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

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

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

(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 \([NOBr]_0\) has been cut in half:

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

The rate is smaller at each value of \(t\):

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

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

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

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

\[
2NO_2(g) \rightarrow 2NO(g) + O_2(g)
\]

\[
\text{Rate} = k[NO_2]^2 \quad k(300^\circ C) = 0.54\ M^{-1}\ s^{-1}
\]
18. *Kinetics—The Course of Chemical Reactions*

**Figure 18.7** A plot of $[\text{NOBr}]$ 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 $1/[\text{NOBr}]$ 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,

\[
\frac{[\text{NO}_2]_t}{[\text{NO}_2]_0} = \frac{0.0925 \, M}{0.1850 \, M} = 0.500
\]

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

\[
t_{1/2} = \frac{1}{k[\text{NO}_2]_0} = \frac{1}{(0.54 \, M^{-1} \, s^{-1})(0.1850 \, M)} = 10. \, s
\]

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 \(1/(k[A]_0)\). 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 \(\text{NO}_2\) is first order, with \(k = 0.54 \, s^{-1}\):

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

(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: \([\text{NO}_2]\) 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):

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

\[
\text{Rate}_2 = k_2[B]^2 \quad k_2 = 1000 \, M^{-1} \, s^{-1}
\]
Figure 18.9  A plot of $[\text{NO}_2]/[\text{NO}_2]_0$ 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 $[\text{NO}_2]/[\text{NO}_2]_0$ versus time for an assumed first-order decomposition reaction ($k = 0.54 \text{ s}^{-1}$), 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 \( t = 0 \):

\[
\text{rate}_2(0) = \text{rate}_1(0)
\]

\[k_2[B]_0^2 = k_1[A]_0
\]

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

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

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

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

**Reaction 1:**

\[t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{1000 \text{ s}^{-1}} = 6.93 \times 10^{-4} \text{ s}
\]

**Reaction 2:**

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

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

<table>
<thead>
<tr>
<th>([A]_0 \text{ (M)})</th>
<th>(t_{1/2} \text{ (s)})</th>
<th>([B]_0 \text{ (M)})</th>
<th>(t_{1/2} \text{ (s)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 1</td>
<td>(6.93 \times 10^{-4})</td>
<td>1</td>
<td>(1.00 \times 10^{-3}) s</td>
</tr>
<tr>
<td>(b) 2</td>
<td>(6.93 \times 10^{-4})</td>
<td>(\sqrt{2})</td>
<td>(7.07 \times 10^{-4}) s</td>
</tr>
<tr>
<td>(c) 3</td>
<td>(6.93 \times 10^{-4})</td>
<td>(\sqrt{3})</td>
<td>(5.77 \times 10^{-4}) s</td>
</tr>
<tr>
<td>(d) 4</td>
<td>(6.93 \times 10^{-4})</td>
<td>2</td>
<td>(5.00 \times 10^{-4}) s</td>
</tr>
</tbody>
</table>

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: \[ [A]_t = [A]_0 \exp(-k_1 t) \quad k_1 = 1000 \text{ s}^{-1} \text{ (first order)} \]

Reaction 2: \[ [B]_t = \frac{[B]_0}{k_2 [B]_0 + 1} \quad k_2 = 1000 \text{ M}^{-1} \text{ s}^{-1} \text{ (second order)} \]

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:

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

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

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

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

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:

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

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

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 \( k_2 \),

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

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:

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

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

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:

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

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$^{-1}$ s$^{-1}$:

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

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

$$\ln A = 26.9838$$

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

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:

\[ T_K = T_C + 273 \]

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:

\[ T_K = T_C + 273.15 \]

Use of the conversion

\[ T_K = T_C + 273.15 \]

results in slightly different values for the slope and intercept:

Slope = −22,122 K \hspace{1cm} E_a = 184 \text{ kJ mol}^{-1} \]

Intercept = 26.9880 \hspace{1cm} A = 5.26 \times 10^{11} \text{ 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 \( E_a = 161 \text{ kJ mol}^{-1} \) and \( A = 4.00 \times 10^{13} \text{ s}^{-1} \):

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

\[ = 161 \text{ kJ mol}^{-1} \]

\[ \ln A = 31.321 \]

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

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 $A$,

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

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

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

$$= \left(4.94 \times 10^{13} \text{ s}^{-1}\right) \exp\left[-\frac{1.03 \times 10^6 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}\right]$$

$$= 5.76 \times 10^{-5} \text{ s}^{-1}$$

The initial rate, directly proportional to the initial concentration, doubles if $[\text{N}_2\text{O}_5]_0$ is doubled. It goes from $5.76 \times 10^{-7} \text{ M s}^{-1}$ when $[\text{N}_2\text{O}_5]_0 = 0.0100 \text{ M}$,

$$\text{Rate} = k[N_2O_5]_0 = \left(5.76 \times 10^{-5} \text{ s}^{-1}\right)(0.0100 \text{ M}) = 5.76 \times 10^{-7} \text{ M s}^{-1}$$

to $1.15 \times 10^{-6} \text{ M s}^{-1}$ when $[\text{N}_2\text{O}_5]_0 = 0.0200 \text{ M}$:

$$\text{Rate} = k[N_2O_5]_0 = \left(5.76 \times 10^{-5} \text{ s}^{-1}\right)(0.0200 \text{ M}) = 1.15 \times 10^{-6} \text{ M s}^{-1}$$

The reaction is first order. Calculations for all the other temperatures are done in the same way. Results are summarized below:

<table>
<thead>
<tr>
<th>$T$</th>
<th>300 K</th>
<th>325 K</th>
<th>350 K</th>
<th>375 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Rate Constant (s$^{-1}$)</td>
<td>$5.76 \times 10^{-5}$</td>
<td>$1.38 \times 10^{-3}$</td>
<td>0.0210</td>
<td>0.222</td>
<td>1.75</td>
</tr>
<tr>
<td>(b) Initial Rate (M s$^{-1}$)</td>
<td>$5.76 \times 10^{-7}$</td>
<td>$1.38 \times 10^{-5}$</td>
<td>0.000210</td>
<td>0.00222</td>
<td>0.0175</td>
</tr>
<tr>
<td>$[N_2O_5]_0 = 0.0100 \text{ M}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Initial Rate (M s$^{-1}$)</td>
<td>$1.15 \times 10^{-6}$</td>
<td>$2.76 \times 10^{-5}$</td>
<td>0.000420</td>
<td>0.00445</td>
<td>0.0350</td>
</tr>
</tbody>
</table>
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. \( E_a = 100 \text{ kJ mol}^{-1} \quad A = 10^{13} \text{ s}^{-1} \)

2. \( E_a = 110 \text{ kJ mol}^{-1} \quad A = 10^{14} \text{ s}^{-1} \)

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

Reaction 1:

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

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

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:

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

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

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 \( E_a \). 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 \(k_2\):

\[
k_1 = k_2
\]

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

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

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

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

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

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

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

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

\[
\text{C}_2\text{H}_3\text{Br(aq)} + \text{OH}^- (aq) \rightarrow \text{C}_2\text{H}_5\text{OH(aq)} + \text{Br}^- (aq)
\]

\[
\text{Rate} = k[\text{C}_2\text{H}_3\text{Br}][\text{OH}^-]
\]

The initial rate quadruples when the initial concentrations \([\text{C}_2\text{H}_3\text{Br}]_0\) and \([\text{OH}^-]_0\) are both doubled.
One sample calculation (at 10°C) should suffice. We use the parameters specified in the problem:

\[ E_a = 89.5 \text{ kJ mol}^{-1} \quad A = 4.30 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \quad T = 283.15 \text{ K} \ (10^\circ \text{C}) \]

Rate constant:

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

\[
= \left( 4.30 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \right) \exp \left[ -\frac{8.95 \times 10^4 \text{ J mol}^{-1}}{\left( 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \right)(283.15 \text{ K})} \right]
\]

\[= 1.3279 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} = 1.33 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \quad (3 \text{ sig fig})\]

Initial rates:

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

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

\[= \left( 1.3279 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \right) (0.100 \text{ M})(0.100 \text{ M})
\]

\[= 1.33 \times 10^{-7} \text{ M s}^{-1}\]

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

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

\[= \left( 1.3279 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \right) (0.200 \text{ M})(0.200 \text{ M})
\]

\[= 5.31 \times 10^{-7} \text{ M s}^{-1}\]

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

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

\[ k_1 = \left(1.49 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}\right) \exp \left[ -\frac{8.66 \times 10^4 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(313.15 \text{ K})} \right] = 5.35 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} \]

Reaction 2:

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

\[ k_2 = \left(2.42 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}\right) \exp \left[ -\frac{8.16 \times 10^4 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(313.15 \text{ K})} \right] = 5.93 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \]
Reaction 3:

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

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

Note that the substitution \( T = 313 \text{ K} \) produces slightly different values for the three rate constants:

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

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

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

where A and B are the two reactants. Since the problem stipulates that \([A]_0 = [B]_0 = 0.10 \text{ M}\) 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

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

directly into the mass-action expression for \( K \):
\[ A + B \rightarrow C + D \]

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

(b) We use the Arrhenius parameters

\[ E_a = 100.0 \text{ kJ mol}^{-1} \quad A = 1.00 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \]

to evaluate the forward rate constant at 700 K:

\[ k_+ = A \exp \left( -\frac{E_a}{RT} \right) \]

\[ = \left(1.00 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\right) \exp \left[ -\frac{1.00 \times 10^5 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)(700 \text{ K})} \right] \]

\[ = 345 \text{ M}^{-1} \text{ s}^{-1} \]

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

\[ \frac{k_+}{k_-} = \frac{A}{k_-} \]

\[ A + B \rightleftharpoons C + D \]

\[ k_- \quad \text{forward rate} = \text{reverse rate} \]

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

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

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

\[ k_- = \frac{k_+}{K} = \frac{345 \text{ M}^{-1} \text{ s}^{-1}}{10.0} = 34.5 \text{ M}^{-1} \text{ s}^{-1} \]

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:

\[ A + B \rightarrow C + D \]

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

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

\[ k_\rightarrow = A \exp\left(-\frac{E_a}{RT}\right) \]

\[ = \left(1.00 \times 10^{10} \, M^{-1} \, s^{-1}\right) \exp\left[-\frac{1.00 \times 10^5 \, J \, mol^{-1}}{(8.3145 \, J \, mol^{-1} \, K^{-1})(800 \, K)}\right] \]

\[ = 2.96 \times 10^3 \, M^{-1} \, s^{-1} \]

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

\[ k_\leftarrow = \frac{k_\rightarrow}{K} = \frac{2.96 \times 10^3 \, M^{-1} \, s^{-1}}{3.0 \times 10^3} = 0.99 \, M^{-1} \, s^{-1} \]

(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 \( k_\rightarrow \), a kinetic (nonthermodynamic) parameter determined by \( E_a, A, \) and \( T \), does not enter into the argument. The value of \( k_\rightarrow \) grows exponentially with temperature,

\[ k_\rightarrow = A \exp\left(-\frac{E_a}{RT}\right) \]

regardless of the endothermicity or exothermicity of the process.
46. We are given a forward rate constant \( k_+ \) and \( \Delta G^\circ \) for the gas-phase formation of HI from \( H_2 \) and \( I_2 \) at 500 K:

\[
\begin{align*}
H_2(g) + I_2(g) & \rightleftharpoons 2HI(g) & k_+(500 \text{ K}) &= 4.3 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1} \\
\end{align*}
\]

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

(a) See Section 14-8 and Example 14-8 for the relationship between the equilibrium constant \( K \) and the difference in standard free energy \( \Delta G^\circ \):

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

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

\[
\text{forward rate} = \text{reverse rate} \quad \text{(at equilibrium)}
\]

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

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

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

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

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. \( I_2 + M \rightleftharpoons I + I + M \) (rapid, equilibrium)
2. \( H_2 + I + I \rightleftharpoons 2HI \) (slow)

Net: \( H_2 + I_2 \rightleftharpoons 2HI \)
We shall see subsequently that our current $k_1$ is effectively a composite rate constant equal to $k_1k_2/k_{-1}$, whereas our current $k_2$ 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:

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

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

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$$

Mechanism 1 consists of only a single, bimolecular step:

$$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$$

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

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

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

1. $\frac{k_1}{k_{-1}} \quad \text{I}_2 + \text{M} \rightleftharpoons \text{I} + \text{I} + \text{M} \quad \text{(rapid, equilibrium)}$

2. $\text{H}_2 + \text{I} + \text{I} \xrightarrow{k_2} 2\text{HI} \quad \text{(slow)}$

Net: $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$

The system comes to a pre-equilibrium in step 1, with the proportions of $\text{I}_2$ and the reactive intermediate $\text{I}$ determined by the equilibrium constant $K_1$:

$$K_1 = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{k_1}{k_{-1}}$$

$$[\text{I}]^2 = K_1[\text{I}_2]$$
The quantity \([I]^2\) is then inserted into the rate law that comes from the slow, *rate-determining* step 2,

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

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

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

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 and 18-11.

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

\[
\begin{align*}
1. & \quad A \rightleftharpoons S \\
& \quad k_1 \\
& \quad k_{-1} & = k_1 = 10 \\
2. & \quad S \rightleftharpoons B \\
& \quad k_2 & = k_2 = 3 \\
& \quad k_{-2} & = k_{-2} = 30
\end{align*}
\]

Net: \(A \rightleftharpoons B\)

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

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

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 \(B\):

\[
\begin{align*}
[B]_{eq} &= \frac{k_1k_2}{k_{-1}k_{-2}} \\
[A]_{eq} &= \frac{k_1}{k_{-1}} \times \frac{3}{30} \\
[B]_{eq} &= \frac{k_1k_2}{k_{-1}k_{-2}} [A]_{eq} = 10 \times 3 \times 1 = 1 M
\end{align*}
\]

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

\[ 2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g) \]

contains a slow step followed by a fast step:

1. \[ \text{NO}_2 + \text{F}_2 \xrightleftharpoons{\kappa_1} \text{NO}_2\text{F} + \text{F} \quad \text{(slow)} \]

2. \[ \text{F} + \text{NO}_2 \xrightarrow{\kappa_2} \text{NO}_2\text{F} \quad \text{(fast)} \]

Net: \[ 2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F} \]

(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:

\[ \text{Rate} = \kappa_1[\text{NO}_2][\text{F}_2] \]

50. Consider the following reaction and proposed mechanism:

1. \[ \text{OCl}^- + \text{H}_2\text{O} \xrightleftharpoons{\kappa_1} \text{HOCl} + \text{OH}^- \quad \text{(rapid, equilibrium)} \]

2. \[ \text{I}^- + \text{HOCl} \xrightarrow{\kappa_2} \text{HOI} + \text{Cl}^- \quad \text{(slow)} \]

3. \[ \text{OH}^- + \text{HOI} \xrightarrow{\kappa_3} \text{H}_2\text{O} + \text{OI}^- \quad \text{(fast)} \]

Net: \[ \text{OCl}^- (\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{Cl}^- (\text{aq}) + \text{OI}^- (\text{aq}) \]

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

\[ 2. \ \text{I}^- + \text{HOCl} \xrightarrow{\kappa_2} \text{HOI} + \text{Cl}^- \quad \text{(slow)} \]

\[ \text{Rate} = \kappa_2[\text{I}^-][\text{HOCl}] \]

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\text{2O}(\ell)]:
1. \[ \text{OC}^- + \text{H}_2\text{O} \xleftrightarrow{\text{k}_1} \text{HOCl} + \text{OH}^- \quad \text{(rapid, equilibrium)} \]

\[ K_1 = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OC}^-]} \]

\[ [\text{HOCl}] = \frac{K_1[\text{OC}^-]}{[\text{OH}^-]} \]

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

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

(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. \[ \text{O}_3 \xleftrightarrow{\text{k}_1} \text{O}_2 + \text{O} \quad \text{(rapid, equilibrium)} \]

\[ \text{Net:} \quad \text{2O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g}) \]

(a) Oxygen radicals build up to a steady concentration during the first step, reaching a quasi equilibrium after some short time:
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1. \[ \text{O}_3 \xrightleftharpoons[k_1]{k_{-1}} \text{O}_2 + \text{O} \] (rapid, equilibrium)

\[ K_1 = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \]

\[ [\text{O}] = \frac{K_1[\text{O}_3]}{[\text{O}_2]} \]

The slow second step is rate determining:

2. \[ \text{O}_3 + \text{O} \xrightarrow{k_2} 2\text{O}_2 \] (slow)

\[ \text{Rate} = k_2[\text{O}_3][\text{O}] = k_2[\text{O}_3] \frac{K_1[\text{O}_3]}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad (k = k_2K_1) \]

(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).