In studying a chemical reaction, it is important to consider not only the chemical properties of the reactants, but also the conditions under which the reaction occurs, the mechanism by which it takes place, the rate at which it occurs, and the equilibrium toward which it proceeds. According to the law of mass action, the rate of a chemical reaction at a constant temperature depends only on the concentrations of the substances that influence the rate. The substances that influence the rate of reaction are usually one or more of the reactants, but can occasionally include products. Catalysts, which do not appear in the balanced overall chemical equation, can also influence reaction rate. The rate law is experimentally determined and can be used to predict the relationship between the rate of a reaction and the concentrations of reactants.

Introduction

The relationship between the rate of a reaction and the concentrations of reactants is expressed by a rate law. For example, the rate of the gas-phase decomposition of dinitrogen pentoxide,

\[
2\text{N}_2\text{O}_5 \rightleftharpoons 4\text{NO}_2 + \text{O}_2 \tag{1} \]

is directly proportional to the concentration of \(\text{N}_2\text{O}_5\):

\[
\text{rate} = k[\text{N}_2\text{O}_5] \tag{2} \]

Care must be taken not to confuse equilibrium constant expressions with rate law expressions. The expression for \(K_{\text{eq}}\) can always be written by inspecting the balanced reaction equation and contains a term for each species of the reaction (raised to the power of its coefficient) whose concentration changes during the reaction. The equilibrium constant for the above reaction is given below:

\[
K_{\text{eq}} = \dfrac{[\text{NO}_2]^4[\text{O}_2]}{[\text{N}_2\text{O}_5]^2} \tag{3} \]

In contrast, the expression for the rate law generally bears no relation to the reaction equation, and must be determined experimentally.

More generally, for a reaction of the form

\[
n_{\text{AA}} + n_{\text{BB}} + \ldots \rightarrow \text{products} \tag{4} \]

with no intermediate steps, the rate law is given by the following:

\[
\text{rate} = k[\text{A}]^a[\text{B}]^b \tag{5} \]

in which the exponents \(a\) and \(b\) are usually (but not always) integers and, it must be emphasized, bear no relation to the coefficients \(n_{\text{A}}\) and \(n_{\text{B}}\). Because the rate of a reaction has dimensions of concentration per unit time, the dimensions of the rate constant \(k\) depend on the exponents of the concentration terms in the rate law. If \(p\) is the sum of the exponents of the concentration terms in the rate law,

\[
p = a + b + \ldots \tag{6} \]

then \(k\) has dimensions of \(\dfrac{\text{concentration}^{1-p}}{\text{time}}\).
How quickly a reaction proceeds depends on the reaction mechanism—the step-by-step molecular pathway leading from reactants to products. Chemical kinetics is concerned with how chemical reaction rates are measured, how they can be predicted, and how reaction rate data is used to deduce probable reactions.

Example

Consider the following reaction:

\[2A + B \rightarrow C\]

The reaction rate is expressed as a derivative of the concentration of reactant A or product C, with respect to time, t:

\[
\begin{align*}
\text{rate} &= \lim_{\Delta t \to 0} - \frac{\Delta [A]}{\Delta t} = -\frac{d[A]}{dt} \\
\text{rate} &= \lim_{\Delta t \to 0} \frac{\Delta [C]}{\Delta t} = \frac{d[C]}{dt}
\end{align*}
\]

In this reaction, one mole of C is produced from every 2 moles of A and one mole of B. The rate of this reaction may be described in terms of either the disappearance of reactants over time, or the appearance of products over time:

\[
\begin{align*}
\text{rate} &= \frac{\text{decrease in concentration of reactants}}{\text{time}} \\
&= \frac{\text{increase in concentration of products}}{\text{time}}
\end{align*}
\]

Because the concentration of a reactant decreases during the reaction, a negative sign is placed before a rate that is expressed in terms of reactants to make the rate positive. For the reaction above, the rate of reaction with respect to A is \(-\Delta[A]/\Delta t\), the rate with respect to B is \(-\Delta[B]/\Delta t\), and the rate with respect to C is \(\Delta[C]/\Delta t\). In this particular reaction, the three rates are not equal. According to the stoichiometry of the reaction, A is used up twice as fast as B, and A is consumed twice as fast as C is produced. To show a standard rate of reaction in which the rates with respect to all substances are equal, the rate for each substance should be divided by its stoichiometric coefficient:

\[
\begin{align*}
\text{rate} &= \frac{-1}{2} \frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{\Delta t} = \frac{\Delta [C]}{\Delta t}
\end{align*}
\]

Differential and Integral Rate Laws

Measuring instantaneous rates is the most direct way of determining the rate law of a reaction, but it is not always convenient, and it may not be possible to do so with precision.

- If the reaction is very fast, its rate may change more rapidly than the time required to measure it; the reaction may be finished before even an initial rate can be observed.
- In the case of very slow reactions, observable changes in concentrations occur so slowly that the observation of a truly "instantaneous" rate becomes impractical.

The ordinary rate law (more precisely known as the instantaneous or differential rate law) shows how the rate of a reaction depends on the concentrations of the reactants. However, for many practical purposes, it is more important to know how the concentrations of reactants (and products) change with time. For example, when carrying out a reaction on an industrial scale, it is important to know how long it will take for, as an example, 95% of the reactants to be converted into products. This is the purpose of an integrated rate law and examples are discussed further below.
For nearly all forward, irreversible reactions, the rate is proportional to the product of the concentrations of only the reactants, each raised to an exponent. For the general reaction

\[aA + bB \rightarrow cC + dD\]

the rate is proportional to \([A]^m[B]^n\):

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

This expression is the rate law for the general reaction above, where \(k\) is the rate constant. Multiplying the units of \(k\) by the concentration factors raised to the appropriate powers give the rate in units of concentration/time.

The dependence of the rate of reaction on the reactant concentrations can often be expressed as a direct proportionality, in which the concentrations may be raised to be the zeroth, first, or second power. The exponent is known as the order of the reaction with respect to that substance. In the reaction above, the overall order of reaction is given by the following:

\[\text{order} = m + n\]

The order of the chemical equation can only be determined experimentally, i.e., \(m\) and \(n\) cannot be determined from a balanced chemical equation alone (e.g., Equation 11). The overall order of a reaction is the sum of the orders with respect to the sum of the exponents (Equation 13). Furthermore, the order of a reaction is stated with respect to a named substance in the reaction. The exponents in the rate law are not equal to the stoichiometric coefficients unless the reaction actually occurs via a single step mechanism (an elementary step); however, the exponents are equal to the stoichiometric coefficients of the rate-determining step. In general, the rate law can calculate the rate of reaction from known concentrations for reactants and derive an equation that expresses a reactant as a function of time.

The proportionality factor \(k\), called the rate constant, is a constant at a fixed temperature; nonetheless, the rate constant varies with temperature. There are dimensions to \(k\) and that be determined with simple dimensional analysis of the particular rate law. The units should be expressed when the \(k\) values are tabulated. The higher the \(k\) value, the faster the reaction proceeds.

### Experimental Determination of Rate Law

The values of \(k\), \(m\), and \(n\) in the rate law equation must be determined experimentally for a given reaction at a given temperature. The rate is usually measured as a function of the initial concentrations of the reactants, \([A]\) and \([B]\).

**Example 1**

Given the data below, find the rate law for the following reaction at 300 K and the corresponding rate constant.

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

<table>
<thead>
<tr>
<th>Trial</th>
<th>(\text{[A]_{initial}} \text{ (M)})</th>
<th>(\text{[B]_{initial}} \text{ (M)})</th>
<th>(r_{initial} \text{ (M/sec)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
SOLUTION

First, look for two trials in which the concentrations of all but one of the substances are held constant.

a. In trials 1 and 2, the concentration of A is kept constant while the concentration of B is doubled. The rate increases by a factor of approximately 4. Write down the rate expression of the two trials.

- Trial 1: \( r_1 = k[A]^x[B]^y = k(1.00)^x(1.00)^y \)
- Trial 2: \( r_2 = k[A]^x[B]^y = k(1.00)^x(2.00)^y \)

Divide the second equation by the first, which yields:

\[
\frac{4}{1} = (2.00)^y
\]

\[
y = 2
\]

b. In trials 2 and 3, the concentration of B is kept constant while the concentration of A is doubled; the rate is increased by a factor of approximately 2. The rate expressions of the two trials are as follows:

- Trial 2: \( r_2 = k[A]^x[B]^y = k(1.00)^x(2.00)^y \)
- Trial 3: \( r_3 = k[A]^x[B]^y = k(2.00)^x(1.00)^y \)

Divide the second equation by the third which yields:

\[
\frac{2}{1} = (2.00)^x
\]

\[
x = 1
\]

Therefore, the rate law is

\[
r = 2.0[A][B]^2
\]

The order of the reaction with respect to A is 1 and with respect to B is 2; the overall reaction order is as follows:

\[
1 + 2 = 3
\]

To calculate \( k \), substitute the values from any one of the above trials into the rate law:

\[
2.0 \text{ M/sec} = k(1.00 \text{ M})(1.00\text{M})^2
\]

\[
k = 2.0; \text{ M}^{-2}; \text{ sec}^{-1}\]
Order of Reactions

Chemical reactions are often classified as zero-order, first-order, second-order, mixed-order, or higher-order. The general reaction \( aA + bB \rightarrow cC + dD \) will be used in the following discussion. First, the meanings of these orders are defined in terms of initial rate of reaction effect:

- Zero-order in the reactant: there is no effect on the initial rate of reaction
- First-order in the reactant: the initial rate of reaction doubles when the reactant is doubled
- Second order in the reactant: the initial rate of the reaction quadruples when the reactant is doubled
- Third order in the reactant: the initial rate of reaction increases eightfold when the reactant is doubled

Zero-Order Reactions

A zero-order reaction has a constant rate that is independent of the reactant's concentrations. The rate law is as follows:

\[
\text{rate} = k \tag{14}
\]

where \( k \) has units of \( M \cdot s^{-1} \). In other words, a zero-order reaction has a rate law in which the sum of the exponents is equal to zero. A reaction is zero order if concentration data are plotted versus time and the result is a straight line. The slope of this resulting line is the negative of the zero order rate constant, \(-k\).

At times, chemists and researchers are also concerned with the relationship between the concentration of a reactant and time. An expression that shows this relationship is called an integrated rate law, in which the equation expresses the concentration of a reactant as a function of time (remember, each order of reaction has its own unique integrated rate law). The integrated rate law of a zero-order reaction is given below:

\[
[A]_t = -kt + [A]_0 \tag{15}
\]

See the article on zero-order reactions for the derivation of this law. Notice, however, that this model is not entirely accurate because this equation predicts negative concentrations at sufficiently large times. In other words, if one were to graph the concentration of \( [A] \) as a function of time, at some point, the line would cross the x-axis. This is physically impossible because concentrations cannot be negative. Nevertheless, this model is a sufficient model for ranges of time where concentration is predicted to be greater than zero.

The half life \((t_{1/2})\) of a reaction is the time required for the concentration of the radioactive substance to decrease to one-half of its original value. The half-life of a zero-order reaction can be derived as follows:

For a reaction involving reactant A and from the definition of a half-life, \((t_{1/2})\) is the time it takes for half of the initial concentration of reactant A to react. These new conditions can be substituted into the integrated rate law form to obtain the following:

\[
\frac{1}{2} [A]_0 = -kt_{1/2} + [A]_0 \tag{16}
\]
Solving for \( t_{1/2} \) gives the following:

\[
\frac{[A]_0}{2k} \tag{17}
\]

First-Order Reactions

A first-order reaction has a rate proportional to the concentration of one reactant.

\[
\text{rate} = k[A] \quad \text{or} \quad \text{rate} = k[B] \tag{18}
\]

First-order rate constants have units of \( \text{sec}^{-1} \). In other words, a first-order reaction has a rate law in which the sum of the exponents is equal to 1.

The integrated rate law of a first-order reaction is the following:

\[
\ln[A]_t = -kt + \ln[A]_0 \tag{9}
\]

or

\[
\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \tag{20}
\]

or

\[
[A] = [A]_0 e^{-kt} \tag{20} \]

Moreover, a first-order reaction can be determined by plotting a graph of \( \ln[A] \) vs. time \( t \): a straight line is produced with slope \(-k\).

The classic example of a first-order reaction is the process of radioactive decay. The concentration of radioactive substance A at any time \( t \) can be expressed mathematically below:

\[
[A]_t = [A]_0 e^{-kt} \tag{21}\]

where \([A]_0\) is initial concentration of A, \([A]_t\) is the concentration of A at time \( t \), \( k \) is the rate constant, and \( t \) is the elapsed time.

The half-life of a first-order reaction can be calculated in a similar fashion as with the half-life of the zero order reaction, giving the following:

\[
\frac{\ln(2)}{k} \tag{22}
\]

where \( k \) is the first-order rate constant. Notice that the half-life associated with the first-order reaction is the only case in which half-life is independent of concentration of a reactant or product. In other words, \([A]\) does not appear in the half-life formula above.
Second-Order Reactions

A second-order reaction has a rate proportional to the product of the concentrations of two reactants, or to the square of
the concentration of a single reactant. For example, each of the equations below describe a second-order reaction:

\[
\begin{eqnarray}
\text{rate} &=& k[A]^2 \\
\text{rate} &=& k[B]^2 \\
\text{rate} &=& k[A][B]
\end{eqnarray}
\]

In other words, a second-order reaction has a rate law in which the sum of the exponents is equal to 2.

The integrated rate law of a second-order reaction is as follow (see second-order reactions for the derivation):

\[
\frac{1}{[A]} = \frac{1}{[A]_0} + kt
\tag{23}
\]

The half-life of a second-order reaction is given below:

\[
t_{1/2} = \frac{1}{k[A]_0}
\tag{24}
\]

Determining Reaction Rate

In the laboratory, a sample of data consisting of measured concentrations of a certain reactant A at different times may be
collected. This sample data may look like the following table. [A], ln[A], and 1/[A] can be plotted versus time to see which
plot yields a straight line. The reaction order is the determined by the plot that gives a straight line (this is made trivial by
spreadsheet software with formula capabilities).
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration (M)</th>
<th>$\ln([A])$</th>
<th>$\dfrac{1}{[A]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.906</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.9184</td>
<td>0.8739</td>
<td>-0.085122253</td>
<td>1.088850174</td>
</tr>
<tr>
<td>9.0875</td>
<td>0.5622</td>
<td>2.206899843</td>
<td>0.110041265</td>
</tr>
<tr>
<td>11.2485</td>
<td>0.5156</td>
<td>2.420234786</td>
<td>0.088900742</td>
</tr>
<tr>
<td>17.5255</td>
<td>0.3718</td>
<td>2.863656963</td>
<td>0.057059713</td>
</tr>
<tr>
<td>23.9993</td>
<td>0.2702</td>
<td>3.178024663</td>
<td>0.041667882</td>
</tr>
<tr>
<td>27.7949</td>
<td>0.2238</td>
<td>3.324852551</td>
<td>0.035977823</td>
</tr>
<tr>
<td>31.9783</td>
<td>0.1761</td>
<td>3.465057548</td>
<td>0.031271206</td>
</tr>
</tbody>
</table>
Plotting the three data sets shows that the graph of ln[A] vs. time is a straight line. Therefore, the reaction is a first-order reaction.

### Problems

1. A reaction involving reactant A has a rate constant of $1.4 \times 10^{-4}$ s$^{-1}$. If 1.0 M of reactant reacts for 25 minutes, how much is left?

2. If the reactant concentration for a second-order reaction decreases from 0.10 M to 0.03 M in 1.00 hour, what is the rate constant for the reaction?

3. How long does it take 2.00 M of reactant to decrease in concentration to 0.75 M if the rate constant is 0.67 M/min?

4. What is the rate constant for a first-order reaction with a half-life of 300.0 seconds?

5. A first-order reaction has a half-life of 0.500 hours. If the initial concentration was 1.00 M, how much remains after 1.13 hour?

6. A second-order reaction has a half-life of 0.50 hours. If the initial concentration is 0.80 M, what is the concentration after 1.50 hours?

7. What is the half-life of a reaction with an initial concentration of 0.300 M and a rate constant of $0.00385$ M$^{-1}\text{s}^{-1}$?
Additional Problems

1. In a third-order reaction involving two reactants and two products, doubling the concentration of the first reaction causes the rate to increase by a factor of 2. If the concentration of the second reactant is cut in half, what is the effect on the rate?

Solution: The rate is directly proportional to the concentration of the first reactant. When the concentration of the reactant doubles, the rate also doubles. Because the reaction is third-order, the sum of the exponents in the rate law must be equal to 3. Therefore, the rate law is defined as follows: rate = k[A][B]^2. Reactant A has no exponent because its concentration is directly proportional to the rate. For this reason, the concentration of reactant B must be squared in order to write a law that represents a third-order reaction. When the concentration of reactant B is multiplied by 1/2, the rate will be multiplied by 1/4. Therefore, the rate of reaction will decrease by a factor of 4.

2. A certain chemical reaction follows the rate law, rate = k[NO][Cl_2]). Which of the following statements describe the kinetics of this reaction?

1. The reaction is second-order
2. The amount of NO consumed is equal to the amount of Cl_2 consumed
3. The rate is not affected by the addition of a compound other than NO and Cl_2

3. The data in the following table is collected for the combustion of the theoretical compound XH_4:

\[ \text{XH}_4 + 2\text{O}_2 \rightarrow \text{XO}_2 + 2\text{H}_2\text{O} \]

What is the rate law for the reaction described?

<table>
<thead>
<tr>
<th>Trial</th>
<th>XH_4 (initial)</th>
<th>O_2 (initial)</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>0.6</td>
<td>12.4</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>2.4</td>
<td>49.9</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>2.4</td>
<td>198.3</td>
</tr>
</tbody>
</table>

Contributors

If you want future readers to know that you worked on this module (not required)