Chemistry, The Central Science, 11th edition
Theodore L. Brown; H. Eugene LeMay, Jr.;
and Bruce E. Bursten

Chapter 14
Chemical Kinetics

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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).

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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.

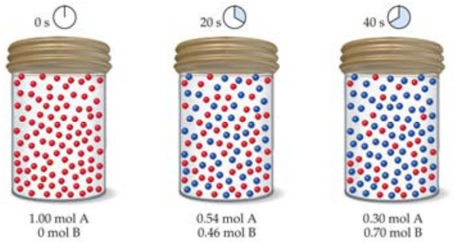
Factors That Affect Reaction Rates

- 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.

Reaction Rates



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

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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.

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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:

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

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		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.

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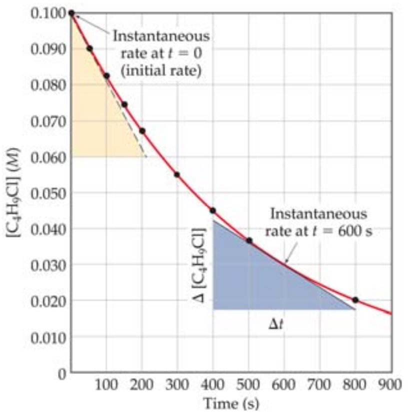
Reaction Rates

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

- 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.



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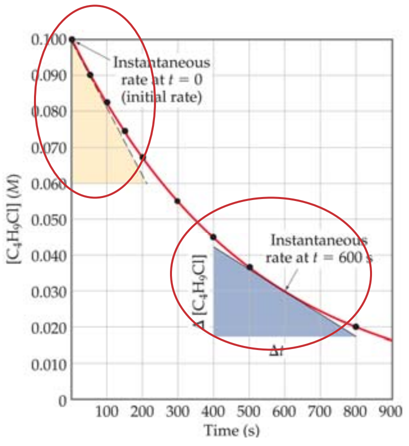
Reaction Rates

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

- 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.



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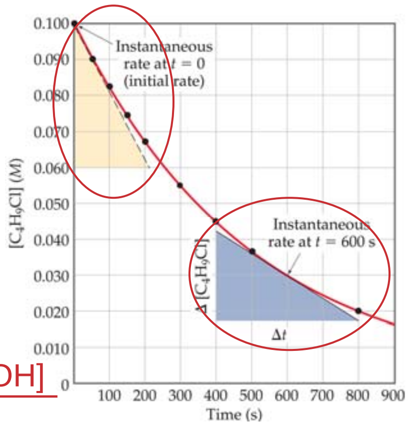
Reaction Rates and Stoichiometry

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

- 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?

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

- 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

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

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

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Sample Exercise 14.1 Calculating an Average Rate of Reaction

From the data given in the caption of Figure 14.3, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

Solution

Analyze: We are given the concentration of A at 20 s (0.54 *M*) and at 40 s (0.30 *M*) and asked to calculate the average rate of reaction over this time interval.
Plan: The average rate is given by the change in concentration, Δ[A], divided by the corresponding change in time, Δ*t*. Because A is a reactant, a minus sign is used in the calculation to make the rate a positive quantity.

Solve: $\text{Average rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.30\,M - 0.54\,M}{40\text{ s} - 20\text{ s}} = 1.2 \times 10^{-2}\,M/\text{s}$

Practice Exercise

For the reaction pictured in Figure 14.3, calculate the average rate of appearance of B over the time interval from 0 to 40 s.
Answer: $1.8 \times 10^{-2}\,M/\text{s}$

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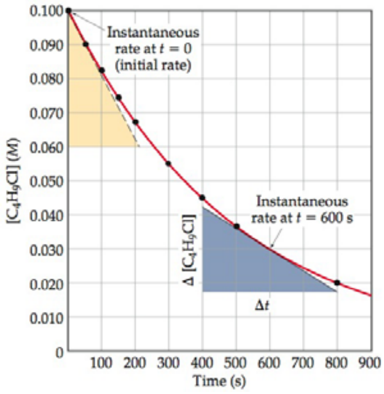
Sample Exercise 14.2 Calculating an Instantaneous Rate of Reaction

Using Figure 14.4, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).

Solution

Analyze: We are asked to determine an instantaneous rate from a graph of concentration versus time.
Plan: To obtain the instantaneous rate at $t = 0$, we must determine the slope of the curve at $t = 0$. The tangent is drawn on the graph.



Sample Exercise 14.2 Calculating an Instantaneous Rate of Reaction

Using Figure 14.4, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).

Solution

The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (that is, change in molarity over change in time).
Solve: The straight line falls from $[C_4H_9Cl] = 0.100\ M$ to $0.060\ M$ in the time change from 0 s to 210 s, as indicated by the tan triangle shown in Figure 14.4. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\ M}{(210 - 0)\ \text{s}} = 1.9 \times 10^{-4}\ M/\text{s}$$

Practice Exercise

Using Figure 14.4, determine the instantaneous rate of disappearance of C_4H_9Cl at $t = 300$ s.
Answer: $1.1 \times 10^{-4}\ M/\text{s}$

Sample Exercise 14.3 Relating Rates at Which Products Appear and Reactants Disappear

(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, $-\Delta[O_3]/\Delta t$?

Solution

Analyze: We are given a balanced chemical equation and asked to relate the rate of appearance of the product to the rate of disappearance of the reactant.

Plan: We can use the coefficients in the chemical equation as shown in Equation 14.4 to express the relative rates of reactions.

Solve: (a) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

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

(b) Solving the equation from part (a) for the rate at which O_3disappears, $-\Delta[O_3]/\Delta t$ we have:

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

Check: We can directly apply a stoichiometric factor to convert the O_2 formation rate to the rate at which the O_3 disappears:

$$-\frac{\Delta[O_3]}{\Delta t} = \left(6.0 \times 10^{-5}\frac{\text{mol } O_2/\text{L}}{\text{s}}\right)\left(\frac{2 \text{ mol } O_3}{3 \text{ mol } O_2}\right) = 4.0 \times 10^{-5}\frac{\text{mol } O_3/\text{L}}{\text{s}}$$

$$= 4.0 \times 10^{-5}\ M/s$$

Sample Exercise 14.3 Relating Rates at Which Products Appear and Reactants Disappear

Practice Exercise

The decomposition of N_2O_5 proceeds according to the following equation:

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

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7} M/s, what is the rate of appearance of (a) NO_2, (b) O_2?

Answer: **(a)** 8.4×10^{-7} M/s, **(b)** 2.1×10^{-7} M/s

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Concentration and Rate

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

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Concentration and Rate

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.

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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.

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Concentration and Rate

- This means

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

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

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

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.

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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 $[NO_2^-]$.

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Rate Laws

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

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

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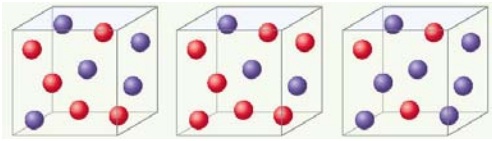
Sample Exercise 14.4 Relating a Rate Law to the Effect of concentration on Rate

Consider a reaction A + B → C for which = $k[A][B]^2$. 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.



Solution

Analyze: We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan: Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Solve: Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Sample Exercise 14.4 Relating a Rate Law to the Effect of concentration on Rate

Solution (continued)

Check: Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a higher reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

Practice Exercise

Assuming that rate = $k[A][B]$, rank the mixtures represented in this Sample Exercise in order of increasing rate.

Answer: $2 = 3 < 1$

Sample Exercise 14.5 Determining Reaction Order and Units of Rate Constants

(a) What are the overall reaction orders for the reactions described in Equations 14.9 and 14.10? **(b)** What are the units of the rate constant for the rate law in Equation 14.9?

Solution

Analyze: We are given two rate laws and asked to express **(a)** the overall reaction order for each and **(b)** the units for the rate constant for the first reaction.
Plan: The overall reaction order is the sum of the exponents in the rate law. The units for the rate constant, *k*, are found by using the normal units for rate (*M*/s) and concentration (*M*) in the rate law and applying algebra to solve for *k*.
Solve: (a) The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.10 is first order in $CHCl_3$ and one-half order in Cl_2. The overall reaction order is three halves.
(b) For the rate law for Equation 14.9, we have

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

So

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

on changes.

Practice Exercise

(a) What is the reaction order of the reactant H_2 in Equation 14.11? **(b)** What are the units of the rate constant for Equation 14.11?
Answer: **(a)** 1, **(b)** M^{-1} s^{-1}

Sample Exercise 14.6 Determining a Rate Law from Initial Rate Data

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] = 0.050 *M* and [B] = 0.100 *M*.

Solution

Analyze: We are given a table of data that relates concentrations of reactants with initial rates of reaction and asked to determine **(a)** the rate law, **(b)** the rate constant, and **(c)** the rate of reaction for a set of concentrations not listed in the table.
Plan: (a) We assume that the rate law has the following form: Rate = $k[A]^m[B]^n$ so we must use the given data to deduce the reaction orders *m* and *n*. We do so by determining how changes in the concentration change the rate. **(b)** Once we know *m* and *n*, we can use the rate law and one of the sets of data to determine the rate constant *k*. **(c)** Now that we know both the rate constant and the reaction orders, we can use the rate law with the given concentrations to calculate rate.

Sample Exercise 14.6 Determining a Rate Law from Initial Rate Data

Solution (continued)

Solve: (a) As we move from experiment 1 to experiment 2, [A] is held constant and [B] is doubled. Thus, this pair of experiments shows how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B. Because the rate remains the same when [B] is doubled, the concentration of B has no effect on the reaction rate. The rate law is therefore zero order in B (that is, $n = 0$).

In experiments 1 and 3, [B] is held constant so these data show how [A] affects rate. Holding [B] constant while doubling [A] increases the rate fourfold. This result indicates that rate is proportional to $[A]^2$ (that is, the reaction is second order in A). Hence, the rate law is

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

This rate law could be reached in a more formal way by taking the ratio of the rates from two experiments:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.0 \times 10^{-5}\ M/s}{4.0 \times 10^{-5}\ M/s} = 1$$

Using the rate law, we have

$$1 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{\cancel{k[0.100\ M]^m}[0.200\ M]^n}{\cancel{k[0.100\ M]^m}[0.100\ M]^n} = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

2^n equals 1 under only one condition:

$$n = 0$$

We can deduce the value of m in a similar fashion:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{16.0 \times 10^{-5}\ M/s}{4.0 \times 10^{-5}\ M/s} = 4$$

Using the rate law gives

$$4 = \frac{\text{rate 3}}{\text{rate 1}} = \frac{k[0.200\ M]^m\cancel{[0.100\ M]^n}}{k[0.100\ M]^m\cancel{[0.100\ M]^n}} = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

Sample Exercise 14.6 Determining a Rate Law from Initial Rate Data

Solution (continued)

Because $2^m = 4$, we conclude that

$$m = 2$$

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

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

(c) Using the rate law from part (a) and the rate constant from part (b), we have

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

Because [B] is not part of the rate law, it is irrelevant to the rate, if there is at least some B present to react with A.

Check: A good way to check our rate law is to use the concentrations in experiment 2 or 3 and see if we can correctly calculate the rate. Using data from experiment 3, we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3}\ M^{-1}\ s^{-1})(0.200\ M)^2 = 1.6 \times 10^{-4}\ M/s$$

Thus, the rate law correctly reproduces the data, giving both the correct number and the correct units for the rate.

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Sample Exercise 14.6 Determining a Rate Law from Initial Rate Data

Practice Exercise

The following data were measured for the reaction of nitric oxide with hydrogen:

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Experiment Number	[NO] (*M*)	$[H_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. **(b)** Calculate the rate constant. **(c)** Calculate the rate when [NO] = 0.050 *M* and $[H_2]$ = 0.150 *M*

Answers: **(a)** rate = $k[NO]^2[H_2]$; **(b)** $k = 1.2\ M^{-2}\ s^{-1}$; **(c)** rate = 4.5×10^{-4} *M*/s

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 $y = mx + b$

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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*.

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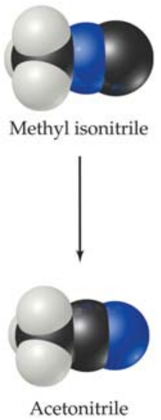
First-Order Processes



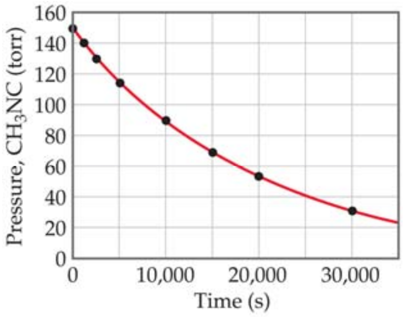
Consider the process in which methyl isonitrile is converted to acetonitrile.

$CH_3NC \longrightarrow CH_3CN$

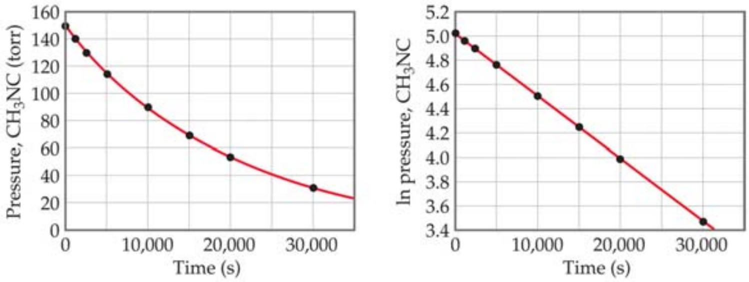
First-Order Processes

$CH_3NC \longrightarrow CH_3CN$

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 of the 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

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

also in the form

$$y = mx + b$$

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* 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

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

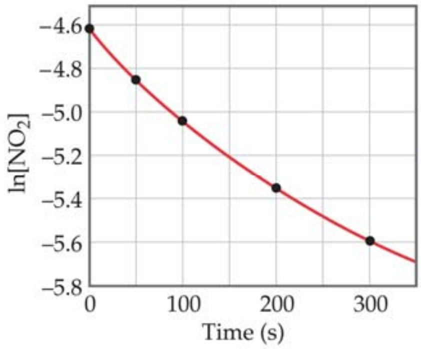
and yields data comparable to this:

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

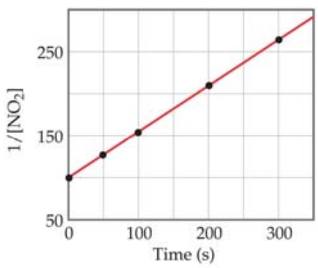
Second-Order Processes

- 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



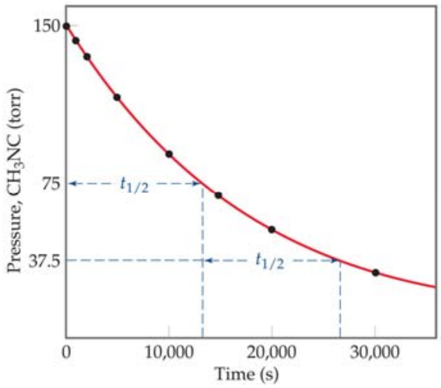
Second-Order Processes



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.
- 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 $[A]_0$.

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Half-Life

For a second-order process,

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

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

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

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

Sample Exercise 14.7 Using the Integrated First-Order Rate Law

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?

Solution

Analyze: We are given the rate constant for a reaction that obeys first-order kinetics, as well as information about concentrations and times, and asked to calculate how much reactant (insecticide) remains after one year. We must also determine the time interval needed to reach a particular insecticide concentration. Because the exercise gives time in (a) and asks for time in (b), we know that the integrated rate law, Equation 14.13, is required.

Plan: (a) We are given $k = 1.45$ yr^{-1}, $t = 1.00$ yr and $[\text{insecticide}]_0 = 5.0 \times 10^{-7}$ g/cm^3, and so Equation 14.13 can be solved for $[\text{insecticide}]_t$. **(b)** We have $k = 1.45$ yr^{-1}, $[\text{insecticide}]_0 = 5.0 \times 10^{-7}$ g/cm^3, and $[\text{insecticide}]_t = 3.0 \times 10^{-7}$ g/cm^3, and so we can solve Equation 14.13 for time, *t*.

Solve: (a) Substituting the known quantities into Equation 14.13, we have

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

We use the ln function on a calculator to evaluate the secondterm on the right, giving

$$\ln[\text{insecticide}]_{t=1\text{ yr}} = -1.45 + (-14.51) = -15.96$$

To obtain $[\text{insecticide}]_{t=1\text{ yr}}$, we use the inverse natural logarithm, or e^x, function on the calculator:

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

Sample Exercise 14.7 Using the Integrated First-Order Rate Law

Solution (continued)

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(b) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7}$ g/cm^3, gives

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

Solving for *t* gives

$$t = -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45\ \text{yr}^{-1}$$
$$= -(-15.02 + 14.51)/1.45\ \text{yr}^{-1} = 0.35\ \text{yr}$$

Check: In part (a) the concentration remaining after 1.00 yr (that is, 1.2×10^{-7} g/cm^3) is less than the original concentration (5.0×10^{-7} g/cm^3), as it should be. In (b) the given concentration (3.0×10^{-7} g/cm^3) is greater than that remaining after 1.00 yr, indicating that the time must be less than a year. Thus, *t* = 0.35 yr is a reasonable answer.

Practice Exercise

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510 °C is a first-order process with a rate constant of 6.8×10^{-4} s^{-1}:

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?
Answer: 51 torr

Sample Exercise 14.8 Determining Reaction Order from the Integrated Rate Law

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C,
$NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$:

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

Is the reaction first or second order in NO_2?

Solution

Analyze: We are given the concentrations of a reactant at various times during a reaction and asked to determine whether the reaction is first or second order.
Plan: We can plot $\ln[NO_2]$ and $1/[NO_2]$ against time. One or the other will be linear, indicating whether the reaction is first or second order.

Sample Exercise 14.8 Determining Reaction Order from the Integrated Rate Law

Solution (continued)

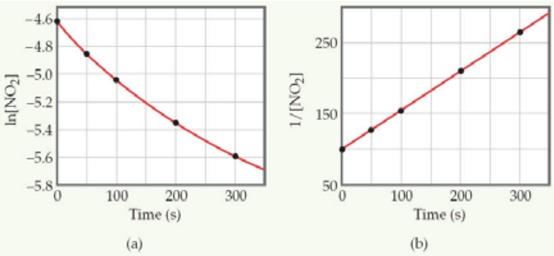
Solve: To graph $\ln[NO_2]$ and $1/[NO_2]$ against time, we will first prepare the following table from the data given:

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

As Figure 14.8 shows, only the plot of $1/[NO_2]$ versus time is linear. Thus, the reaction obeys a second-order rate law: Rate = $k[NO_2]^2$. From the slope of this straight-line graph, we determine that $k = 0.543\ M^{-1}\ s^{-1}$ for the disappearance of NO_2.

Sample Exercise 14.8 Determining Reaction Order from the Integrated Rate Law

Solution (continued)



▲ **Figure 14.8 Kinetic data for decomposition of NO_2.** The reaction is $NO_2(g) \longrightarrow NO(g) + \frac{1}{2} O_2(g)$, and the data were collected at 300 °C. (a) A plot of $\ln[NO_2]$ versus time is not linear, indicating that the reaction is not first order in NO_2. (b) A plot of $1/[NO_2]$ versus time is linear, indicating that the reaction is second order in NO_2.

Practice Exercise

Consider again the decomposition of NO_2 discussed in the Sample Exercise. The reaction is second order in NO_2 with $k = 0.543\ M^{-1}\ s^{-1}$. If the initial concentration of NO_2 in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 h?
Answer: Using Equation 14.14, we find $[NO_2] = 1.00 \times 10^{-3}\ M$

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Sample Exercise 14.9 Determining the Half-Life of a First-Order Reaction

The reaction of C_4H_9Cl with water is a first-order reaction. Figure 14.4 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.

Solution

Analyze: We are asked to estimate the half-life of a reaction from a graph of concentration versus time and then to use the half-life to calculate the rate constant for the reaction.
Plan: (a) To estimate a half-life, we can select a concentration and then determine the time required for the concentration to decrease to half of that value. **(b)** Equation 14.15 is used to calculate the rate constant from the half-life.
Solve: (a) From the graph, we see that the initial value of $[C_4H_9Cl]$ is 0.100 *M*. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 *M*, which we can read off the graph. This point occurs at approximately 340 s. **(b)** Solving Equation 14.15 for *k*, we have

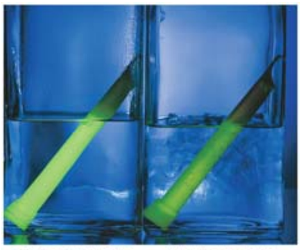
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340 \text{ s}} = 2.0 \times 10^{-3} \text{ s}^{-1}$$

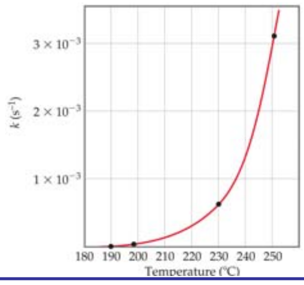
Check: At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 *M*. Inspection of the graph shows that this is indeed the case.

Practice Exercise

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. **(b)** How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?
Answer: 0.478 yr = 1.51×10^7 s; **(b)** it takes two half-lives, 2(0.478 yr) = 0.956 yr

Temperature and Rate





- 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.

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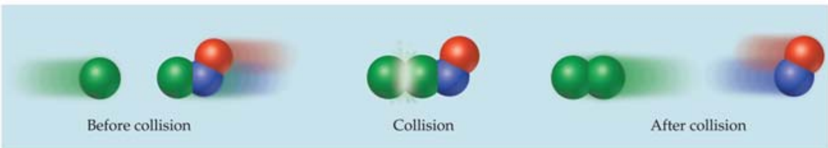
The Collision Model

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



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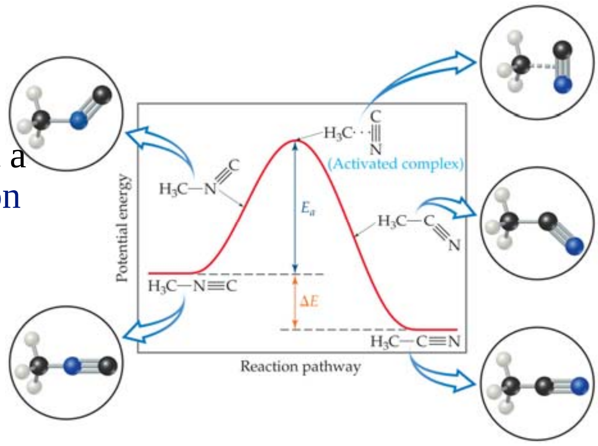
Activation Energy

- 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.

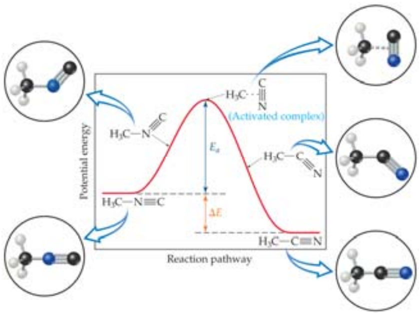
Reaction Coordinate Diagrams

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



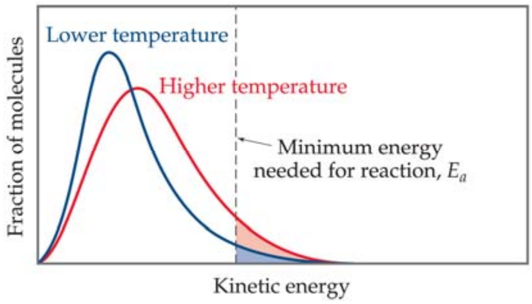
Reaction Coordinate Diagrams

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



- 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.

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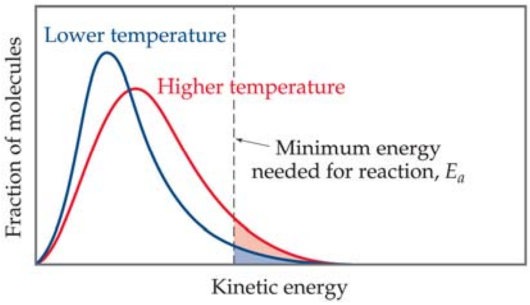
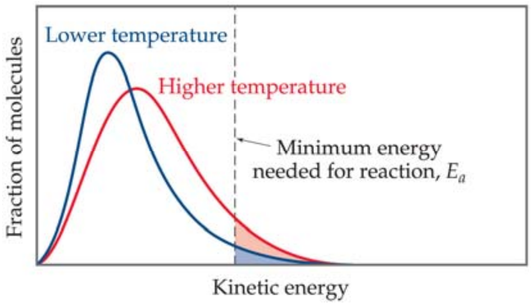
Maxwell–Boltzmann Distributions



- 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.



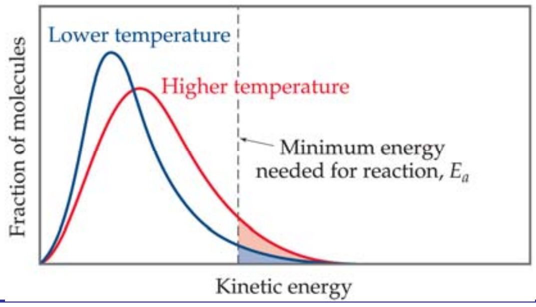
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

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

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



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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.

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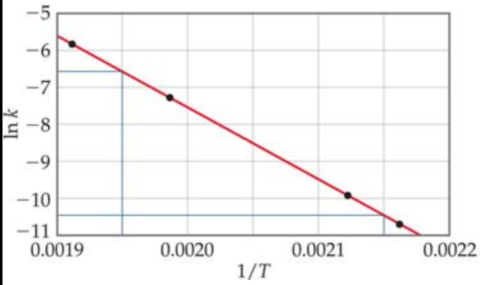
Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

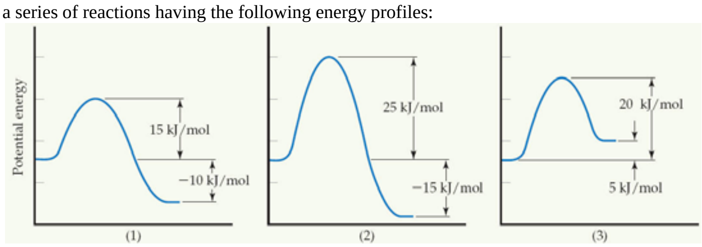
$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

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

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

Sample Exercise 14.10 Relating Energy Profiles to Activation Energies and Speed of Reaction

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.

Solution

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).

Practice Exercise

Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest.
Answer: (2) < (1) < (3) because E_a values are 40, 25, and 15 kJ/mol, respectively

Sample Exercise 14.11 Determining the Energy of Activation

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data in Figure 14.12):

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}

(a) From these data, calculate the activation energy for the reaction. **(b)** What is the value of the rate constant at 430.0 K?

Solution

Analyze: We are given rate constants, k, measured at several temperatures and asked to determine the activation energy, E_a, and the rate constant, k, at a particular temperature.
Plan: We can obtain E_a from the slope of a graph of ln k versus $1/T$. and the rate constant, k, at a particular temperature. Once we know E_a, we can use Equation 14.21 together with the given rate data to calculate the rate constant at 430.0 K.

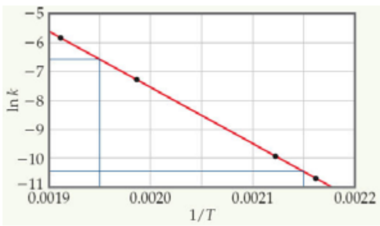
Sample Exercise 14.11 Determining the Energy of Activation

Solution (continued)

Solve: (a) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, ln k. This gives us the table shown at the right:

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

A graph of ln k versus $1/T$ results in a straight line, as shown in Figure 14.17.



◀ Figure 14.17 **Graphical determination of activation energy.** The natural logarithm of the rate constant for the rearrangement of methyl isonitrile is plotted as a function of $1/T$. The linear relationship is predicted by the Arrhenius equation giving a slope equal to $-E_a/R$.

Sample Exercise 14.11 Determining the Energy of Activation

Solution (continued)

The slope of the line is obtained by choosing two well-separated points, as shown, and using the coordinates of each:

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

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1}. Thus, the overall units for the slope are K. The slope equals $-E_a/R$. We use the value for the molar gas constant R in units of J/mol-K (Table 10.2). We thus obtain

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

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

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

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.17.

(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:

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

Thus,

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

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

Note that the units of k_1 are the same as those of k_2.

Sample Exercise 14.11 Determining the Energy of Activation

Practice Exercise

Using the data in Sample Exercise 14.11, calculate the rate constant for the rearrangement of methyl isonitrile at 280 °C.

Answer: $2.2 \times 10^{-2}\ s^{-1}$

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