Reaction Rates and Rate Laws

In this section, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations.

Reaction Rates

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

The progress of a simple reaction (A → B) is shown in Figure 14.5; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 14.5. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.
Figure 14.5 The Progress of a Simple Reaction \((A \rightarrow B)\). The mixture initially contains only \(A\) molecules (purple). Over time, the number of \(A\) molecules decreases and more \(B\) molecules (green) are formed (top). The graph shows the change in the number of \(A\) and \(B\) molecules in the reaction as a function of time over a 1 min period (bottom).

\[
\text{rate} = \frac{\Delta [\text{B}]}{\Delta t} = -\frac{\Delta [\text{A}]}{\Delta t} \tag{14.4}
\]

Square brackets indicate molar concentrations, and the capital Greek delta (\(\Delta\)) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of \(\Delta[A]/\Delta t\) to convert that expression to a positive number. The reaction rate calculated for the reaction \(A \rightarrow B\) using Equation 14.4 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first. This is consistent with the concentration effects described in Section 14.1.

Note

Reaction rates generally decrease with time as reactant concentrations decrease.

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 14.4 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 14.6.
Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 14.1 and are shown in the graph in Figure 14.7. These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Table 14.1 Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>[Aspirin] (M)</th>
<th>[Salicylic Acid] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$5.55 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>2.0</td>
<td>$5.51 \times 10^{-3}$</td>
<td>$0.040 \times 10^{-3}$</td>
</tr>
<tr>
<td>5.0</td>
<td>$5.45 \times 10^{-3}$</td>
<td>$0.10 \times 10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>$5.35 \times 10^{-3}$</td>
<td>$0.20 \times 10^{-3}$</td>
</tr>
<tr>
<td>20</td>
<td>$5.15 \times 10^{-3}$</td>
<td>$0.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>30</td>
<td>$4.96 \times 10^{-3}$</td>
<td>$0.59 \times 10^{-3}$</td>
</tr>
<tr>
<td>40</td>
<td>$4.78 \times 10^{-3}$</td>
<td>$0.77 \times 10^{-3}$</td>
</tr>
<tr>
<td>50</td>
<td>$4.61 \times 10^{-3}$</td>
<td>$0.94 \times 10^{-3}$</td>
</tr>
<tr>
<td>100</td>
<td>$3.83 \times 10^{-3}$</td>
<td>$1.72 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$2.64 \times 10^{-3}$</td>
<td>$2.91 \times 10^{-3}$</td>
</tr>
<tr>
<td>300</td>
<td>$1.82 \times 10^{-3}$</td>
<td>$3.73 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.
Figure 14.7 The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

The average reaction rate for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t₀) and at the end of the interval (t₁). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

\[
\begin{align*}
\text{rate}_{(t=0-2.0\,\text{h})} &= \frac{[\text{salicylic acid}]_2 - [\text{salicylic acid}]_0}{2.0\,\text{h} - 0\,\text{h}} \\
&= \frac{0.040 \times 10^{-3}\,\text{M} - 0\,\text{M}}{2.0\,\text{h}} = 2.0 \times 10^{-5}\,\text{M/h}
\end{align*}
\]

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

\[
\begin{align*}
\text{rate}_{(t=0-2.0\,\text{h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\,\text{h} - 0\,\text{h}} \\
&= -\frac{(5.51 \times 10^{-3}\,\text{M}) - (5.55 \times 10^{-3}\,\text{M})}{2.0\,\text{h}} = 2 \times 10^{-5}\,\text{M/h}
\end{align*}
\]

If the reaction rate is calculated during the last interval given in Table 14.1 (the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

\[
\begin{align*}
\text{rate}_{(t=200-300\,\text{h})} &= \frac{[\text{salicylic acid}]_{300} - [\text{salicylic acid}]_{200}}{300\,\text{h} - 200\,\text{h}} \\
&= -\frac{(3.73 \times 10^{-3}\,\text{M}) - (2.91 \times 10^{-3}\,\text{M})}{100\,\text{h}} = 8.2 \times 10^{-6}\,\text{M/h}
\end{align*}
\]
Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq) + \text{H}_2\text{O}(l) \rightarrow 4\text{C}_2\text{H}_5\text{OH}(aq) + 4\text{CO}_2(g) \tag{14.5}
\]

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10 "Gases", the volume of CO\textsubscript{2} gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

\[
\frac{\Delta[\text{C}_2\text{H}_5\text{OH}]}{\Delta t} = -4\frac{\Delta[\text{sucrose}]}{\Delta t} \tag{14.6}
\]

The concentration of the reactant—in this case sucrose—decreases with time, so the value of \(\Delta[\text{sucrose}]\) is negative. Consequently, a minus sign is inserted in front of \(\Delta[\text{sucrose}]\) in Equation 14.6 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration increases with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 14.5) corresponds to sucrose, so the reaction rate is generally defined as follows:

\[
\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[\text{C}_2\text{H}_5\text{OH}]}{\Delta t}\right) \tag{14.7}
\]

Example 1

Consider the thermal decomposition of gaseous N\textsubscript{2}O\textsubscript{5} to NO\textsubscript{2} and O\textsubscript{2} via the following equation:

\[
2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)
\]

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

**Given:** balanced chemical equation

**Asked for:** reaction rate expressions

**Strategy:**

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

SOLUTION

A. Because $O_2$ has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of $O_2$ and write that expression.

B. The balanced chemical equation shows that 2 mol of $N_2O_5$ must decompose for each 1 mol of $O_2$ produced and that 4 mol of $NO_2$ are produced for every 1 mol of $O_2$ produced. The molar ratios of $O_2$ to $N_2O_5$ and to $NO_2$ are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because $NO_2$ is produced at four times the rate of $O_2$, the rate of production of $NO_2$ is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{\Delta [\text{NO}_2]}{4 \Delta t} = -\frac{\Delta [\text{N}_2\text{O}_5]}{2 \Delta t}$$

Exercise 1

The key step in the industrial production of sulfuric acid is the reaction of $SO_2$ with $O_2$ to produce $SO_3$.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer:

$$\text{rate} = -\frac{\Delta [\text{O}_2]}{\Delta t} = -\frac{\Delta [\text{SO}_2]}{2 \Delta t} = \frac{\Delta [\text{SO}_3]}{2 \Delta t}$$

Example 2

Using the reaction shown in Example 1, calculate the reaction rate from the following data taken at 56°C:

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

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$[N_2O_5]$ (M)</th>
<th>$[NO_2]$ (M)</th>
<th>$[O_2]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>0.0388</td>
<td>0.0314</td>
<td>0.00792</td>
</tr>
<tr>
<td>600</td>
<td>0.0197</td>
<td>0.0699</td>
<td>0.0175</td>
</tr>
</tbody>
</table>

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:
A. Using the equations in Example 1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

**SOLUTION**

A Calculate the reaction rate in the interval between \( t_1 = 240 \text{ s} \) and \( t_2 = 600 \text{ s} \). From Example 1, the reaction rate can be evaluated using any of three expressions:

\[
\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{\Delta [\text{NO}_2]}{4\Delta t} = -\frac{\Delta [\text{N}_2\text{O}_5]}{2\Delta t}
\]

Subtracting the initial concentration from the final concentration of \( \text{N}_2\text{O}_5 \) and inserting the corresponding time interval into the rate expression for \( \text{N}_2\text{O}_5 \),

\[
\text{rate} = -\frac{\Delta [\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\text{ s} - 240\text{ s})}
\]

B Substituting actual values into the expression,

\[
\text{rate} = -\frac{\text{0.0197 M - 0.0388 M}}{2(360\text{ s})} = 2.65 \times 10^{-5} \text{ M/s}
\]

Similarly, \( \text{NO}_2 \) can be used to calculate the reaction rate:

\[
\text{rate} = \frac{\Delta [\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699 \text{ M} - 0.0314 \text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5} \text{ M/s}
\]

Allowing for experimental error, this is the same rate obtained using the data for \( \text{N}_2\text{O}_5 \). The data for \( \text{O}_2 \) can also be used:

\[
\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175 \text{ M} - 0.00792 \text{ M}}{360\text{ s}} = 2.66 \times 10^{-5} \text{ M/s}
\]

Again, this is the same value obtained from the \( \text{N}_2\text{O}_5 \) and \( \text{NO}_2 \) data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

**Exercise 2**

Using the data in the following table, calculate the reaction rate of \( \text{SO}_2(g) \) with \( \text{O}_2(g) \) to give \( \text{SO}_3(g) \).

\[
\text{2SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)
\]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[SO(_2)] (M)</th>
<th>[O(_2)] (M)</th>
<th>[SO(_3)] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0270</td>
<td>0.0500</td>
<td>0.0072</td>
</tr>
<tr>
<td>720</td>
<td>0.0194</td>
<td>0.0462</td>
<td>0.0148</td>
</tr>
</tbody>
</table>

**Answer:** \( 9.0 \times 10^{-6} \text{ M/s} \)
Instantaneous Rates of Reaction

The instantaneous rate of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, \( t = 0 \). Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to \( t = 0 \).

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called rate laws, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A differential rate law expresses the reaction rate in terms of changes in the concentration of one or more reactants (\( \Delta [R] \)) over a specific time interval (\( \Delta t \)). In contrast, an integrated rate law describes the reaction rate in terms of the initial concentration ([R]_0) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail in Section 14.3. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:
the experimentally determined rate law usually has the following form:

\[
\text{rate} = k[A]^m[B]^n \tag{14.9}\]

The proportionality constant \(k\) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of \(k\), however, does not change as the reaction progresses under a given set of conditions.

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers \(m\) and \(n\), respectively. The values of \(m\) and \(n\) are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; \(m\) and \(n\) need not be integers. For example, Equation 14.9 tells us that Equation 14.8 is \(m\)th order in reactant A and \(n\)th order in reactant B. It is important to remember that \(n\) and \(m\) are not related to the stoichiometric coefficients \(a\) and \(b\) in the balanced chemical equation and must be determined experimentally. The overall reaction order is the sum of all the exponents in the rate law: \(m + n\).

Note

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (Click the link for a presentation of the general forms for integrated rate laws.) To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of \(t\)-butyl bromide in 70% aqueous acetone. This reaction produces \(t\)-butanol according to the following equation:

\[
(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{14.10}\]

Combining the rate expression in Equation 14.4 and Equation 14.9 gives a general expression for the differential rate law:

\[
\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^m[B]^n \tag{14.11}\]

Inserting the identities of the reactants into Equation 14.11 gives the following expression for the differential rate law for the reaction:

\[
\text{rate} = -\frac{\Delta[(CH_3)_3CBr]}{\Delta t} = k[(CH_3)_3CBr]^m[H_2O]^n \tag{14.12}\]

Experiments to determine the rate law for the hydrolysis of \(t\)-butyl bromide show that the reaction rate is directly proportional to the concentration of \((CH_3)_3CBr\) but is independent of the concentration of water. Therefore, \(m\) and \(n\) in Equation 14.12 are 1 and 0, respectively, and,
\[
\text{rate} = k[(\text{CH}_3)_3\text{CBr}]^1[\text{H}_2\text{O}]^0 = k[(\text{CH}_3)_3\text{CBr}] \tag{14.13}
\]

Because the exponent for the reactant is 1, the reaction is first order in (CH$_3$)$_3$CBr. It is zeroth order in water because the exponent for [H$_2$O] is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of (CH$_3$)$_3$CBr doubles the reaction rate of the hydrolysis reaction, halving the concentration of (CH$_3$)$_3$CBr halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of $k$, $m$, and $n$ in the rate law must be determined experimentally.) Experimental data show that $k$ has the value 5.15 × 10$^{-4}$ s$^{-1}$ at 25°C. The rate constant has units of reciprocal seconds (s$^{-1}$) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the $t$-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH$_3$Br) is as follows:

\[
\text{rate} = -\frac{\Delta [\text{CH}_3\text{Br}]}{\Delta t} = k'\text{[CH}_3\text{Br}] \tag{14.14}\]

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.14 is approximately 10$^6$ times smaller than that for $t$-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than $t$-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when $t$-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH$^-$ ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. For methyl bromide, in contrast, the differential rate law becomes rate = $k''[\text{CH}_3\text{Br}][\text{OH}^-]$, with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Note

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

Example 3
Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

1. \[
\ce{2HI(g) \xrightarrow{\text{Pt}} H_2(g) + I_2(g)}
\]
\[
\text{rate} = -\frac{1}{2}\left(\frac{\Delta [\text{HI}]}{\Delta t}\right) = k[\text{HI}]^2
\]

2. \[
\ce{2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)}
\]
\[
\text{rate} = -\frac{1}{2}\left(\frac{\Delta [\text{N}_2\text{O}]}{\Delta t}\right) = k
\]

3. \[
\ce{\text{cyclopropane(g)} \rightarrow \text{propane(g)}}
\]
\[
\text{rate} = -\frac{\Delta [\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]
\]

**Given:** balanced chemical equations and differential rate laws

**Asked for:** units of rate constant, reaction orders, and effect of doubling reactant concentration

**Strategy:**

A. Express the reaction rate as moles per liter per second \([\text{mol}/(\text{L} \cdot \text{s}), \text{or M/s}].\) Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.

C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

**Solution:**

1. A \([\text{HI}]^2\) will give units of \((\text{moles per liter})^2.\) For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units \([1/(\text{M} \cdot \text{s})]:\)

\[
\langle k \rangle = \frac{\text{mole}}{\text{L} \cdot \text{s}}.\]

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from \(k[\text{HI}]_0^2\) to \(k(2[\text{HI}])^2 = 4k[\text{HI}]_0^2.\) The reaction rate will therefore quadruple.

2. A Because no concentration term appears in the rate law, the rate constant must have \(\text{M/s}\) units for the reaction rate to have \(\text{M/s}\) units.

B The rate law tells us that the reaction rate is constant and independent of the \(\text{N}_2\text{O}\) concentration. That is, the reaction is zeroth order in \(\text{N}_2\text{O}\) and zeroth order overall.

C Because the reaction rate is independent of the \(\text{N}_2\text{O}\) concentration, doubling the concentration will have no effect on the reaction rate.

3. A The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds \((\text{s}^{-1})\) to have units of moles per liter per second for the reaction rate: \(\text{M} \cdot \text{s}^{-1} = \text{M/s}.)
The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

Doubling the initial cyclopropane concentration will increase the reaction rate from \( k[c\text{yclopropane}]_0 \) to \( 2k[c\text{yclopropane}]_0 \). This doubles the reaction rate.

Exercise 3

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

1. \[
\begin{align}
\text{CH}_3\text{N=NC}_3\text{H}_6(\text{g}) + \text{N}_2(\text{g}) &\rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{N}_2(\text{g}) \\
&\text{rate} = -\frac{\Delta [\text{CH}_3\text{N=NC}_3\text{H}_6]}{\Delta t} = k[\text{CH}_3\text{N=NC}_3\text{H}_6]
\end{align}
\]

2. \[
\begin{align}
2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) &\rightarrow 2\text{NO}_2\text{F}(\text{g}) \\
&\text{rate} = -\frac{1}{2}\frac{\Delta [\text{F}_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta [\text{NO}_2]}{\Delta t} = k[\text{NO}_2][\text{F}_2]
\end{align}
\]

Answer:

1. \( \text{s}^{-1} \); first order in \( \text{CH}_3\text{N}=\text{NC}_3\); first order overall; doubling \( \text{CH}_3\text{N}=\text{NC}_3 \) will double the reaction rate.
2. \( \text{M}^{-1}\text{s}^{-1} \); first order in \( \text{NO}_2 \), first order in \( \text{F}_2 \); second order overall; doubling \( \text{NO}_2 \) will double the reaction rate.

Summary

Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant \( (k) \) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

Conceptual Problems

1. Explain why the reaction rate is generally fastest at early time intervals. For the second-order \( \text{A} + \text{B} \rightarrow \text{C} \), what would the plot of the concentration of \( \text{C} \) versus time look like during the course of the reaction?
2. Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?
3. Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order
of $10^{10}$ L/(mol·s). Are the reactions expected to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+ + \text{N(CH}_3)_3 \rightarrow \text{H}_2\text{O} + \text{HN(CH}_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?

4. What information can be obtained from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?

5. During the hydrolysis reaction $\text{A} + \text{H}_2\text{O} \rightarrow \text{B} + \text{C}$, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How would this effect be reflected in the overall reaction order?

Conceptual Answers

1. Reactant concentrations are highest at the beginning of a reaction. The plot of $[\text{C}]$ versus $t$ is a curve with a slope that becomes steadily less positive.

3. Faster in a less viscous solvent because the rate of diffusion is higher; the $\text{H}_3\text{O}^+/\text{OH}^-$ reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

Numerical Problems

1. The reaction rate of a particular reaction in which A and B react to make C is as follows:

\[ \text{rate} = \frac{\text{[A]}}{\text{[B]}} = \frac{\Delta \text{[C]}}{\Delta t} \]

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

2. While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

3. Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[A] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.158</td>
</tr>
<tr>
<td>240</td>
<td>0.089</td>
</tr>
<tr>
<td>360</td>
<td>0.062</td>
</tr>
</tbody>
</table>

4. Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.
   a. $\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$: rate = $k[\text{C}_2\text{H}_5\text{I}]$
   b. $\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$: rate = $k[\text{SO}][\text{O}_2]$
   c. $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$: rate = $k[\text{CH}_3]^2$
   d. $\text{ClOO} \rightarrow \text{Cl} + \text{O}_2$: rate = $k$
5. Cleavage of C₂H₆ to produce two CH₃ radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with \( k = 5.46 \times 10^{-4} \text{ s}^{-1} \). How long will it take for the reaction to go to 15% completion? to 50% completion?

6. Three chemical processes occur at an altitude of approximately 100 km in Earth’s atmosphere.

\[
\begin{align*}
\text{N}_2^+ + \text{O}_2 & \xrightarrow{k_1} \text{N}_2 + \text{O}_2^+ \\
\text{O}_2^+ + \text{O} & \xrightarrow{k_2} \text{O}_2 + \text{O}^+ \\
\text{O}^+ + \text{N}_2 & \xrightarrow{k_3} \text{NO}^+ + \text{N}
\end{align*}
\]

Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = \( k[N_2^+][O_2] \), which one of the steps is rate limiting?

7. The oxidation of aqueous iodide by arsenic acid to give I₃⁻ and arsenous acid proceeds via the following reaction:

\[
\text{H}_3\text{AsO}_4(aq) + 3\text{I}^-(aq) + 2\text{H}^+(aq) \overset{k_f}{\underset{k_r}{\rightleftharpoons}} \text{H}_3\text{AsO}_3(aq) + \text{I}_3^-(aq) + \text{H}_2\text{O}(l)
\]

Write an expression for the initial rate of decrease of \([\text{I}_3^-]\), \(\Delta[\text{I}_3^-]/\Delta t\). When the reaction rate of the forward reaction is equal to that of the reverse reaction: \(k_f/k_r = \frac{[\text{H}_3\text{AsO}_3][\text{I}_3^-]}{[\text{H}_3\text{AsO}_4][\text{I}^-]^3[\text{H}^+]^2}\). Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

**Numerical Answer**

5. 298 s; 1270 s