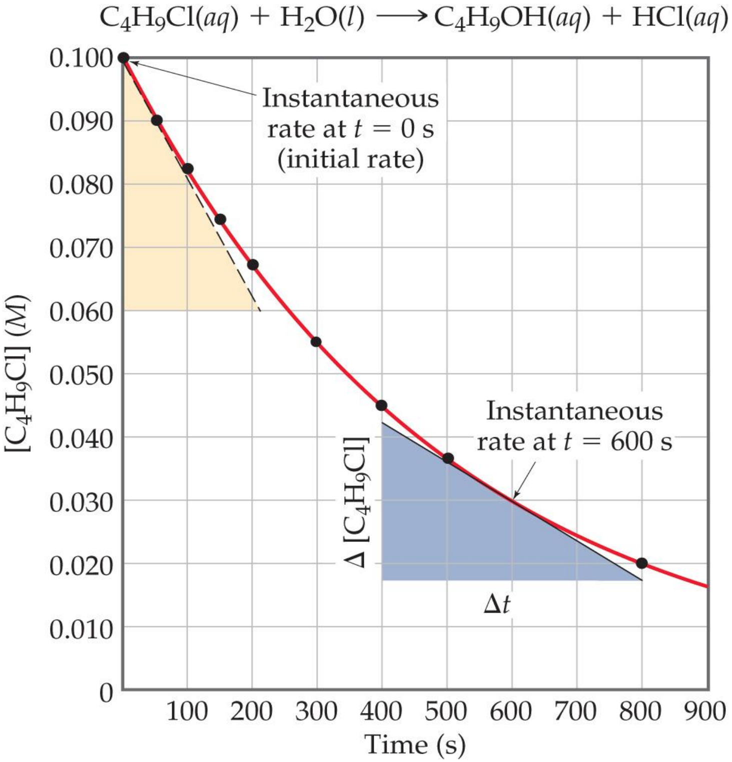
- All reactions slow down over time.
- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the *beginning* of the reaction.



Reaction Rates

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

- 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.



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

Reaction Rates and Stoichiometry

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

$$2\ HI(g) \longrightarrow H_2(g) + I_2(g)$$

- In such a case,

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

Reaction Rates and Stoichiometry

- To generalize, then, for the reaction

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

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

Concentration and Rate

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

Concentration and Rate

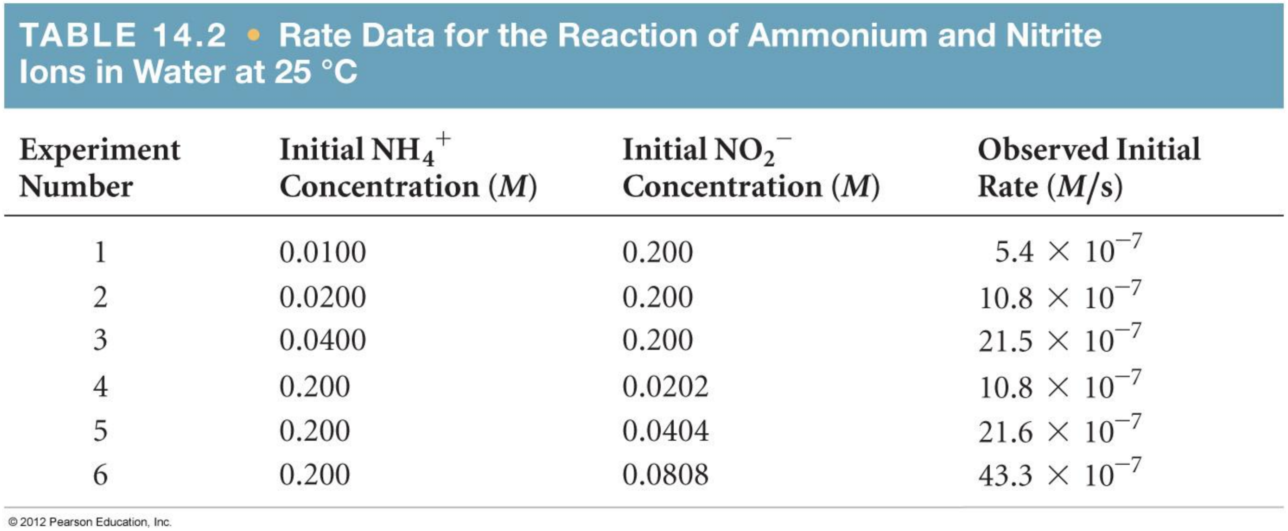


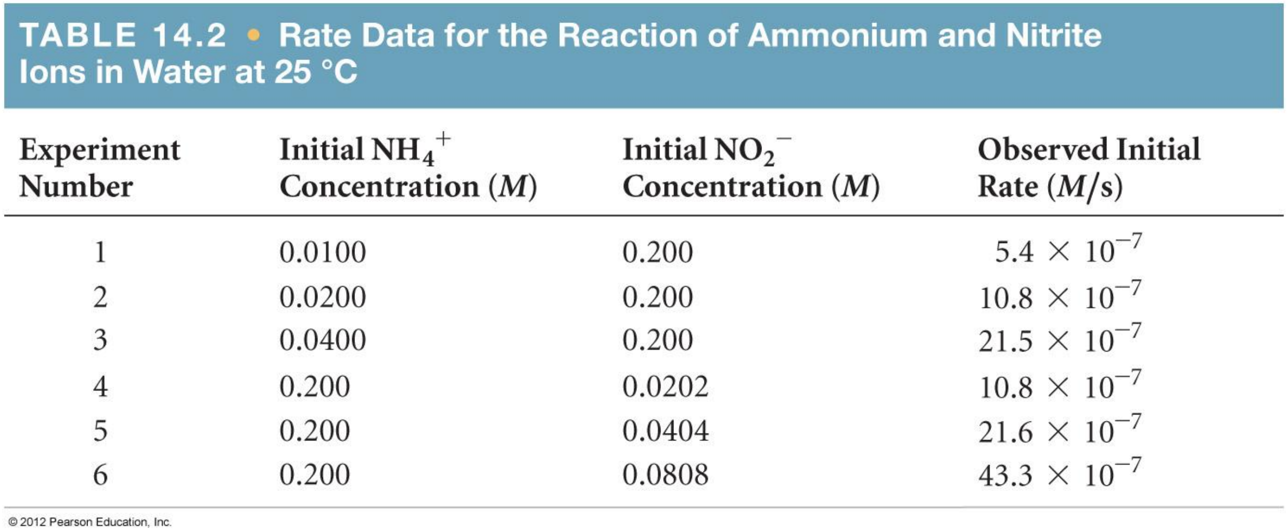
TABLE 14.2 • Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

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	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

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

If we compare Experiments 1 and 2, we see that when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate



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4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

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

Likewise, when we compare Experiments 5 and 6, we see that when $[NO_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

- This means

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

Therefore,

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

which, when written as an equation, becomes

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

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

Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The exponents tell the **order** of the reaction with respect to each reactant.
- Since the rate law is

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

the reaction is

First-order in $[\mathrm{NH_4^+}]$

and

First-order in $[\mathrm{NO_2^-}]$

Rate Laws

$$\text{Rate} = k[\text{NH}_4^+]\,[\text{NO}_2^-]$$

- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is second-order overall.

Integrated Rate Laws

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

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

where

$[A]_0$ is the initial concentration of A, and

$[A]_t$ is the concentration of A at some time, t, during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces

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

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

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

which is in the form

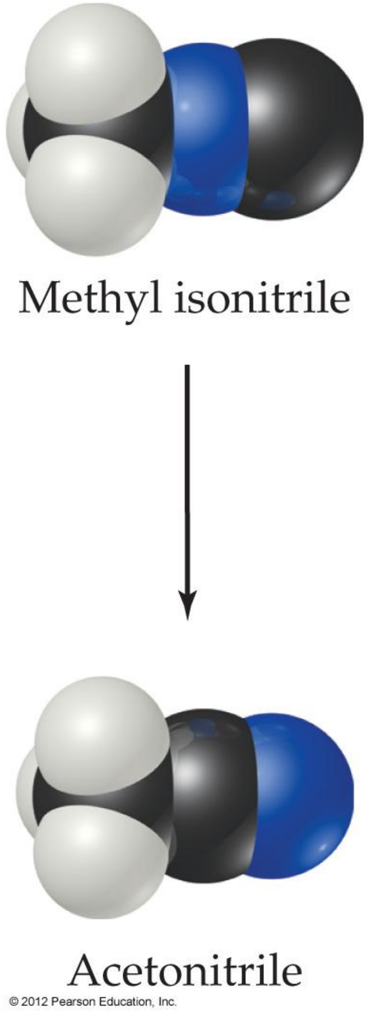
$$\boldsymbol{y = mx + b}$$

First-Order Processes

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

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



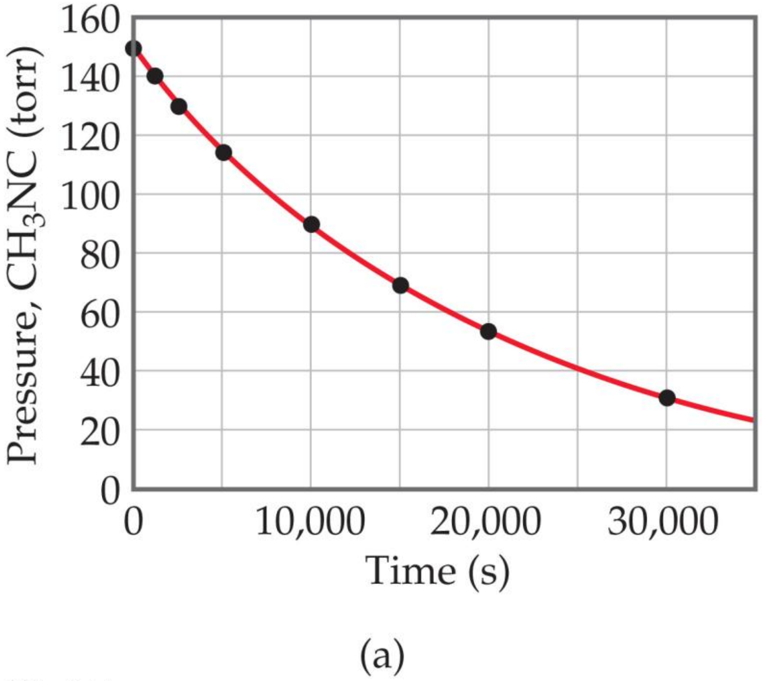
Consider the process in which methyl isonitrile is converted to acetonitrile.

$$CH_3NC \longrightarrow CH_3CN$$

First-Order Processes

$$CH_3NC \longrightarrow CH_3CN$$

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



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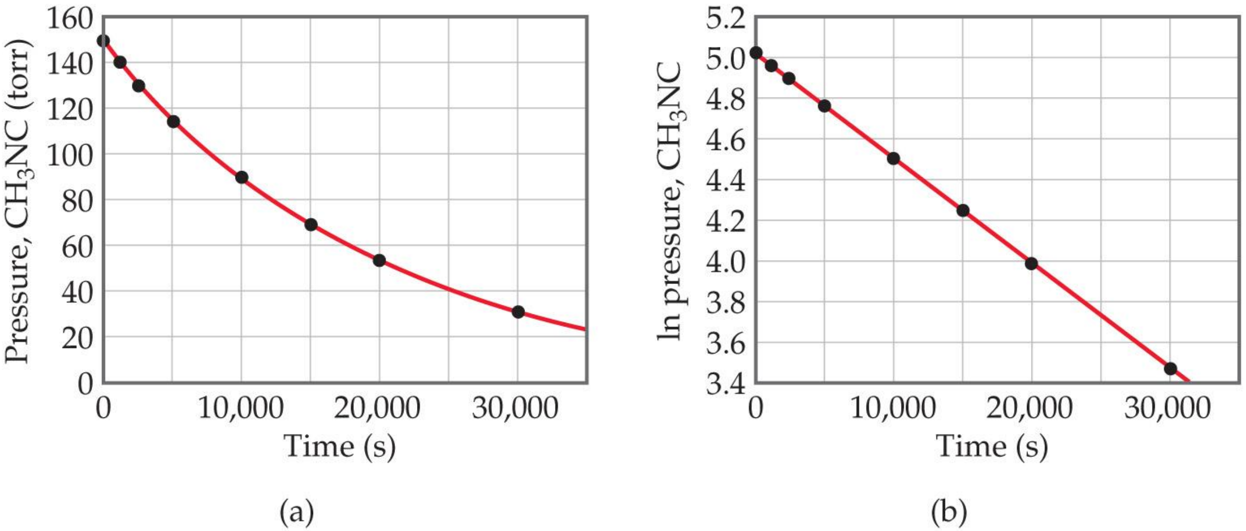
First-Order Processes



(a) (b)

- When ln *P* is plotted as a function of time, a straight line results.
- Therefore,
  - The process is first-order.
  - *k* is the negative of the slope: 5.1×10^{-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

$$\boldsymbol{y = mx + b}$$

Second-Order Processes

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

So if a process is second-order in A, a plot of $\frac{1}{[A]}$ vs. *t* yields 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

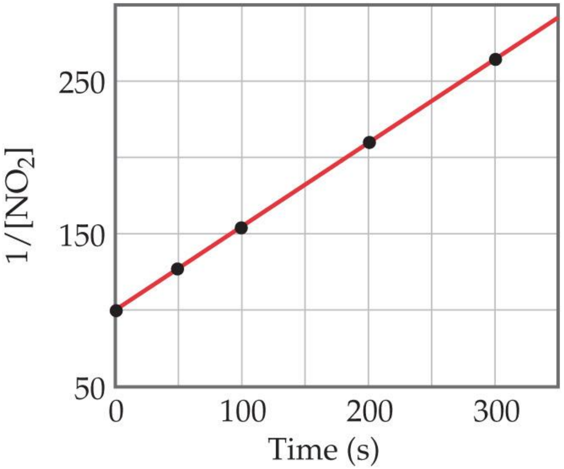
$$NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$$

and yields data comparable to this table:

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

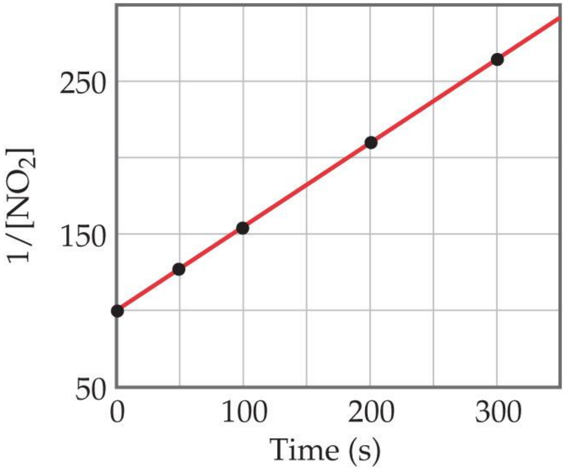
Second-Order Processes

- Plotting ln $[NO_2]$ vs. *t* yields the graph at the right.
- 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

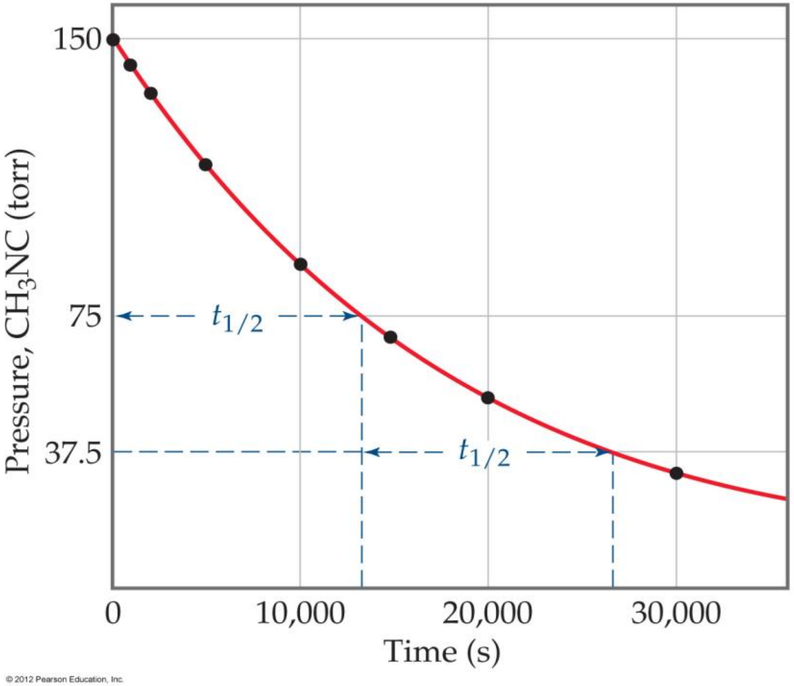
Second-Order Processes



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 $\frac{1}{[NO_2]}$ vs. *t*, however, gives this plot Fig. 14.9(b).
- Because this *is* a straight line, the process is second-order in [A].

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

For a first-order process, this becomes

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

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

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

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

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

Half-Life

For a second-order process,

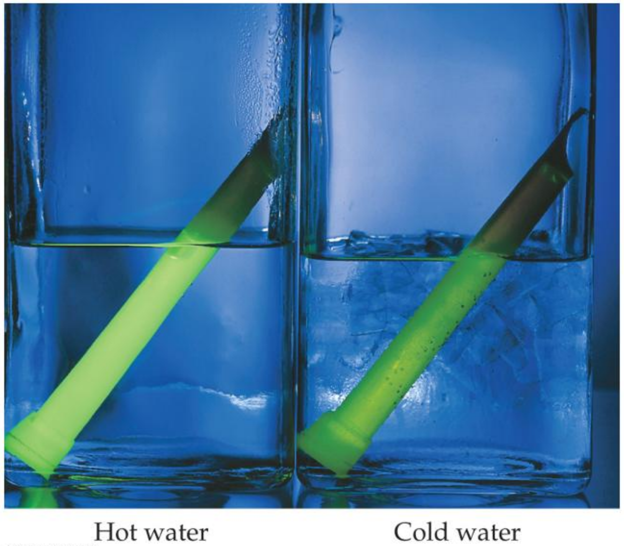
$$\frac{1}{0.5\ [\mathrm{A}]_0} = kt_{1/2} + \frac{1}{[\mathrm{A}]_0}$$

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

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

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

Temperature and Rate



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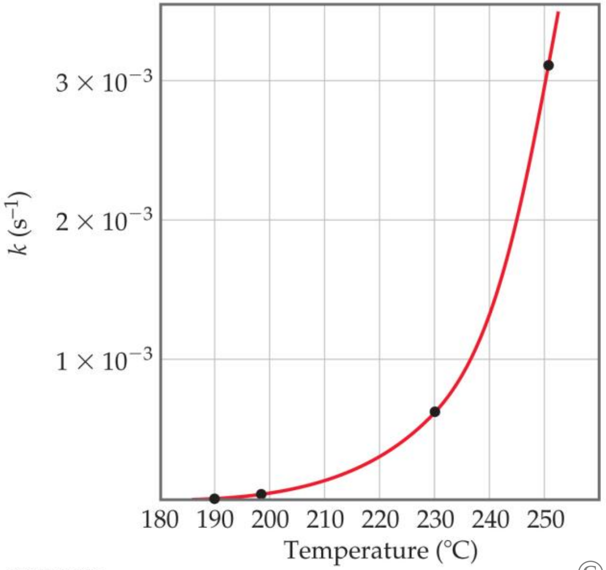

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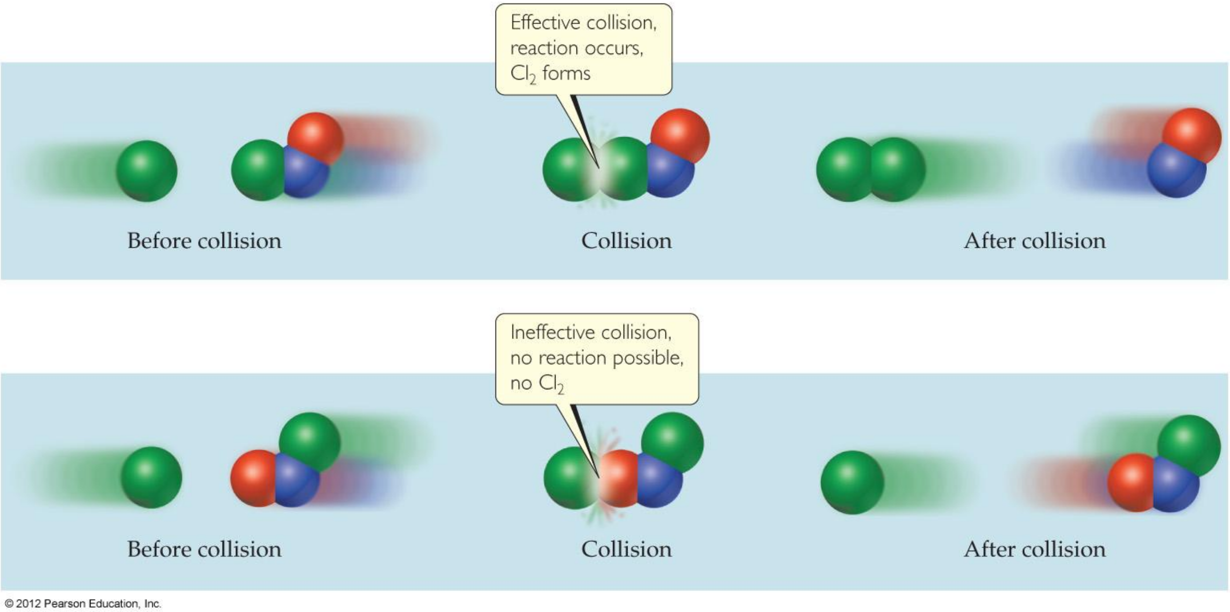
- Generally, as temperature increases, so does the reaction rate.
- This is because *k* is temperature-dependent.

The Collision Model

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

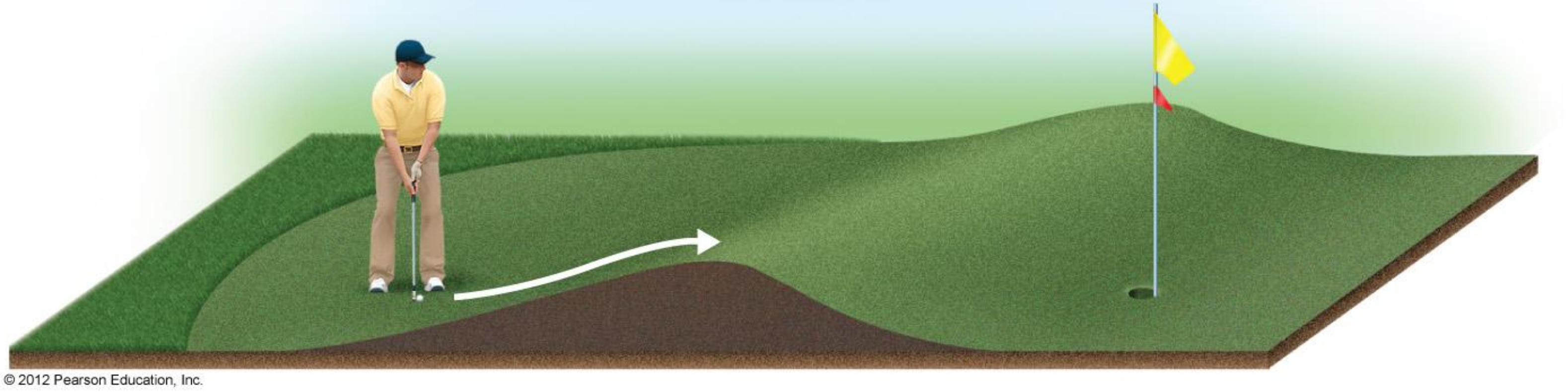
The Collision Model

Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.



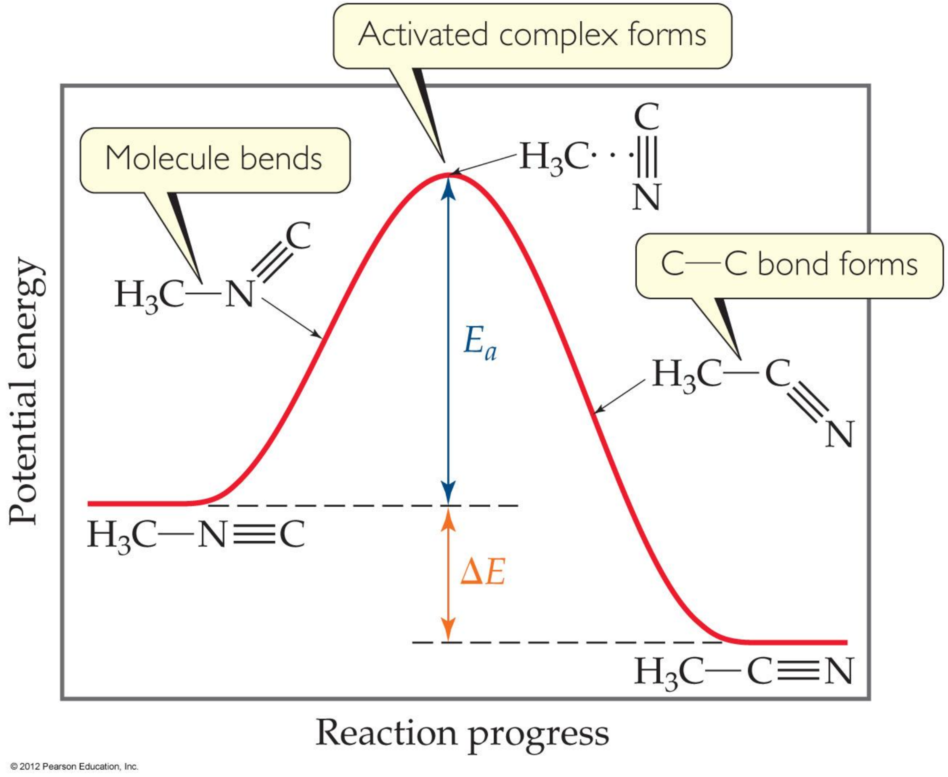
Activation Energy

- In other words, 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.



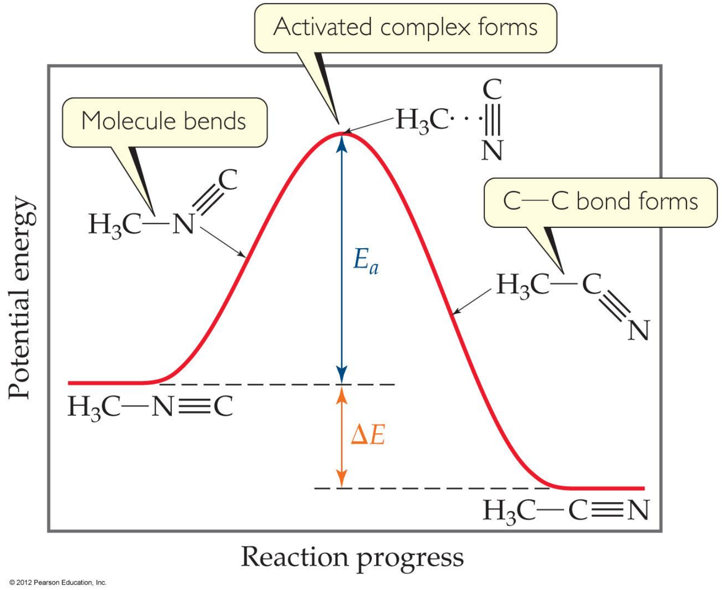
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a **reaction coordinate diagram** like this one for the rearrangement of methyl isonitrile.



Reaction Coordinate Diagrams

- The diagram shows the energy of the reactants and products (and, therefore, ΔE).
- The high point on the diagram is the **transition state**.



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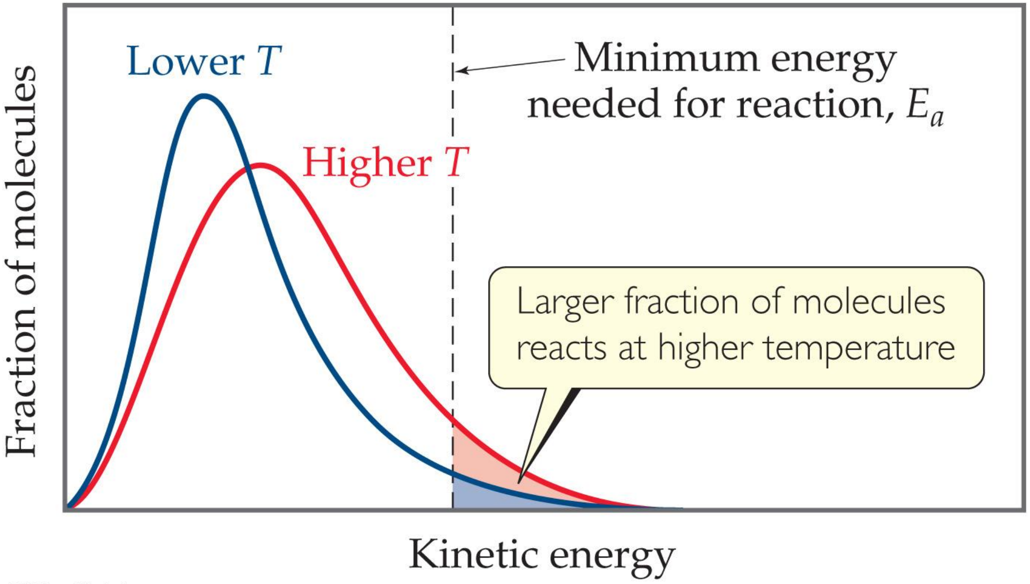
- The species present at the transition state is called the **activated complex**.
- The energy gap between the reactants and the activated complex is the **activation-energy barrier**.

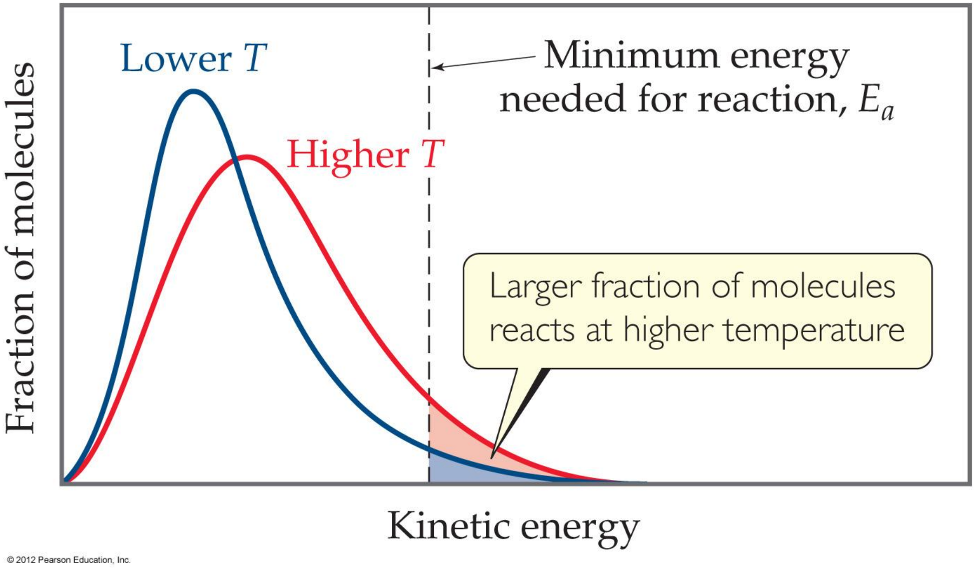
Maxwell–Boltzmann Distributions



- 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.

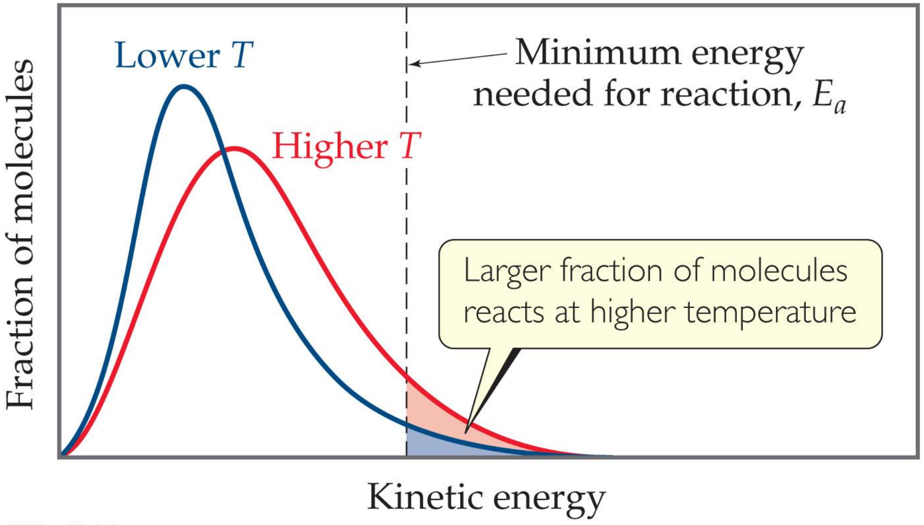
Maxwell–Boltzmann Distributions



- 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, then as the temperature increases, so does the fraction of molecules that can overcome the activation-energy barrier.



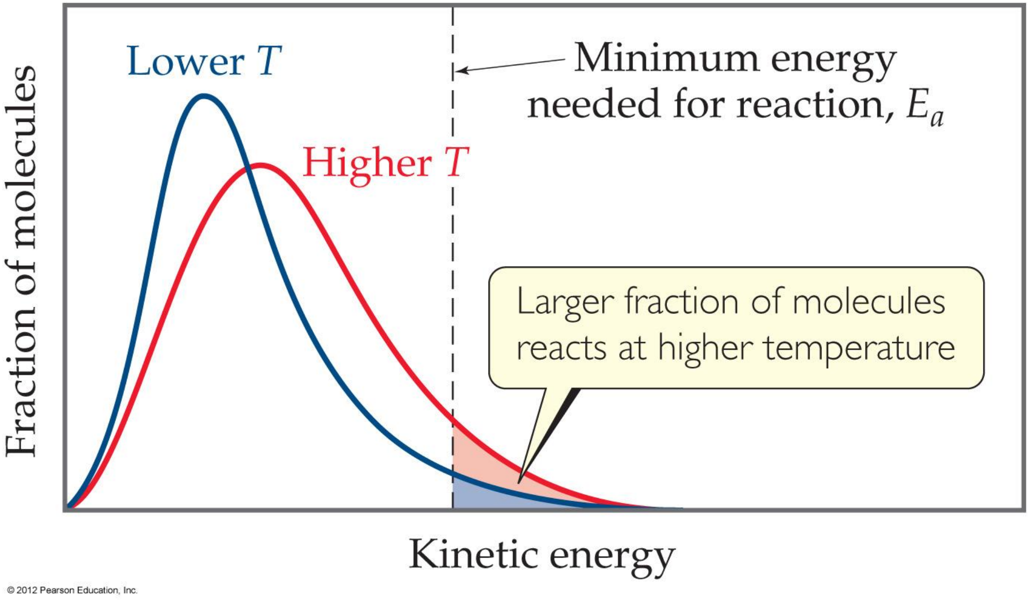
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

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

where R is the gas constant and T is the Kelvin temperature.



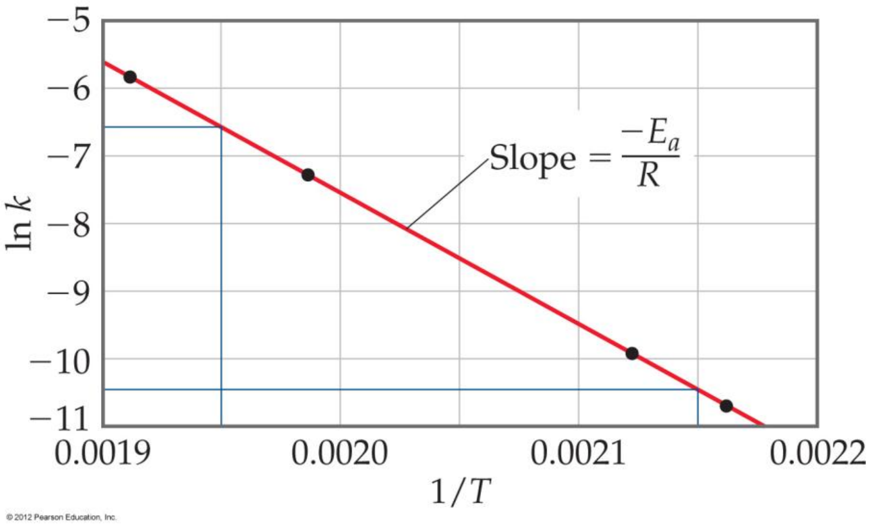
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

$$k = Ae^{-E_a/RT}$$

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

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

$$\boldsymbol{y = mx + b}$$

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

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

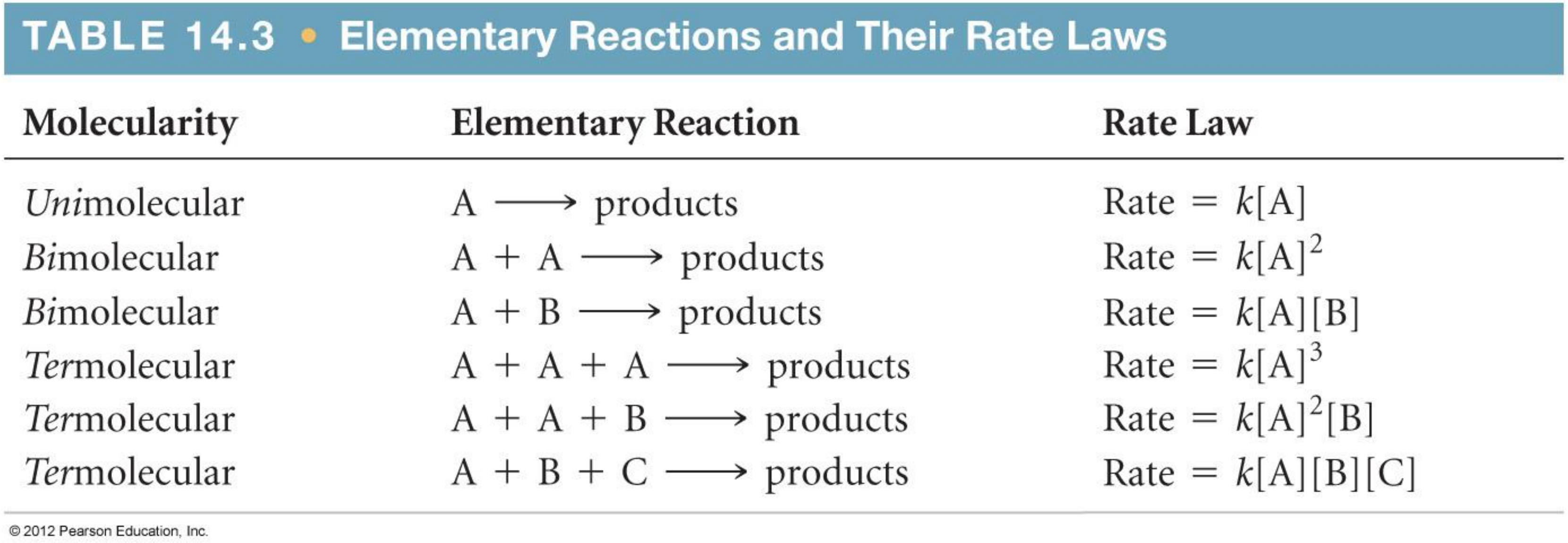


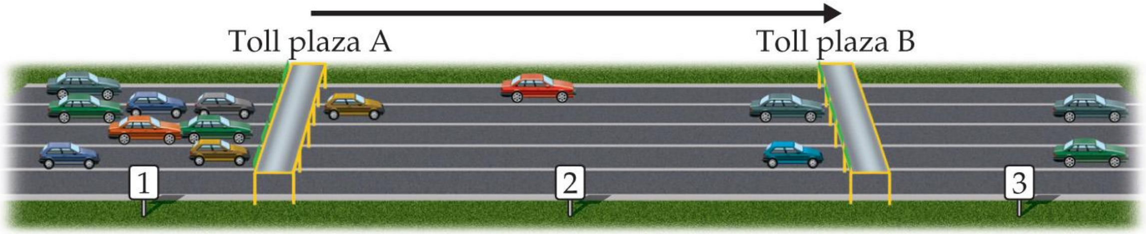
TABLE 14.3 • Elementary Reactions and Their Rate Laws

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

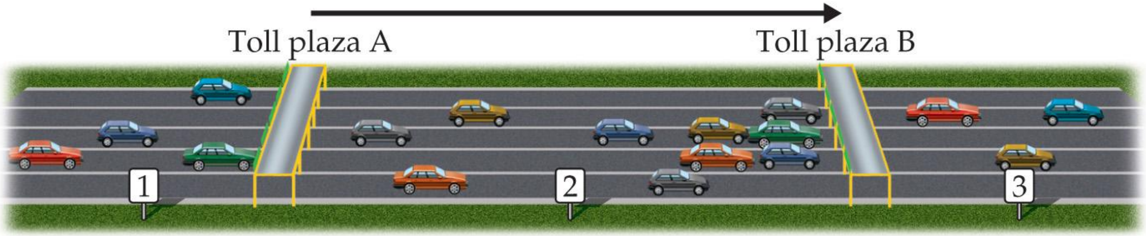
The **molecularity** of a process tells how many molecules are involved in the process.

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**.



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



(b) Cars slowed at toll plaza B, rate-determining step is passage through 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 that the reaction occurs in two steps.

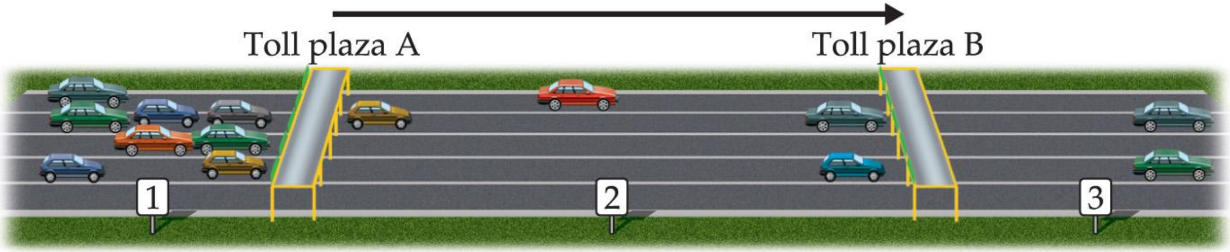
Slow Initial Step

- A proposed mechanism for this reaction is

Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

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



(a) Cars slowed at toll plaza A, rate-determining step is passage through A

Fast Initial Step

$$2\ NO(g) + Br_2(g) \longrightarrow 2\ NOBr(g)$$

- The rate law for this reaction is found to be

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

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

Fast Initial Step

- A proposed mechanism is

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

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

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

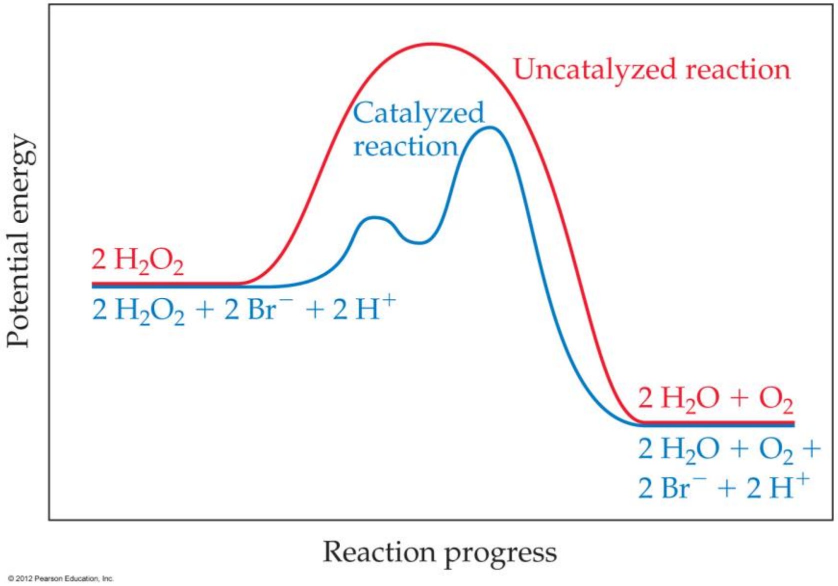
Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step, gives

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

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

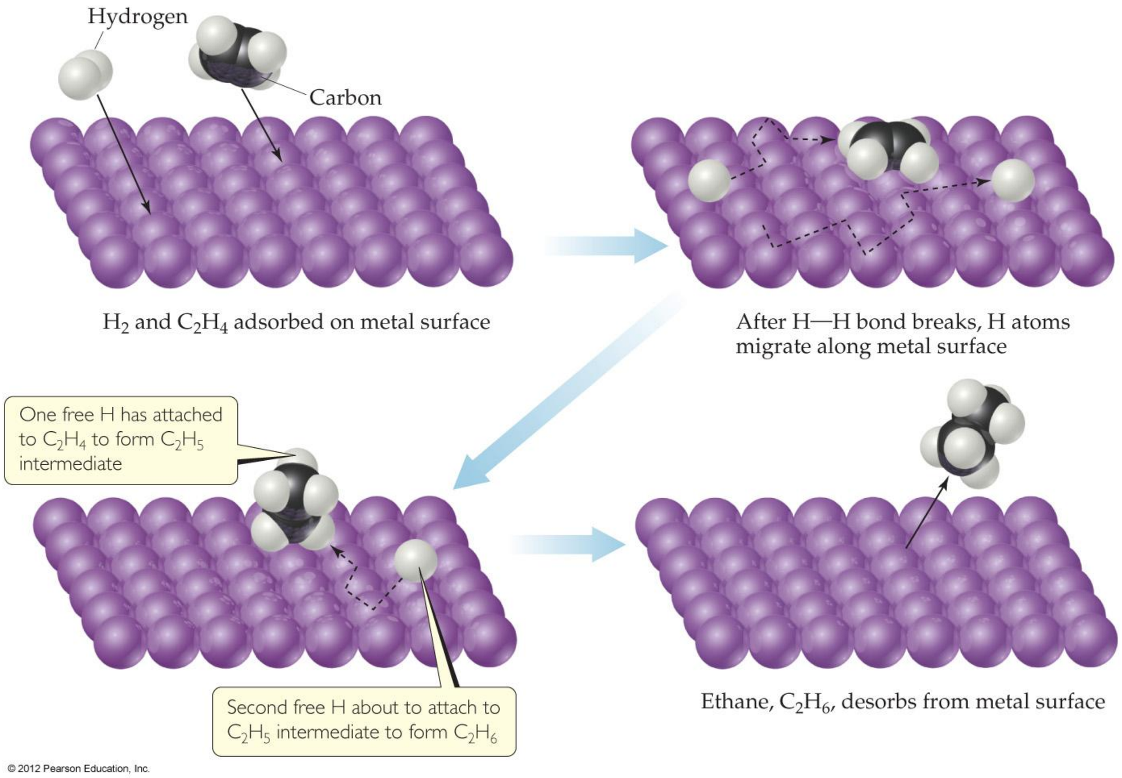
Catalysts

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

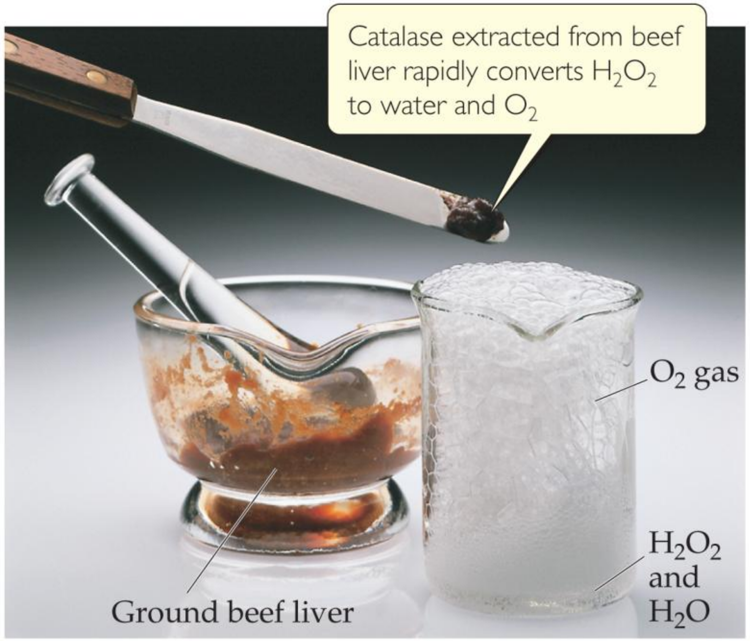


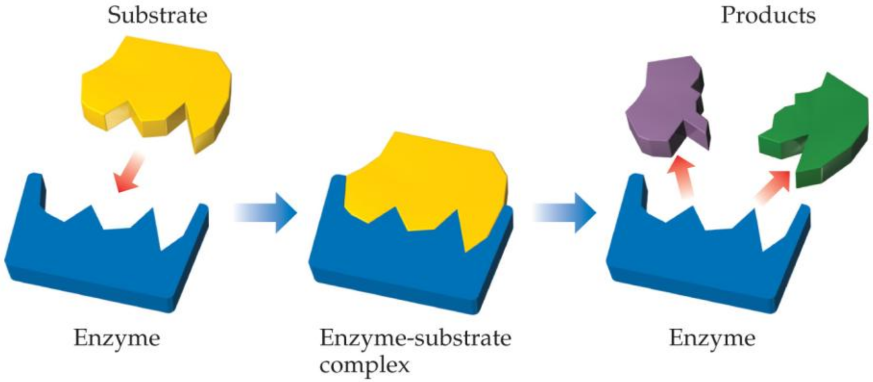
Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.



Enzymes





- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.