18.5 The Progress of Chemical Reactions

Rate Laws

The rate of a reaction depends in part on the concentrations of the reactants. For a reaction in which reactant A forms product B in one step, you can write a simple equation.

\[ A \rightarrow B \]

The rate at which A forms B can be expressed as the change in A (\( \Delta A \)) with time, where concentration \( A_t \) is the initial concentration of A at time \( t \), and concentration \( A_{t_2} \) is the concentration of A at a later time, \( t_2 \).

\[
\text{Rate} = -\frac{\Delta A}{\Delta t} = \frac{\text{concentration } A_{t_2} - \text{concentration } A_t}{t_2 - t_1}
\]

Because A, the reactant, is decreasing, the concentration of A is smaller at a later time than initially and so \( \Delta A \) will always be negative. The negative sign in the expression is needed to make the rate positive, as all rates must be. The rate of disappearance of A is proportional to the concentration of A.

\[
-\frac{\Delta A}{\Delta t} \propto [A]
\]

The proportionality becomes an equation with the insertion of a constant (\( k \)).

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

This equation, called a rate law, is an expression for the rate of a reaction in terms of the concentration of reactants. The specific rate constant (\( k \)) for a reaction is a proportionality constant relating the concentrations of reactants to the rate of the reaction. The magnitude of the specific rate constant depends on the conditions of the reaction and is determined experimentally.

The value of the specific rate constant, \( k \), is large if the products form quickly; the value is small if the products form slowly.

Guide for Reading

Key Concepts

- What is the general relationship between the value of the specific rate constant, \( k \), and the speed of a chemical reaction?
- What do the hills and valleys in a reaction progress curve represent?

Vocabulary

- Rate law
- Specific rate constant
- First-order reaction
- Elementary reaction
- Reaction mechanism
- Intermediate

Reading Strategy

Monitoring Your Understanding After you read the section, identify what you don’t yet understand. Reread the section or ask for help, then write your clarified understanding.

18.5.1 Describe the general relationship between the value of the specific rate constant, \( k \), and the speed of a chemical reaction.

18.5.2 Interpret the hills and valleys in a reaction progress curve.
Section 18.5 (continued)

Rate Laws

Use Visuals

Figure 18.27 Explain that the slope of a straight line is the ratio of the rise ($y$) to the run ($x$). Demonstrate how to calculate the slope for several straight lines. Explain that the slope of the tangent to a curve at any point is the slope of the curve at that point. Discuss how to calculate the rate of reaction by determining the slope of the tangent line for the two points shown on the graph. Have students calculate the initial rate of reaction. (rate = (10 – 7.5)/(0.5 – 0) = 5 concentration/time units) Next have students calculate the rate at time $t = 2.5$. (rate = (5.5 – 2.5)/(3.7 – 1.7) = 1.5 concentration/time units) Point out that the rate decreases, as expected, as the concentration of reactant $A$ decreases.

Discuss how the effect of concentration on the reaction rate is expressed as a quantitative relationship. Each rate expression contains a rate constant, $k$, which is specific to the reaction. A knowledge of this dependence not only allows prediction of the actual rate, but also gives clues to the step-by-step mechanism by which the reaction occurs. Demonstrate how to set up the rate equation for a chemical reaction such as the formation of water from hydrogen and oxygen.

Interpreting Graphs

Interpreting Graphs

a. Navigate What is the dependent variable?
b. Read What happens to the relative concentration of reactant $A$ as time progresses?
c. Interpret The short colored lines illustrate the reaction rates at two distinct points of time. Is the initial rate or the subsequent rate faster?

The rate of blooming for the century plant ($Agave americana$) is one time per 10 to 15 years.

The Rate of a First-Order Reaction

The order of a reaction is the power to which the concentration of a reactant must be raised to give the experimentally observed relationship between concentration and rate. In a first-order reaction, the reaction rate is directly proportional to the concentration of only one reactant. The conversion of $A$ to $B$ in a one-step reaction is an example of a first-order reaction; the reaction rate is proportional to the concentration of $A$ raised to the first power: $[A]^1 = [A]$. As a first-order reaction progresses, the rate of reaction decreases, as shown in Figure 18.27. This decrease occurs because the concentration of reactant is decreasing. On a graph, the rate ($\Delta[A]/\Delta t$) at any point equals the slope of the tangent to the curve at that point. For a first-order reaction, a reduction of $[A]$ by one-half reduces the reaction rate by one-half.

In some kinds of reactions, such as double-replacement, two substances react to give products. The coefficients in the general equation for such a reaction are represented by lowercase letters.

$$aA + bB \rightarrow cC + dD$$

For a one-step reaction of $A$ with $B$, the rate of reaction is dependent on the concentrations of both $A$ and $B$.

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

When each of the exponents $a$ and $b$ in the rate law equals 1, the reaction is said to be first-order in $A$, first-order in $B$, and second-order overall. The overall order of a reaction is the sum of the exponents for the individual reactants.

For any one-step reaction, the experimentally determined exponents in the rate law are the same as the coefficients $a$ and $b$ in the chemical equation. However, the exponents in the rate law and the coefficients in the equation do not correspond in most real reactions because most reactions are more complex than the one-step reactions used in the examples. The actual order of a reaction must be determined by experiment.

**Checkpoint** How can you determine the rate of a reaction from a graph of reactant concentration versus time?
Reaction Rates and Equilibrium

Discuss
Point out that most reactions are more complex than the one-step reactions used as examples in the text. In most cases, reaction order cannot be predicted solely on the basis of a balanced equation; it must be determined experimentally. This is because the rate depends primarily on the slowest step in the reaction mechanism.

Conceptual Problem 18.2

Answers

36. Rate = \( k[A] \); rate is moles per liter per second. \([A]\) is moles per liter. \( k = \frac{\text{rate}}{[A]} \).
   \( k = 1/\text{s} = \text{s}^{-1} \)

37. 0.25 mol/Ls; 0.125 mol/Ls

Practice Problems

36. Show that the unit of \( k \) for a first-order reaction is a reciprocal unit of time, such as a reciprocal second (s\(^{-1}\)).

37. Suppose a first-order reaction initially proceeds at a rate of 0.5 mol/Ls. What is the rate when half the starting material remains? When one-fourth of the starting material remains?
Section 18.5 (continued)

**Reaction Mechanisms**

**Discuss**

Explain that even complex reactions occur as a series of simple steps. Each step usually involves the collision of no more than two different particles. Use the reaction between hydrogen and bromine as an example. The overall reaction \( H_2 + Br_2 \rightarrow 2HBr \) occurs as a sequence of three elementary steps.

\[
\begin{align*}
Br_2 & \rightarrow 2Br \\
Br + H_2 & \rightarrow HBr + H \\
H + Br & \rightarrow HBr
\end{align*}
\]

**Interpreting Graphs**

**Enrichment Question**

**How would a catalyst affect this graph?** (It would lower the activation energy for the slowest step in the reaction mechanism.)

**Math Handbook**

For help with making and interpreting graphs, go to page R74.

**Use Visuals**

Figure 18.28 The energy of a reaction (y-axis), determined experimentally, is plotted versus time or reaction progress (x-axis). The graph shows that the slope changes from positive to negative frequently during the course of the reaction. The usual way to construct such a graph is to measure the energy at several points, most likely at the tops of the energy barriers and at the positions of the intermediate. The remaining points can be interpolated. Displaying the data in a graph provides a more complete picture than a table of data.

**Facts and Figures**

**Ozone**

Ozone is an essential gas in the stratosphere. It absorbs UV radiation from the sun, keeping the UV levels at Earth’s surface below a lethal level. The Chapman cycle describes the equilibrium of \( O_2 \) and \( O_3 \) in the stratosphere. In the first step, \( O_2 + \text{ solar radiation} \rightarrow 2O \). Then, \( O + O_2 \) combine to make \( O_3 \). Natural levels of nitrogen oxides react with \( O \) and \( O_3 \) to keep \( O_3 \) at an equilibrium of 6 ppm. Human-generated chemicals such as chlorinated fluorocarbons change the equilibrium, so that less ozone is produced. UV radiation levels at Earth’s surface go up as a result.
## Professor of Chemistry

If you study chemistry in college, your teacher probably will be a Professor of Chemistry. Chemistry professors train the next generation of chemists. In addition to their classroom teaching, they often undertake fundamental research projects to learn more about the how and why of chemical interactions.

For example, a professor who is interested in reaction rates could study a particular reaction and determine its rate and reaction mechanism. Both graduate and undergraduate students gain valuable experience by assisting the professor in carrying out the work in the laboratory. Together, professor and students publish the results of their research in scientific journals. Much of the basic research reported in journals is done in university laboratories.

Many chemistry professors specialize in one kind of chemistry, for example, inorganic chemistry, organic chemistry, biochemistry, or analytical chemistry. As experts in their particular field, they may share what they know by writing books.

A new member of the Chemistry faculty might start at the level of Instructor. The usual steps in advancement are Assistant Professor, Associate Professor, and then Professor. The minimum qualification for Instructor is usually a PhD in chemistry. Often candidates for a position also have completed a number of years of post-doctoral research at a university.

### 18.5 Section Assessment

38. **Key Concept** How does the size of the specific rate constant ($k$) for a reaction relate to the speed of the reaction?

39. **Key Concept** What do the hills and valleys in a reaction progress curve represent?

40. Define each of the following terms as applied to chemical reactions.
   a. elementary reaction
   b. intermediate
   c. reaction mechanism
   d. activation energy

41. Show that the unit of $k$ for a reaction that is second-order in A and second-order overall can be expressed in L/(mol·s).

42. The rate law for this reaction is first-order in NO and O₃, and second-order overall.

   \[
   \text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)
   \]

   Write the complete rate law for this reaction.

## Evaluation Understanding

Ask students to construct a reaction rate equation for the production of NO₂F from NO₂ and F₂. The two-step reaction mechanism is

\[
\text{NO}_2 + \text{F}_2 = \text{NO}_2\text{F} + \text{F} \quad \text{(slow)}
\]

\[
\text{NO}_2 + \text{F} = \text{NO}_2\text{F} \quad \text{(fast)}
\]

Because the first step is the slower, it is the rate-determining step. The rate law is $\text{rate} = k[\text{NO}_2][\text{F}_2]$.

## Reteach

Have students note the difference between rate determination and the calculation of an equilibrium constant, which can be determined from the overall reaction. Stress that there is no correlation between the equilibrium constant and the rate of a chemical reaction. Remind students that many familiar reactions have multiple steps. Ask them to suggest possible mechanisms for the following reactions:

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

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

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

## Solar Radiation and the Stratosphere

Solar radiation in the stratosphere breaks CF₂Cl₂ into active substances Cl and CCl₂F. These react in several ways with O₃ to produce O₂.