31. Repeat the calculations of the preceding exercise, but this time start with $[\text{NOBr}]_0 = 0.100\ M$ (half the initial concentration from before).

(a) The half-life doubles when $[\text{NOBr}]_0$ is halved, going from 6.25 s in Exercise 30(a) to 12.5 s in the present system:

$$t_{1/2} = \frac{1}{k[\text{NOBr}]_0} = \frac{1}{\left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left(0.100\ M\right)} = 12.5\ \text{s} = 13\ \text{s} \qquad \text{(2 sig fig)}$$

(b) See Figure 18.7.

(c) See Figure 18.8.

(d) Compared with the conditions in Exercise 30, the reaction proceeds more slowly now that $[\text{NOBr}]_0$ has been cut in half:

$$\text{Rate}(t) = k\left(\frac{[\text{NOBr}]_0}{kt[\text{NOBr}]_0 + 1}\right)^2$$

The rate is smaller at each value of t:

$$\text{Rate}(0) = \left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left[\frac{0.100\ M}{\left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left(0\ \text{s}\right)\left(0.100\ M\right)+1}\right]^2 = 8.0 \times 10^{-3}\ M\ \text{s}^{-1}$$

$$\text{Rate}(15\ \text{s}) = \left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left[\frac{0.100\ M}{\left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left(15\ \text{s}\right)\left(0.100\ M\right)+1}\right]^2 = 1.7 \times 10^{-3}\ M\ \text{s}^{-1}$$

$$\text{Rate}(30\ \text{s}) = \left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left[\frac{0.100\ M}{\left(0.80\ M^{-1}\ \text{s}^{-1}\right)\left(30\ \text{s}\right)\left(0.100\ M\right)+1}\right]^2 = 6.9 \times 10^{-4}\ M\ \text{s}^{-1}$$

32. The gas-phase decomposition of NO_2 displays second-order kinetics:

$$2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

$$\text{Rate} = k[\text{NO}_2]^2 \qquad k(300°\text{C}) = 0.54\ M^{-1}\ \text{s}^{-1}$$

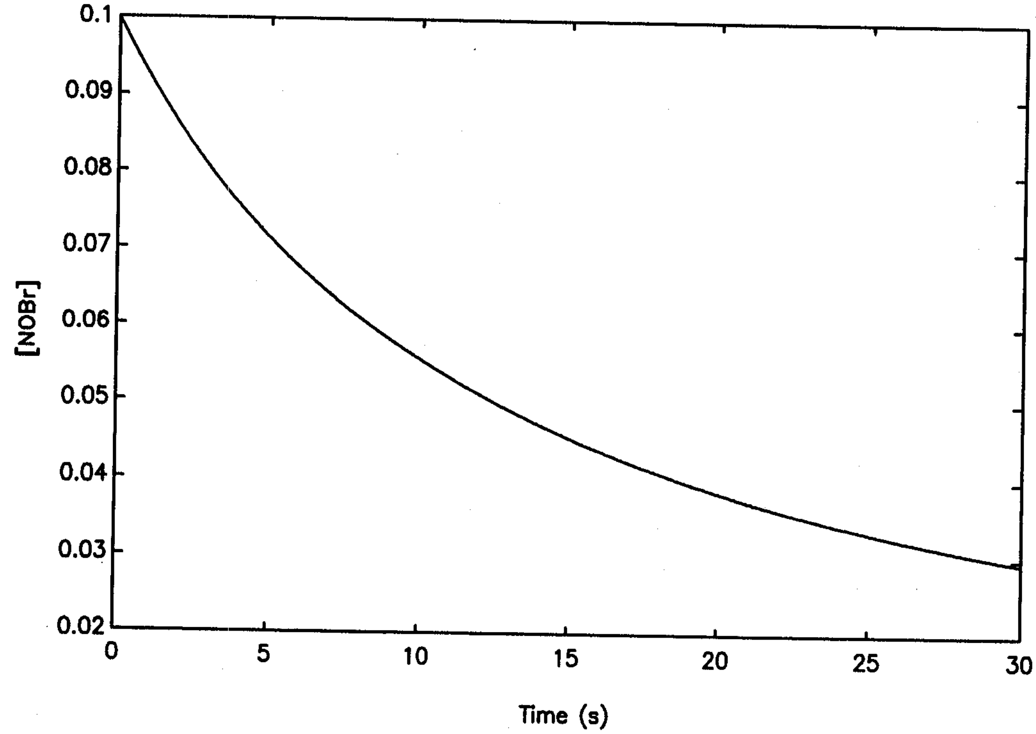


FIGURE 18.7 A plot of [NOBr] versus time for the second-order reaction described in Exercise 31. The concentration is measured in moles per liter, M.

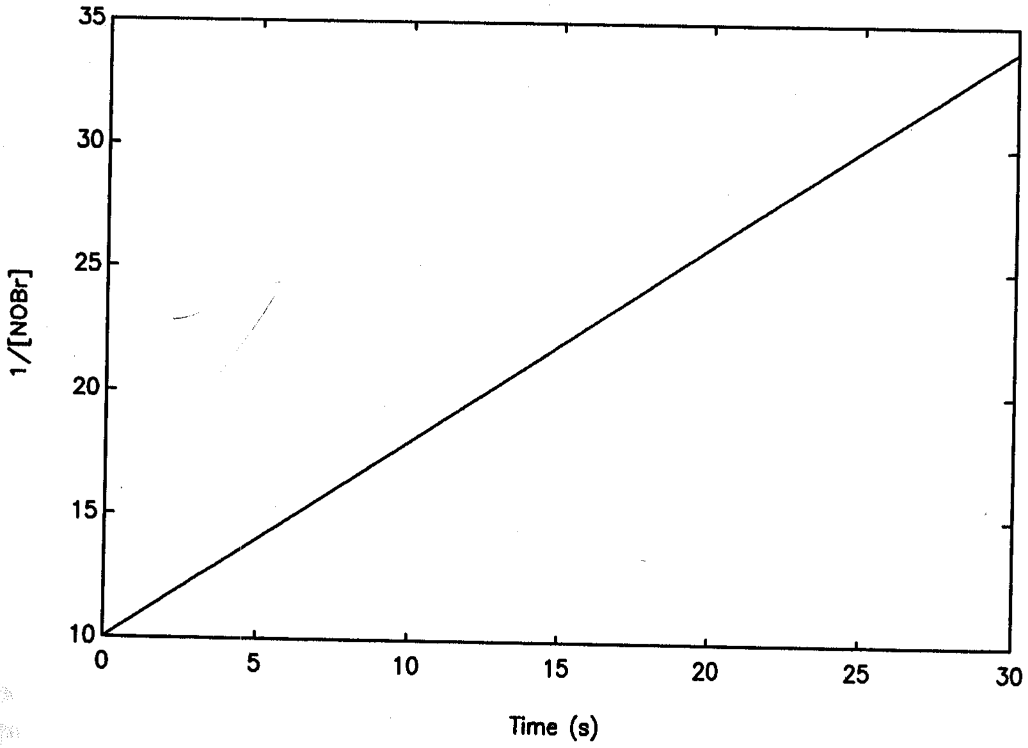


FIGURE 18.8 A plot of 1/[NOBr] versus time for the second-order reaction described in Exercise 31. The reciprocal concentration is measured in units of M^{-1}.

(a) Since the initial concentration decreases by exactly half,

$$\frac{[NO_2]_t}{[NO_2]_0} = \frac{0.0925\ M}{0.1850\ M} = 0.500$$

we simply compute the initial half-life of the second-order process:

$$t_{1/2} = \frac{1}{k[NO_2]_0} = \frac{1}{(0.54\ M^{-1}\ s^{-1})(0.1850\ M)} = 10.\ s$$

See page 656 and Example 18-6 in *PoC*.

(b) The half-life *changes* with time during the course of a second-order reaction, varying each instant as $1/(k[A]_t)$. As a result, the concentration does not decrease uniformly by $\frac{1}{2}$ over each interval $t_{1/2}$. See Figure 18.9.

33. Contrary to fact, we assume that the decomposition of NO_2 is first order, with $k = 0.54\ s^{-1}$:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

(a) Calculate the half-life of the assumed first-order process:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.54\ s^{-1}} = 1.3\ s$$

(b) See Figure 18.10.

(c) The half-life of a first-order process is a constant, independent of concentration: $[NO_2]$ would decrease uniformly by $\frac{1}{2}$ over each interval $t_{1/2}$ if the reaction were first order.

34. We have two hypothetical processes, a first-order reaction (1) and a second-order reaction (2):

$$\text{Rate}_1 = k_1[A] \qquad k_1 = 1000\ s^{-1}$$

$$\text{Rate}_2 = k_2[B]^2 \qquad k_2 = 1000\ M^{-1}\ s^{-1}$$

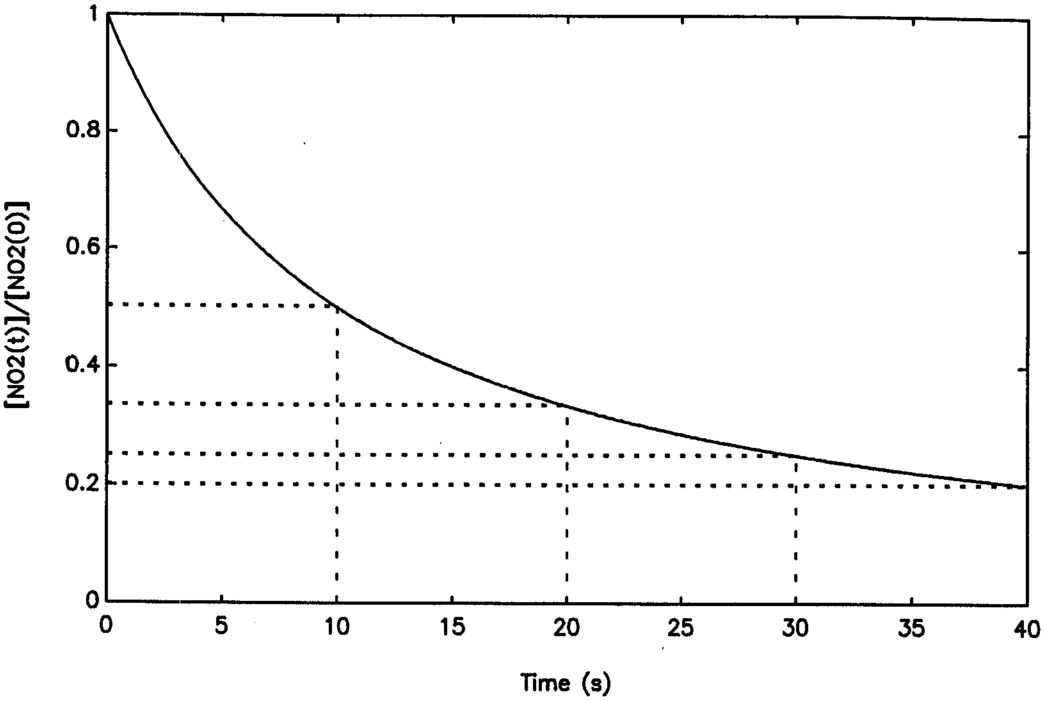


FIGURE 18.9 A plot of $[NO_2]_t/[NO_2]_0$ versus time during the second-order reaction described in Exercise 32. Broken lines mark the passage of four *initial* half-lives, as determined by the conditions prevailing at $t = 0$. The fractional concentration falls to $(n + 1)^{-1}$ rather than 2^{-n} after n such intervals.

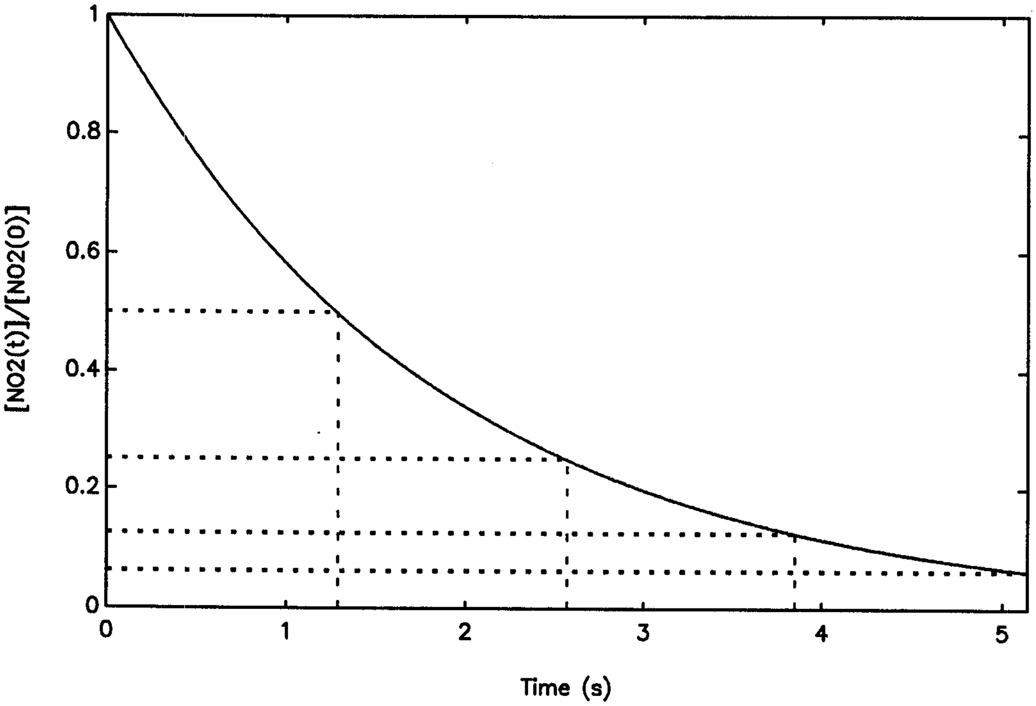


FIGURE 18.10 A plot of $[NO_2]_t/[NO_2]_0$ versus time for an assumed *first*-order decomposition reaction ($k = 0.54\ s^{-1}$), with broken lines marking the passage of each successive half-life. The incorrect assumption of first-order kinetics is made only for the sake of argument in Exercise 33. Compare the time dependence shown here with the proper second-order profile depicted in Figure 18.9.

First, we calculate the initial concentration of B that will equalize the two rates at $t = 0$:

$$\text{rate}_2(0) = \text{rate}_1(0)$$

$$k_2[\text{B}]_0^2 = k_1[\text{A}]_0$$

$$[\text{B}]_0 = \sqrt{\frac{k_1[\text{A}]_0}{k_2}}$$

With $[\text{A}]_0 = 1\ M$, for example, the matching concentration $[\text{B}]_0$ is also equal to 1 M:

$$[\text{B}]_0 = \sqrt{\frac{k_1[\text{A}]_0}{k_2}} = \sqrt{\frac{(1000\ \text{s}^{-1})(1\ M)}{1000\ M^{-1}\ \text{s}^{-1}}} = 1\ M$$

Next, we calculate the half-lives. The first-order and second-order values are $(\ln 2)/k$ and $1/(k[\text{B}]_0)$, respectively:

$$\text{Reaction 1:} \qquad t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{1000\ \text{s}^{-1}} = 6.93 \times 10^{-4}\ \text{s}$$

$$\text{Reaction 2:} \qquad t_{1/2} = \frac{1}{k[\text{B}]_0} = \frac{1}{(1000\ M^{-1}\ \text{s}^{-1})(1\ M)} = 1.00 \times 10^{-3}\ \text{s} \quad ([\text{B}]_0 = 1\ M)$$

The first-order half-life is independent of initial concentration; the second-order half-life is not:

	REACTION 1		REACTION 2	
	$[\text{A}]_0$ (M)	$t_{1/2}$ (s)	$[\text{B}]_0$ (M)	$t_{1/2}$ (s)
(a)	1	6.93×10^{-4}	1	1.00×10^{-3} s
(b)	2	6.93×10^{-4}	$\sqrt{2}$	7.07×10^{-4} s
(c)	3	6.93×10^{-4}	$\sqrt{3}$	5.77×10^{-4} s
(d)	4	6.93×10^{-4}	2	5.00×10^{-4} s

Values are written with an arbitrary number of digits for the sake of this hypothetical exercise. The approximate decimal equivalents of $\sqrt{2}$ and $\sqrt{3}$ are 1.414 and 1.732.

35. The concentrations of A and B vary with time in the following ways:

Reaction 1:	$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-k_1 t)$	$k_1 = 1000\ \mathrm{s}^{-1}$	(first order)
Reaction 2:	$[\mathrm{B}]_t = \dfrac{[\mathrm{B}]_0}{k_2 t[\mathrm{B}]_0 + 1}$	$k_2 = 1000\ M^{-1}\ \mathrm{s}^{-1}$	(second order)

See Figure 18.11 (overleaf). The relevant equations are discussed on pages 653–656 of *PoC* and demonstrated in Examples 18-4 through 18-6.

Exercises 36 through 43 deal with activation, temperature, and the Arrhenius law. See pages 656–659 and Examples 18-7 through 18-9 in PoC.

36. The Arrhenius expression for the rate constant,

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

makes use of two parameters: the activation energy (E_a) and the pre-exponential factor (A).

(a) Start with the ratio of the two rate constants, and isolate E_a on the left-hand side:

$$\frac{k_2}{k_1} = \frac{A\exp\left(-\dfrac{E_a}{RT_2}\right)}{A\exp\left(-\dfrac{E_a}{RT_1}\right)} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

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

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

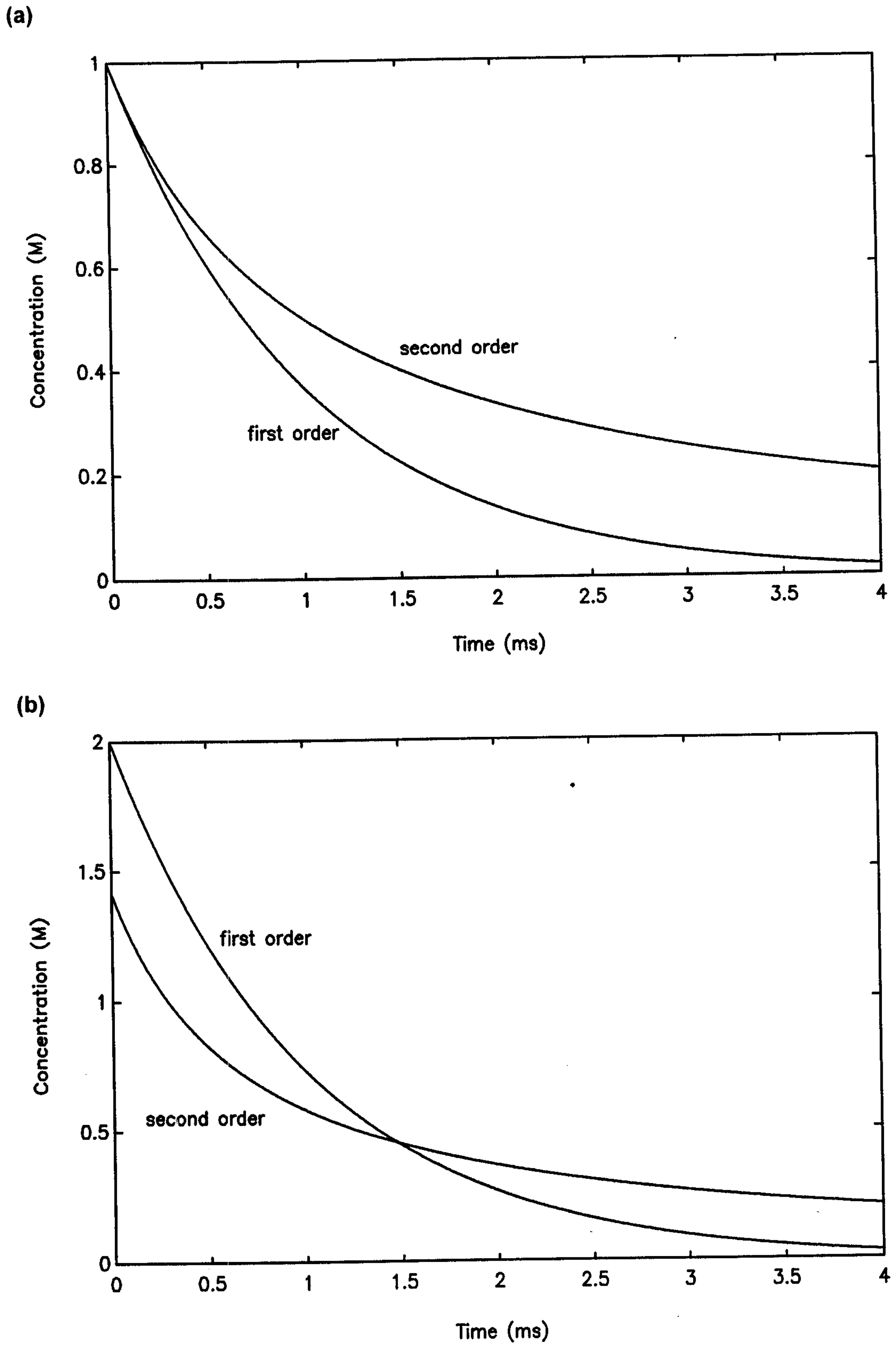
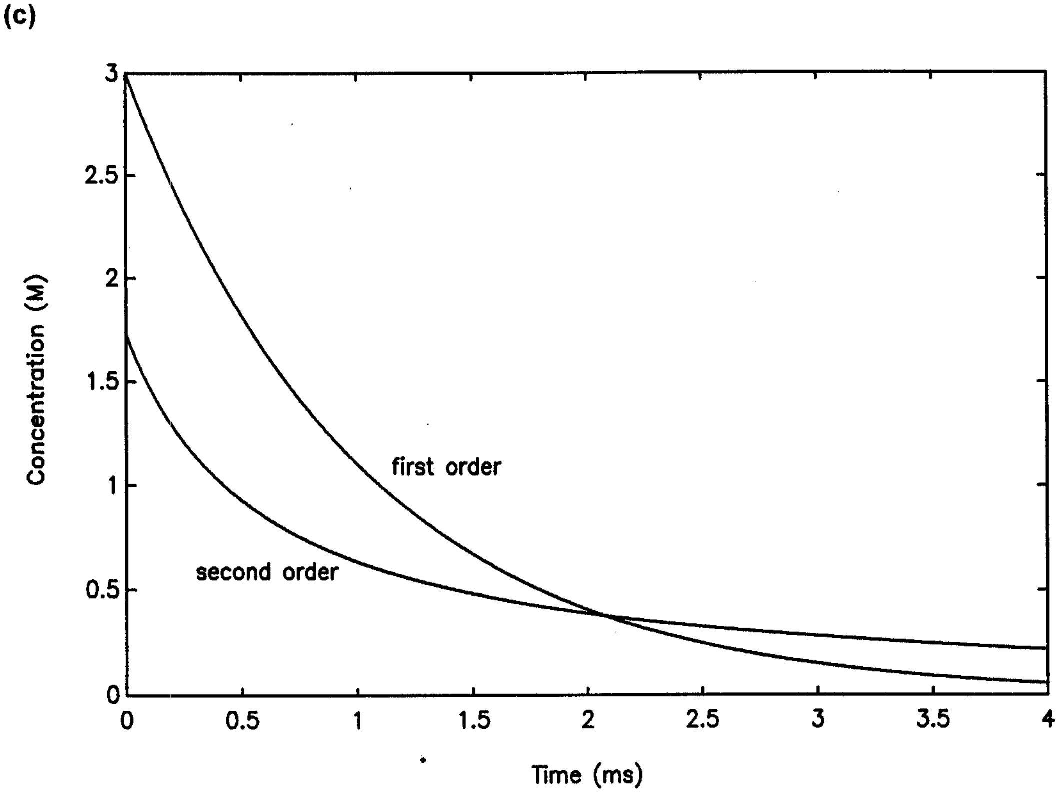


FIGURE 18.11 Concentration versus time for the first-order and second-order processes considered in Exercises 34 and 35. (Figure continues on next page.)



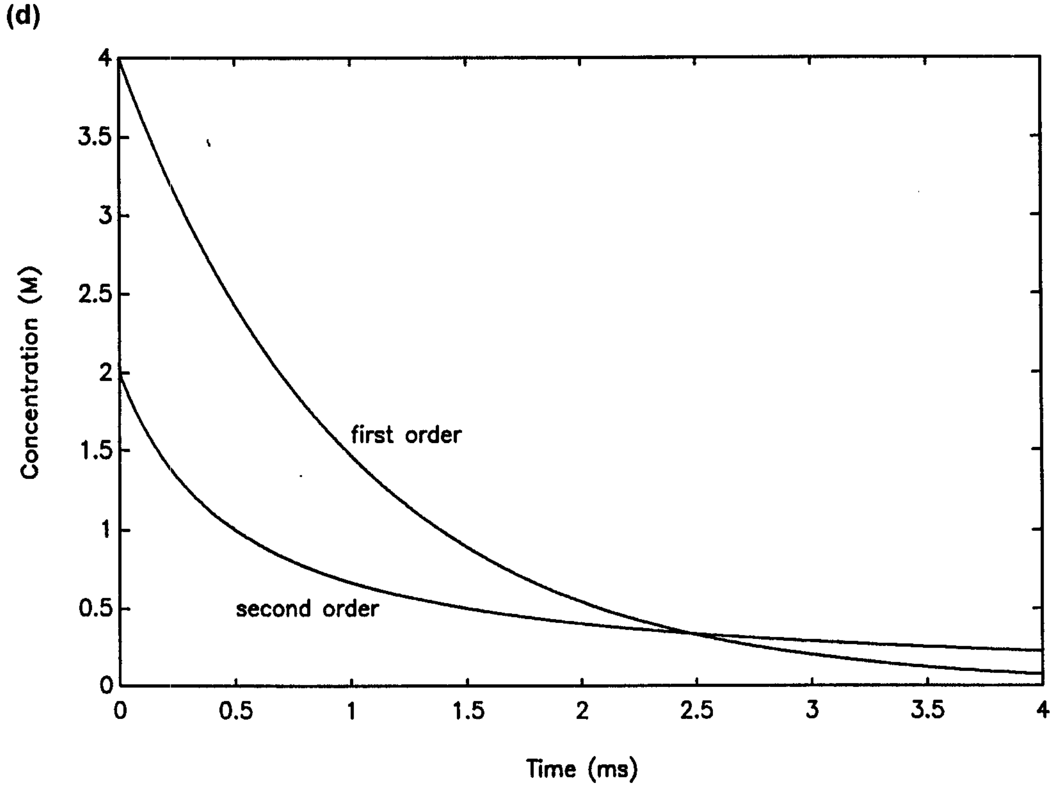


FIGURE 18.11 Continued.

Given the following data,

$$\frac{k_2}{k_1} = 2 \qquad T_1 = 283.15\text{ K (10°C)} \qquad T_2 = 293.15\text{ K (20°C)}$$

we then obtain a numerical value for the activation energy:

$$E_a = \frac{R\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{\left(8.3145\text{ J mol}^{-1}\text{ K}^{-1}\right)\ln 2}{\frac{1}{283.15\text{ K}} - \frac{1}{293.15\text{ K}}} = 4.78 \times 10^4\text{ J mol}^{-1}$$

$$= 47.8\text{ kJ mol}^{-1}$$

See Example 18-9 in *PoC* (beginning on page R18.20).

(b) Knowing the activation energy, we can now calculate the ratio of rate constants at any two temperatures:

$$E_a = 4.78 \times 10^4\text{ J mol}^{-1} \qquad T_1 = 283.15\text{ K} \qquad T_2 = 289.15\text{ K}$$

$$\frac{k_2}{k_1} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \exp\left[-\frac{4.78 \times 10^4\text{ J mol}^{-1}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}} \times \left(\frac{1}{289.15\text{ K}} - \frac{1}{283.15\text{ K}}\right)\right] = 1.52$$

See Example 18-7 in *PoC* (beginning on page R18.16).

37. The procedures are largely the same as in Exercise 36. See also Examples 18-7 and 18-9 in *PoC.*

(a) Given a ratio of rate constants k_1 and k_2,

$$\frac{k_2}{k_1} = \frac{600\text{ s}^{-1}}{100\text{ s}^{-1}} = 6.00 \qquad T_1 = 298\text{ K} \qquad T_2 = 350\text{ K}$$

we first calculate the activation energy:

$$E_a = \frac{R\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{\left(8.3145\text{ J mol}^{-1}\text{ K}^{-1}\right)\ln 6.00}{\frac{1}{298\text{ K}} - \frac{1}{350\text{ K}}} = 2.988 \times 10^4\text{ J mol}^{-1}$$

$$= 29.9\text{ kJ mol}^{-1}$$

We then solve for the pre-exponential factor A by substituting E_a, T_1, and k_1 into the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

$$A = k_1 \exp\left(\frac{E_a}{RT_1}\right) = \left(100\ \text{s}^{-1}\right)\exp\left[\frac{2.988 \times 10^4\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(298\ \text{K}\right)}\right] = 1.73 \times 10^7\ \text{s}^{-1}$$

Substitution of T_2 and k_2 (rather than T_1 and k_1) leads to the same result.

(b) Having values for both A and E_a, we can now compute the rate constant at any temperature:

$$k = A\exp\left(-\frac{E_a}{RT}\right) = \left(1.73 \times 10^7\ \text{s}^{-1}\right)\exp\left[-\frac{2.988 \times 10^4\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(320\ \text{K}\right)}\right] = 229\ \text{s}^{-1}$$

38. If the rate constant k obeys the Arrhenius equation,

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

then a plot of ln k versus $1/T$ yields a straight line with slope equal to $-E_a/R$ and vertical intercept equal to ln A:

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

See pages 656–659 and Example 18-9 in *PoC*.

From the slope (–22,115 K) and intercept (26.9838) of the line in Figure 18.12, we thus establish that $E_a = 184$ kJ mol^{-1} and $A = 5.23 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$:

$$E_a = -R \times \text{slope} = -\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(-22{,}115\ \text{K}\right) = 1.84 \times 10^5\ \text{J mol}^{-1}$$

$$= 184\ \text{kJ mol}^{-1}$$

$$\ln A = 26.9838$$

$$A = \exp(\ln A) = \exp 26.9838 = 5.23 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$$

The line itself is calculated to be the "best fit" through the data, as determined by a *least-squares* (or linear regression) analysis. This method, in general, ensures that the

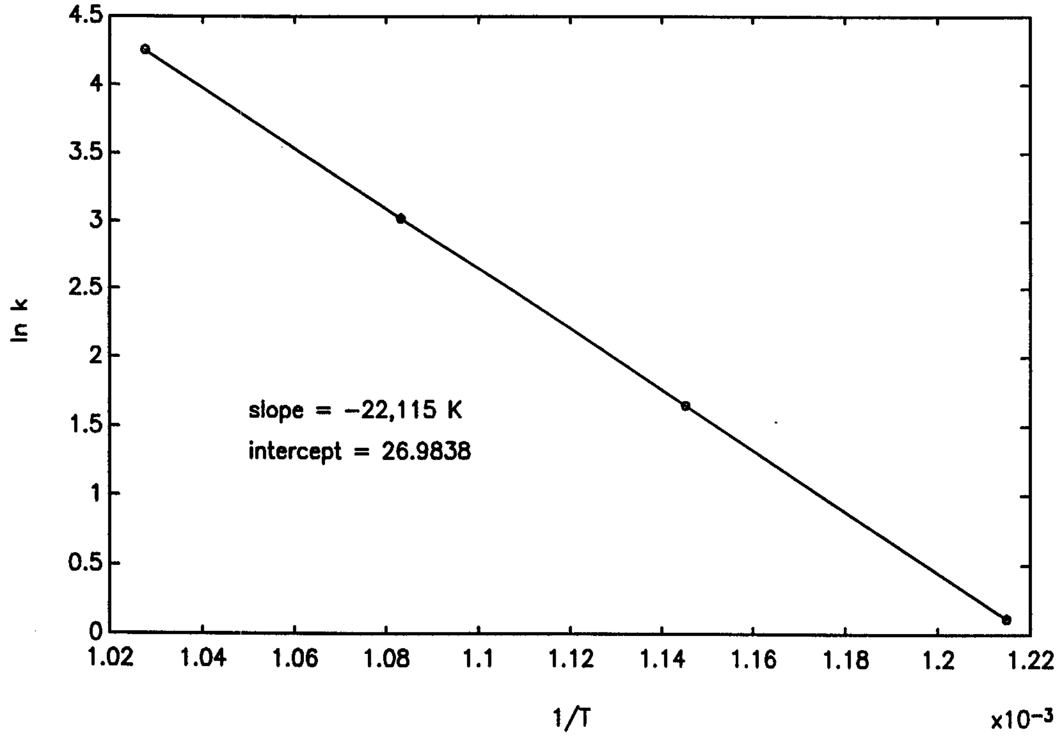


FIGURE 18.12 An Arrhenius plot (ln k versus $1/T$) of the data in Exercise 38. The reciprocal absolute temperature, $1/T$, is expressed in units of K^{-1}.

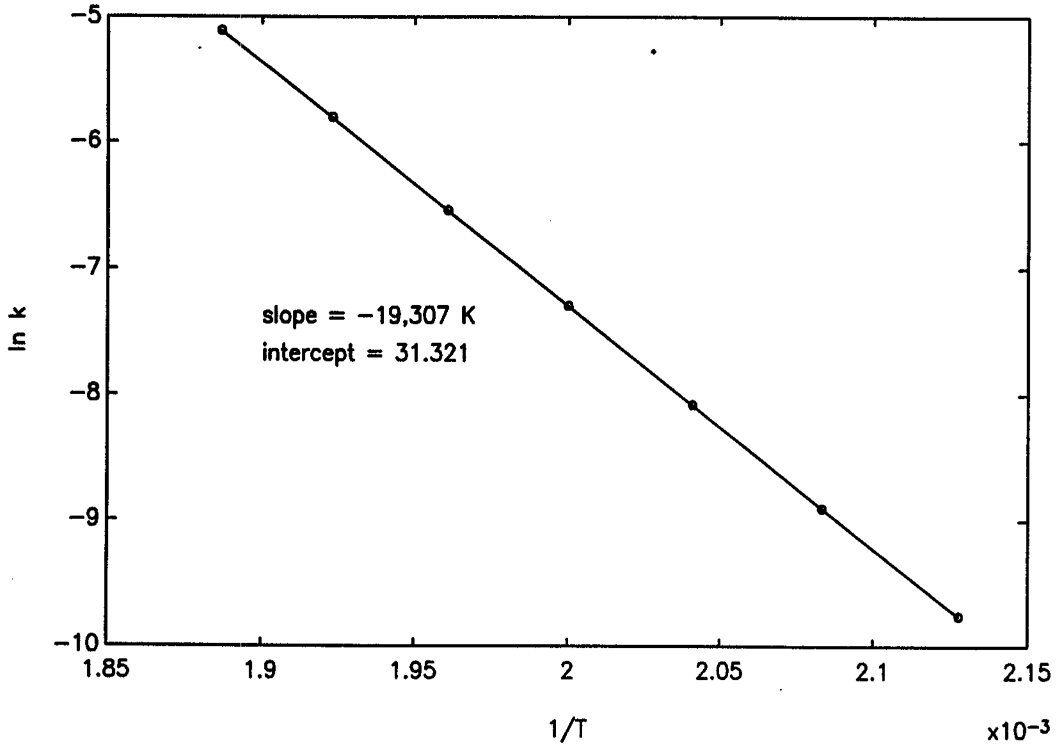
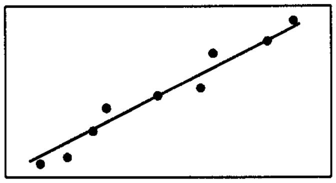


FIGURE 18.13 An Arrhenius plot (ln k versus $1/T$) of the data in Exercise 39. The reciprocal absolute temperature, $1/T$, is expressed in units of K^{-1}.

points in any experimental data set are scattered equally above and below the theoretical line:



Linear regression is available as an automatic function on many scientific calculators. Alternatively, a manual estimation of the slope (as demonstrated in Example 18-9) will provide an acceptable estimate.

Note that the units of A are assigned for consistency with second-order kinetics. Note also that the slope and intercept in Figure 18.12 were obtained by adding 273 (rather than 273.15) to the Celsius temperatures:

$$T_K = T_C + 273$$

Use of the conversion

$$T_K = T_C + 273.15$$

results in slightly different values for the slope and intercept:

Slope = –22,122 K $\qquad E_a = 184$ kJ mol^{-1}

Intercept = 26.9880 $\qquad A = 5.26 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$

39. The method is the same as in Exercise 38. Plot ln k versus $1/T$, and determine the parameters E_a and A from the resulting straight line:

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

Measuring the slope (–19,307 K) and intercept (31.321) of the line in Figure 18.13, we obtain $E_a = 161$ kJ mol^{-1} and $A = 4.00 \times 10^{13}$ s^{-1}:

$$E_a = -R \times \text{slope} = -\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(-19{,}307\ \text{K}\right) = 1.605 \times 10^5\ \text{J mol}^{-1}$$

$$= 161\ \text{kJ mol}^{-1}$$

$$\ln A = 31.321$$

$$A = \exp(\ln A) = \exp 31.321 = 4.00 \times 10^{13}\ \text{s}^{-1}$$

The units of A (s^{-1}) are assigned for consistency with first-order kinetics, as implied in the problem.

40. Given the parameters E_a and A,

$$E_a = 103 \text{ kJ mol}^{-1} \qquad A = 4.94 \times 10^{13} \text{ s}^{-1}$$

start by inserting $T = 300$ K into the Arrhenius equation for the rate constant:

$$\begin{aligned} k &= A \exp\left(-\frac{E_a}{RT}\right) \\ &= \left(4.94 \times 10^{13} \text{ s}^{-1}\right) \exp\left[-\frac{1.03 \times 10^5 \text{ J.mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(300 \text{ K}\right)}\right] \\ &= 5.76 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

The initial rate, directly proportional to the initial concentration, doubles if $[N_2O_5]_0$ is doubled. It goes from 5.76×10^{-7} M s^{-1} when $[N_2O_5]_0 = 0.0100$ M,

$$\text{Rate} = k[\text{N}_2\text{O}_5]_0 = \left(5.76 \times 10^{-5} \text{ s}^{-1}\right)\left(0.0100 \ M\right) = 5.76 \times 10^{-7} \ M \text{ s}^{-1}$$

to 1.15×10^{-6} M s^{-1} when $[N_2O_5]_0 = 0.0200$ M:

$$\text{Rate} = k[\text{N}_2\text{O}_5]_0 = \left(5.76 \times 10^{-5} \text{ s}^{-1}\right)\left(0.0200 \ M\right) = 1.15 \times 10^{-6} \ M \text{ s}^{-1}$$

The reaction is first order.

Calculations for all the other temperatures are done in the same way. Results are summarized below:

T =	300 K	325 K	350 K	375 K	400 K
(a) Rate Constant (s^{-1})	5.76×10^{-5}	1.38×10^{-3}	0.0210	0.222	1.75
(b) Initial Rate (M s^{-1}) $[N_2O_5]_0 = 0.0100$ M	5.76×10^{-7}	1.38×10^{-5}	0.000210	0.00222	0.0175
(c) Initial Rate (M s^{-1}) $[N_2O_5]_0 = 0.0200$ M	1.15×10^{-6}	2.76×10^{-5}	0.000420	0.00445	0.0350

41. We continue to work with the Arrhenius formulation of the rate constant,

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

specifying parameters for two hypothetical first-order reactions:

1. $E_a = 100\ \text{kJ mol}^{-1}$ $\qquad A = 10^{13}\ \text{s}^{-1}$
2. $E_a = 110\ \text{kJ mol}^{-1}$ $\qquad A = 10^{14}\ \text{s}^{-1}$

(a) Insert the appropriate temperature and parameters for each system, and evaluate the rate constant:

Reaction 1:

$$k_1(300\ \text{K}) = \left(10^{13}\ \text{s}^{-1}\right)\exp\left[-\frac{1.00\times10^{5}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(300\ \text{K}\right)}\right] = 3.88\times10^{-5}\ \text{s}^{-1}$$

$$k_1(1000\ \text{K}) = \left(10^{13}\ \text{s}^{-1}\right)\exp\left[-\frac{1.00\times10^{5}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(1000\ \text{K}\right)}\right] = 5.98\times10^{7}\ \text{s}^{-1}$$

The value of k increases by more than 12 orders of magnitude (a factor greater than 1 trillion) when the absolute temperature is raised from 300 K to 1000 K.

Reaction 2:

$$k_2(300\ \text{K}) = \left(10^{14}\ \text{s}^{-1}\right)\exp\left[-\frac{1.10\times10^{5}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(300\ \text{K}\right)}\right] = 7.04\times10^{-6}\ \text{s}^{-1}$$

$$k_2(1000\ \text{K}) = \left(10^{14}\ \text{s}^{-1}\right)\exp\left[-\frac{1.10\times10^{5}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(1000\ \text{K}\right)}\right] = 1.80\times10^{8}\ \text{s}^{-1}$$

With the activation energy 10% larger, the rate constant k_2 grows by more than 13 orders of magnitude over the same range of temperature.

(b) Reaction 1 has the smaller activation energy (which tends to increase the rate) but also the smaller pre-exponential factor (which tends to decrease the rate).

At the lower temperature, the activation energy dominates and reaction 1 goes faster than reaction 2 at 300 K. Comparatively more molecules have sufficient energy to overcome the smaller activation barrier E_{a1}. The advantage of a lower activation energy in reaction 1 more than compensates for the greater pre-exponential factor in reaction 2.

At the higher temperature, the frequency of collisions becomes more important. Since the exponential factors $\exp(-E_{a1}/RT)$ and $\exp(-E_{a2}/RT)$ are now closer in magnitude, the kinetic advantage goes to the process in which the proportion of productive collisions is greater. Reaction 2, with a tenfold larger pre-exponential factor, goes faster than reaction 1 at 1000 K.

(c) Solve for the temperature at which k_1 becomes equal to k_2:

$$k_1 = k_2$$

$$A_1 \exp\left(-\frac{E_{a1}}{RT}\right) = A_2 \exp\left(-\frac{E_{a2}}{RT}\right)$$

$$\ln A_1 - \frac{E_{a1}}{RT} = \ln A_2 - \frac{E_{a2}}{RT}$$

$$\frac{E_{a2} - E_{a1}}{RT} = \ln A_2 - \ln A_1 = \ln\left(\frac{A_2}{A_1}\right)$$

$$T = \frac{E_{a2} - E_{a1}}{R \ln\left(\frac{A_2}{A_1}\right)} = \frac{110{,}000 \text{ J mol}^{-1} - 100{,}000 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\ln\left(\frac{10^{14} \text{ s}^{-1}}{10^{13} \text{ s}^{-1}}\right)} = 522 \text{ K}$$

Finally, to check the result, we evaluate both k_1 and k_2 at 522 K (more accurately, 522.334 K before round-off):

$$k_1(522.334 \text{ K}) = \left(10^{13} \text{ s}^{-1}\right)\exp\left[-\frac{1.00 \times 10^5 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(522.334 \text{ K}\right)}\right] = 1000.0 \text{ s}^{-1}$$

$$k_2(522.334 \text{ K}) = \left(10^{14} \text{ s}^{-1}\right)\exp\left[-\frac{1.10 \times 10^5 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(522.334 \text{ K}\right)}\right] = 1000.0 \text{ s}^{-1}$$

42. The method is similar to that used in Exercise 40, except now the reaction is governed by second-order kinetics:

$$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$$

$$\text{Rate} = k[C_2H_5Br][OH^-]$$

The initial rate quadruples when the initial concentrations $[C_2H_5Br]_0$ and $[OH^-]_0$ are both doubled.

One sample calculation (at 10°C) should suffice. We use the parameters specified in the problem:

$$E_a = 89.5 \text{ kJ mol}^{-1} \qquad A = 4.30 \times 10^{11}\ M^{-1}\ \text{s}^{-1} \qquad T = 283.15 \text{ K} \ \ (10°\text{C})$$

Rate constant:

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

$$= \left(4.30\times10^{11}\ M^{-1}\ \text{s}^{-1}\right)\exp\left[-\frac{8.95\times10^{4}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(283.15\ \text{K}\right)}\right]$$

$$= 1.3279\times10^{-5}\ M^{-1}\ \text{s}^{-1} = 1.33\times10^{-5}\ M^{-1}\ \text{s}^{-1} \quad (3 \text{ sig fig})$$

Initial rates:

$$[\text{C}_2\text{H}_5\text{Br}]_0 = [\text{OH}^-]_0 = 0.100\ M$$

$$\text{Rate}(0) = k[\text{C}_2\text{H}_5\text{Br}]_0[\text{OH}^-]_0$$

$$= \left(1.3279\times10^{-5}\ M^{-1}\ \text{s}^{-1}\right)\left(0.100\ M\right)\left(0.100\ M\right)$$

$$= 1.33\times10^{-7}\ M\ \text{s}^{-1}$$

$$[\text{C}_2\text{H}_5\text{Br}]_0 = [\text{OH}^-]_0 = 0.200\ M$$

$$\text{Rate}(0) = k[\text{C}_2\text{H}_5\text{Br}]_0[\text{OH}^-]_0$$

$$= \left(1.3279\times10^{-5}\ M^{-1}\ \text{s}^{-1}\right)\left(0.200\ M\right)\left(0.200\ M\right)$$

$$= 5.31\times10^{-7}\ M\ \text{s}^{-1}$$

A full set of results is presented in the following table:

	$T =$ 283.15 K	293.15 K	303.15 K	313.15 K	323.15 K
(a) Rate Constant (M^{-1} s^{-1})	1.33×10^{-5}	4.86×10^{-5}	1.63×10^{-4}	5.07×10^{-4}	1.47×10^{-3}
(b) Initial Rate (M s^{-1}) $[\mathrm{A}]_0 = [\mathrm{B}]_0 = 0.100\ M$	1.33×10^{-7}	4.86×10^{-7}	1.63×10^{-6}	5.07×10^{-6}	1.47×10^{-5}
(c) Initial Rate (M s^{-1}) $[\mathrm{A}]_0 = [\mathrm{B}]_0 = 0.200\ M$	5.31×10^{-7}	1.94×10^{-6}	6.52×10^{-6}	2.03×10^{-5}	5.87×10^{-5}

43. We use the Arrhenius equation one last time, applying the formula to a set of second-order nucleophilic substitution reactions.

(a) Insert the appropriate parameters for each system, and use the equation

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

to calculate the second-order rate constant at 40°C.

Reaction 1:

$E_{a1} = 86.6\ \text{kJ mol}^{-1}$ $\qquad A_1 = 1.49 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$ $\qquad T = 313.15\ \text{K}\ \ (40°\text{C})$

$$k_1 = \left(1.49\times10^{11}\ M^{-1}\ \text{s}^{-1}\right)\exp\left[-\frac{8.66\times10^{4}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(313.15\ \text{K}\right)}\right] = 5.35\times10^{-4}\ M^{-1}\ \text{s}^{-1}$$

Reaction 2:

$E_{a2} = 81.6\ \text{kJ mol}^{-1}$ $\qquad A_2 = 2.42 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$ $\qquad T = 313.15\ \text{K}\ \ (40°\text{C})$

$$k_2 = \left(2.42\times10^{11}\ M^{-1}\ \text{s}^{-1}\right)\exp\left[-\frac{8.16\times10^{4}\ \text{J mol}^{-1}}{\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(313.15\ \text{K}\right)}\right] = 5.93\times10^{-3}\ M^{-1}\ \text{s}^{-1}$$

Reaction 3:

$E_{a3} = 89.5 \text{ kJ mol}^{-1}$ $\quad A_3 = 4.30 \times 10^{11}\ M^{-1}\ \text{s}^{-1}$ $\quad T = 313.15 \text{ K}\ (40°\text{C})$

$$k_3 = \left(4.30 \times 10^{11}\ M^{-1}\ \text{s}^{-1}\right)\exp\left[-\frac{8.95 \times 10^4 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1}\ \text{K}^{-1}\right)\left(313.15 \text{ K}\right)}\right] = 5.07 \times 10^{-4}\ M^{-1}\ \text{s}^{-1}$$

Note that the substitution $T = 313$ K produces slightly different values for the three rate constants:

$k_1 = 5.26 \times 10^{-4}\ M^{-1}\ \text{s}^{-1}$ $\quad k_2 = 5.84 \times 10^{-3}\ M^{-1}\ \text{s}^{-1}$ $\quad k_3 = 4.99 \times 10^{-4}\ M^{-1}\ \text{s}^{-1}$

(b) For each S_N2 reaction, the rate law is given by the equation

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

where A and B are the two reactants. Since the problem stipulates that $[\text{A}]_0 = [\text{B}]_0 = 0.10\ M$ for the whole set, the initial rates are directly proportional to k.

Reaction 2 has the largest rate constant. Its initial rate is highest of the three.

(c) Activation energies and other kinetic parameters for the forward reaction are insufficient to fix the value of an equilibrium constant. To predict the composition at equilibrium, we need the standard difference in free energy between reactants and products. Alternatively, we need rate constants for both the forward and reverse reactions at each step. See the next several exercises.

This final block of exercises deals with the mechanistic considerations of Section 18-6. For sample problems, see Examples 18-10 through 18-12.

44. The following material in *PoC* is relevant to the present exercise and the next:

Law of mass action: Section 12-4 and Example 12-2
Arrhenius law: pages 656–659 and Examples 18-7 through 18-9
Principle of detailed balance: pages 682–684 and Example 18-12

(a) Insert the specified equilibrium concentrations

$[\text{A}]_{\text{eq}} = 1.00\ M$ $\quad [\text{B}]_{\text{eq}} = 2.00\ M$ $\quad [\text{C}]_{\text{eq}} = 5.00\ M$ $\quad [\text{D}]_{\text{eq}} = 4.00\ M$

directly into the mass-action expression for K:

$$\mathrm{A + B \rightarrow C + D}$$

$$K = \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} = \frac{(5.00)(4.00)}{(1.00)(2.00)} = 10.0$$

(b) We use the Arrhenius parameters

$$E_{\mathrm{a}} = 100.0 \text{ kJ mol}^{-1} \qquad A = 1.00 \times 10^{10}\ M^{-1}\ \mathrm{s}^{-1}$$

to evaluate the forward rate constant at 700 K:

$$\begin{aligned} k_+ &= A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \\ &= \left(1.00 \times 10^{10}\ M^{-1}\ \mathrm{s}^{-1}\right)\exp\left[-\frac{1.000 \times 10^5 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1}\ \mathrm{K}^{-1}\right)\left(700 \text{ K}\right)}\right] \\ &= 345\ M^{-1}\ \mathrm{s}^{-1} \end{aligned}$$

(c) Forward and reverse rates for the elementary reaction are equal at equilibrium:

$$\mathrm{A + B \underset{k_-}{\overset{k_+}{\rightleftarrows}} C + D}$$

$$\text{forward rate} = \text{reverse rate}$$

$$k_+[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} = k_-[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}$$

$$\frac{k_+}{k_-} = \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} = K$$

Having established values for K and k_+ in (a) and (b) above, we now solve for the rate constant k_- in the reverse direction:

$$k_- = \frac{k_+}{K} = \frac{345\ M^{-1}\ \mathrm{s}^{-1}}{10.0} = 34.5\ M^{-1}\ \mathrm{s}^{-1}$$

45. We rework the preceding calculation at 800 K, looking to discern the effect of temperature on both the equilibrium position and kinetics of the reaction. The method is the same as in Exercise 44.

(a) The equilibrium constant increases 300-fold as the system goes from 700 K to 800 K:

$$\mathrm{A + B \rightarrow C + D}$$

$$K = \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} = \frac{(10.00)(15.00)}{(0.10)(0.50)} = 3.0 \times 10^3$$

(b) The forward rate constant (k_+) increases from $3.45 \times 10^2\ M^{-1}\ \mathrm{s}^{-1}$ at 700 K to $2.96 \times 10^3\ M^{-1}\ \mathrm{s}^{-1}$ at 800 K:

$$\begin{aligned} k_+ &= A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \\ &= \left(1.00 \times 10^{10}\ M^{-1}\ \mathrm{s}^{-1}\right)\exp\left[-\frac{1.000 \times 10^5\ \mathrm{J\ mol^{-1}}}{\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\left(800\ \mathrm{K}\right)}\right] \\ &= 2.96 \times 10^3\ M^{-1}\ \mathrm{s}^{-1} \end{aligned}$$

(c) The reverse rate constant (k_-) decreases from $34.5\ M^{-1}\ \mathrm{s}^{-1}$ at 700 K to $0.99\ M^{-1}\ \mathrm{s}^{-1}$ at 800 K, conforming to the larger value of K at the higher temperature:

$$k_- = \frac{k_+}{K} = \frac{2.96 \times 10^3\ M^{-1}\ \mathrm{s}^{-1}}{3.0 \times 10^3} = 0.99\ M^{-1}\ \mathrm{s}^{-1}$$

(d) The reaction is endothermic. Its equilibrium constant increases with temperature, in accordance with Le Châtelier's principle: Heat functions as a reactant, and the system relieves the stress of a higher temperature by moving to the right—toward the consumption of heat and the manufacture of product. See Section 12-6 and Examples 12-15 and 15-9 in *PoC.*

Note that the rate constant k_+, a *kinetic* (nonthermodynamic) parameter determined by E_a, A, and T, does not enter into the argument. The value of k_+ grows exponentially with temperature,

$$k_+ = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)$$

regardless of the endothermicity or exothermicity of the process.

46. We are given a forward rate constant (k_+) and ΔG° for the gas-phase formation of HI from H_2 and I_2 at 500 K:

$$H_2(g) + I_2(g) \underset{k_-}{\overset{k_+}{\rightleftarrows}} 2HI(g) \qquad k_+(500\text{ K}) = 4.3 \times 10^{-7}\ M^{-1}\ s^{-1}$$

$$K = \frac{[HI]^2}{[H_2][I_2]} \qquad \Delta G^\circ(500\text{ K}) = -20.2\text{ kJ} \text{ (per mole of } H_2)$$

(a) See Section 14-8 and Example 14-8 for the relationship between the equilibrium constant (K) and the difference in standard free energy (ΔG°):

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{(-2.02 \times 10^4\text{ J mol}^{-1})}{(8.3145\text{ J mol}^{-1}\text{ K}^{-1})(500\text{ K})}\right] = 129 \qquad (T = 500\text{ K})$$

(b) We assume, for now, that the transformation is elementary (second order in both directions), and we apply the principle of detailed balance:

forward rate = reverse rate (at equilibrium)

$$k_+[H_2]_{eq}[I_2]_{eq} = k_-[HI]^2_{eq}$$

$$\frac{k_+}{k_-} = \frac{[HI]^2_{eq}}{[H_2]_{eq}[I_2]_{eq}} = K$$

Insertion of $k_+ = 4.3 \times 10^{-7}\ M^{-1}\ s^{-1}$ and $K = 129$ gives us a value for k_-:

$$k_- = \frac{k_+}{K} = \frac{4.3 \times 10^{-7}\ M^{-1}\ s^{-1}}{129} = 3.3 \times 10^{-9}\ M^{-1}\ s^{-1}$$

See pages 682–684 and Example 18-12 in *PoC.*

Note that the reaction actually occurs in two steps, as described in the next exercise:

1. $I_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I + I + M$ (rapid, equilibrium)

2. $H_2 + I + I \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2HI$ (slow)

Net: $H_2 + I_2 \rightleftarrows 2HI$

We shall see subsequently that our current k_+ is effectively a composite rate constant equal to k_1k_2/k_{-1}, whereas our current k_- is equal to k_{-2}. Applying the principle of detailed balance to each step, we then recover the same expression previously obtained for the overall equilibrium constant:

$$K = \frac{k_1k_2}{k_{-1}k_{-2}} = \frac{\left(\dfrac{k_1k_2}{k_{-1}}\right)}{k_{-2}} = \frac{k_+}{k_-}$$

47. We have two mechanisms to evaluate, each of which yields the same macroscopic rate law for the gas-phase formation of hydrogen iodide:

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

Mechanism 1 consists of only a single, bimolecular step:

$$H_2 + I_2 \rightarrow 2HI$$

Here the rate law happens to follow the stoichiometry, since the reaction is elementary:

$$\text{Rate} = k[H_2][I_2]$$

Mechanism 2, by contrast, posits a rapid first step involving a third species (M), followed by a slow second step:

$$\begin{array}{lllll}
1. & I_2 + M & \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & I + I + M & \text{(rapid, equilibrium)} \\
2. & H_2 + I + I & \xrightarrow{k_2} & 2HI & \text{(slow)} \\
\hline
\text{Net:} & H_2 + I_2 & \longrightarrow & 2HI &
\end{array}$$

The system comes to a pre-equilibrium in step 1, with the proportions of I_2 and the reactive intermediate I determined by the equilibrium constant K_1:

$$K_1 = \frac{[I]^2}{[I_2]} = \frac{k_1}{k_{-1}}$$

$$[I]^2 = K_1[I_2]$$

The quantity $[\mathrm{I}]^2$ is then inserted into the rate law that comes from the slow, *rate-determining* step 2,

$$\text{Rate} = k_2[\mathrm{H_2}][\mathrm{I}]^2$$

to yield a final form that involves only the reactants H_2 and I_2:

$$\text{Rate} = k_2[\mathrm{H_2}]K_1[\mathrm{I_2}] = k[\mathrm{H_2}][\mathrm{I_2}]$$

The overall rate forward rate constant, k, is equal to K_1k_2 (equivalently, k_1k_2/k_{-1}).
See Section 18-6 in *PoC*, as well as Examples 18-10 and18-11.

48. Imagine that the reaction proceeds through some transient species S:

$$1.\quad \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{S} \qquad k_1 = 10 \qquad k_{-1} = 1$$

$$2.\quad \mathrm{S} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{B} \qquad k_2 = 3 \qquad k_{-2} = 30$$

$$\text{Net:}\quad \mathrm{A} \rightleftarrows \mathrm{B}$$

At system-wide equilibrium, the principle of detailed balance requires that

$$K = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_1K_2 = \frac{[\mathrm{S}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \times \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{S}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}}$$

for the two-step mechanism. Given the equilibrium concentration of A, together with values for the four rate constants, we can then solve for the equilibrium concentration of B:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1k_2}{k_{-1}k_{-2}}$$

$$[\mathrm{B}]_{\mathrm{eq}} = \frac{k_1k_2}{k_{-1}k_{-2}}[\mathrm{A}]_{\mathrm{eq}} = \frac{10 \times 3}{1 \times 30} \times 1\ M = 1\ M$$

For a related calculation see Example 18-12. The principle of detailed balance is covered on pages 682–684 of *PoC*.

49. The suggested mechanism for the reaction

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

contains a slow step followed by a fast step:

1. $NO_2 + F_2 \xrightarrow{k_1} NO_2F + F$ (slow)

2. $F + NO_2 \xrightarrow{k_2} NO_2F$ (fast)

Net: $2NO_2 + F_2 \longrightarrow 2NO_2F$

(a) The *slow* step (step 1) determines the rate. See pages 678–680 and Example 18-11 in *PoC.*

(b) The rate law derives directly from the rate-determining elementary step:

$$\text{Rate} = k_1[NO_2][F_2]$$

50. Consider the following reaction and proposed mechanism:

1. $OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HOCl + OH^-$ (rapid, equilibrium)

2. $I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$ (slow)

3. $OH^- + HOI \xrightarrow{k_3} H_2O + OI^-$ (fast)

Net: $OCl^-(aq) + I^-(aq) \longrightarrow Cl^-(aq) + OI^-(aq)$

(a) Step 2, specified as slow, determines the overall rate of reaction:

2. $I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$ (slow)

$$\text{Rate} = k_2[I^-][HOCl]$$

The concentration of HOCl, an intermediate, is obtained from the pre-equilibrium established in step 1. As usual, the equilibrium constant does not include a factor $[H_2O(\ell)]$:

$$1. \qquad OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HOCl + OH^- \qquad \text{(rapid, equilibrium)}$$

$$K_1 = \frac{[HOCl][OH^-]}{[OCl^-]}$$

$$[HOCl] = \frac{K_1[OCl^-]}{[OH^-]}$$

The overall rate law follows upon substitution of this latter value for [HOCl]:

$$\text{Rate} = k_2[I^-][HOCl] = k_2[I^-]\frac{K_1[OCl^-]}{[OH^-]} = k\frac{[I^-][OCl^-]}{[OH^-]} \qquad (k = k_2K_1)$$

(b) Substitute the equivalent form

$$K_1 = \frac{k_1}{k_{-1}}$$

into the rate law to express the overall rate constant, k, in terms of k_1, k_{-1}, and k_2:

$$k = k_2K_1 = k_2\frac{k_1}{k_{-1}}$$

The substitution is justified by the principle of detailed balance (pages 682–684 and Example 18-12 in *PoC*).

51. We are given a two-step mechanism for the production of molecular oxygen from ozone:

$$1. \qquad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \qquad \text{(rapid, equilibrium)}$$

$$2. \qquad O_3 + O \xrightarrow{k_2} 2O_2 \qquad \text{(slow)}$$

$$\text{Net:} \qquad 2O_3(g) \longrightarrow 3O_2(g)$$

(a) Oxygen radicals build up to a steady concentration during the first step, reaching a quasi equilibrium after some short time:

$$1. \quad O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \qquad \text{(rapid, equilibrium)}$$

$$K_1 = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_1[O_3]}{[O_2]}$$

The slow second step is rate determining:

$$2. \quad O_3 + O \xrightarrow{k_2} 2O_2 \qquad \text{(slow)}$$

$$\text{Rate} = k_2[O_3][O] = k_2[O_3]\frac{K_1[O_3]}{[O_2]} = k\frac{[O_3]^2}{[O_2]} \qquad (k = k_2K_1)$$

(b) Replace the first-stage equilibrium constant by the expression

$$K_1 = \frac{k_1}{k_{-1}}$$

to express the overall rate constant k in terms of the individual rate constants k_1, k_{-1}, and k_2:

$$k = k_2K_1 = k_2\frac{k_1}{k_{-1}}$$

The substitution is justified by the principle of detailed balance (pages 682–684 and Example 18-12 in *PoC*).