In a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form \( A \rightarrow \text{products} \). The differential rate for a first-order reaction is as follows:

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

If the concentration of \( A \) is doubled, the reaction rate doubles; if the concentration of \( A \) is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds \( (s^{-1}) \).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

\[
[A] = [A]_0e^{-kt}
\]

where \([A]_0\) is the initial concentration of reactant \( A \) at \( t = 0 \); \( k \) is the rate constant; and \( e \) is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation (14.4.6) predicts that the concentration of \( A \) will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation (14.4.6) and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of \( A \) and \( t \):

\[
\ln[A] = \ln[A]_0 - kt
\]

Because Equation (14.4.7) has the form of the algebraic equation for a straight line, \( y = mx + b \), with \( y = \ln[A] \) and \( b = \ln[A]_0 \), a plot of \( \ln[A] \) versus \( t \) for a first-order reaction should give a straight line with a slope of \(-k\) and an intercept of \( \ln[A]_0 \). Either the differential rate law (Equation (14.4.5)) or the integrated rate law (Equation (14.4.7)) can be used to determine whether a particular reaction is first order.

First-order reactions are very common. We have already encountered two examples of first-order reactions: the hydrolysis of aspirin and the reaction of \( t \)-butyl bromide with water to give \( t \)-butanol. Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:
Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure \(\PageIndex{1}\) is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure \(\PageIndex{1}\) have been studied extensively to find ways of maximizing the concentration of the active species.

Note

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table \(\PageIndex{1}\). The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table \(\PageIndex{1}\) shows that the reaction rate doubles \([1.8 \times 10^{-5} \text{ M/min}] ÷ [9.0 \times 10^{-6} \text{ M/min}] = 2.0]\) when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 \([4.5 \times 10^{-5} \text{ M/min}] ÷ [9.0 \times 10^{-6} \text{ M/min}] = 5.0]\) when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = \(k[\text{cisplatin}]^1\). Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table \(\PageIndex{1}\). For example, substituting the values for Experiment 3 into Equation \(\ref{14.4.5}\),

\[
3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})
\]

\[
1.5 \times 10^{-3} \text{ min}^{-1} = k
\]

Table \(\PageIndex{1}\): Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[Cisplatin]₀ (M)</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0060</td>
<td>9.0 \times 10^{-6}</td>
</tr>
<tr>
<td>2</td>
<td>0.012</td>
<td>1.8 \times 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>0.024</td>
<td>3.6 \times 10^{-5}</td>
</tr>
</tbody>
</table>
Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

\[
\text{CH}_3\text{CH}_2\text{Cl}(g) \rightarrow \Delta \text{HCl}(g) + \text{C}_2\text{H}_4(g)
\]

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{Cisplatin}]_0 \text{ (M)})</th>
<th>Initial Rate \text{ (M/min)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>1.6 × 10^{-8}</td>
</tr>
<tr>
<td>2</td>
<td>0.030</td>
<td>4.8 × 10^{-8}</td>
</tr>
<tr>
<td>3</td>
<td>0.040</td>
<td>6.4 × 10^{-8}</td>
</tr>
<tr>
<td>4</td>
<td>0.075</td>
<td>9.6 × 10^{-8}</td>
</tr>
</tbody>
</table>

**Given:** balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

**Asked for:** reaction order and rate constant

**Strategy:**

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C. Use measured concentrations and rate data from any of the experiments to find the rate constant.

**Solution:**

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.
Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to \([\text{CH}_3\text{CH}_2\text{Cl}]\). Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to \([\text{CH}_3\text{CH}_2\text{Cl}]\).

This behavior is characteristic of a first-order reaction, for which the rate law is \(\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}]\).

We can calculate the rate constant \((k)\) using any row in the table. Selecting Experiment 1 gives the following:

\[
1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})
\]

\[
1.6 \times 10^{-6} \text{ s}^{-1} = k
\]

Exercise \(\PageIndex{1}\)

Sulfuryl chloride (SO\(_2\)Cl\(_2\)) decomposes to SO\(_2\) and Cl\(_2\) by the following reaction:

\[
\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})
\]

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{SO}_2\text{Cl}_2]_0 \text{ (M)})</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0050</td>
<td>(1.10 \times 10^{-7})</td>
</tr>
<tr>
<td>2</td>
<td>0.0075</td>
<td>(1.65 \times 10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>0.0100</td>
<td>(2.20 \times 10^{-7})</td>
</tr>
<tr>
<td>4</td>
<td>0.0125</td>
<td>(2.75 \times 10^{-7})</td>
</tr>
</tbody>
</table>

**Answer:** first order; \(k = 2.2 \times 10^{-5} \text{ s}^{-1}\)

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Part (a) in Figure \(\PageIndex{3}\) shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.
The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure \(\PageIndex{3}\)). The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure \(\PageIndex{3}\)) for \(t = 100\) min \([\text{cisplatin}] = 0.0086\) M and \(t = 1000\) min \([\text{cisplatin}] = 0.0022\) M,

\[
\begin{align*}
\text{slope}&=\frac{\ln [\text{cisplatin}]_{1000}-\ln [\text{cisplatin}]_{100}}{1000\text{ min}-100\text{ min}} \\
-\text{k}&=\frac{\ln 0.0022-\ln 0.0086}{1000\text{ min}-100\text{ min}}=\frac{\ln 0.0022-\ln 0.0086}{1000\text{ min}-100\text{ min}}=\frac{-6.12-(-4.76)}{900\text{ min}}=-1.51\times10^{-3}\text{ min}^{-1} \\
\text{k}&=1.5\times10^{-3}\text{ min}^{-1}
\end{align*}
\]

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of \(\text{min}^{-1}\) because the times plotted on the horizontal axes in parts (a) and (b) in Figure \(\PageIndex{3}\)) are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

Example \(\PageIndex{2}\))

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M \((k = 1.6 \times 10^{-6}\text{ s}^{-1})\) ?

**Given:** initial concentration, rate constant, and time interval

**Asked for:** concentration at specified time and time required to obtain particular concentration

**Strategy:**
A. Substitute values for the initial concentration \([A]_0\) and the calculated rate constant for the reaction \(k\) into the integrated rate law for a first-order reaction. Calculate the concentration \([A]\) at the given time \(t\).

B. Given a concentration \([A]\), solve the integrated rate law for time \(t\).

Solution:

The exponential form of the integrated rate law for a first-order reaction (Equation \(\text{(14.4.6)}\)) is \([A] = [A]_0 e^{-kt}\).

A Having been given the initial concentration of ethyl chloride \([A]_0\) and having the rate constant of \(k = 1.6 \times 10^{-6} \text{ s}^{-1}\), we can use the rate law to calculate the concentration of the reactant at a given time \(t\). Substituting the known values into the integrated rate law,

\[
\begin{align*}
[A]_{10 \text{ h}} &= [A]_0 e^{-kt} \\
&= 0.0200 \text{ M}(e^{-(1.6 \times 10^{-6} \text{ s}^{-1})[(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})]}) \\
&= 0.0189 \text{ M}
\end{align*}
\]

We could also have used the logarithmic form of the integrated rate law (Equation \(\text{(14.4.7)}\)):

\[
\begin{align*}
\ln[A]_{10 \text{ h}} &= \ln [A]_0 - kt \\
&= \ln 0.0200 - (1.6 \times 10^{-6} \text{ s}^{-1})[(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})] \\
&= -3.912 - 0.0576 = -3.970 \\
[A]_{10 \text{ h}} &= e^{-3.970} \text{ M} \\
&= 0.0189 \text{ M}
\end{align*}
\]

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for \(t\). Equation \(\text{(14.4.7)}\) gives the following:

\[
\begin{align*}
\ln[A]_t &= \ln [A]_0 - kt \\
kt &= \ln[A]_0 - \ln[A]_t = \ln\left(\frac{[A]_0}{[A]_t}\right) \\
t &= \frac{1}{k}\left(\ln\left(\frac{[A]_0}{[A]_t}\right)\right) = \frac{1}{1.6 \times 10^{-6} \text{ s}^{-1}}\left(\ln \frac{0.0200 \text{ M}}{0.0050 \text{ M}}\right) \\
&= \frac{\ln 4.0}{1.6 times 10^{-6} \text{ M}} = 8.7 times 10^5 \text{ s} = 240 \text{ h} = 2.4 \times 10^2 \text{ h}
\end{align*}
\]

Exercise \(\PageIndex{2}\)

In the exercise above, you found that the decomposition of sulfuryl chloride \((\text{SO}_2\text{Cl}_2)\) is first order, and you calculated the rate constant at 320° C. Use the form(s) of the integrated rate law to find the amount of \text{SO}_2\text{Cl}_2\) that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320° C. How long would it take for 90% of the \text{SO}_2\text{Cl}_2\) to decompose?

Answer: 0.0252 M; 29 h