WORKED EXAMPLE 12.1 Finding Relative Rates of Product Formation and Reactant Consumption

Ethanol (C_2H_5OH), the active ingredient in alcoholic beverages and an octane booster in gasoline, is produced by the fermentation of glucose. The balanced equation is

$$C_6H_{12}O_6(aq) \longrightarrow 2\ C_2H_5OH(aq) + 2\,CO_2(g)$$

(a) How is the rate of formation of ethanol related to the rate of consumption of glucose?

(b) Write this relationship in terms of $\Delta[C_2H_5OH]/\Delta t$ and $\Delta[C_6H_{12}O_6]/\Delta t$.

Strategy

To find the relative rates, look at the coefficients in the balanced chemical equation.

Solution

(a) According to the balanced equation, 2 mol of ethanol are produced for each mole of glucose that reacts. Therefore, the rate of formation of ethanol is twice the rate of consumption of glucose.

(b) Since the rate of formation of ethanol is $\Delta[C_2H_5OH]/\Delta t$ and the rate of consumption of glucose is $-\Delta[C_6H_{12}O_6]/\Delta t$ (note the minus sign), we can write

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -2\,\frac{\Delta[C_6H_{12}O_6]}{\Delta t}$$

WORKED EXAMPLE 12.1 Finding Relative Rates of Product Formation and Reactant Consumption

Continued

PROBLEM 12.1 The oxidation of iodide ion by arsenic acid, H_3AsO_4, is described by the balanced equation

$$3\,I^-(aq) + H_3AsO_4(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + H_3AsO_3(aq) + H_2O(l)$$

(a) If $-\Delta[I^-]/\Delta t = 4.8 \times 10^{-4}$ M/s, what is the value of $\Delta[I_3^-]/\Delta t$ during the same time interval?

(b) What is the average rate of consumption of H^+ during that time interval?

PROBLEM 12.2 Use the data in Table 12.1 to calculate the average rate of decomposition of N_2O_5 and the average rate of formation of O_2 during the time interval 200–300 s.

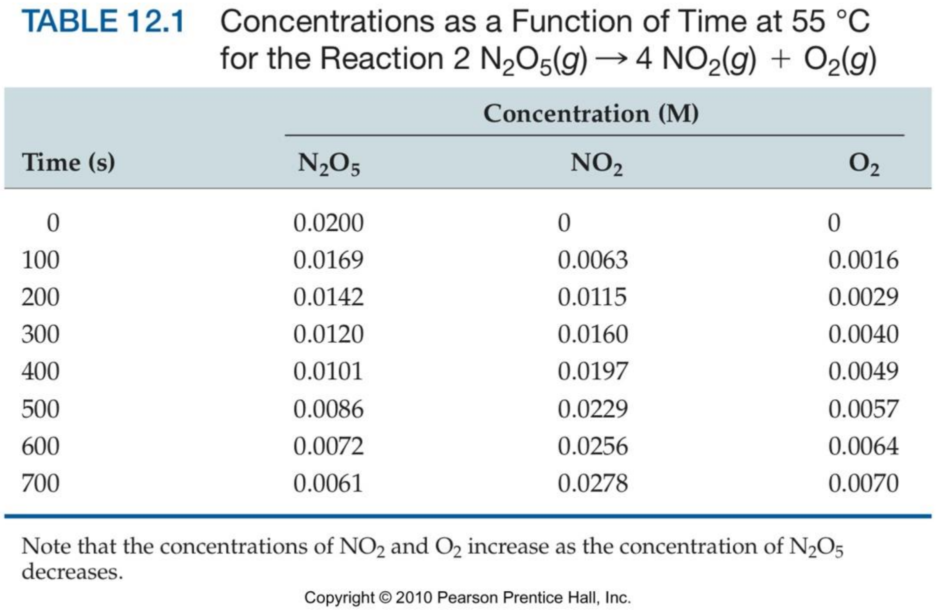


TABLE 12.1 Concentrations as a Function of Time at 55 °C for the Reaction $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$

	Concentration (M)		
Time (s)	**N_2O_5**	**NO_2**	**O_2**
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note that the concentrations of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.

WORKED EXAMPLE 12.2 Finding Reaction Order from a Rate Law

The second reaction in Table 12.2, shown in progress in Figure 12.4, is

TABLE 12.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

Reaction	Rate Law
$(CH_3)_3CBr(soln) + H_2O(soln) \rightarrow (CH_3)_3COH(soln) + H^+(soln) + Br^-(soln)$	$\text{Rate} = k[(CH_3)_3CBr]$
$HCO_2H(aq) + Br_2(aq) \rightarrow 2\,H^+(aq) + 2\,Br^-(aq) + CO_2(g)$	$\text{Rate} = k[Br_2]$
$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$	$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$
$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$	$\text{Rate} = k[H_2][I_2]$

In general, the exponents in the rate law are not the same as the stoichiometric coefficients in the balanced chemical equation for the reaction.

$$\underset{\text{Colorless}}{HCO_2H(aq)} + \underset{\text{Red}}{Br_2(aq)} \longrightarrow \underset{\text{Colorless}}{2\,H^+(aq) + 2\,Br^-(aq)} + CO_2(g)$$

What is the order of the reaction with respect to each of the reactants? What is the overall reaction order?

FIGURE 12.4

The reaction of formic acid (HCO_2H) and bromine (Br_2). As time passes (left to right), the red color of bromine disappears because Br_2 is reduced to the colorless Br^- ion. The concentration of Br_2 as a function of time, and thus the reaction rate, can be determined by measuring the intensity of the color.

WORKED EXAMPLE 12.2 Finding Reaction Order from a Rate Law

Continued

Strategy

To find the reaction order with respect to each reactant, look at the exponents in the rate law, not the coefficients in the balanced chemical equation. Then sum the exponents to obtain the overall reaction order.

Solution

The rate law for the second reaction in Table 12.2 is

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

Because HCO_2H (formic acid) does not appear in the rate law, the rate is independent of the HCO_2H concentration, and so the reaction is zeroth order in HCO_2H. Because the exponent on $[Br_2]$ (understood) is 1, the reaction is first order in Br_2. The reaction is first order overall because the sum of the exponents is 1.

PROBLEM 12.3 Consider the last two reactions in Table 12.2. What is the order of each reaction in the various reactants? What is the overall reaction order for each?

WORKED EXAMPLE 12.3 Determining a Rate Law from Initial Rates

Initial rate data for the decomposition of gaseous N_2O_5 at 55 °C are as follows:

Experiment	Initial N_2O_5	Initial Rate of Decomposition of N_2O_5 (M/s)
1	0.020	3.4×10^{-5}
2	0.050	8.5×10^{-5}

(a) What is the rate law?

(b) What is the value of the rate constant?

(c) What is the initial rate of decomposition of N_2O_5 at 55 °C when its initial concentration is 0.030 M?

Strategy

(a) The rate law for the decomposition of N_2O_5 can be written as

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]^m$$

where *m* is both the order of the reaction in N_2O_5 and the overall reaction order. To find the value of the exponent *m*, compare the change in the initial concentration of N_2O_5 for experiments 1 and 2 with the change in the initial rate.

(b) To find the value of the rate constant *k*, solve the rate law for *k* and then substitute in the data from either experiment.

(c) To calculate the initial rate, substitute the rate constant found in part **(b)** and the given initial concentration (0.030 M) into the rate law.

WORKED EXAMPLE 12.3 Determining a Rate Law from Initial Rates

Continued

Solution

(a) Comparing experiments 1 and 2 shows that an increase in the initial concentration of N_2O_5 by a factor of 2.5 increases the initial rate by a factor of 2.5:

$$\frac{[N_2O_5]_2}{[N_2O_5]_1} = \frac{0.050\ \text{M}}{0.020\ \text{M}} = 2.5 \qquad \frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{8.5 \times 10^{-5}\ \text{M/s}}{3.4 \times 10^{-5}\ \text{M/s}} = 2.5$$

The rate is proportional to the concentration of N_2O_5, and therefore the rate law is first order in N_2O_5:

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]$$

If the rate had increased by a factor of $(2.5)^2 = 6.25$, the reaction would have been second order in N_2O_5. If the rate had increased by a factor of $(2.5)^3 = 15.6$, the reaction would have been third order in N_2O_5, and so forth.

A more formal way to approach this problem is to write the rate law for each experiment:

$$(\text{Rate})_1 = k[N_2O_5]_1 = k(0.020\ \text{M})^m \qquad (\text{Rate})_2 = k[N_2O_5]_2 = k(0.050\ \text{M})^m$$

If we then divide the second equation by the first, we obtain

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k(0.050\ \text{M})^m}{k(0.020\ \text{M})^m} = (2.5)^m$$

Comparing this ratio to the ratio of the experimental rates,

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{8.5 \times 10^{-5}\ \text{M/s}}{3.4 \times 10^{-5}\ \text{M/s}} = 2.5$$

shows that the exponent m must have a value of 1. Therefore, the rate law is

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k\,[N_2O_5]$$

WORKED EXAMPLE 12.3 Determining a Rate Law from Initial Rates

Continued

(b) Solving the rate law for *k* and substituting in the data from the first experiment gives

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{3.4 \times 10^{-5}\ \text{M/s}}{0.020\ \text{M}} = 1.7 \times 10^{-3}\ \text{s}^{-1}$$

(c) Substituting the initial concentration (0.030 M) and the rate constant from part **(b)** ($1.7 \times 10^{-3}\text{s}^{-1}$) into the rate law gives

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5] = \left(\frac{1.7 \times 10^{-3}}{\text{s}}\right)(0.030\ \text{M}) = 5.1 \times 10^{-5}\ \text{M/s}$$

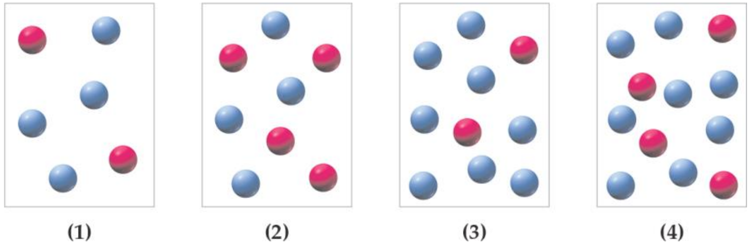
Ballpark Check

(b) It’s a good idea to check the units of the rate constant. The units of *k*, 1/s or s^{-1}, are the expected units for a first-order reaction.

(c) Because the reaction is first order in N_2O_5 and the initial concentration of N_2O_5 is 3/2 times that in experiment 1, the decomposition rate will increase by a factor of 3/2 from 3.4×10^{-5} M/s to about 5×10^{-5} M/s, which agrees with the detailed solution.

WORKED KEY CONCEPT EXAMPLE 12.4 Using the Method of Initial Rates

The relative rates of the reaction A + 2 B → products in vessels (1)–(4) are 1 : 2 : 2 : 4. Red spheres represent A molecules, and blue spheres represent B molecules.



(a) What is the order of the reaction in A and B? What is the overall reaction order?

(b) Write the rate law.

Strategy

(a) To find the reaction order, apply the method of initial rates. Count the number of A and B molecules in vessels (1)–(4), and compare the relative rates with the relative number of molecules of each type. Assume that all four vessels have the same volume, so the concentrations are proportional to the number of molecules.

(b) The rate law can be written as rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$, where the exponents m and n are the orders of the reaction in A and B, respectively.

WORKED KEY CONCEPT EXAMPLE 12.4 Using the Method of Initial Rates

Continued

Solution

(a) Compare pairs of vessels in which the concentration of one reactant varies while the concentration of the other reactant remains constant. The concentration of A molecules in vessel (2) is twice that in vessel (1) while the concentration of B remains constant. Because the reaction rate in vessel (2) is twice that in vessel (1), the rate is proportional to [A], and therefore the reaction is first order in A. When the concentration of B is doubled while the concentration of A remains constant [compare vessels (1) and (3)], the rate doubles, so the reaction is first order in B. When the concentrations of both A and B are doubled, the rate increases by a factor of 4 [compare vessels (1) and (4)], in accord with a reaction that is first order in A and first order in B. The overall reaction order is the sum of the orders in A and B, or $1 + 1 = 2$.

(b) Since the reaction is first order in A and first order in B, the rate law is rate = $k[A][B]$. Note that the exponents in the rate law differ from the coefficients in the balanced chemical equation, $A + 2B \rightarrow \text{products}$.

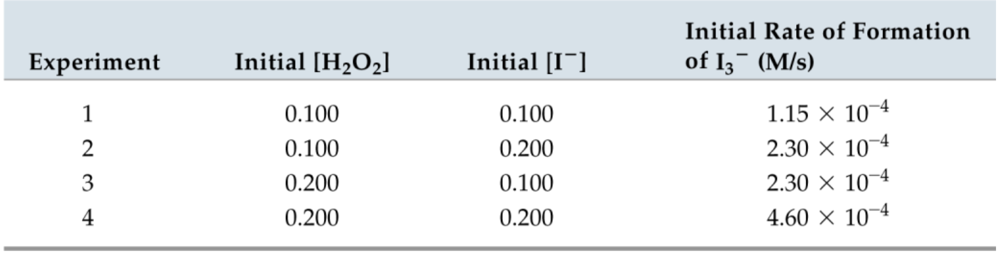
PROBLEM 12.4 The oxidation of iodide ion by hydrogen peroxide in an acidic solution is described by the balanced equation

$$H_2O_2(aq) + 3\,I^-(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + 2\,H_2O(l)$$

WORKED KEY CONCEPT EXAMPLE 12.4 Using the Method of Initial Rates

Continued

The rate of formation of the red triiodide ion, $\Delta[I_3^-]/\Delta t$, can be determined by measuring the rate of appearance of the color (Figure 12.5). Initial rate data at 25 ° C are as follows:



Experiment	Initial $[H_2O_2]$	Initial $[I^-]$	Initial Rate of Formation of I_3^- (M/s)
1	0.100	0.100	1.15×10^{-4}
2	0.100	0.200	2.30×10^{-4}
3	0.200	0.100	2.30×10^{-4}
4	0.200	0.200	4.60×10^{-4}

(a) What is the rate law for the formation of I_3^-?
(b) What is the value of the rate constant?
(c) What is the initial rate of formation of I_3^- when the initial concentrations are $[H_2O_2]$ = 0.300 M and $[I^-]$ = 0.400 M?

FIGURE 12.5
A sequence of photographs showing the progress of the reaction of hydrogen peroxide (H_2O_2) and iodide ion (I^-). As time passes (left to right), the red color due to the triiodide ion (I_3^-) increases in intensity.

WORKED KEY CONCEPT EXAMPLE 12.4 Using the Method of Initial Rates

Continued

PROBLEM 12.5 What are the units of the rate constant for each of the reactions in Table 12.2?

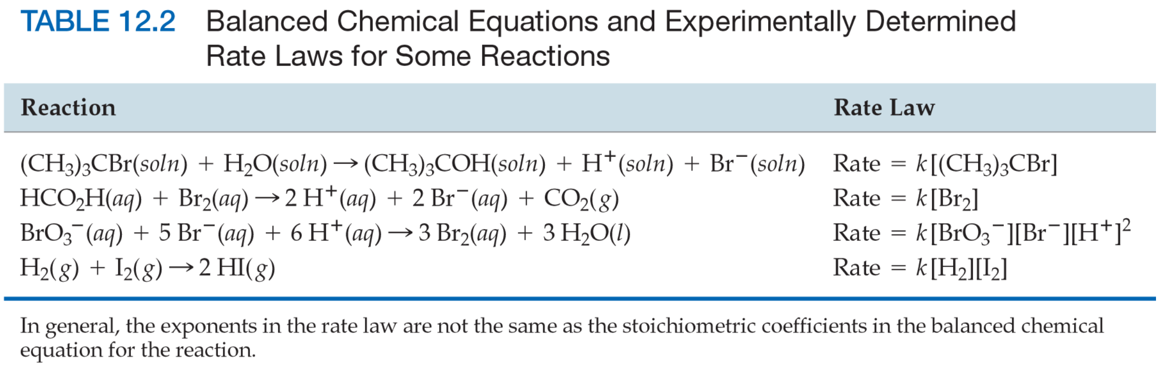
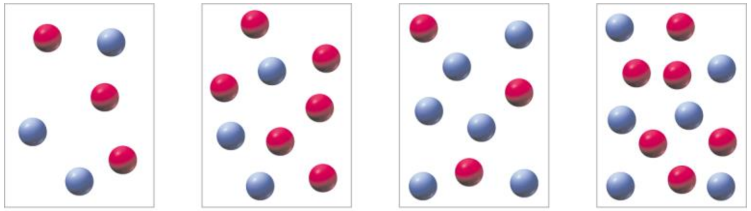


TABLE 12.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

Reaction	Rate Law
$(CH_3)_3CBr(soln) + H_2O(soln) \rightarrow (CH_3)_3COH(soln) + H^+(soln) + Br^-(soln)$	Rate $= k[(CH_3)_3CBr]$
$HCO_2H(aq) + Br_2(aq) \rightarrow 2\,H^+(aq) + 2\,Br^-(aq) + CO_2(g)$	Rate $= k[Br_2]$
$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$	Rate $= k[BrO_3^-][Br^-][H^+]^2$
$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$	Rate $= k[H_2][I_2]$

In general, the exponents in the rate law are not the same as the stoichiometric coefficients in the balanced chemical equation for the reaction.

KEY CONCEPT PROBLEM 12.6 The relative rates of the reaction A + B → products in vessels (1)–(4) are 1 : 1 : 4 : 4. Red spheres represent A molecules, and blue spheres represent B molecules.



(1) (2) (3) (4)

(a) What is the order of the reaction in A and B? What is the overall reaction order?

(b) Write the rate law.

WORKED EXAMPLE 12.5 Using the Integrated Rate Law for a First-Order Reaction

The decomposition of hydrogen peroxide in dilute sodium hydroxide solution is described by the equation

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

The reaction is first order in H_2O_2, the rate constant for the consumption of H_2O_2 at 20 °C is $1.8 \times 10^{-5} s^{-1}$, and the initial concentration of H_2O_2 is 0.30 M.

(a) What is the concentration of H_2O_2 after 4.00 h?

(b) How long will it take for the H_2O_2 concentration to drop to 0.12 M?

(c) How long will it take for 90% of the H_2O_2 to decompose?

Strategy

Since this reaction has a first-order rate law, $-\Delta[H_2O_2]/\,\Delta t = k[H_2O_2]$, we can use the corresponding concentration–time equation for a first-order reaction:

$$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt$$

In each part, we substitute the known quantities into this equation and solve for the unknown.

Solution

(a) Because k has units of s^{-1}, we must first convert the time from hours to seconds:

$$t = (4.00\ \text{h})\left(\frac{60\ \text{min}}{\text{h}}\right)\left(\frac{60\ \text{s}}{\text{min}}\right) = 1.44 \times 10^4\ \text{s}$$

Then, substitute the values of $[H_2O_2]_0$, k, and t into the concentration–time equation:

$$\ln \frac{[H_2O_2]_t}{0.30\ \text{M}} = -(1.8 \times 10^{-5}\ \text{s}^{-1})(1.44 \times 10^4\ \text{s}) = -0.259$$

WORKED EXAMPLE 12.5 Using the Integrated Rate Law for a First-Order Reaction

Continued

Taking the antilogarithm (antiln) of both sides gives

$$\frac{[H_2O_2]_t}{0.30\ \text{M}} = e^{-0.259} = 0.772$$

$$[H_2O_2]_t = (0.772)(0.30\ \text{M}) = 0.23\ \text{M}$$

(b) First, solve the concentration–time equation for the time:

$$t = -\frac{1}{k}\ \ln\frac{[H_2O_2]_t}{[H_2O_2]_0}$$

Then evaluate the time by substituting the concentrations and the value of *k*:

$$t = -\left(\frac{1}{1.8 \times 10^{-5}\ \text{s}^{-1}}\right)\left(\ln\frac{0.12\ \text{M}}{0.30\ \text{M}}\right) = -\left(\frac{1}{1.8 \times 10^{-5}\ \text{s}^{-1}}\right)(-0.916) = 5.1 \times 10^4\ \text{s}$$

Thus, the H_2O_2 concentration reaches 0.12 M at a time of 5.1×10^4s (14 h).

(c) When 90% of the H_2O_2 has decomposed, 10% remains. Therefore,

$$\frac{[H_2O_2]_t}{[H_2O_2]_0} = \frac{(0.10)(0.30\ \text{M})}{0.30\ \text{M}} = 0.10$$

The time required for 90% decomposition is

$$t = -\left(\frac{1}{1.8 \times 10^{-5}\ \text{s}^{-1}}\right)(\ln 0.10) = -\left(\frac{1}{1.8 \times 10^{-5}\ \text{s}^{-1}}\right)(-2.30) = 1.3 \times 10^5\ \text{s}\ (36\ \text{h})$$

Ballpark Check

The concentration of H_2O_2 (0.23 M) after 4.00 h is less than the initial concentration (0.30 M). A longer period of time (14 h) is required for the concentration to drop to 0.12 M, and still more time (36 h) is needed for the concentration to fall to 0.030 M (10% of the original concentration). These results look reasonable. A plot of $[H_2O_2]$ versus time would exhibit an exponential decay of the H_2O_2 concentration, as expected for a first-order reaction.

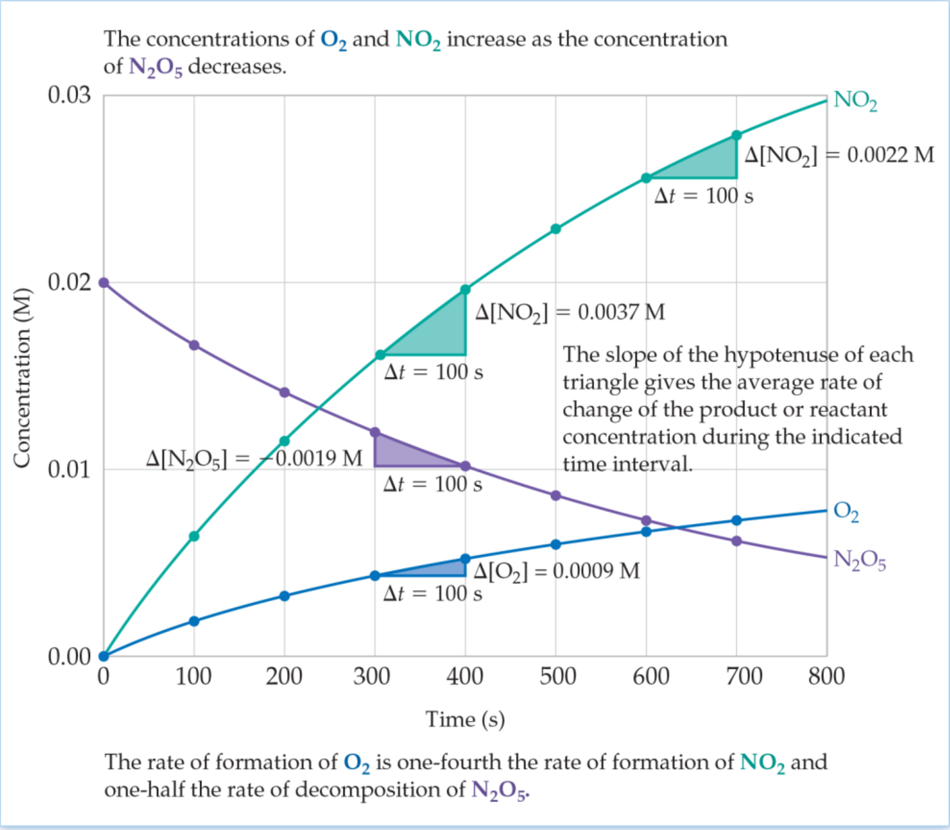
WORKED EXAMPLE 12.6 Plotting Data for a First-Order Reaction

Experimental concentration-versus-time data for the decomposition of gaseous N_2O_5 at 55 °C are listed in Table 12.1 and are plotted in Figure 12.1. Use those data to confirm that the decomposition of N_2O_5 is a first-order reaction. What is the value of the rate constant for the consumption of N_2O_5?

TABLE 12.1 Concentrations as a Function of Time at 55 °C for the Reaction $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

	Concentration (M)		
Time (s)	**N_2O_5**	**NO_2**	**O_2**
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note that the concentrations of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.



The concentrations of O_2 and NO_2 increase as the concentration of N_2O_5 decreases.

The slope of the hypotenuse of each triangle gives the average rate of change of the product or reactant concentration during the indicated time interval.

The rate of formation of O_2 is one-fourth the rate of formation of NO_2 and one-half the rate of decomposition of N_2O_5.

FIGURE 12.1

Concentrations measured as a function of time when gaseous N_2O_5 at an initial concentration of 0.0200 M decomposes to gaseous NO_2 and O_2 at 55 °C.

WORKED EXAMPLE 12.6 Plotting Data for a First-Order Reaction

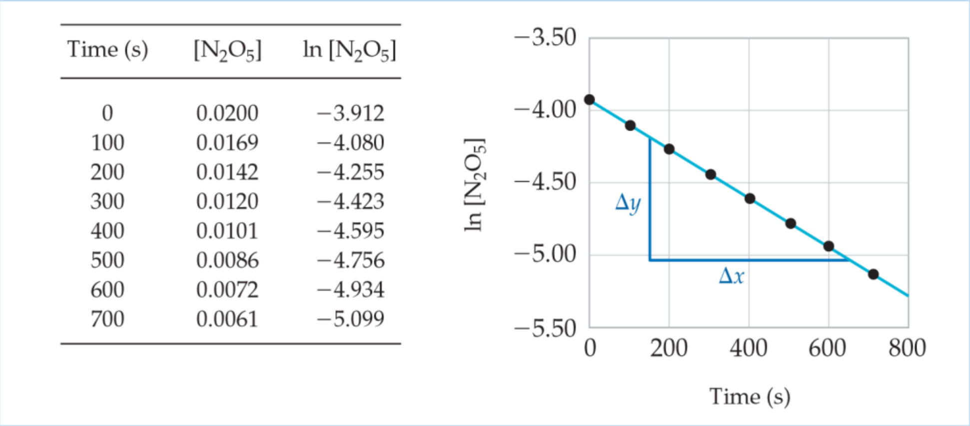
Continued

Strategy

To confirm that the reaction is first order, check to see whether a plot of ln [N_2O_5] versus time gives a straight line. The rate constant for a first-order reaction equals minus the slope of the straight line.

Solution

Values of ln [N_2O_5] are listed in the following table and are plotted versus time in the graph:



Time (s)	[N_2O_5]	ln [N_2O_5]
0	0.0200	−3.912
100	0.0169	−4.080
200	0.0142	−4.255
300	0.0120	−4.423
400	0.0101	−4.595
500	0.0086	−4.756
600	0.0072	−4.934
700	0.0061	−5.099

Because the data points lie on a straight line, the reaction is first order in N_2O_5. The slope of the line can be determined from the coordinates of any two widely separated points on the line, and the rate constant k can be calculated from the slope:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{(-5.02) - (-4.17)}{650\ \text{s} - 150\ \text{s}} = \frac{-0.85}{500\ \text{s}} = -1.7 \times 10^{-3}\ \text{s}^{-1}$$

$$k = -(\text{Slope}) = 1.7 \times 10^{-3}\ \text{s}^{-1}$$

Note that the slope is negative, k is positive, and the value of k agrees with the value obtained earlier in Worked Example 12.3 by the method of initial rates.

WORKED EXAMPLE 12.6 Plotting Data for a First-Order Reaction

Continued

PROBLEM 12.7 In acidic aqueous solution, the purple complex ion $Co(NH_3)_5Br^{2+}$ undergoes a slow reaction in which the bromide ion is replaced by a water molecule, yielding the pinkish-orange complex ion $Co(NH_3)_5(H_2O)^{3+}$:

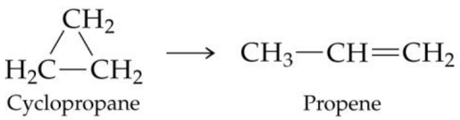
$$\underset{\text{Purple}}{Co(NH_3)_5Br^{2+}(aq)} + H_2O(l) \longrightarrow \underset{\text{Pinkish-orange}}{Co(NH_3)_5(H_2O)^{3+}(aq)} + Br^-(aq)$$

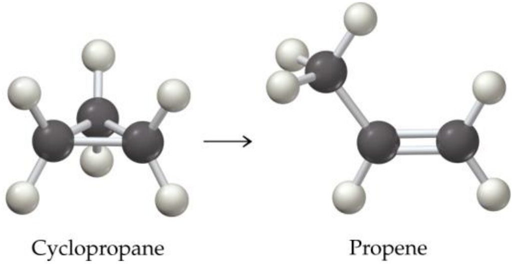
The reaction is first order in $Co(NH_3)_5Br^{2+}$, the rate constant at 25 °C is $6.3 \times 10^{-6}\ s^{-1}$, and the initial concentration of $Co(NH_3)_5Br^{2+}$ is 0.100 M.

(a) What is its molarity after a reaction time of 10.0 h?

(b) How many hours are required for 75% of the $Co(NH_3)_5Br^{2+}$ to react?

PROBLEM 12.8 At high temperatures, cyclopropane is converted to propene, the material from which polypropylene plastics are made:





Given the following concentration data, test whether the reaction is first order and calculate the value of the rate constant.

Time (min)	0	5.0	10.0	15.0	20.0
Cyclopropane	0.098	0.080	0.066	0.054	0.044

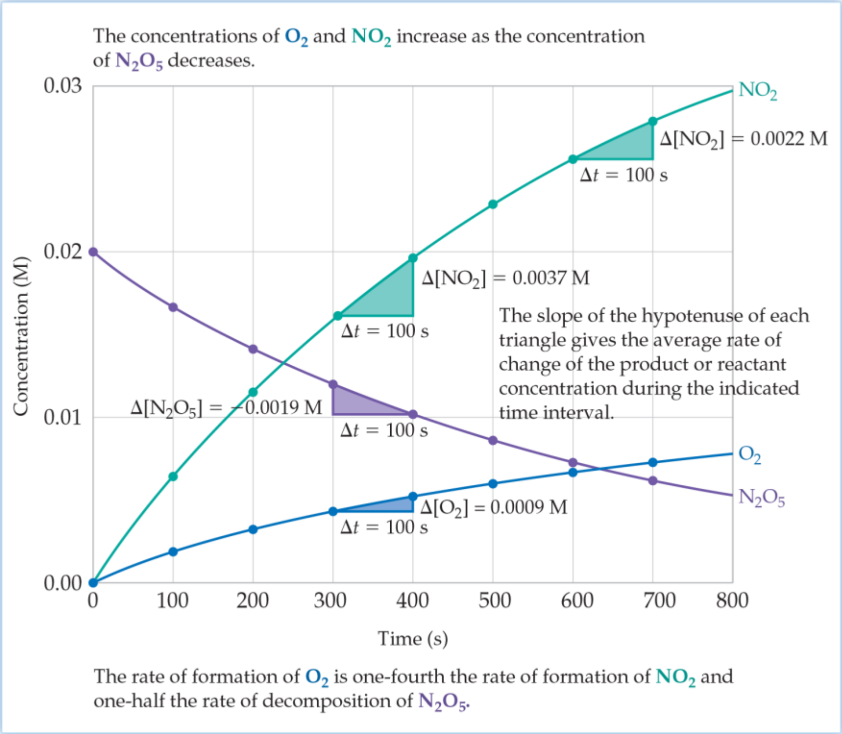
WORKED EXAMPLE 12.7 Determining the Half-Life for a First-Order Reaction

(a) Estimate the half-life for the decomposition of gaseous N_2O_5 at 55 °C from the concentration-versus-time plot in Figure 12.1.

(b) Calculate the half-life from the rate constant ($1.7 \times 10^{-3} s^{-1}$).

(c) If the initial concentration of N_2O_5 is 0.020 M, what is the concentration of N_2O_5 after five half-lives?

(d) How long will it take for the N_2O_5 concentration to fall to 12.5% of its initial value?



The concentrations of O_2 and NO_2 increase as the concentration of N_2O_5 decreases.

The slope of the hypotenuse of each triangle gives the average rate of change of the product or reactant concentration during the indicated time interval.

The rate of formation of O_2 is one-fourth the rate of formation of NO_2 and one-half the rate of decomposition of N_2O_5.

FIGURE 12.1
Concentrations measured as a function of time when gaseous N_2O_5 at an initial concentration of 0.0200 M decomposes to gaseous NO_2 and O_2 at 55 °C.

WORKED EXAMPLE 12.7 Determining the Half-Life for a First-Order Reaction

Continued

Strategy

Because the decomposition of N_2O_5 is a first-order reaction (Worked Example 12.6), we can determine its half-life either from the time required for $[N_2O_5]$ to drop to 1/2 of its initial value or from the equation $t_{1/2} = 0.693/k$. To find $[N_2O_5]$ after n half-lives, multiply its initial concentration by $(1/2)^n$ because $[N_2O_5]$ drops by a factor of 2 during each successive half-life.

Solution

(a) Figure 12.1 shows that the concentration of N_2O_5 falls from 0.020 M to 0.010 M during a time period of approximately 400 s. At 800 s, $[N_2O_5]$ has decreased by another factor of 2, to 0.0050 M. Therefore, $t_{1/2} \approx 400$ s.

(b) Based on the value of the rate constant,

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{1.7 \times 10^{-3}\ \text{s}^{-1}} = 4.1 \times 10^{2}\ \text{s}\ (6.8\ \text{min})$$

(c) At $5t_{1/2}$, $[N_2O_5]$ will be $(1/2)^5 = 1/32$ of its initial value. Therefore,

$$[N_2O_5] = \frac{0.020\ \text{M}}{32} = 0.000\,62\ \text{M}$$

(d) Since 12.5% of the initial concentration corresponds to 1/8 or $(1/2)^3$ of the initial concentration, the time required is three half-lives:

$$t = 3t_{1/2} = 3\,(4.1 \times 10^{2}\ \text{s}) = 1.2 \times 10^{3}\ \text{s}\ (20\ \text{min})$$

WORKED EXAMPLE 12.7 Determining the Half-Life for a First-Order Reaction

Continued

PROBLEM 12.9 Consider the first-order decomposition of H_2O_2 in Worked Example 12.5.

(a) What is the half-life (in hours) of the reaction at 20 °C?

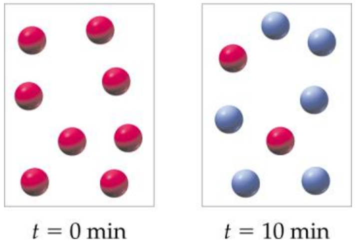
(b) What is the molarity of H_2O_2 after four half-lives if the initial concentration of H_2O_2 is 0.30 M?

(c) How many hours will it take for the concentration to drop to 25% of its initial value?

KEY CONCEPT PROBLEM 12.10 Consider the first-order reaction A → B in which A molecules (red spheres) are converted to B molecules (blue spheres).

(a) Given the following pictures at $t = 0$ min and $t = 10$ min, what is the half-life of the reaction?

(b) Draw a picture that shows the number of A and B molecules present at $t = 15$ min.



WORKED EXAMPLE 12.8 Calculating a Half-Life from a Decay Constant

The decay constant for sodium-24, a radioisotope used medically in blood studies, is $4.63 \times 10^{-2}\ \text{h}^{-1}$. What is the half-life of ^{24}Na?

Strategy

Half-life can be calculated from the decay constant by using the equation

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

Solution

Substituting the values $k = 4.63 \times 10^{-2}\ \text{h}^{-1}$ and $\ln 2 = 0.693$ into the equation gives

$$t_{1/2} = \frac{0.693}{4.63 \times 10^{-2}\ \text{h}^{-1}} = 15.0\ \text{h}$$

WORKED EXAMPLE 12.9 Calculating a Decay Constant from a Half-Life

The half-life of radon-222, a radioactive gas of concern as a health hazard in some homes, is 3.82 days. What is the decay constant of ^{222}Rn?

Strategy

A decay constant can be calculated from the half-life by using the equation

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

Solution

Substituting the values $t_{1/2} = 3.82$ days and $\ln 2 = 0.693$ into the equation gives

$$k = \frac{0.693}{3.82 \text{ days}} = 0.181 \text{ day}^{-1}$$

WORKED EXAMPLE 12.10 Using Half-Life to Calculate an Amount Remaining

Phosphorus-32, a radioisotope used in leukemia therapy, has a half-life of 14.26 days. What percent of a sample remains after 35.0 days?

Strategy

The ratio of remaining (N_t) and initial (N_0) amounts of a radioactive sample at time t is given by the equation

$$\ln\left(\frac{N_t}{N_0}\right) = (-\ln 2)\left(\frac{t}{t_{1/2}}\right)$$

Taking N_0 as 100%, N_t can then be obtained.

Solution

Substituting values for t and for $t_{1/2}$ into the equation gives

$$\ln\left(\frac{N_t}{N_0}\right) = (-0.693)\left(\frac{35.0 \text{ days}}{14.26 \text{ days}}\right) = -1.70$$

Taking the natural antilog of –1.70 then gives the ratio N_t/N_0:

$$\frac{N_t}{N_0} = \text{antiln}\,(-1.70) = e^{-1.70} = 0.183$$

Since the initial amount of ^{32}P was 100%, we can set $N_0 = 100\%$ and solve for N_t:

$$\frac{N_t}{100\%} = 0.183 \quad \text{so} \quad N_t = (0.183)(100\%) = 18.3\%$$

After 35.0 days, 18.3% of a ^{32}P sample remains and 100% – 18.3% = 81.7% has decayed.

WORKED EXAMPLE 12.11 Using Decay Rates to Calculate a Half-Life

A sample of ^{41}Ar, a radioisotope used to measure the flow of gases from smokestacks, decays initially at a rate of 34,500 disintegrations/min, but the decay rate falls to 21,500 disintegrations/min after 75.0 min. What is the half-life of ^{41}Ar?

Strategy

The half-life of a radioactive decay process is given by finding $t_{1/2}$ in the equation

$$\ln\left(\frac{N_t}{N_0}\right) = (-\ln 2)\left(\frac{t}{t_{1/2}}\right)$$

In the present instance, though, we are given decay rates at two different times rather than values of N_t and N_0. Nevertheless, for a first-order process like radioactive decay, in which rate = kN, the ratio of the decay rate at any time t to the decay rate at time $t = 0$ is the same as the ratio of N_t to N_0:

$$\frac{\text{Decay rate at time } t}{\text{Decay rate at time } t = 0} = \frac{kN_t}{kN_0} = \frac{N_t}{N_0}$$

Solution

Substituting the proper values into the equation gives

$$\ln\left(\frac{21{,}500}{34{,}500}\right) = (-0.693)\left(\frac{75.0 \text{ min}}{t_{1/2}}\right) \quad \text{or} \quad -0.473 = \frac{-52.0 \text{ min}}{t_{1/2}}$$

$$\text{so} \qquad t_{1/2} = \frac{-52.0 \text{ min}}{-0.473} = 110 \text{ min}$$

The half-life of ^{41}Ar is 110 min.

WORKED EXAMPLE 12.11 Using Decay Rates to Calculate a Half-Life

Continued

PROBLEM 12.11 The decay constant for mercury-197, a radioisotope used medically in kidney scans, is $1.08 \times 10^{-2}\ \text{h}^{-1}$. What is the half-life of mercury-197?

PROBLEM 12.12 The half-life of carbon-14 is 5715 years. What is its decay constant?

PROBLEM 12.13 What percentage of $^{14}_{6}\text{C}(t_{1/2} = 5715\ \text{years})$ remains in a sample estimated to be 16,230 years old?

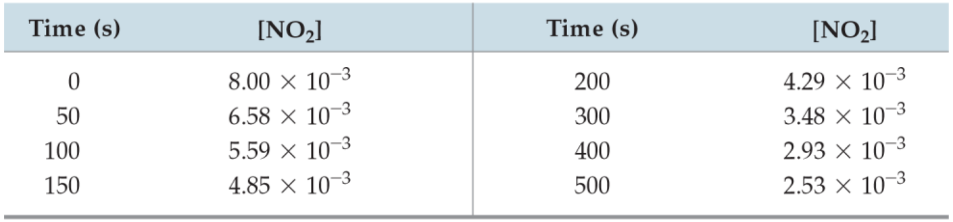
PROBLEM 12.14 What is the half-life of iron-59, a radioisotope used medically in the diagnosis of anemia, if a sample with an initial decay rate of 16,800 disintegrations/min decays at a rate of 10,860 disintegrations/min after 28.0 days?

WORKED EXAMPLE 12.12 Determining Reaction Order Graphically

At elevated temperatures, nitrogen dioxide decomposes to nitric oxide and molecular oxygen:

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

Concentration–time data for the consumption of NO_2 at 300 °C are as follows:



Time (s)	$[NO_2]$	Time (s)	$[NO_2]$
0	8.00×10^{-3}	200	4.29×10^{-3}
50	6.58×10^{-3}	300	3.48×10^{-3}
100	5.59×10^{-3}	400	2.93×10^{-3}
150	4.85×10^{-3}	500	2.53×10^{-3}

(a) Is the reaction first order or second order?
(b) What is the value of the rate constant?
(c) What is the concentration of NO_2 at $t = 20.0$ min
(d) What is the half-life of the reaction when the initial concentration of NO_2 is 6.00×10^{-3} M?
(e) What is $t_{1/2}$ when $[NO_2]_0$ is 3.00×10^{-3} M?

Strategy

To determine whether the reaction is first order or second order, calculate values of ln $[NO_2]$ and $1/[NO_2]$ and then graph these values versus time. The rate constant can be obtained from the slope of the straight-line plot, and concentrations and half-lives can be calculated from the appropriate equation in Table 12.4.

WORKED EXAMPLE 12.12 Determining Reaction Order Graphically

Continued

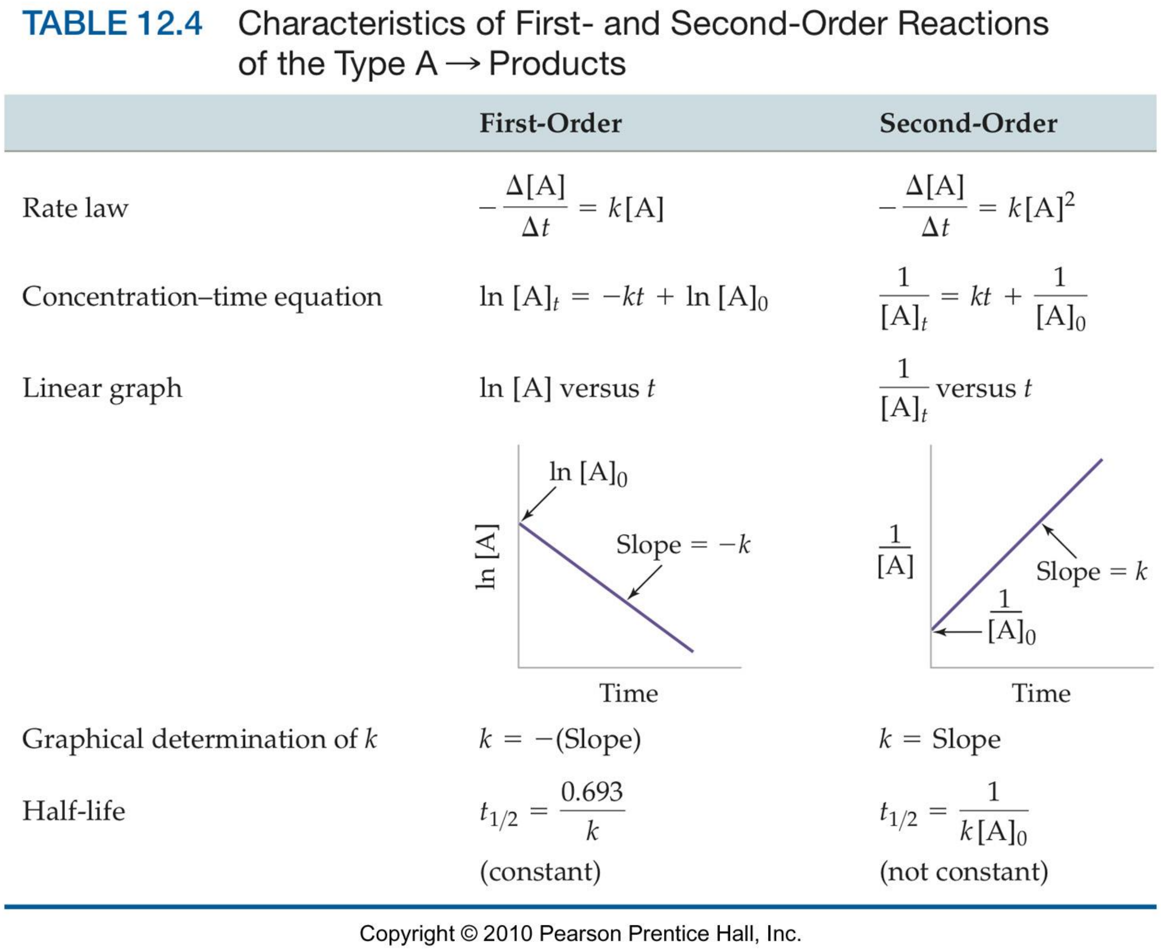


TABLE 12.4 Characteristics of First- and Second-Order Reactions of the Type A $\longrightarrow$ Products

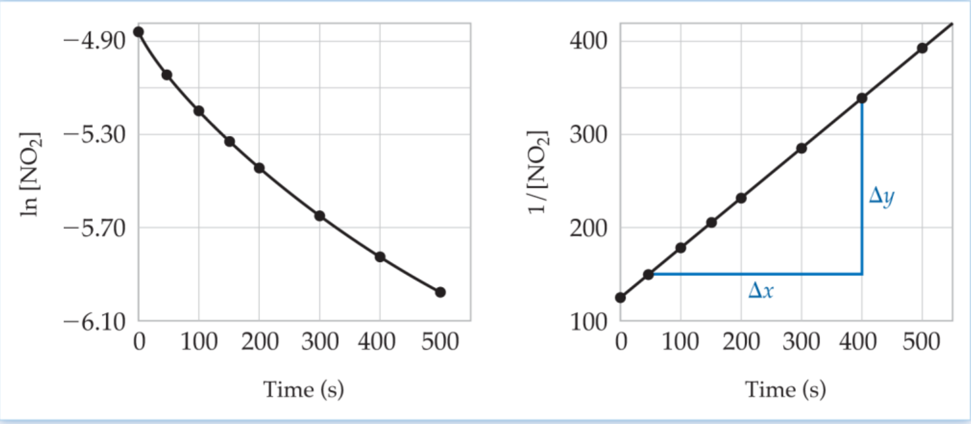
	First-Order	Second-Order
Rate law	$-\dfrac{\Delta[A]}{\Delta t} = k[A]$	$-\dfrac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration–time equation	$\ln [A]_t = -kt + \ln [A]_0$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$
Linear graph	$\ln [A]$ versus t	$\dfrac{1}{[A]_t}$ versus t
Graphical determination of k	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \dfrac{0.693}{k}$ (constant)	$t_{1/2} = \dfrac{1}{k[A]_0}$ (not constant)

WORKED EXAMPLE 12.12 Determining Reaction Order Graphically

Continued

Solution

Time (s)	$[NO_2]$	$\ln [NO_2]$	$1/[NO_2]$
0	8.00×10^{-3}	−4.828	125
50	6.58×10^{-3}	−5.024	152
100	5.59×10^{-3}	−5.187	179
150	4.85×10^{-3}	−5.329	206
200	4.29×10^{-3}	−5.451	233
300	3.48×10^{-3}	−5.661	287
400	2.93×10^{-3}	−5.833	341
500	2.53×10^{-3}	−5.980	395



WORKED EXAMPLE 12.12 Determining Reaction Order Graphically

Continued

(a) The plot of ln $[NO_2]$ versus time is curved, but the plot of $1/[NO_2]$ versus time is a straight line. The reaction is therefore second order in NO_2.

(b) The rate constant equals the slope of the straight line in the plot of $1/[NO_2]$ versus time, which we can estimate from the coordinates of two widely separated points on the line:

$$k = \text{Slope} = \frac{\Delta y}{\Delta x} = \frac{340\ \text{M}^{-1} - 150\ \text{M}^{-1}}{400\ \text{s} - 50\ \text{s}} = \frac{190\ \text{M}^{-1}}{350\ \text{s}} = 0.54/(\text{M}\cdot\text{s})$$

(c) The concentration of NO_2 at $t = 20.0$ min (1.20×10^3 s) can be calculated using the integrated rate law:

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0}$$

Substituting the values of k, t, and $[NO_2]_0$ gives

$$\frac{1}{[NO_2]_t} = \left(\frac{0.54}{\text{M}\cdot\text{s}}\right)\left(1.20 \times 10^3\ \text{s}\right) + \frac{1}{8.00 \times 10^{-3}\ \text{M}}$$

$$= \frac{648}{\text{M}} + \frac{125}{\text{M}} = \frac{773}{\text{M}}$$

$$[NO_2]_t = 1.3 \times 10^{-3}\ \text{M}$$

(d) The half-life of this second-order reaction can be calculated from the rate constant and the initial concentration of NO_2 (6.00×10^{-3} M):

$$t_{1/2} = \frac{1}{k[NO_2]_0} = \frac{1}{\left(\frac{0.54}{\text{M}\cdot\text{s}}\right)(6.00 \times 10^{-3}\ \text{M})} = 3.1 \times 10^2\ \text{s}$$

(e) When $[NO_2]_0$ is 3.00×10^{-3} M, $t_{1/2} = 6.2 \times 10^2$ s (twice as long as when $[NO_2]_0$ is 6.00×10^{-3} M because $[NO_2]_0$ is now smaller by a factor of 2).

WORKED EXAMPLE 12.12 Determining Reaction Order Graphically

Continued

PROBLEM 12.15 Hydrogen iodide gas decomposes at 410 ° C:

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

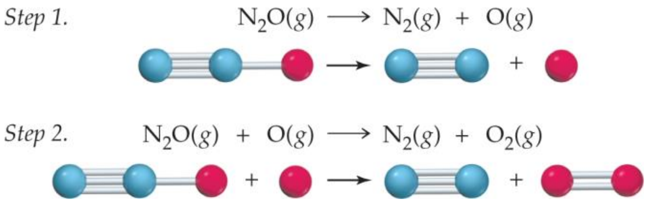
The following data describe this decomposition:

Time (min)	0	20	40	60	80
[HI]	0.500	0.382	0.310	0.260	0.224

(a) Is the reaction first order or second order?
(b) What is the value of the rate constant for consumption of HI?
(c) At what time (in minutes) does the HI concentration reach 0.100 M?
(d) In how many minutes does the HI concentration drop from 0.400 M to 0.200 M?

WORKED EXAMPLE 12.13 Identifying Intermediates and Molecularity in a Reaction Mechanism

The following two-step mechanism has been proposed for the gas-phase decomposition of nitrous oxide (N_2O):



Step 1. $N_2O(g) \longrightarrow N_2(g) + O(g)$

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

(a) Write the chemical equation for the overall reaction.
(b) Identify any reaction intermediates.
(c) What is the molecularity of each of the elementary reactions?
(d) What is the molecularity of the overall reaction?

Strategy

To find the overall reaction, sum the elementary steps. To identify intermediates and molecularity, look at the individual steps.

Solution

(a) The overall reaction is the sum of the two elementary steps:

Step 1.	$N_2O(g) \longrightarrow N_2(g) + O(g)$	Elementary reaction
Step 2.	$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$	Elementary reaction
	$2\,N_2O(g) + \cancel{O(g)} \longrightarrow 2\,N_2(g) + \cancel{O(g)} + O_2(g)$	
	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$	Overall reaction

(b) The oxygen atom is a reaction intermediate because it is formed in the first elementary step and consumed in the second step.

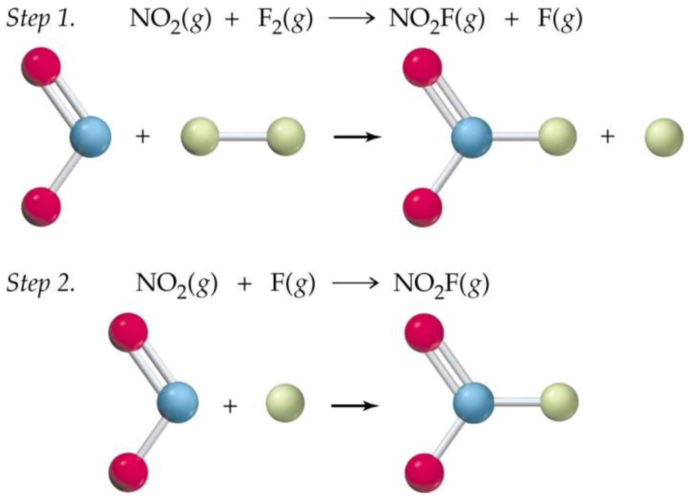
(c) The first elementary reaction is unimolecular because it involves a single reactant molecule. The second step is bimolecular because it involves two reactant atoms or molecules.

(d) It's inappropriate to use the word *molecularity* in connection with the overall reaction because the overall reaction does not describe an individual molecular event. Only an elementary reaction can have a molecularity.

WORKED EXAMPLE 12.13 Identifying Intermediates and Molecularity in a Reaction Mechanism

Continued

PROBLEM 12.16 A suggested mechanism for the reaction of nitrogen dioxide and molecular fluorine is



Step 1. $NO_2(g) + F_2(g) \longrightarrow NO_2F(g) + F(g)$

Step 2. $NO_2(g) + F(g) \longrightarrow NO_2F(g)$

(a) Write the chemical equation for the overall reaction, and identify any reaction intermediates.

(b) What is the molecularity of each elementary reaction?

WORKED EXAMPLE 12.14 Suggesting a Mechanism Given the Rate Law: Reactions with an Initial Slow Step

The following reaction has a second-order rate law:

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

Devise a possible reaction mechanism.

Strategy

The reaction doesn’t occur in a single elementary step because, if it did, the rate law would be third order: Rate = $k[H_2][Icl]^2$. The observed rate law will be obtained if the rate-determining step involves the bimolecular reaction of H_2 and ICl.

Solution

A plausible sequence of elementary steps is

$$\begin{array}{ll} H_2(g) + ICl(g) \xrightarrow{k_1} HI(g) + HCl(g) & \text{Slower, rate-determining} \\ HI(g) + ICl(g) \xrightarrow{k_2} I_2(g) + HCl(g) & \text{Faster} \\ \hline H_2(g) + 2\,ICl(g) \longrightarrow I_2(g) + 2\,HCl(g) & \text{Overall reaction} \end{array}$$

The rate law predicted by this mechanism, rate = $k[H_2][Icl]$, agrees with the observed rate law.

WORKED EXAMPLE 12.15 Supporting a Mechanism Given the Rate Law: Reactions with an Initial Fast Step

The experimental rate law for the decomposition of ozone is second order in ozone and inverse first order in molecular oxygen:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \qquad \text{Rate} = -\frac{\Delta[O_3]}{\Delta t} = k\,\frac{[O_3]^2}{[O_2]}$$

Show that the following mechanism is consistent with the experimental rate law, and relate the observed rate constant *k* to the rate constants for the elementary reactions:

$$\begin{array}{rll} O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) & & \text{Faster, reversible} \\ O(g) + O_3(g) \xrightarrow{k_2} 2\,O_2(g) & & \text{Slower, rate-determining} \\ \hline 2\,O_3(g) \longrightarrow 3\,O_2(g) & & \text{Overall reaction} \end{array}$$

Strategy

To show that the mechanism is consistent with the experiment, we must derive the rate law predicted by the mechanism and compare it with the experimental rate law. If we assume that the faster, reversible step is at equilibrium, we can eliminate the concentration of the intermediate O atoms from the predicted rate law.

Solution

The rate law for the rate-determining step is rate = $k_2[O][O_3]$, but the stoichiometry of the reaction indicates that the overall rate of consumption of ozone is twice the rate of the rate-determining step:

$$\text{Rate} = -\frac{\Delta[O_3]}{\Delta t} = 2k_2[O][O_3]$$

(When one O atom and one O_3 molecule react in the rate-determining step, two O_3 molecules are consumed in the overall reaction.)

WORKED EXAMPLE 12.15 Supporting a Mechanism Given the Rate Law: Reactions with an Initial Fast Step

Continued

The rates of the forward and reverse reactions in the faster, reversible step are given by

$$\text{Rate}_{\text{forward}} = k_1[\text{O}_3] \qquad \text{Rate}_{\text{reverse}} = k_{-1}[\text{O}_2][\text{O}]$$

Assuming that the first step is at equilibrium, we can equate the rates of the forward and reverse reactions and then solve for the concentration of the intermediate O atoms:

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}] \qquad \text{so,}\ [\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

Substituting this expression for [O] into the predicted rate law for overall consumption of ozone gives the predicted rate law in terms of only reactants and products:

$$\text{Rate} = -\frac{\Delta[\text{O}_3]}{\Delta t} = 2k_2[\text{O}][\text{O}_3] = 2k_2\frac{k_1}{k_{-1}}\frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Because the predicted and experimental rate laws have the same reaction orders in O_3 and O_2, the proposed mechanism is consistent with the experimental rate law and is a plausible mechanism for the reaction. Comparison of the predicted and experimental rate laws indicates that the observed rate constant k equals $2k_2k_1/k_{-1}$.

PROBLEM 12.18 The following reaction has a first-order rate law:

$$\text{Co(CN)}_5(\text{H}_2\text{O})^{2-}(aq) + \text{I}^-(aq) \longrightarrow \text{Co(CN)}_5\text{I}^{3-}(aq) + \text{H}_2\text{O}(l)$$

$$\text{Rate} = k[\text{Co(CN)}_5(\text{H}_2\text{O})^{2-}]$$

Suggest a possible reaction mechanism, and show that your mechanism agrees with the observed rate law.

WORKED EXAMPLE 12.15 Supporting a Mechanism Given the Rate Law: Reactions with an Initial Fast Step

Continued

PROBLEM 12.19 The following mechanism has been proposed for the oxidation of nitric oxide to nitrogen dioxide:

$$NO(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3(g) \qquad \text{Faster, reversible}$$

$$NO_3(g) + NO(g) \xrightarrow{k_2} 2\,NO_2(g) \qquad \text{Slower, rate-determining}$$

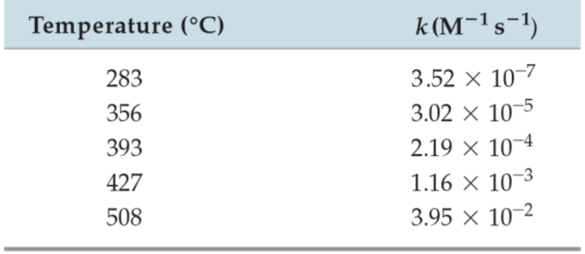
The experimental rate law for the overall reaction is

$$\text{Rate} = -\frac{\Delta[NO]}{\Delta t} = k[NO]^2[O_2]$$

(a) Write a balanced equation for the overall reaction.
(b) Show that the proposed mechanism is consistent with the experimental rate law.
(c) Relate the rate constant *k* to the rate constants for the elementary reactions.

WORKED EXAMPLE 12.16 Using the Arrhenius Equation

Rate constants for the gas-phase decomposition of hydrogen iodide, $2\ HI(g) \rightarrow H_2(g) + I_2(g)$, are listed in the following table:



Temperature (°C)	$k\ (M^{-1}\ s^{-1})$
283	3.52×10^{-7}
356	3.02×10^{-5}
393	2.19×10^{-4}
427	1.16×10^{-3}
508	3.95×10^{-2}

(a) Find the activation energy (in kJ/mol) using all five data points.
(b) Calculate E_a from the rate constants at 283 °C and 508 °C.
(c) Given the rate constant at 283 °C and the value of E_a obtained in part **(b)**, what is the rate constant at 293 °C?

Strategy

(a) The activation energy E_a can be determined from the slope of a linear plot of ln k versus $1/T$.
(b) To calculate E_a from values of the rate constant at two temperatures, use the equation

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

(c) Use the same equation and the known values of E_a and k_1 at T_1 to calculate k_2 at T_2.

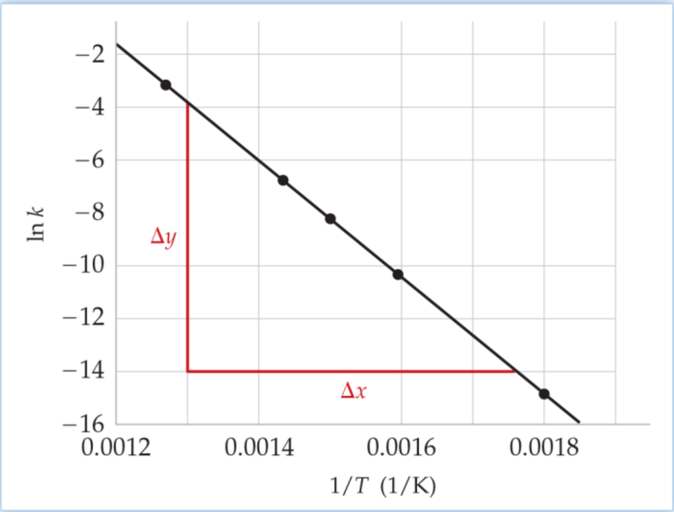
WORKED EXAMPLE 12.16 Using the Arrhenius Equation

Continued

Solution

(a) Since the temperature in the Arrhenius equation is expressed in kelvin, we must first convert the Celsius temperatures to absolute temperatures and then calculate values of $1/T$ and ln k, and plot ln k versus $1/T$. The results are shown in the following table and graph:

t (°C)	T (K)	k ($M^{-1}s^{-1}$)	$1/T$ (1/K)	ln k
283	556	3.52×10^{-7}	0.001 80	–14.860
356	629	3.02×10^{-5}	0.001 59	–10.408
393	666	2.19×10^{-4}	0.001 50	–8.426
427	700	1.16×10^{-3}	0.001 43	–6.759
508	781	3.95×10^{-2}	0.001 28	–3.231



WORKED EXAMPLE 12.16 Using the Arrhenius Equation

Continued

The slope of the straight-line plot can be determined from the coordinates of any two widely separated points on the line:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{(-14.0) - (-3.9)}{(0.001\,75\ \text{K}^{-1}) - (0.001\,30\ \text{K}^{-1})}$$

$$= \frac{-10.1}{0.000\,45\ \text{K}^{-1}} = -2.24 \times 10^4\ \text{K}$$

Finally, calculate the activation energy from the slope:

$$E_a = -R(\text{Slope}) = -\left(8.314\ \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)(-2.24 \times 10^4\ \text{K})$$

$$= 1.9 \times 10^5\ \text{J/mol} = 190\ \text{kJ/mol}$$

Note that the slope of the Arrhenius plot is negative and the activation energy is positive. The greater the activation energy for a particular reaction, the steeper the slope of the ln k versus $1/T$ plot and the greater the increase in the rate constant for a given increase in temperature.

(b) Substituting the values of $k_1 = 3.52 \times 10^{-7}\ \text{M}^{-1}\text{s}^{-1}$ at $T_1 = 556$ K (283 °C) and $k_2 = 3.95 \times 10^{-2}\ \text{M}^{-1}\text{s}^{-1}$ at $T_2 = 781$ K (508 °C) into the equation

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

gives

$$\ln\left(\frac{3.95 \times 10^{-2}\ \text{M}^{-1}\ \text{s}^{-1}}{3.52 \times 10^{-7}\ \text{M}^{-1}\ \text{s}^{-1}}\right) = \left(\frac{-E_a}{8.314\ \frac{\text{J}}{\text{K}\cdot\text{mol}}}\right)\left(\frac{1}{781\ \text{K}} - \frac{1}{556\ \text{K}}\right)$$

Simplifying this equation gives

$$11.628 = \left(\frac{-E_a}{8.314\ \frac{\text{J}}{\text{K}\cdot\text{mol}}}\right)\left(\frac{-5.18 \times 10^{-4}}{\text{K}}\right)$$

$$E_a = 1.87 \times 10^5\ \text{J/mol} = 187\ \text{kJ/mol}$$

WORKED EXAMPLE 12.16 Using the Arrhenius Equation

Continued

(c) Use the same equation as in part **(b)**, but now the known values are $k_1 = 3.52 \times 10^{-7}\ \mathrm{M^{-1}s^{-1}}$ at $T_1 = 556$ K (283 °C) and $E_a = 1.87 \times 10^5$ J/mol, and k_2 at $T_2 = 566$ K (293 °C) is the unknown:

$$\ln\left(\frac{k_2}{3.52 \times 10^{-7}\ \mathrm{M^{-1}\,s^{-1}}}\right) = \left(\frac{-1.87 \times 10^5\ \dfrac{\mathrm{J}}{\mathrm{mol}}}{8.314\ \dfrac{\mathrm{J}}{\mathrm{K \cdot mol}}}\right)\left(\frac{1}{566\ \mathrm{K}} - \frac{1}{556\ \mathrm{K}}\right) = 0.715$$

Taking the antiln of both sides gives

$$\frac{k_2}{3.52 \times 10^{-7}\ \mathrm{M^{-1}\,s^{-1}}} = e^{0.715} = 2.04$$

$$k_2 = 7.18 \times 10^{-7}\ \mathrm{M^{-1}\,s^{-1}}$$

In this temperature range, a rise in temperature of 10 K doubles the rate constant.

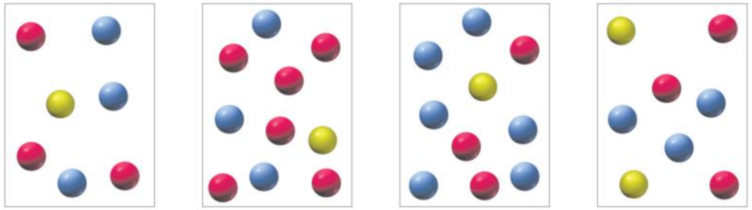
PROBLEM 12.21 Rate constants for the decomposition of gaseous dinitrogen pentoxide are $3.7 \times 10^{-5}\ \mathrm{s^{-1}}$ at 25 °C and $1.7 \times 10^{-3}\ \mathrm{s^{-1}}$ at 55 °C.

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

(a) What is the activation energy for this reaction in kJ/mol?
(b) What is the rate constant at 35 °C?

WORKED KEY CONCEPT EXAMPLE 12.17 Using the Method of Initial Rates for a Catalyzed Reaction

The relative rates of the reaction A + B → AB in vessels (1)–(4) are 1 : 2 : 1 : 2. Red spheres represent A molecules, blue spheres represent B molecules, and yellow spheres represent molecules of a third substance C.



(1) (2) (3) (4)

(a) What is the order of the reaction in A, B, and C?
(b) Write the rate law.
(c) Write a mechanism that agrees with the rate law.
(d) Why doesn't C appear in the equation for the overall reaction?

Strategy and Solution

(a) Count the number of molecules of each type in vessels (1)–(4), and compare the relative rates with the relative numbers of molecules. The concentration of A molecules in vessel (2) is twice that in vessel (1), while the concentrations of B and C remain constant. Because the reaction rate in vessel (2) is twice that in vessel (1), the rate is proportional to [A], and so the reaction is first order in A. When [B] is doubled [compare vessels (1) and (3)], the rate is unchanged, so the reaction is zeroth order in B. When [C] is doubled [compare vessels (1) and (4)], the rate doubles, so the reaction is first order in C.

WORKED KEY CONCEPT EXAMPLE 12.17 Using the Method of Initial Rates for a Catalyzed Reaction

Continued

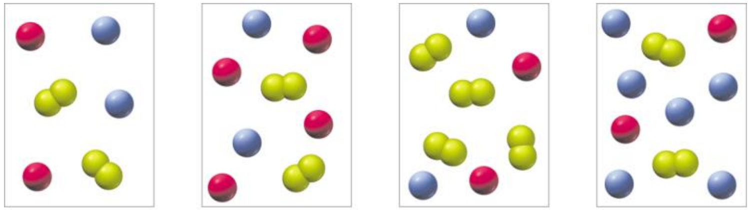
(b) The rate law can be written as rate = $k[A]^m[B]^n[C]^p$, where the exponents m, n, and p specify the reaction orders in A, B, and C, respectively. Since the reaction is first order in A and C, and zeroth order in B, the rate law is rate = $k\,[A][C]$.

(c) The rate law tells us that A and C collide in the rate-determining step because the rate law for the overall reaction is the rate law for the rate-determining step. Subsequent steps in the mechanism are faster than the rate-determining step, and the various steps must sum up to give the overall reaction. Therefore, a plausible mechanism is

$$\begin{array}{lll} A + C \longrightarrow AC & & \text{Slower, rate determining} \\ AC + B \longrightarrow AB + C & & \text{Faster} \\ \hline A + B \longrightarrow AB & & \text{Overall reaction} \end{array}$$

(d) C doesn’t appear in the overall reaction because it is consumed in the first step and regenerated in the second step. C is therefore a catalyst. AC is an intermediate because it is formed in the first step and consumed in the second step.

KEY CONCEPT PROBLEM 12.22 The relative rates of the reaction $2\,A + C_2 \rightarrow 2AC$ in vessels (1)–(4) are 1 : 1 : 2 : 3. Red spheres represent A molecules, blue spheres represent B molecules, and connected yellow spheres represent C_2 molecules.



(1) (2) (3) (4)

WORKED KEY CONCEPT EXAMPLE 12.17 Using the Method of Initial Rates for a Catalyzed Reaction

Continued

(a) What is the order of the reaction in A, B, and C_2?

(b) Write the rate law.

(c) Write a mechanism that agrees with the rate law.

(d) Identify all catalysts and intermediates in your mechanism.