GENERAL CHEMISTRY

Chapter 14

Kinetics

Contents

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).

14-1 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

- 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

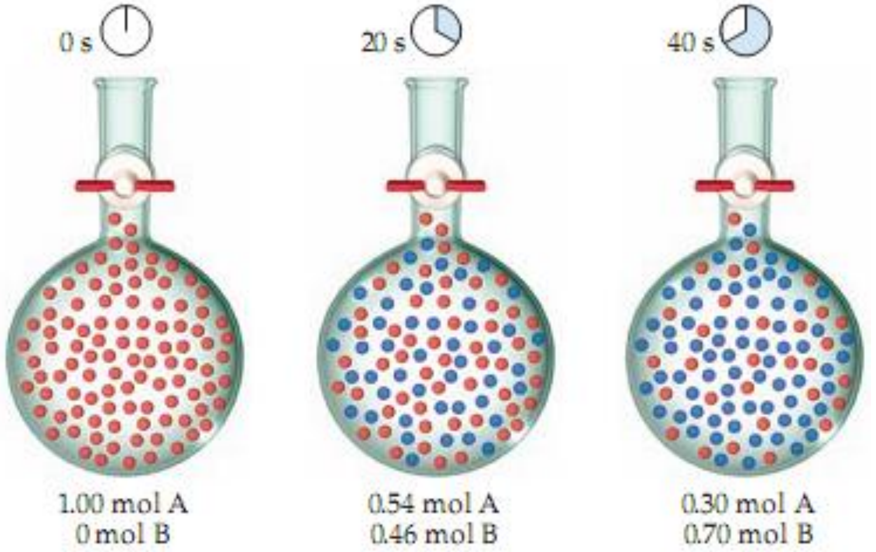
- Presence of a Catalyst
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.

14-2 Reaction Rates

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

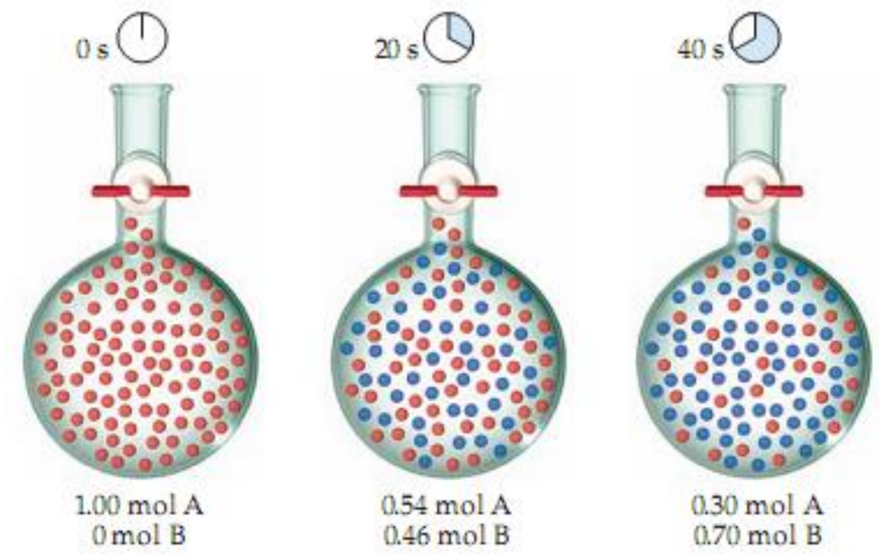
$$\text{Average rate of appearance of B} = \frac{\text{change in concentration of B}}{\text{change in time}}$$

$$= \frac{[\mathrm{B}]\text{ at } t_2 - [\mathrm{B}]\text{ at } t_1}{t_2 - t_1} = \frac{\Delta[\mathrm{B}]}{\Delta t}$$



EXAMPLE

From the data given in the figure, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

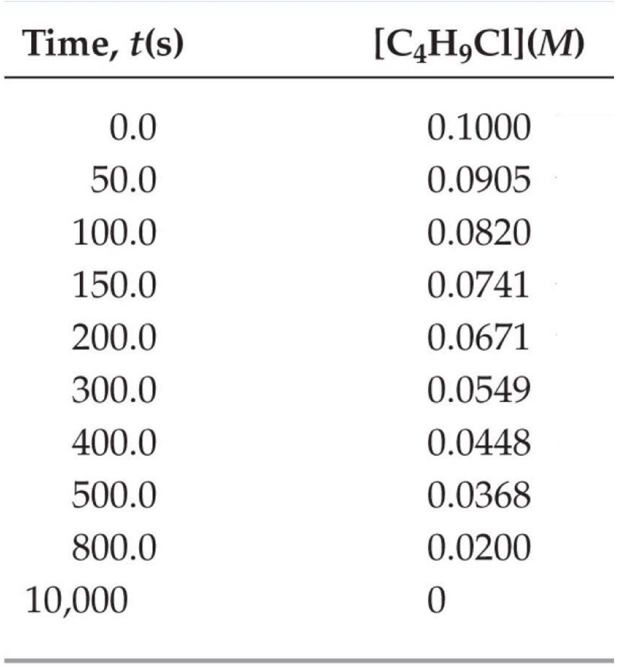


$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30\,M - 0.54\,M}{40\text{ s} - 20\text{ s}}$$

$$= 1.2 \times 10^{-2}\,M/\text{s}$$

Change of Rate with Time

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

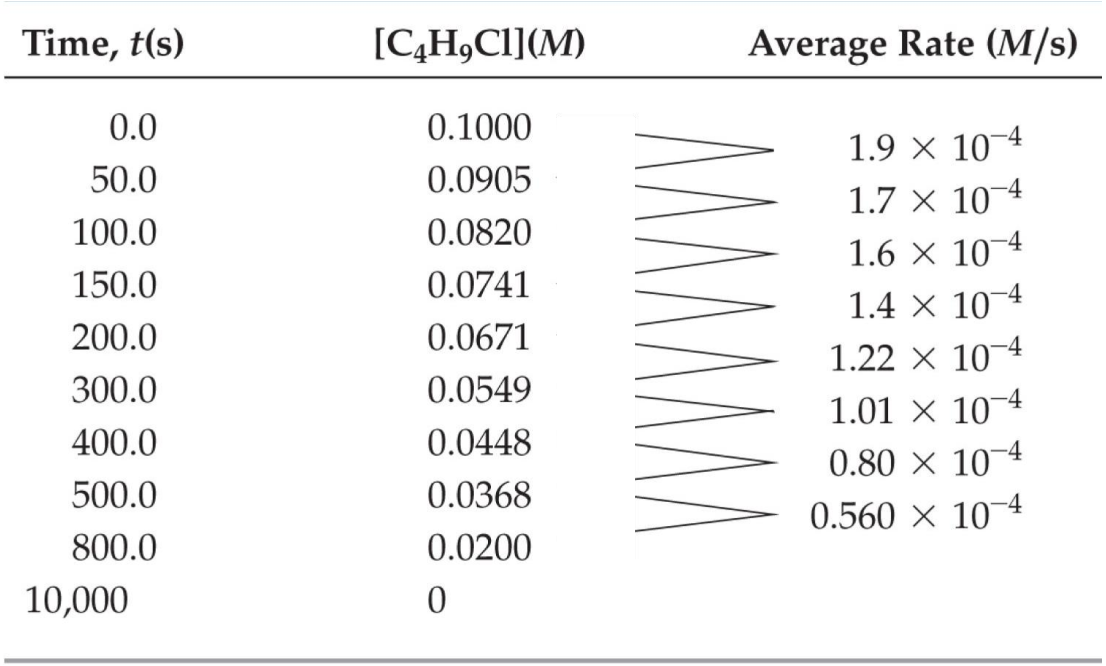


Time, t(s)	$[C_4H_9Cl](M)$
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

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

Change of Rate with Time

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



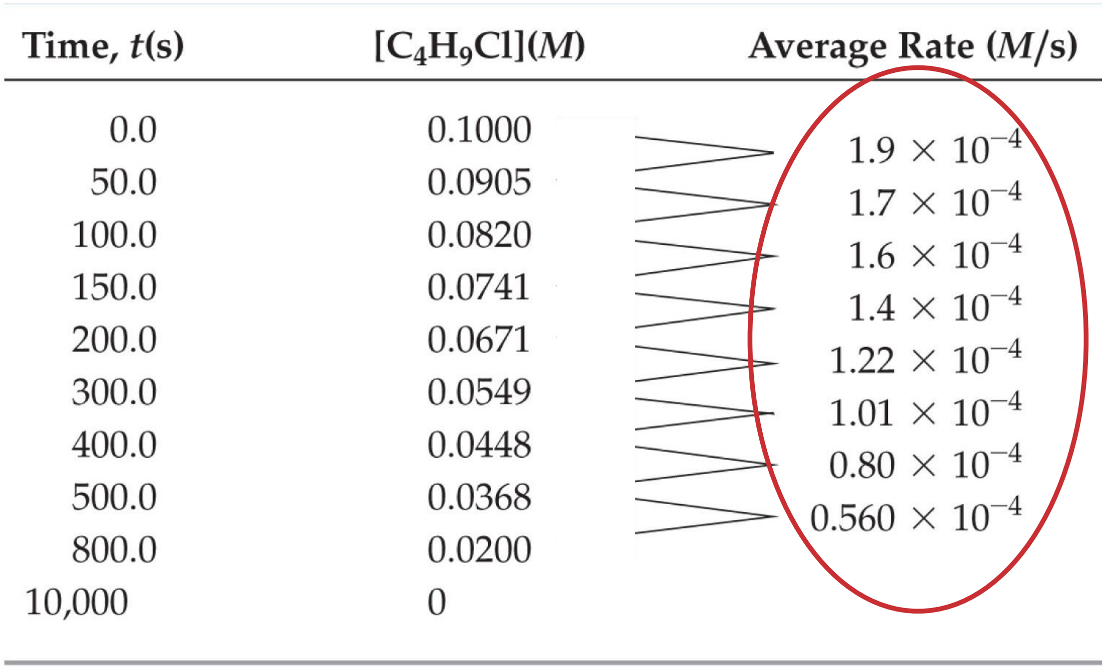
Time, t(s)	$[C_4H_9Cl]$(M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

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

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

Change of Rate with Time

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



Time, t(s)	$[C_4H_9Cl](M)$	Average Rate (M/s)
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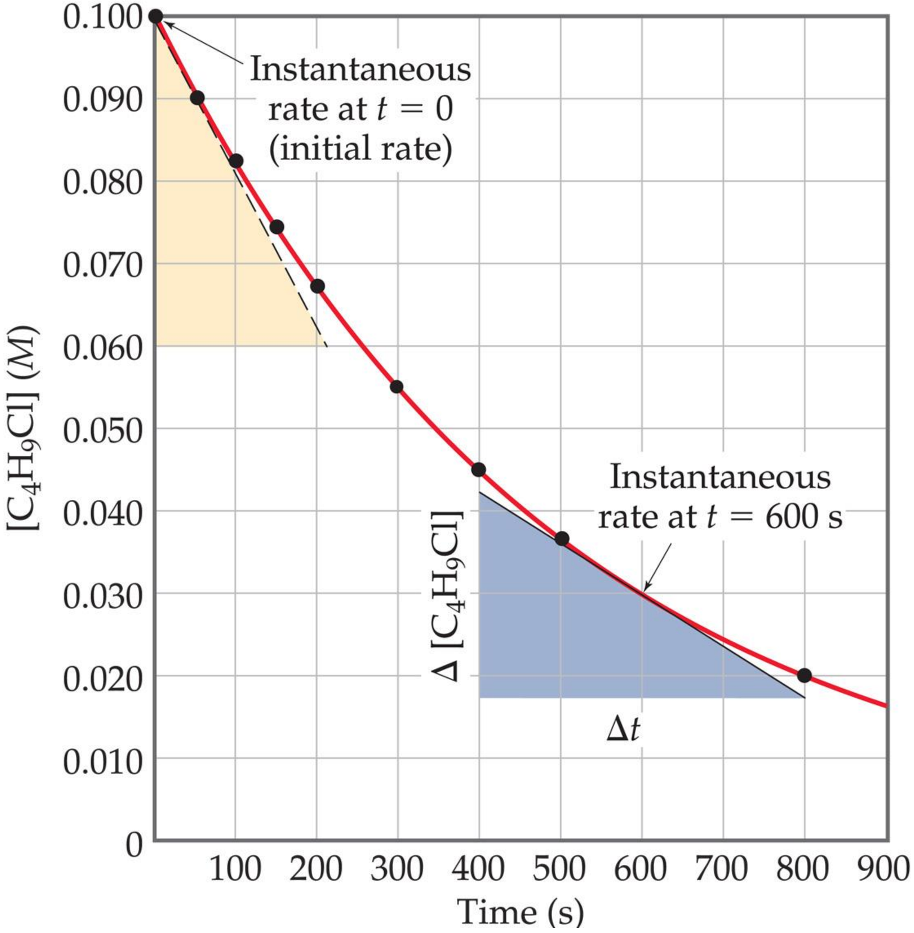
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- 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.

Change of Rate with Time

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

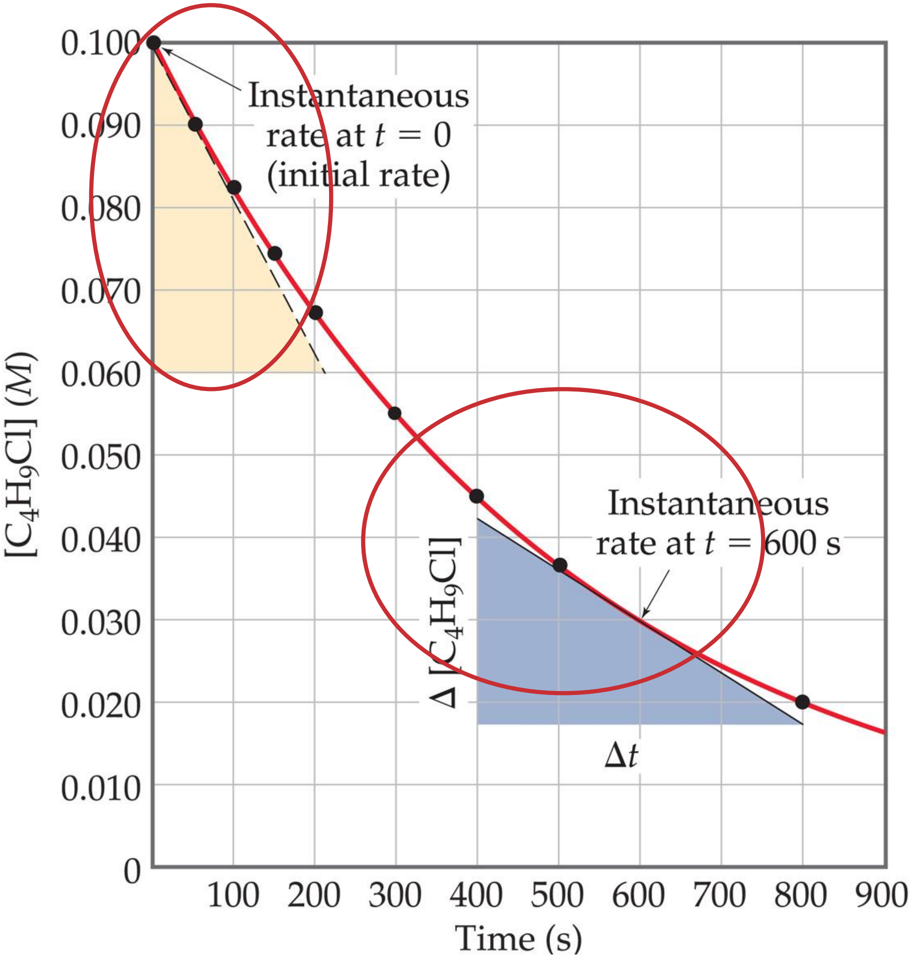
- A plot of [C_4H_9Cl] vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.



Change of Rate with Time

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

- 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.



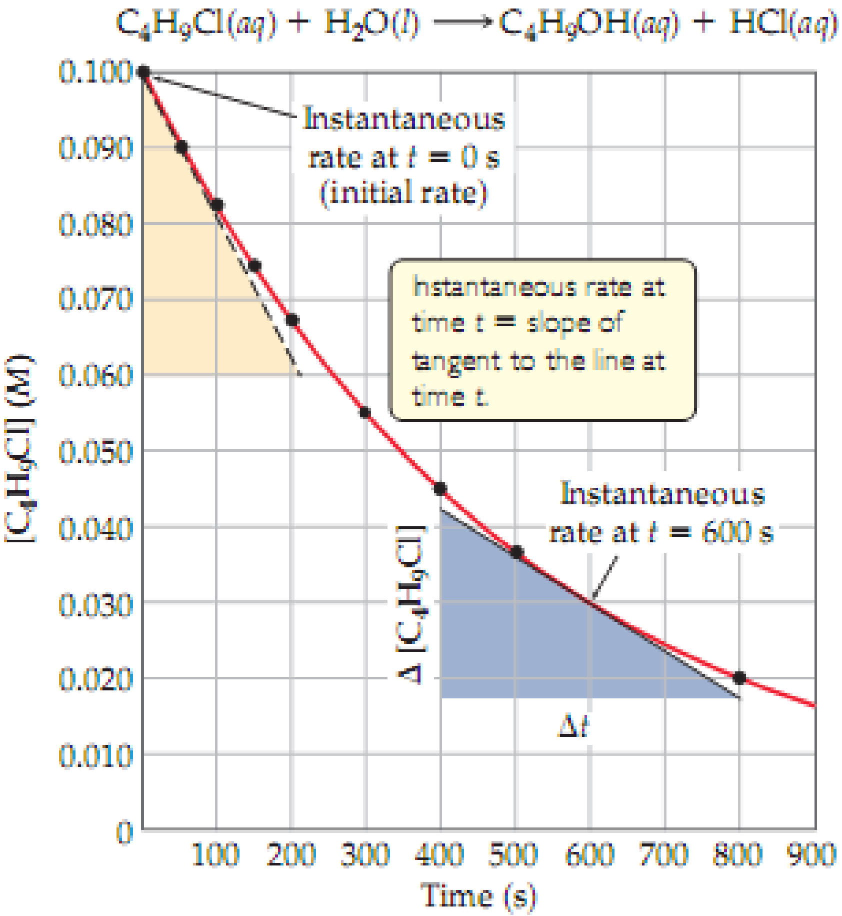
EXAMPLE

Calculate the instantaneous rate of disappearance of C_4H_9Cl at t = 0 s (the initial rate)

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

$$= -\frac{(0.060 - 0.100)\ M}{(210 - 0)\ s}$$

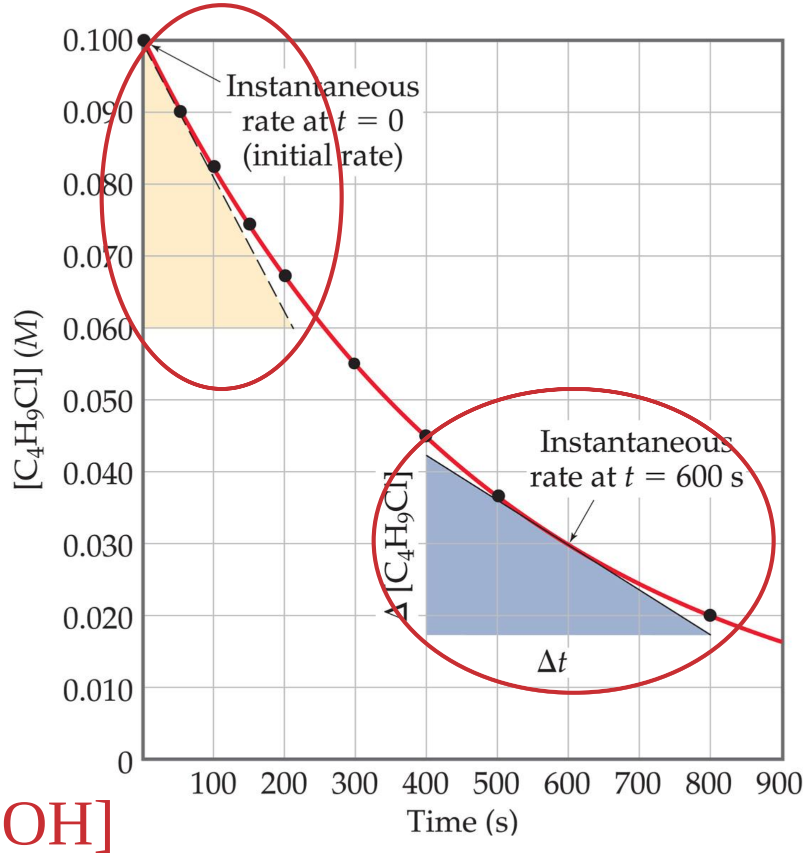
$$= 1.9 \times 10^{-4}\ M/s$$



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?

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

- In such a case,

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

Reaction Rates and Stoichiometry

- To generalize, then, for the reaction

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

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

EXAMPLE

(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction

$$2\ O_3(g) \rightarrow 3\ O_2(g)?$$

(b) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]/\Delta t$?

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

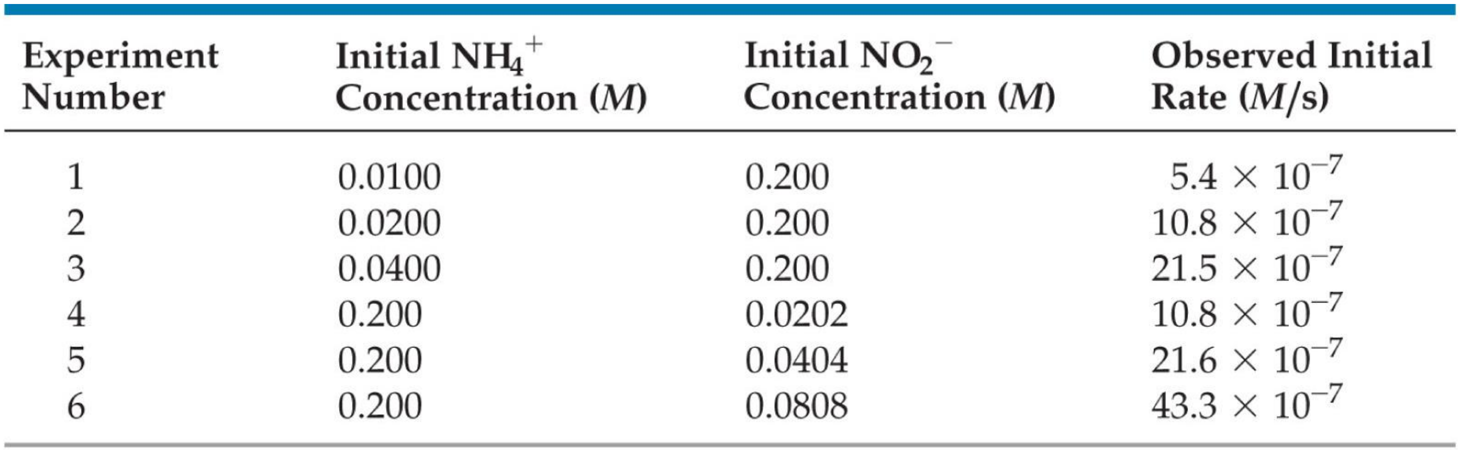
$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}(6.0 \times 10^{-5}\,M/s) = 4.0 \times 10^{-5}\,M/s$$

14-3 Concentration and Rate Law

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

Example:

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



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

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

If 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

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

the reaction is

First-order in $[NH_4^+]$ and

First-order in $[NO_2^-]$.

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

Rate Laws

- For the general reaction

$$aA + bB \rightarrow cC + dD$$

the rate law generally has the form

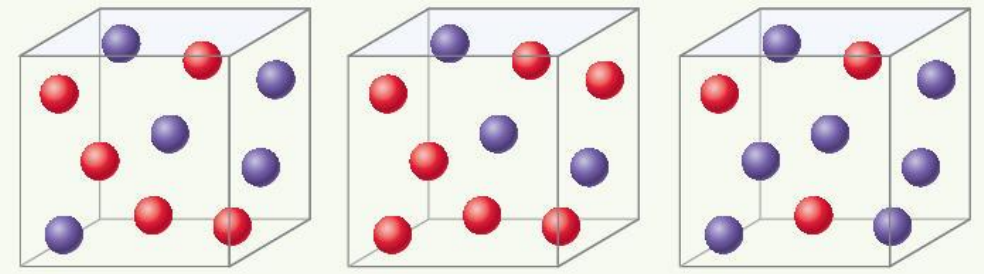
$$\text{Rate} = k\,[A]^m\,[B]^n$$

The exponents *m* and *n* are

- reaction orders
- typically small whole numbers
- Should be determined experimentally although sometimes same as the coefficient in the reaction equation

EXAMPLE

Consider a reaction A + B → C for which = $k[\mathrm{A}][\mathrm{B}]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



Box 1: Rate $= k(5)(5)^2 = 125k$

Box 2: Rate $= k(7)(3)^2 = 63k$

Box 3: Rate $= k(3)(7)^2 = 147k$

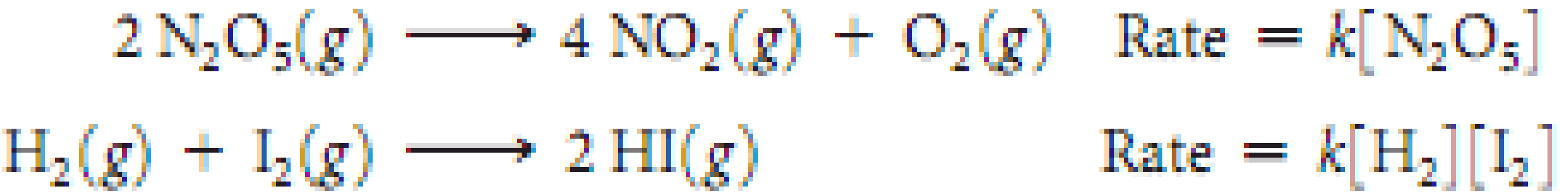
Magnitudes and Units of Rate Constants

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/\text{s}}{M^2} = M^{-1}\,\text{s}^{-1}$$

EXAMPLE

(a) What are the overall reaction orders for the reactions described in Equations (1) and (2)? **(b)** What are the units of the rate constant for the rate law in Equation (1)?

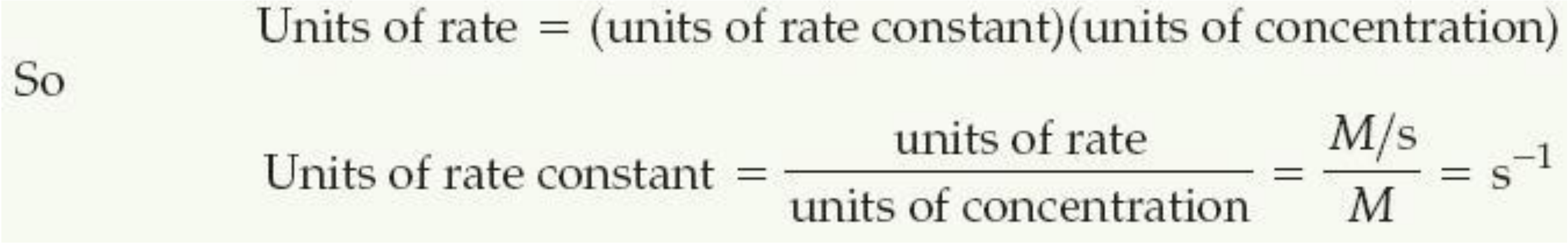


$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \qquad \text{Rate} = k[N_2O_5] \qquad (1)$$

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \qquad \text{Rate} = k[H_2][I_2] \qquad (2)$$

(a) The rate of the reaction in Equation (1) is first order in N_2O_5 and first order overall.
The reaction in Equation (2) is first order in $CHCl_3$ and one-half order in Cl_2. The overall reaction order is three halves.

(b)



$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

So

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{M/\text{s}}{M} = \text{s}^{-1}$$

Using Initial Rates to Determine Rate Laws

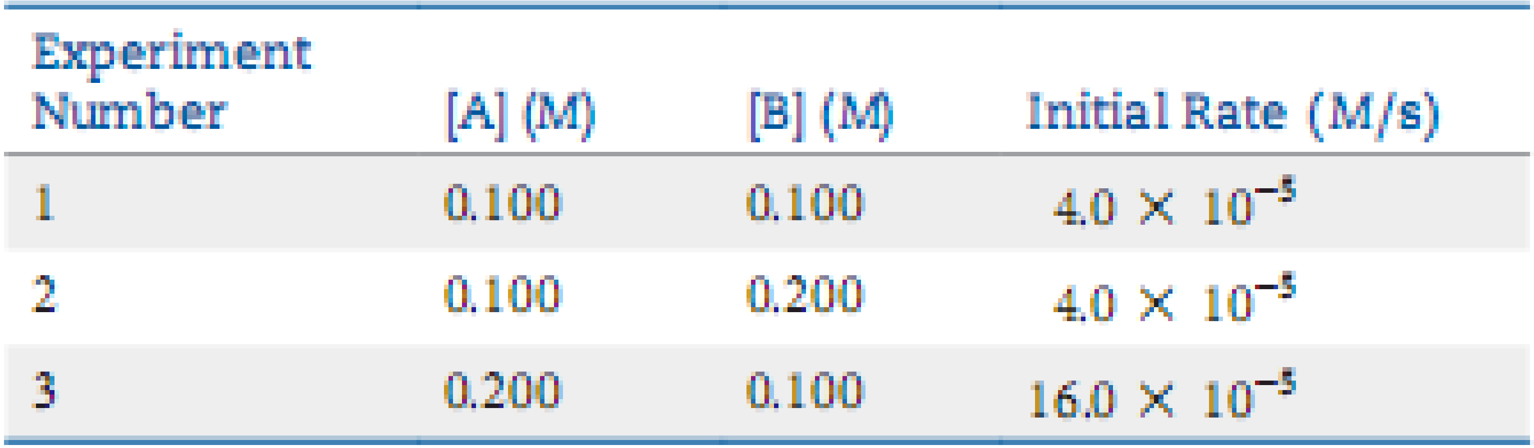
$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots$$

The task of determining the rate law becomes the task of determining the reaction orders, m and n.

In most reactions, the reaction orders are 0, 1, or 2

EXAMPLE

The initial rate of a reaction A + B → C was measured for several different starting concentrations of A and B, and the results are as follows:



Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

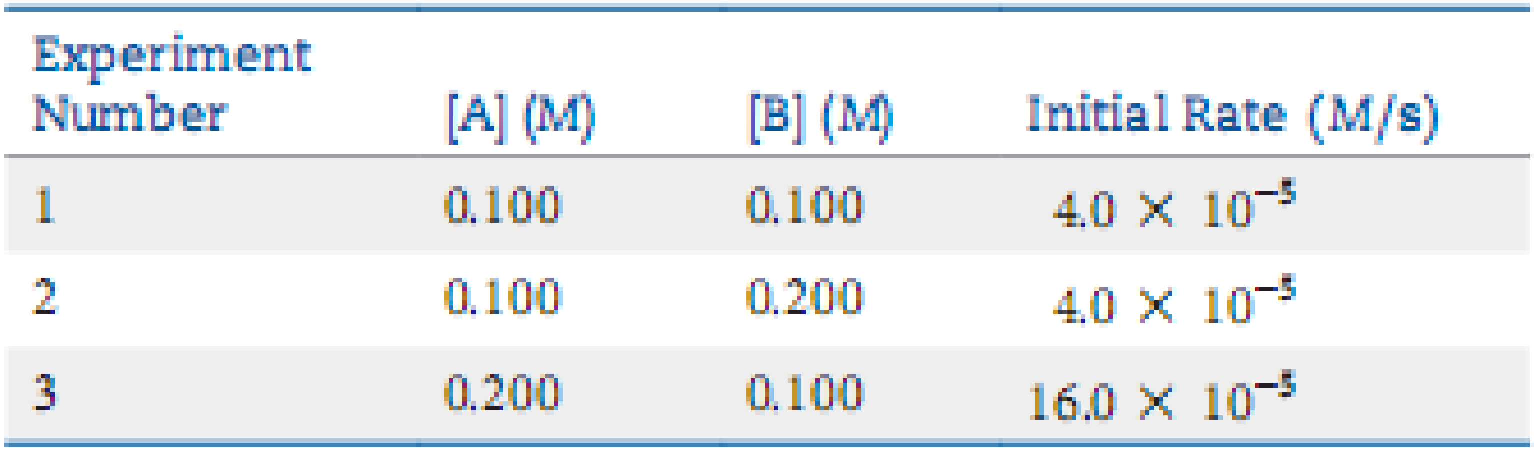
Using these data, determine

(a) the rate law for the reaction,

(b) the rate constant,

(c) the rate of the reaction when [A] = 0.050M and [B] = 0.100 M.

EXAMPLE



Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

(a) the rate law for the reaction:

Compare experiments 1 and 2, we see that [A] is held constant and [B] is doubled.

➔ the concentration of B has no effect on the reaction rate

Compare experiments 1 and 3, we see that [B] is held constant and [A] is doubled, the rate increases fourfold

➔ rate is proportional to $[A]^2$

Therefore, $\text{Rate} = k[A]^2[B]^0 = k[A]^2$

EXAMPLE

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

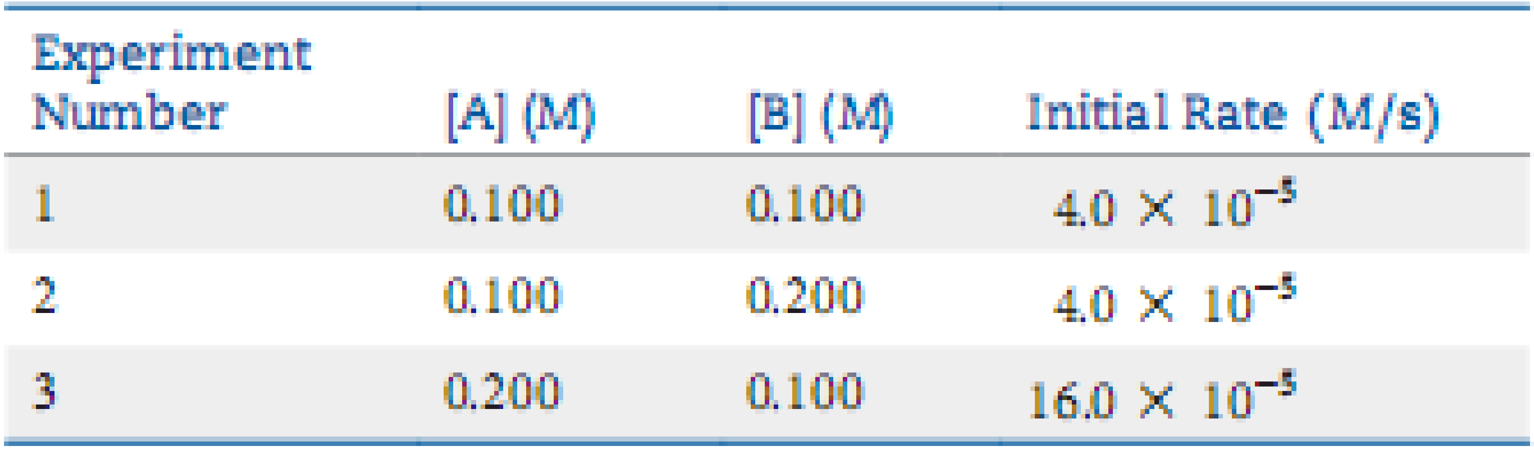
(b) the rate constant

From (a) we have $\text{Rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$

Using the rate law and the data from experiment 1, we have

$$k = \frac{\text{rate}}{[\text{A}]^2} = \frac{4.0 \times 10^{-5}\ M/\text{s}}{(0.100\ M)^2} = 4.0 \times 10^{-3}\ M^{-1}\,\text{s}^{-1}$$

EXAMPLE



Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

(c) the rate of the reaction when [A] = 0.050M and [B] = 0.100 M

From (a) we have $\text{Rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$

From (b), we have $k = 4.0 \times 10^{-3}\, M^{-1} s^{-1}$

Therefore,

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3}\, M^{-1} s^{-1})(0.050\, M)^2 = 1.0 \times 10^{-5}\, M/s$$

14.4 The Change of Concentration with Time

- First order reactions
- Second order reaction
- Zero order reactions
- Half life

First-order reactions

A first-order reaction is one whose rate depends on the concentration of a single reactant raised to the first power

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

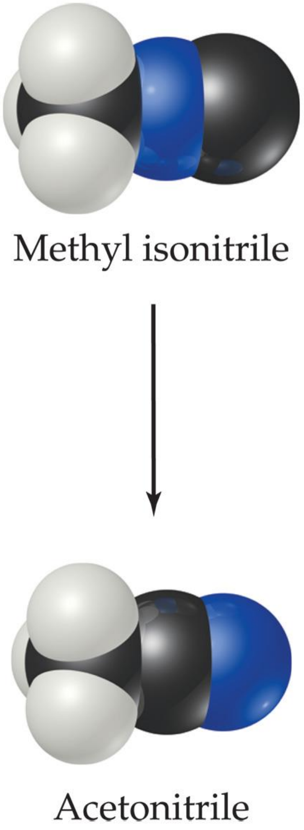
Using integration operation, we see that this relationship can be transformed into an equation known as the integrated rate law

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

$[\text{A}]_0$ is the initial concentration of A, and

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

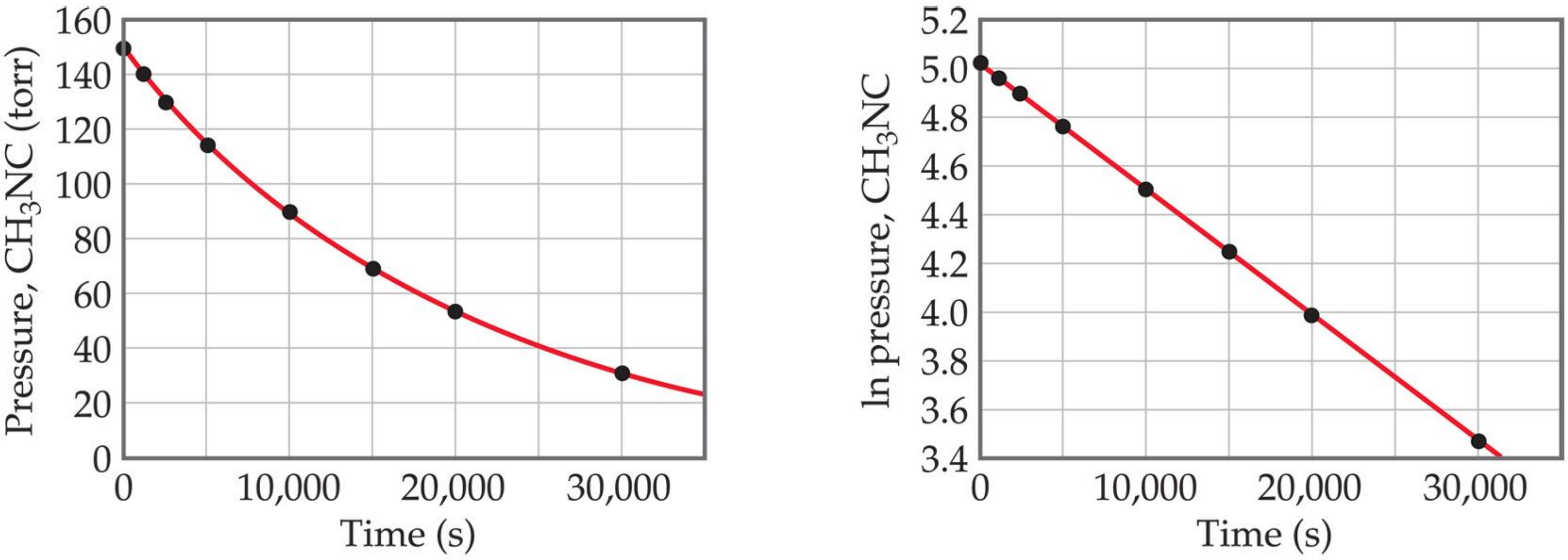
First-Order Reactions



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

$$CH_3NC \longrightarrow CH_3CN$$

First-Order Reactions



- 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: $5.1 \times 10^{-5}\ s^{-1}$.

EXAMPLE

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12 °C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3. Assume that the average temperature of the lake is 12 °C.

(a) What is the concentration of the insecticide on June 1 of the following year?

(b) How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

EXAMPLE

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12 °C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7}\ \text{g/cm}^3$. Assume that the average temperature of the lake is 12 °C.

$k = 1.45\ \text{yr}^{-1}$, $[\text{insecticide}]_o = 5.0 \times 10^{-7}\ \text{g/cm}^3$, T = constant

(a) the concentration of the insecticide on June 1 of the following year

$\Delta t = 1$ year

$$\ln[\text{insecticide}]_{t=1\,\text{yr}} = -(1.45\ \text{yr}^{-1})(1.00\ \text{yr}) + \ln(5.0 \times 10^{-7})$$

$$= -15.96$$

$$[\text{insecticide}]_{t=1\,\text{yr}} = e^{-15.96} = 1.2 \times 10^{-7}\ \text{g/cm}^3$$

EXAMPLE

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12 °C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3. Assume that the average temperature of the lake is 12 °C.

$k = 1.45\ \text{yr}^{-1}$, $[\text{insecticide}]_o = 5.0 \times 10^{-7}\ \text{g/cm}^3$, T = constant

(b) How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

$[\text{insecticide}]_t = 3.0 \times 10^{-7}\ \text{g/cm}^3$

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

$$\ln(3.0 \times 10^{-7}) = -(1.45\,\text{yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

$$t = -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45\,\text{yr}^{-1}$$

$$= -(-15.02 + 14.51)/1.45\,\text{yr}^{-1} = 0.35\,\text{yr}$$

Second-Order Processes

A second-order reaction is one for which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power

Consider reactions of the type A → products or A + B → products that are second order in just one reactant, A

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

Using integration operation, we see that this relationship can be transformed into an equation known as the integrated rate law

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

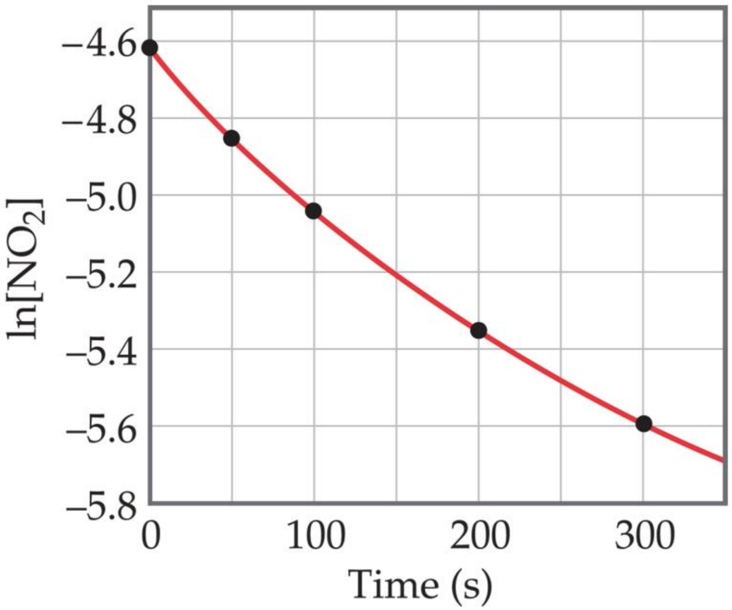
Second-Order Processes

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

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

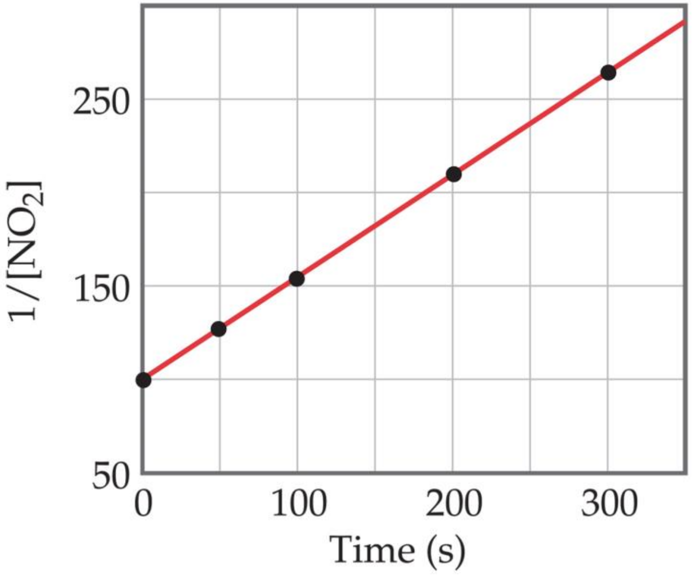
and yields data comparable to this:

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



- The plot is *not* a straight line, so the process is *not* first-order in [A].

Second-Order Reactions

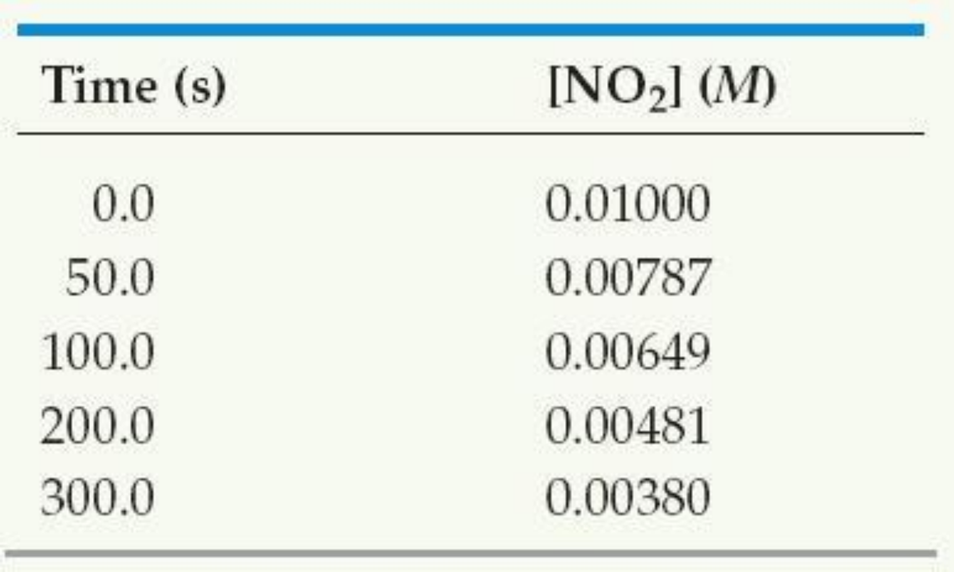


Time (*s*)	$[NO_2]$, *M*	$1/[NO_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

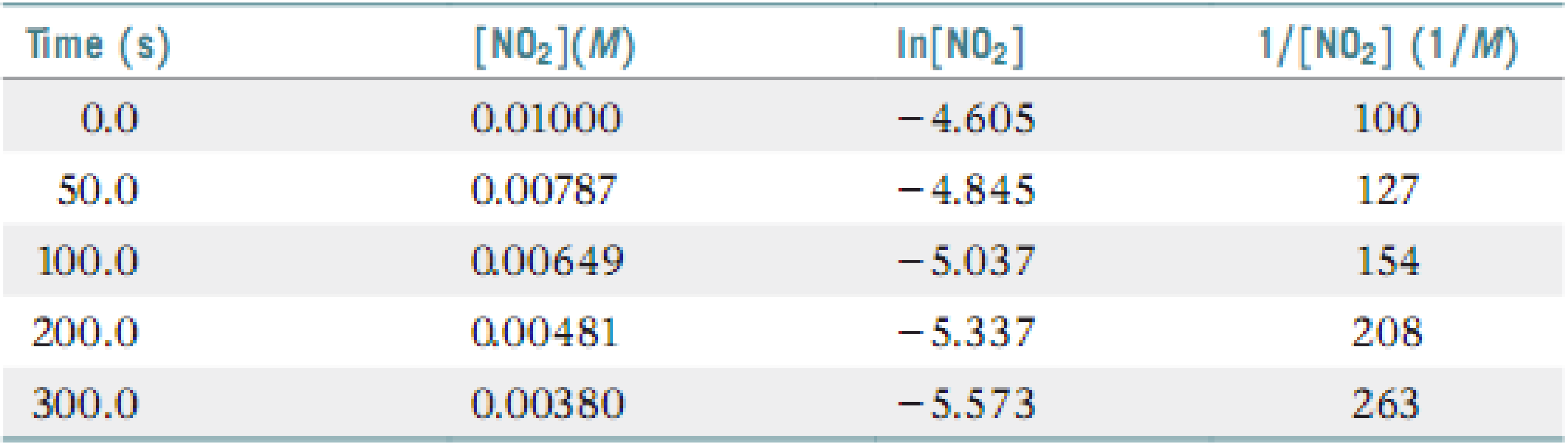
- Graphing ln $\frac{1}{[NO_2]}$ vs. *t*, however, gives this plot.
- Because this *is* a straight line, the process is second-order in [A].

EXAMPLE

The following data were obtained for the gas-phase decomposition of nitrogen dioxide to nitrogen monoxide at 300 °C. Is the reaction first or second order in NO_2?

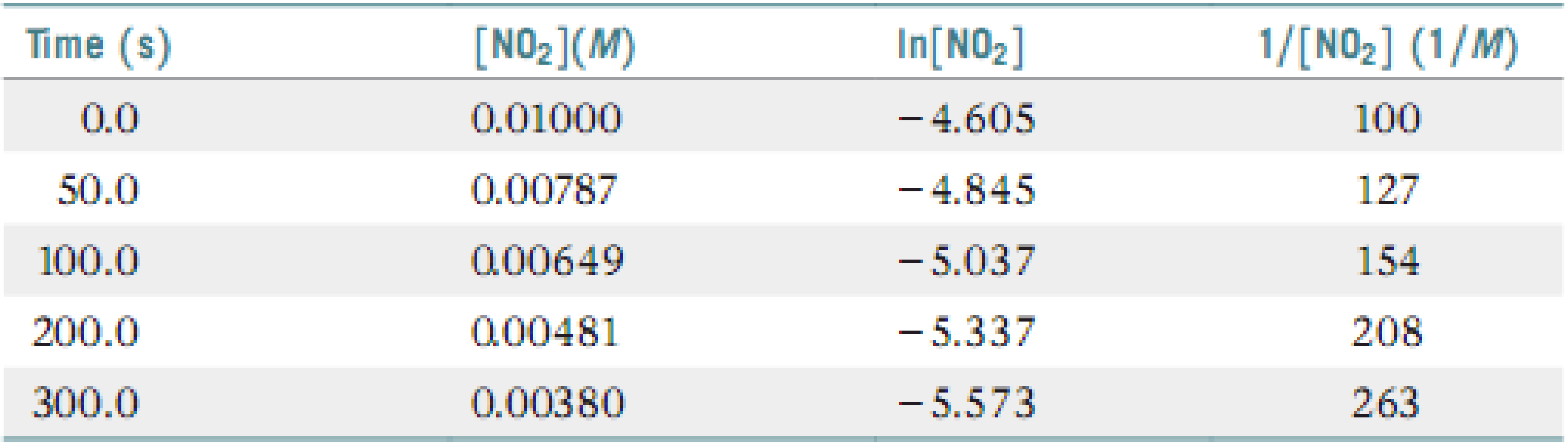


Time (s)	$[NO_2]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380



Time (s)	$[NO_2]$(M)	ln$[NO_2]$	1/$[NO_2]$ (1/M)
0.0	0.01000	−4.605	100
50.0	0.00787	−4.845	127
100.0	0.00649	−5.037	154
200.0	0.00481	−5.337	208
300.0	0.00380	−5.573	263

EXAMPLE



Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$ (1/M)
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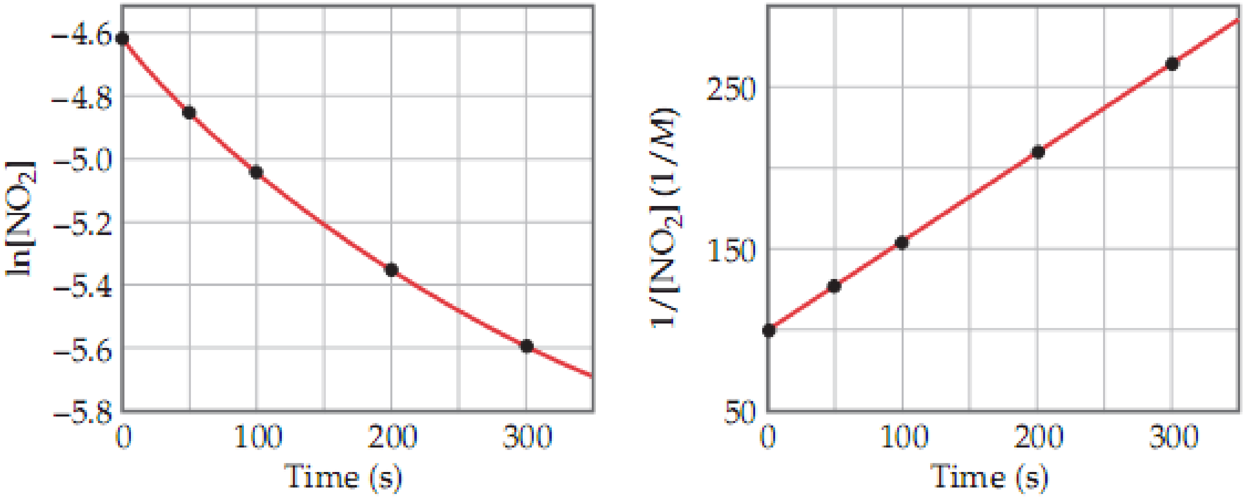
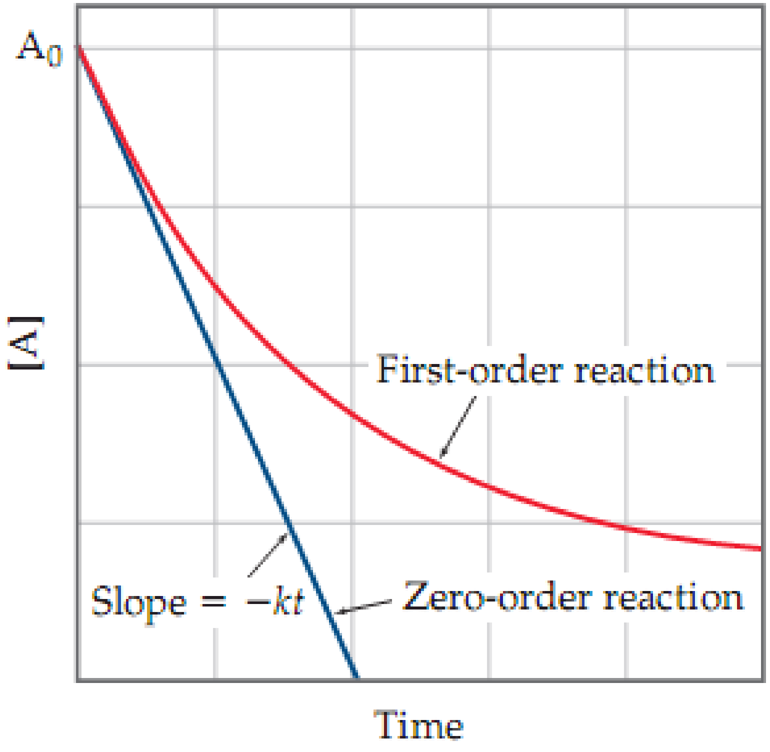


Thus, the reaction obeys a second-order rate law: Rate = $k[NO_2]^2$

Zero-order reactions

A zero-order reaction is one in which the rate of disappearance of A is independent of [A]

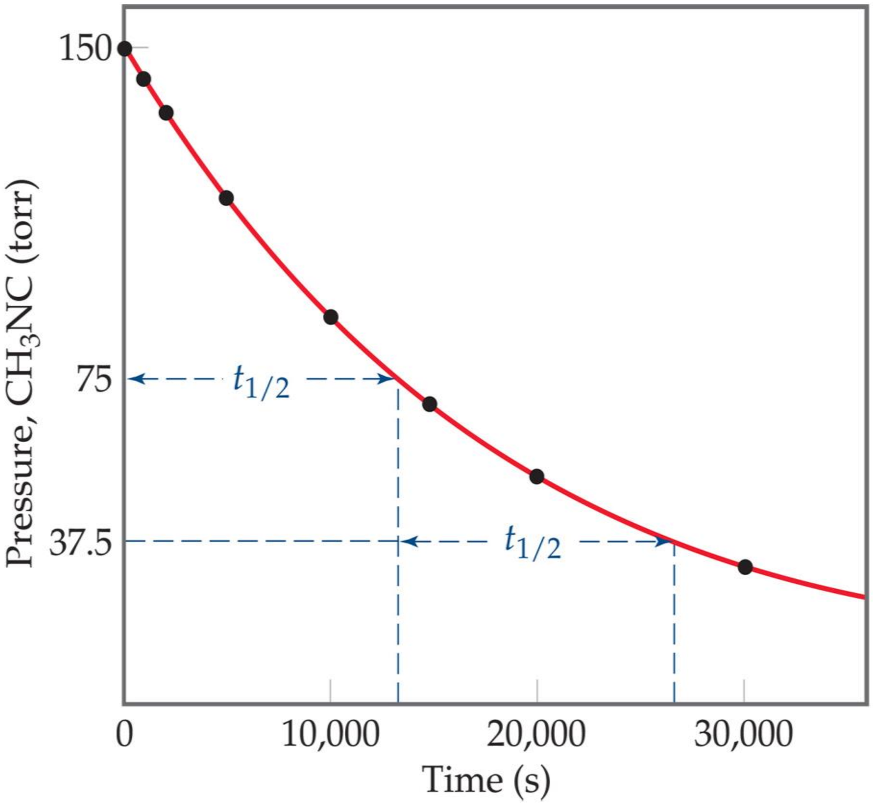
$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$



Using integration operation, we see that this relationship can be transformed into an equation known as the integrated rate law

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

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

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

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

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

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

NOTE: For a first-order process, then, the half-life *does not* depend on $[\mathrm{A}]_0$.

Half-Life

For a second-order process,

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

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

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

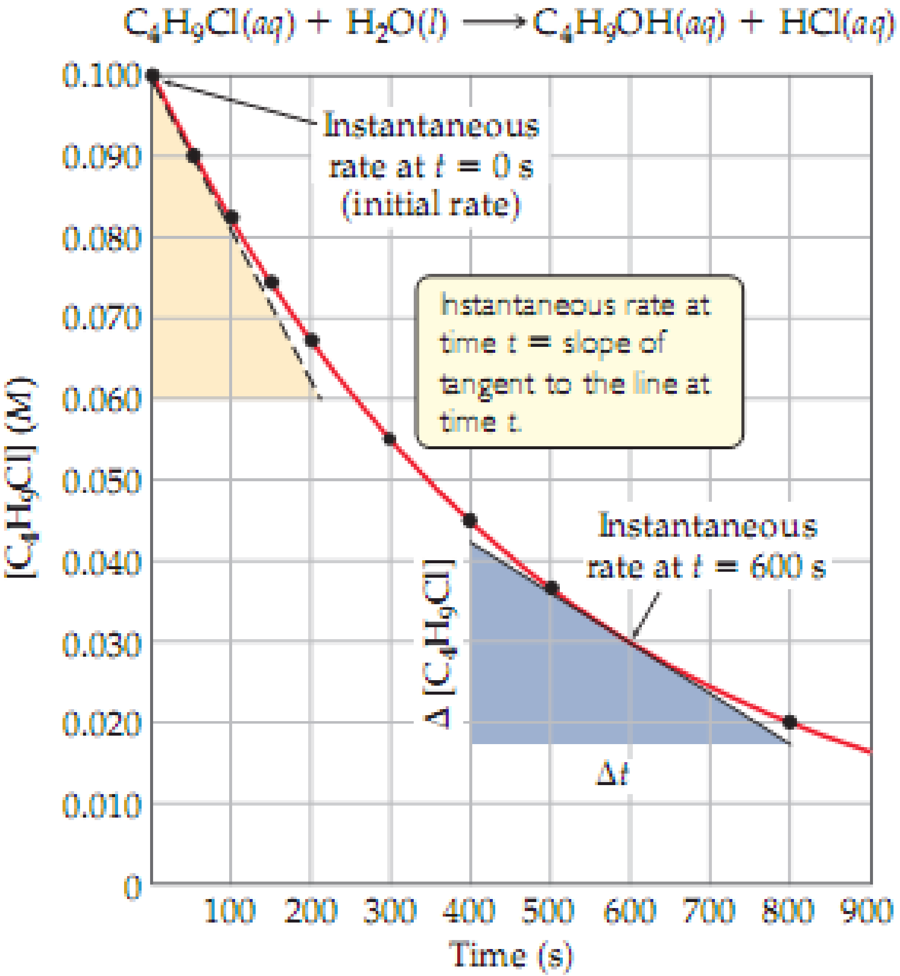
$$\frac{1}{k[\mathrm{A}]_0} = t_{1/2}$$

EXAMPLE

The reaction of C_4H_9Cl with water is a first-order reaction. The figure shows how the concentration of C_4H_9Cl changes with time at a particular temperature.

(a) From that graph, estimate the half-life for this reaction.

(b) Use the half-life from (a) to calculate the rate constant.

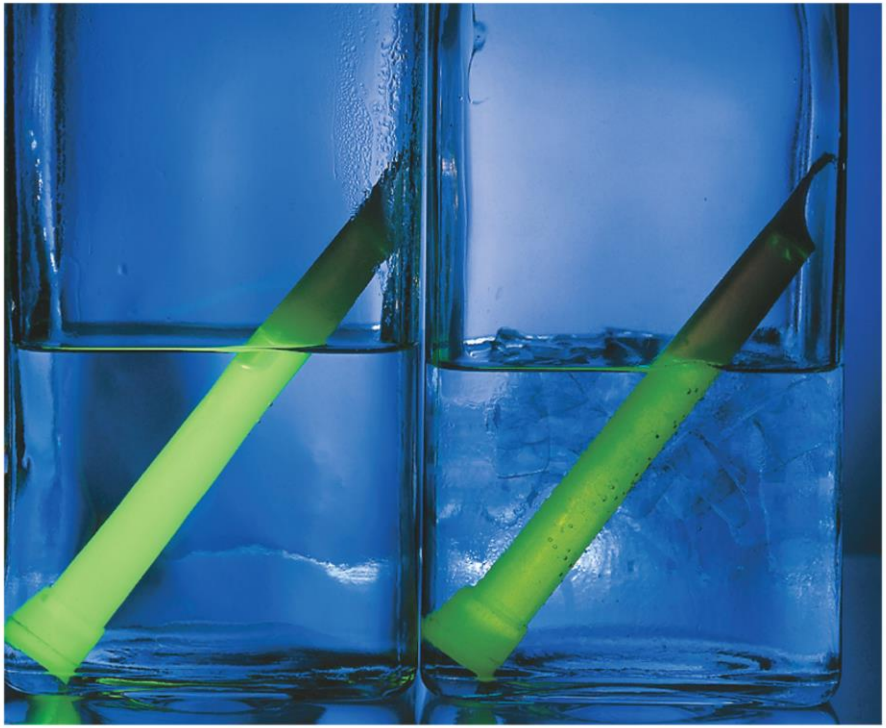


$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

(a) $[C_4H_9Cl]_0$ = is 0.100 M.
$[C_4H_9Cl]$ = 0.050 M at approximatel
340 s

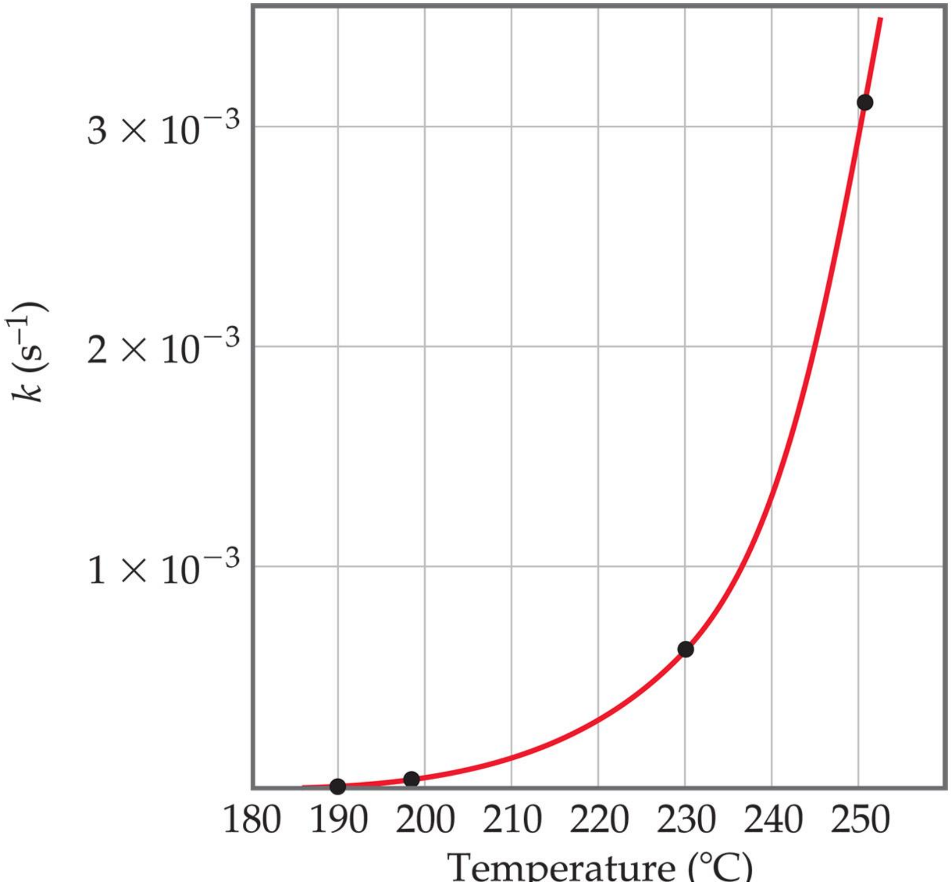
(b) $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\ \text{s}} = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

14-5 Temperature and Rate



Higher temperature

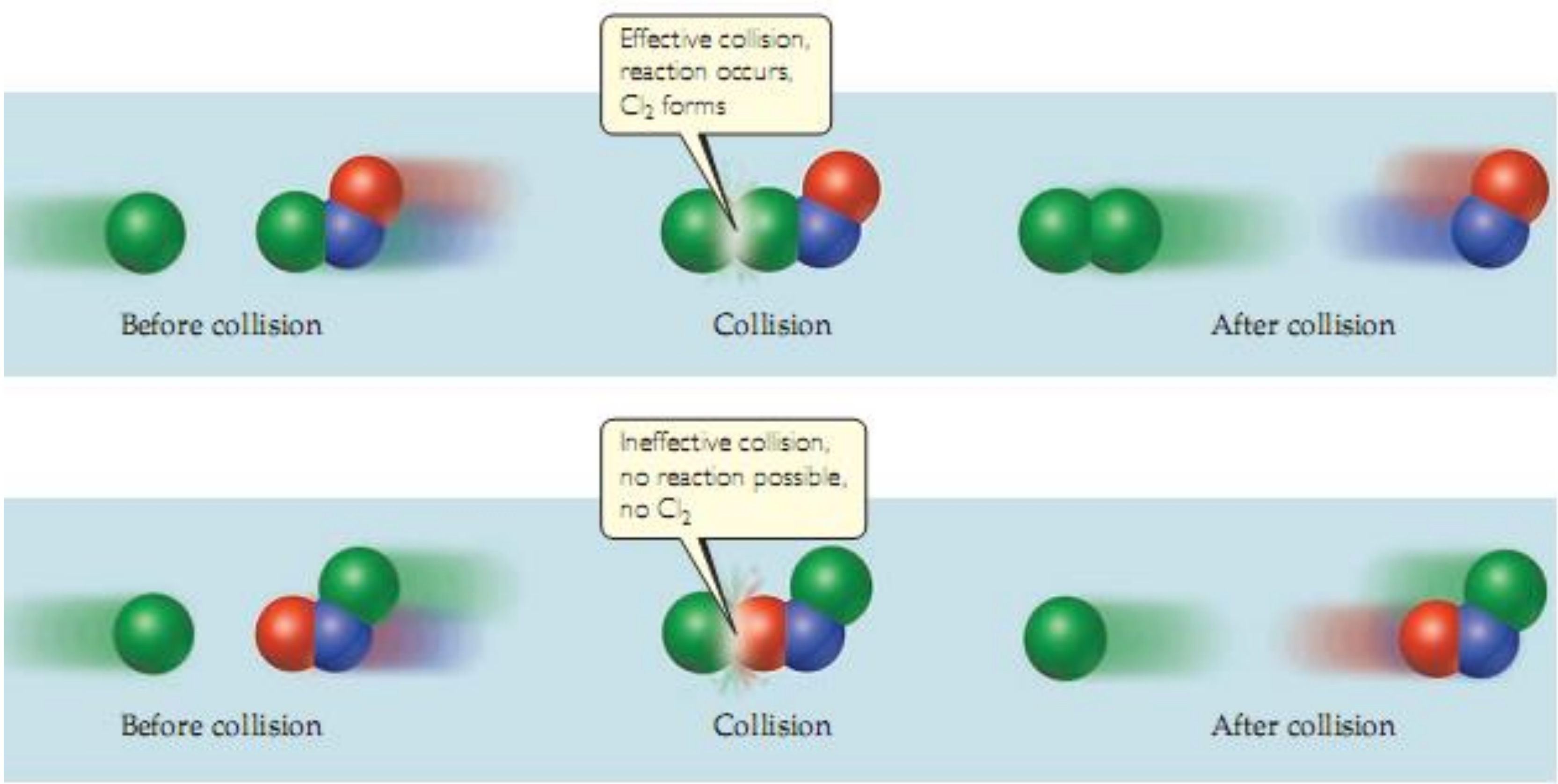
Lower temperature



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

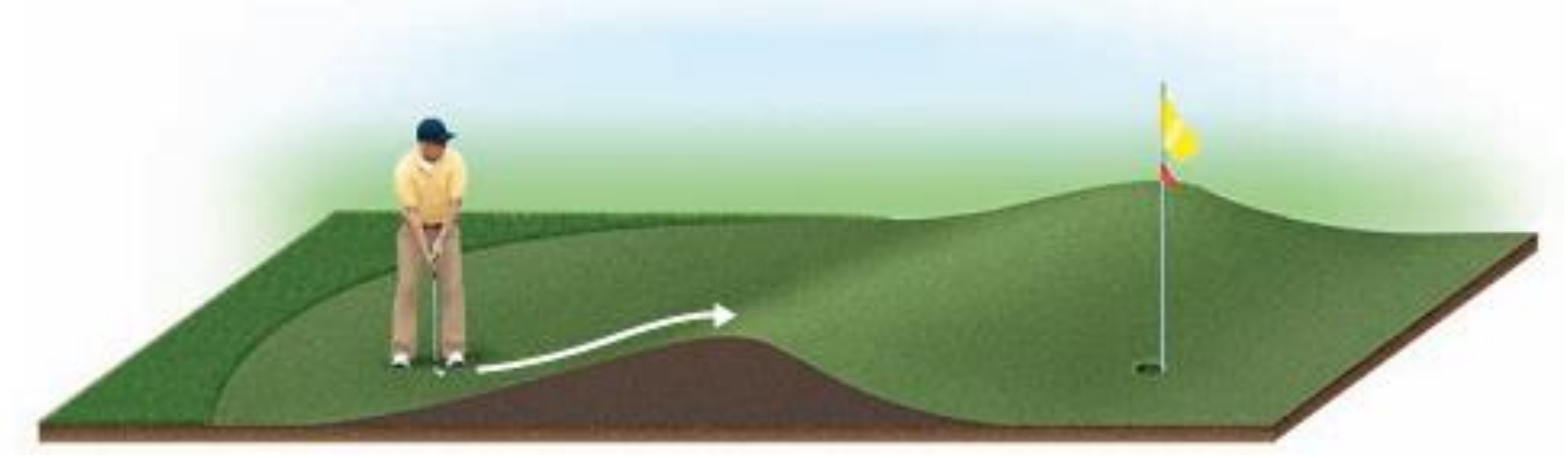
The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.
- Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.



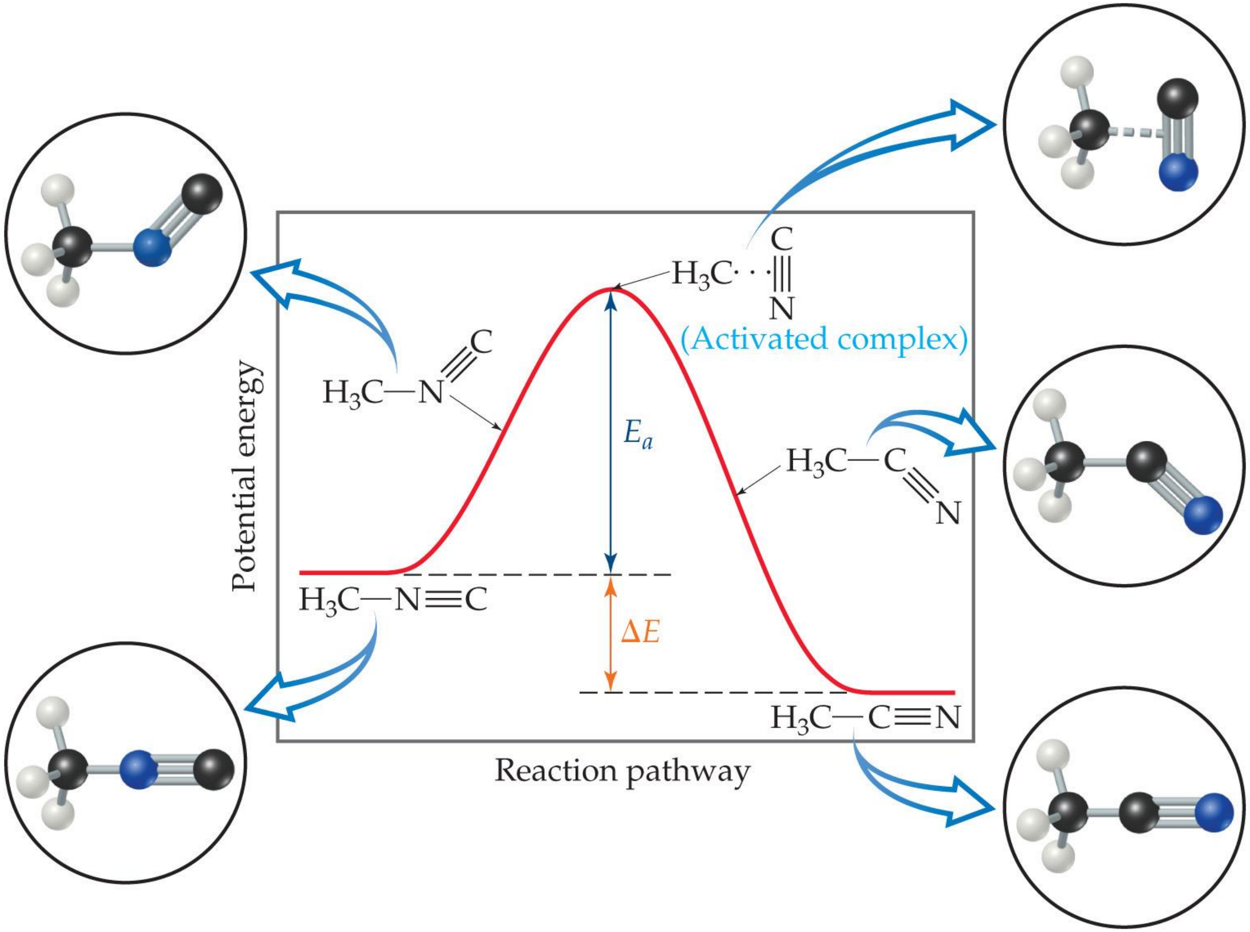
Activation Energy

- There is a minimum amount of energy required for reaction: the activation energy, E_a.



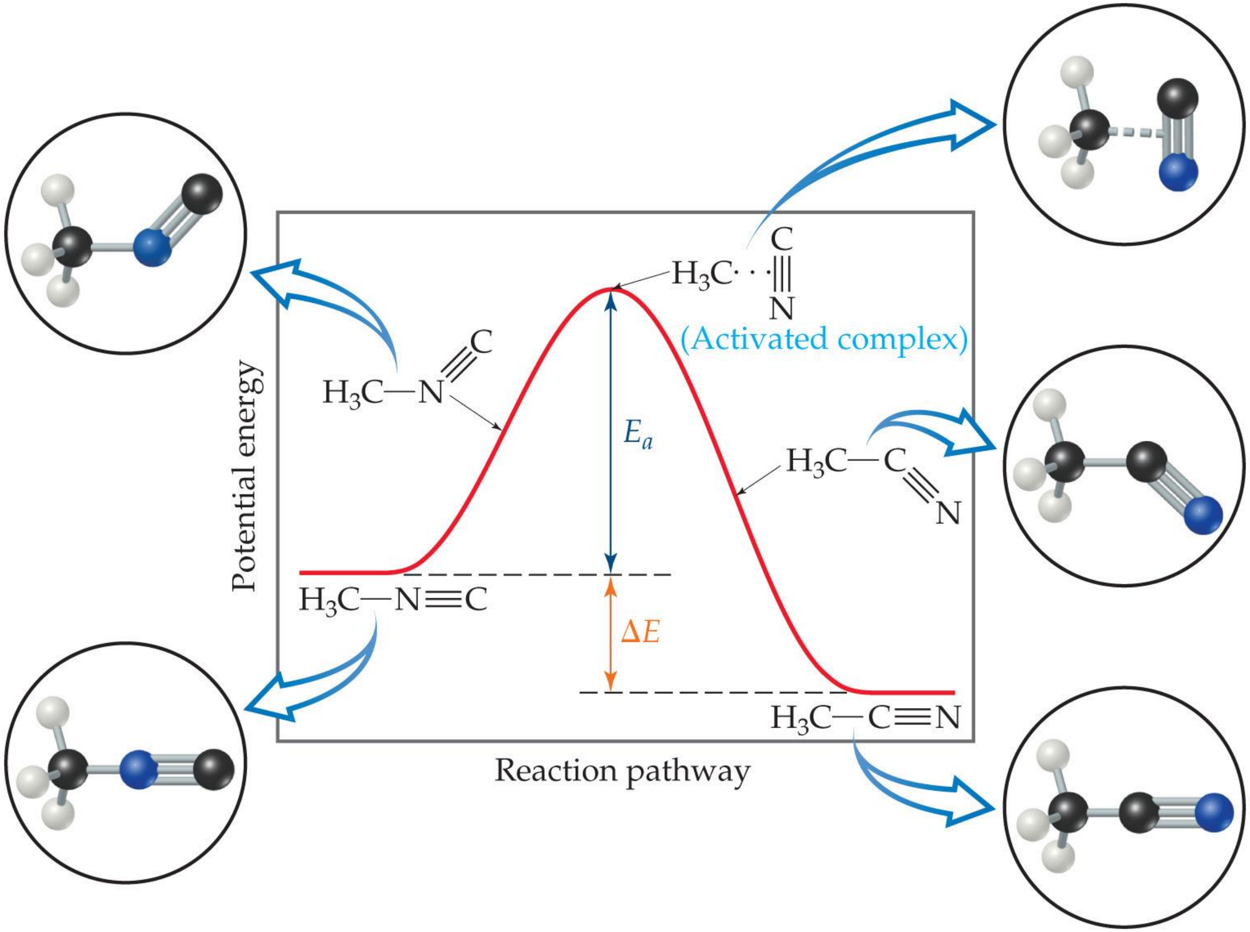
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

Reaction Coordinate Diagrams



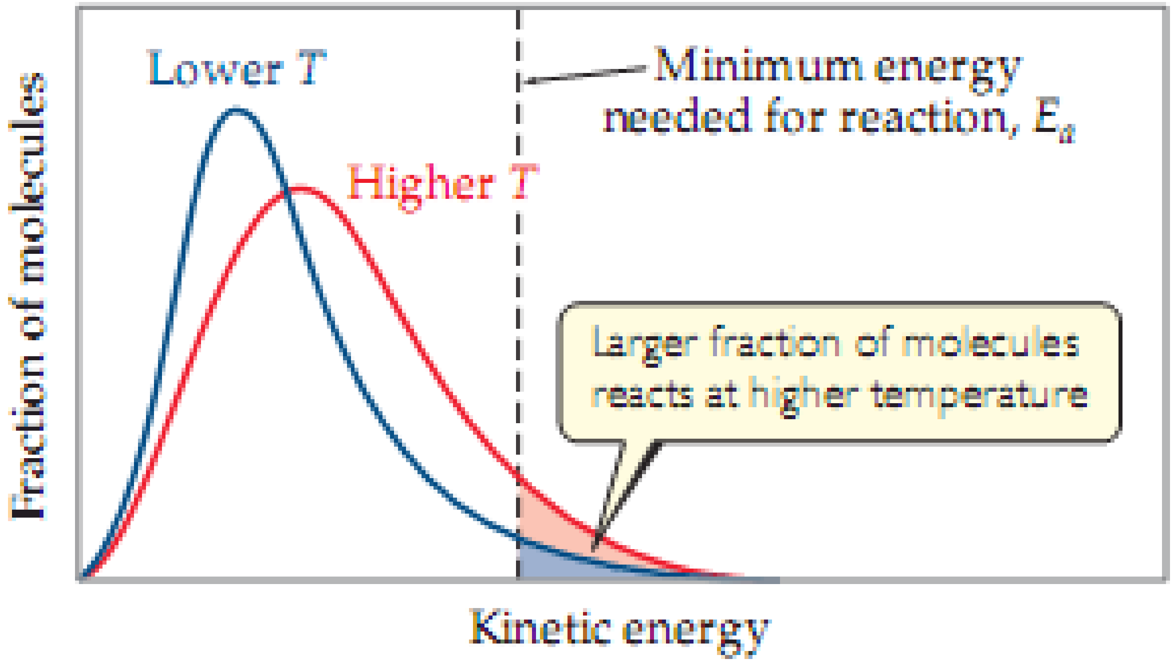
- The diagram shows the energy of the reactants and products (and, therefore, ΔE).
- The high point on the diagram is the transition state.

Reaction Coordinate Diagrams



- 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.

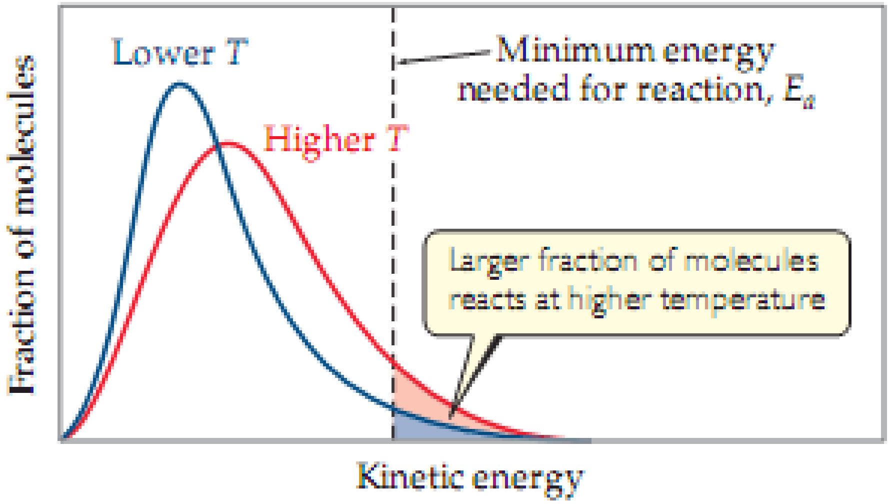
Maxwell–Boltzmann Distributions



◆ 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.
- 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.

This fraction of molecules can be found through the expression

$$f = e^{-\frac{-E_a}{RT}}$$

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

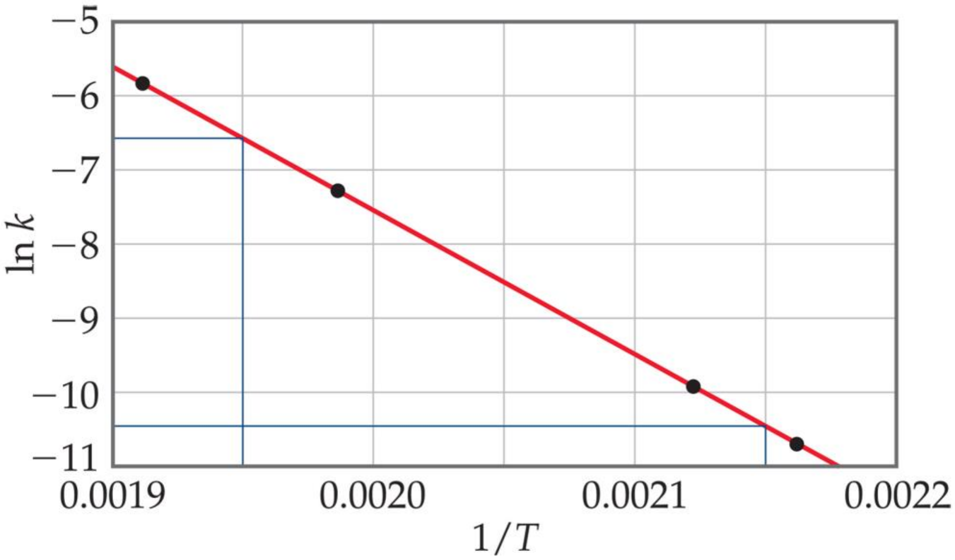
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

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

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

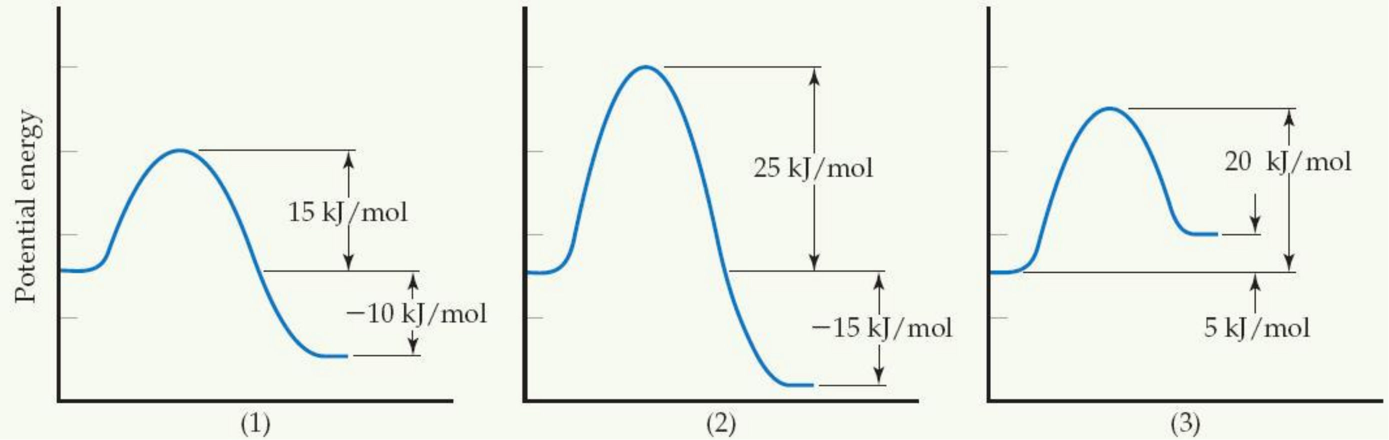
$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y \quad = \quad m \quad x \quad + \quad b$$

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

EXAMPLE

Consider a series of reactions having the following energy profiles: Rank the reactions from slowest to fastest assuming that they have nearly the same frequency factors.



The lower the activation energy, the faster the reaction. The value of ΔE does not affect the rate. Hence the order is (2) < (3) < (1).

Determining the Activation Energy

$$\begin{tikzcd}
\ln k \arrow[d, leftrightarrow] & = & -\frac{E_a}{RT} \arrow[d, leftrightarrow] & + & \ln A \arrow[d, leftrightarrow] \\
y & = & mx \arrow[d, dash] & + & b \arrow[d, dash] \\
 & & \text{slope} & & \text{intercept}
\end{tikzcd}$$

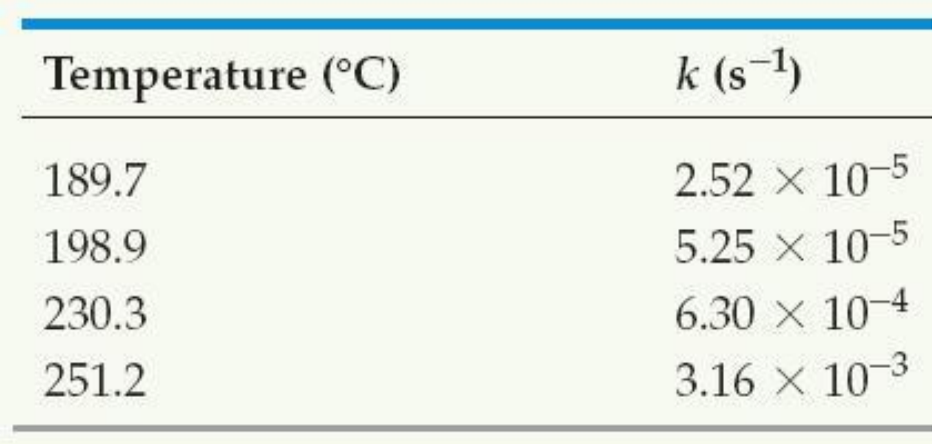
$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

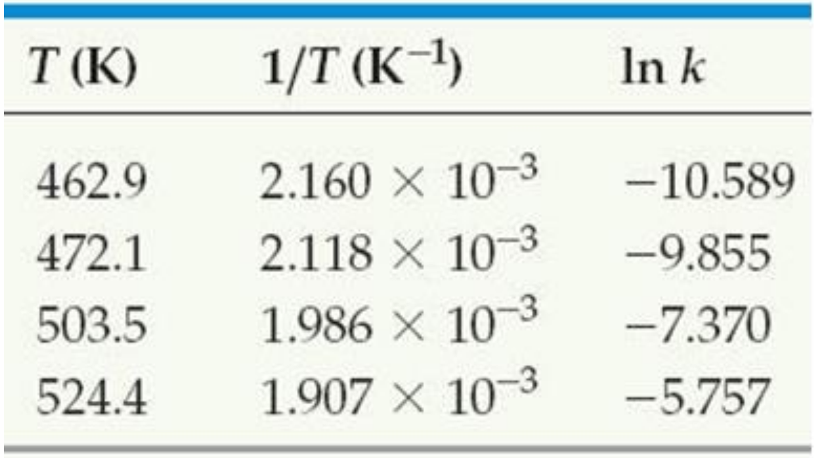
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

EXAMPLE

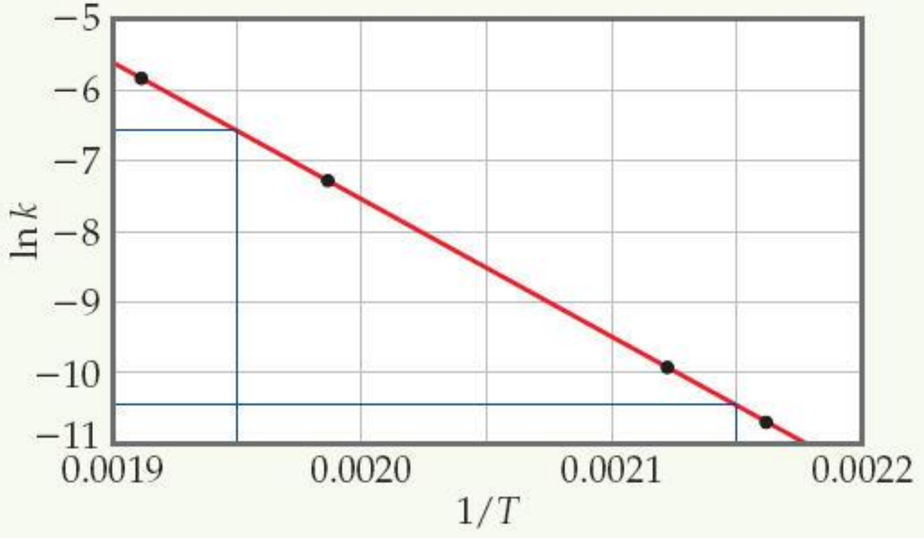
The table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures: **(a)** From these data, calculate the activation energy for the reaction. **(b)** What is the value of the rate constant at 430.0 K?



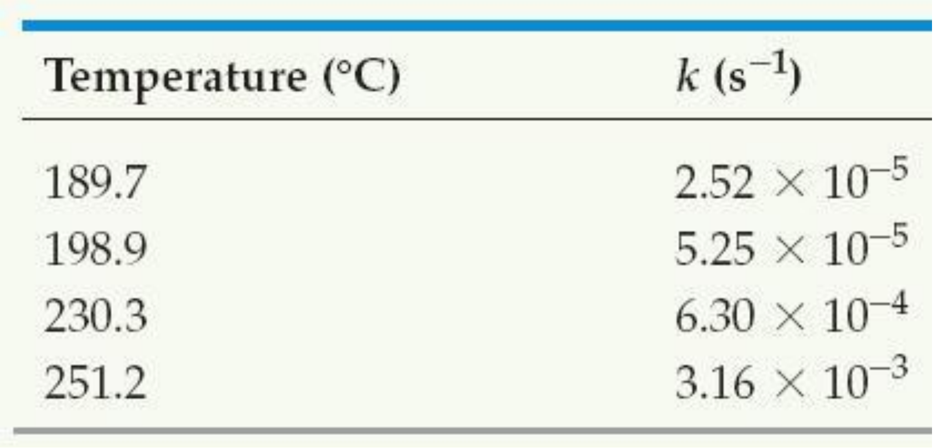
Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}



T (K)	$1/T$ (K^{-1})	$\ln k$
462.9	2.160×10^{-3}	−10.589
472.1	2.118×10^{-3}	−9.855
503.5	1.986×10^{-3}	−7.370
524.4	1.907×10^{-3}	−5.757



EXAMPLE



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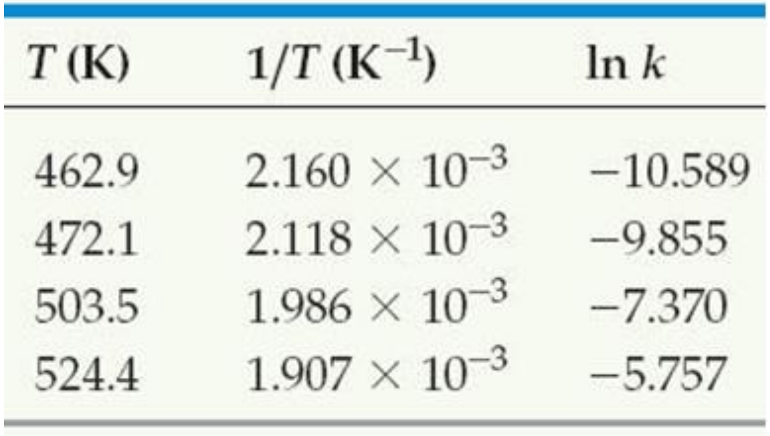

T (K)	$1/T$ (K^{-1})	ln k
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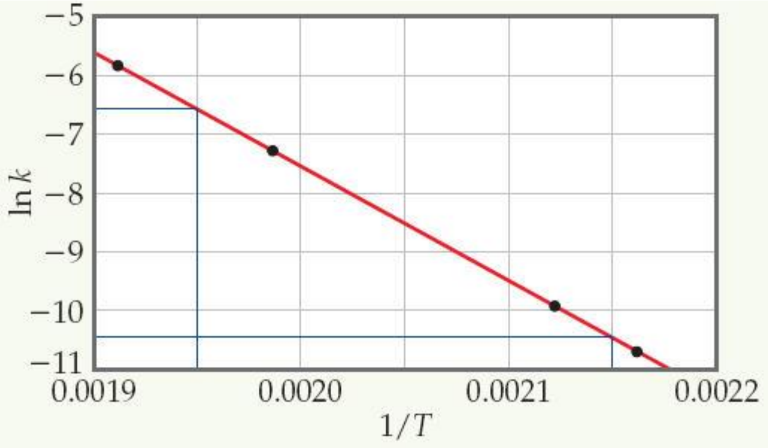
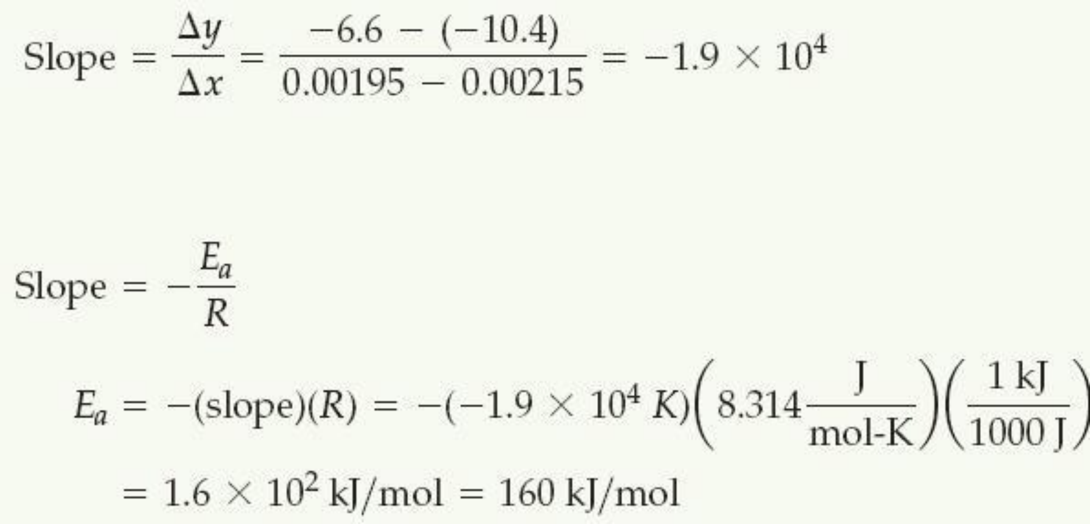




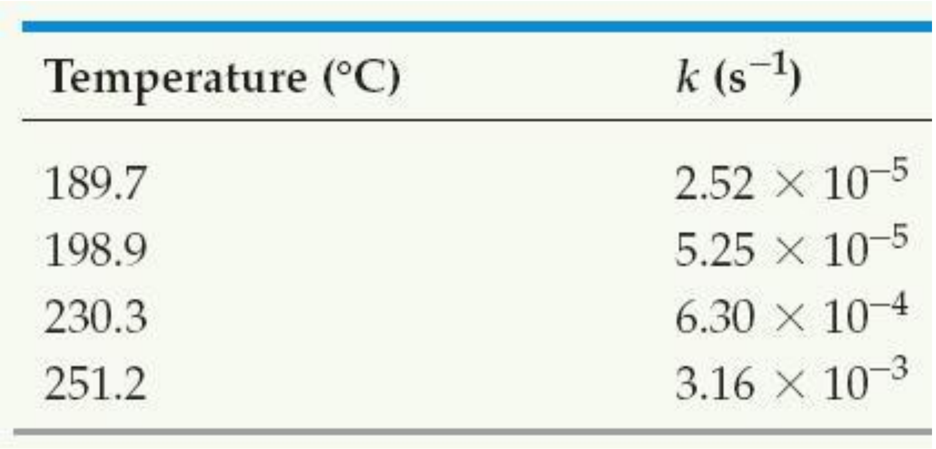
$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

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

$$E_a = -(\text{slope})(R) = -(-1.9 \times 10^4\ K)\left(8.314 \frac{\text{J}}{\text{mol-K}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right.$$

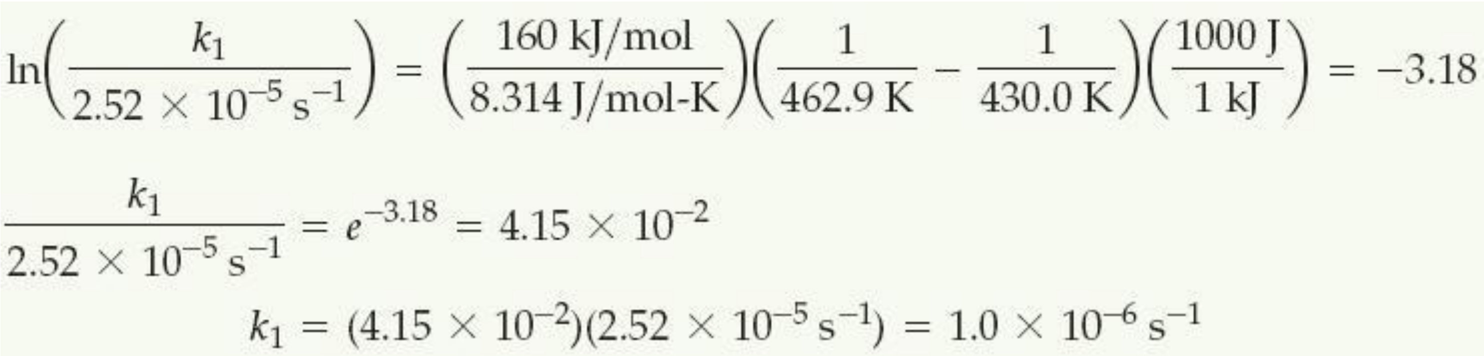
$$= 1.6 \times 10^2\ \text{kJ/mol} = 160\ \text{kJ/mol}$$

EXAMPLE



Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(b) To determine the rate constant, k_1, at $T_1 = 430.0$ K, we can use Equation 14.21 with $E_a = 160$ kJ/mol, and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5}\ s^{-1}$ and $T_2 = 462.9$ K:



$$\ln\left(\frac{k_1}{2.52 \times 10^{-5}\ \mathrm{s}^{-1}}\right) = \left(\frac{160\ \mathrm{kJ/mol}}{8.314\ \mathrm{J/mol\text{-}K}}\right)\left(\frac{1}{462.9\ \mathrm{K}} - \frac{1}{430.0\ \mathrm{K}}\right)\left(\frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}}\right) = -3.18$$

$$\frac{k_1}{2.52 \times 10^{-5}\ \mathrm{s}^{-1}} = e^{-3.18} = 4.15 \times 10^{-2}$$

$$k_1 = (4.15 \times 10^{-2})(2.52 \times 10^{-5}\ \mathrm{s}^{-1}) = 1.0 \times 10^{-6}\ \mathrm{s}^{-1}$$

14-6 Reaction Mechanisms

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

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

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

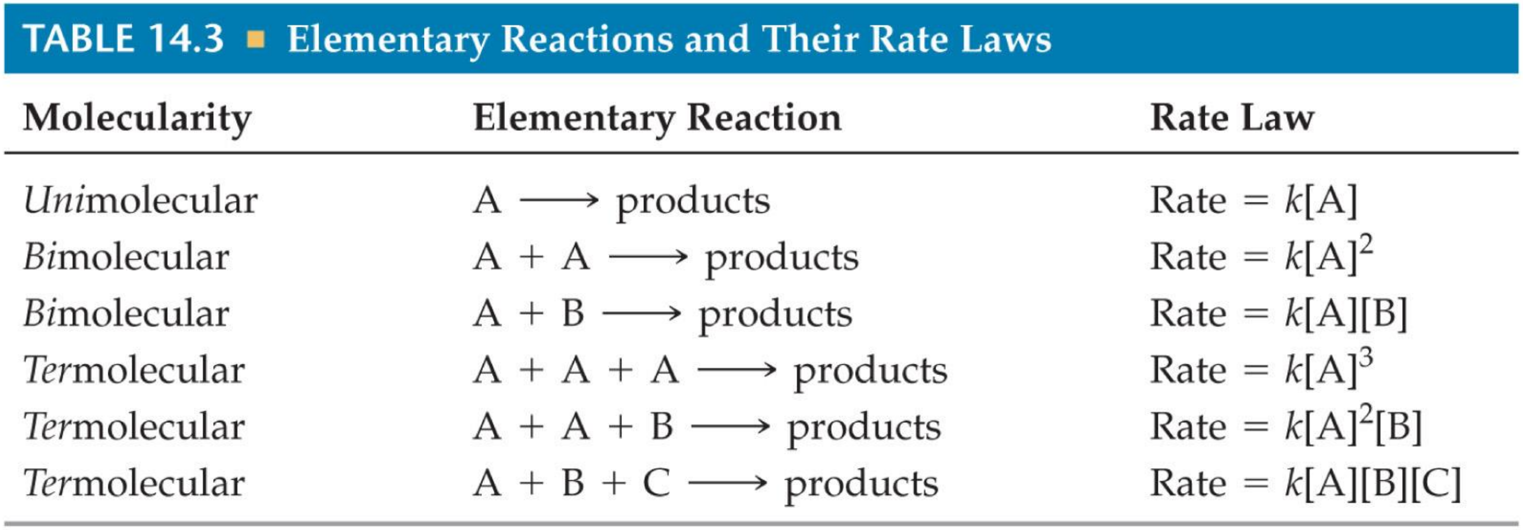


TABLE 14.3 ■ Elementary Reactions and Their Rate Laws

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	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

EXAMPLE

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$

(a) Describe the molecularity of each elementary reaction in this mechanism.
(b) Write the equation for the overall reaction.
(c) Identify the intermediate(s).

(a) The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.

(b)

$$2\,O_3(g) + O(g) \longrightarrow 3\,O_2(g) + O(g)$$
$$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

(c) The intermediate is O(*g*). It is neither an original reactant nor a final product but is formed in the first step of the mechanism and consumed in the second.

EXAMPLE

If the following reaction occurs in a single elementary reaction, predict its rate law

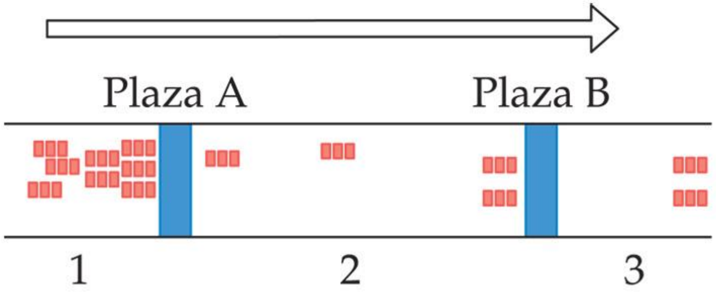
$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$

The reaction is bimolecular, involving one molecule of H_2 with one molecule of Br_2. Thus, the rate law is first order in each reactant and second order overall:

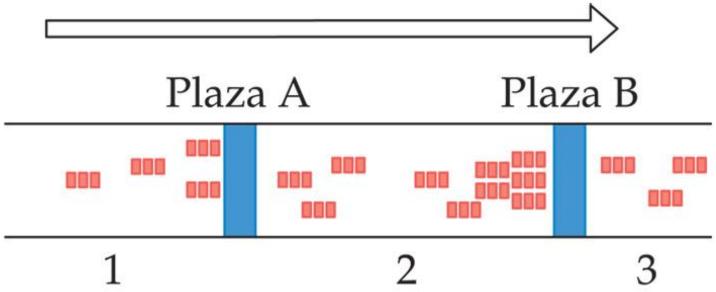
$$\text{Rate} = k[H_2][Br_2]$$

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

EXAMPLE

The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$\begin{array}{lll} N_2O(g) \longrightarrow N_2(g) + O(g) & & \text{(slow)} \\ N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) & & \text{(fast)} \end{array}$$

(a) Write the equation for the overall reaction.
(b) Write the rate law for the overall reaction.

(a) Adding the two elementary reactions gives

$$2\,N_2O(g) + O(g) \longrightarrow 2\,N_2(g) + O_2(g) + O(g)$$

Omitting the intermediate, O(*g*), which occurs on both sides of the equation, gives the overall reaction:

$$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$$

(b) The rate law for the overall reaction is just the rate law for the slow, rate determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

$$\text{Rate} = k[N_2O]$$

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: $NO + Br_2 \rightleftharpoons NOBr_2$ (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

$$\text{Rate} = k_2\,[\mathrm{NOBr_2}]\,[\mathrm{NO}]$$

- But how can we find $[\mathrm{NOBr_2}]$?

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 Rate$_f$ = Rate$_r$,

$$k_1\,[\mathrm{NO}]\,[\mathrm{Br_2}] = k_{-1}\,[\mathrm{NOBr_2}]$$

- Solving for [NOBr$_2$] gives us

$$\frac{k_1}{k_{-1}}\,[\mathrm{NO}]\,[\mathrm{Br_2}] = [\mathrm{NOBr_2}]$$

Fast Initial Step

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

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

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

EXAMPLE

Show that the following mechanism for Equation 14.24 also produces a rate law consistent with the experimentally observed one:

$$\text{Step 1:}\quad \mathrm{NO}(g) + \mathrm{NO}(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2}(g) \qquad \text{(fast equilibrium)}$$

$$\text{Step 2:}\quad \mathrm{N_2O_2}(g) + \mathrm{Br_2}(g) \xrightarrow{k_2} 2\,\mathrm{NOBr}(g) \qquad \text{(slow)}$$

The second step is rate determining, so the overall rate is

$$\text{Rate} = k_2[\mathrm{N_2O_2}][\mathrm{Br_2}]$$

We solve for the concentration of the intermediate N_2O_2 by assuming that an equilibrium is established in step 1; thus, the rates of the forward and reverse reactions in step 1 are equal:

$$k_1[\mathrm{NO}]^2 = k_{-1}[\mathrm{N_2O_2}]$$

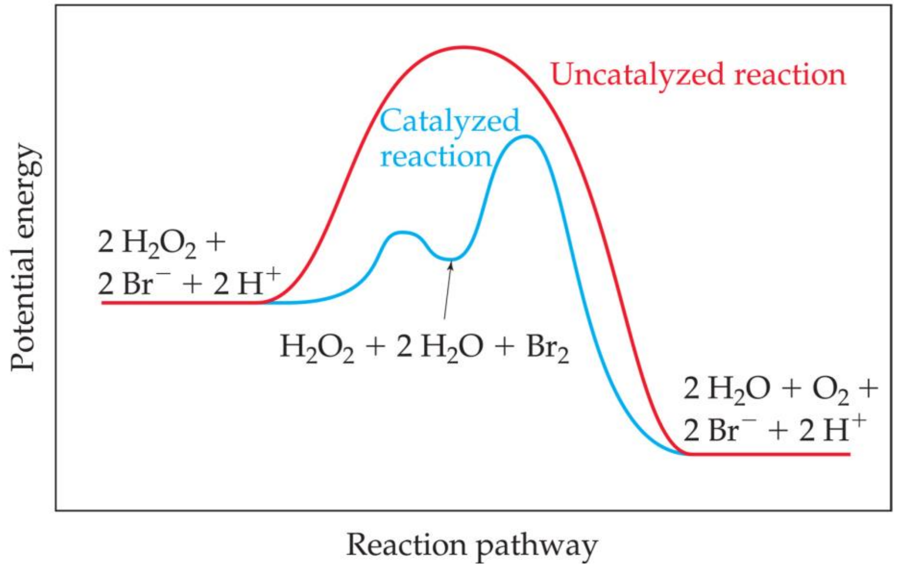
$$[\mathrm{N_2O_2}] = \frac{k_1}{k_{-1}}[\mathrm{NO}]^2$$

$$\text{Rate} = k_2\frac{k_1}{k_{-1}}[\mathrm{NO}]^2[\mathrm{Br_2}] = k[\mathrm{NO}]^2[\mathrm{Br_2}]$$

Thus, this mechanism also yields a rate law consistent with the experimental one.

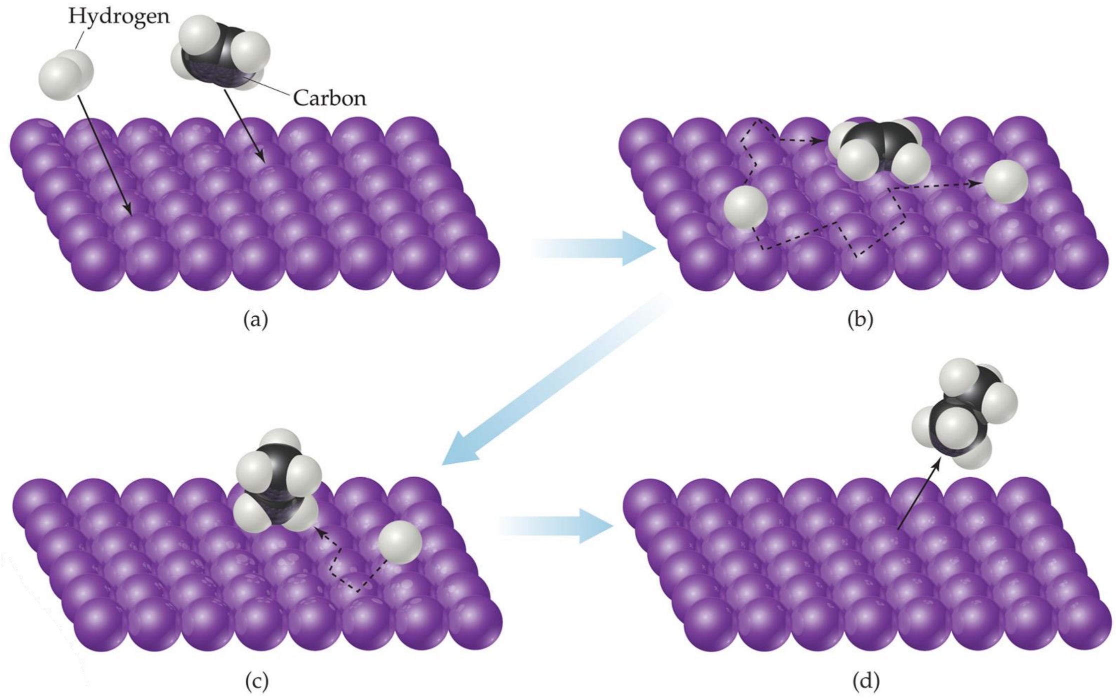
Catalysts

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



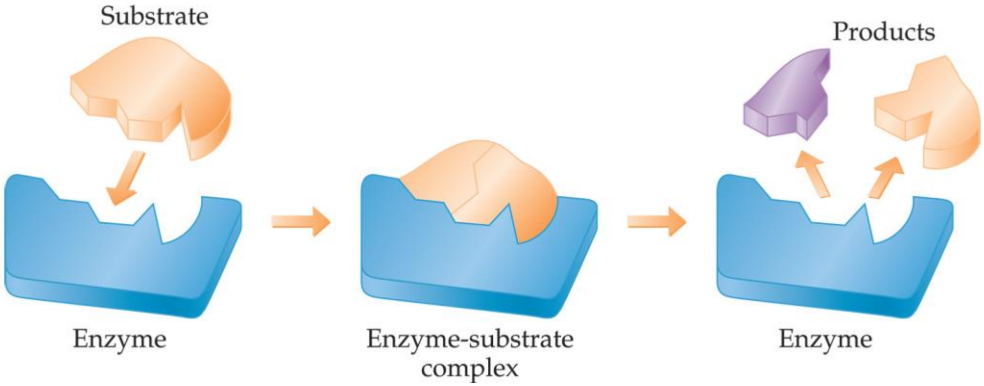
Catalysts

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.

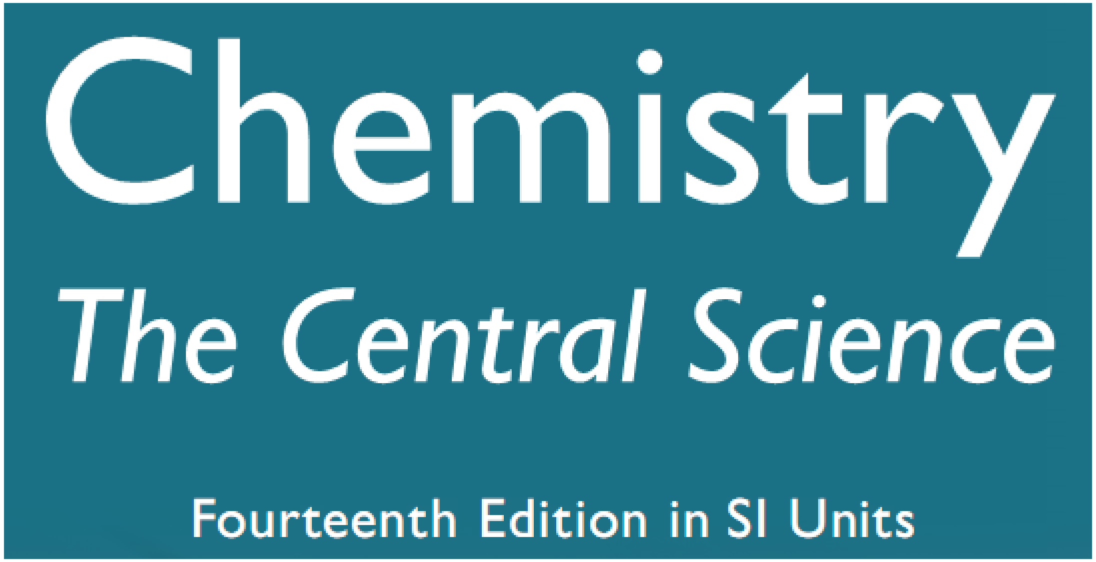


Homeworks

14.117

14.122

Due: July 31st 2019



Chemistry

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