

**Nobody, I suppose,
could devote many years
to the study of chemical
kinetics without being
deeply conscious of the
fascination of time and
change: this is
something that goes
outside science into
poetry. . . .**

—SIR CYRIL N. HINSELWOOD
(1897–1967)

CHAPTER

15

Chemical Kinetics

In this chapter-opening quotation, Oxford chemistry professor Sir Cyril Hinshelwood calls attention to an aspect of chemistry often overlooked by the casual observer—the mystery of change with time. Since the opening chapter of this book, you have learned that the goal of chemistry is to understand the macroscopic world by examining the molecular one. In this chapter, we focus on understanding how this molecular world changes with time, an area of study called chemical kinetics. The molecular world is anything but static. Thermal energy produces constant molecular motion, causing molecules to repeatedly collide with one another. In a tiny fraction of these collisions, something extraordinary happens—the electrons on one molecule or atom are attracted to the nuclei of another. Some bonds weaken and new bonds form—a chemical reaction occurs. Chemical kinetics is the study of how these kinds of changes occur in time.



Pouring ice water on a lizard slows it down, making it easier to catch.

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15.1 Catching Lizards

The children who live in my neighborhood (including my own kids) have a unique way of catching lizards. Armed with cups of ice water, they chase one of these cold-blooded reptiles into a corner, and take aim and pour the cold water directly onto the lizard's body. The lizard's body temperature drops, and it becomes virtually immobilized—easy prey for little hands. The kids scoop up the lizard and place it in a tub filled with sand and leaves. They then watch as the lizard warms back up and becomes active again. They usually release the lizard back into the yard within hours. I guess you could call them catch-and-release lizard hunters.

Unlike mammals, which actively regulate their body temperature through metabolic activity, lizards are *ectotherms*—their body temperature depends on their surroundings. When splashed with cold water, a lizard's body simply gets colder. The drop in body temperature immobilizes the lizard because its movement depends on chemical reactions that occur within its muscles, and the *rates* of those reactions—how fast they occur—are highly sensitive to temperature. In other words, when the temperature drops, the reactions that produce movement in the lizard occur more slowly; therefore, the movement itself slows down. When reptiles get cold, they become lethargic, unable to move very quickly. For this reason, reptiles try to maintain their body temperature within a narrow range by moving between sun and shade.

The rates of chemical reactions, and especially the ability to *control* those rates, are important not just in reptile movement but in many other phenomena as well. For example, a successful rocket launch depends on the rate at which fuel burns—too quickly and the rocket can explode, too slowly and it will not leave the ground. Chemists must always consider reaction rates when synthesizing compounds. No matter how stable a compound might be, its synthesis is impossible if the rate at which it forms is too slow. As we have seen with reptiles, reaction rates are important to life. In fact, the human body's ability to switch a specific reaction on or off at a specific time is achieved partly by controlling the rate of that reaction through the use of enzymes (biological molecules that we explore more fully in Section 15.7).

The first person to measure the rate of a chemical reaction carefully was Ludwig Wilhelmy (1812–1864). In 1850, he measured how fast sucrose, upon treatment with acid, hydrolyzed (broke up with the addition of water) into glucose and fructose. This reaction occurred over several hours, and Wilhelmy was able to show how the rate depended on the initial amount of sugar present—the greater the initial amount, the faster the initial rate. Today we can measure the rates of reactions that occur in times as short as several femtoseconds (femto = 10^{-15}). The knowledge of reaction rates is not only practically important—giving us the ability to control how fast a reaction occurs—but also theoretically important. As we will discuss in Section 15.6, the rate of a reaction can tell us much about how the reaction occurs on the molecular scale.

WATCH NOW!

KEY CONCEPT VIDEO 15.2

 The Rate of a Chemical Reaction

15.2 The Rate of a Chemical Reaction

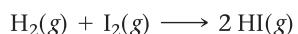
The rate of a chemical reaction is a measure of how fast the reaction occurs, as shown in Figure 15.1▶. If a chemical reaction has a fast rate, a large fraction of molecules react to form products in a given period of time. If a chemical reaction has a slow rate, only a relatively small fraction of molecules reacts to form products in a given period of time.

Definition of Reaction Rate

When we measure how fast something occurs, or more specifically the *rate* at which it occurs, we usually express the measurement as a change in some quantity per unit of time. For example, we measure the speed of a car—the rate at which it travels—in *miles per hour*, and we measure how quickly (or slowly) people lose weight in *pounds per week*. We report these rates in units that represent the change in what we are measuring (distance or weight) divided by the change in time:

$$\text{Speed} = \frac{\text{change in distance}}{\text{change in time}} = \frac{\Delta x}{\Delta t} \quad \text{Weight loss} = \frac{\text{change in weight}}{\text{change in time}} = \frac{\Delta \text{ weight}}{\Delta t}$$

Similarly, the rate of a chemical reaction is measured as a change in the amounts of reactants or products (usually in concentration units) divided by the change in time. For example, consider the gas-phase reaction between $\text{H}_2(g)$ and $\text{I}_2(g)$:

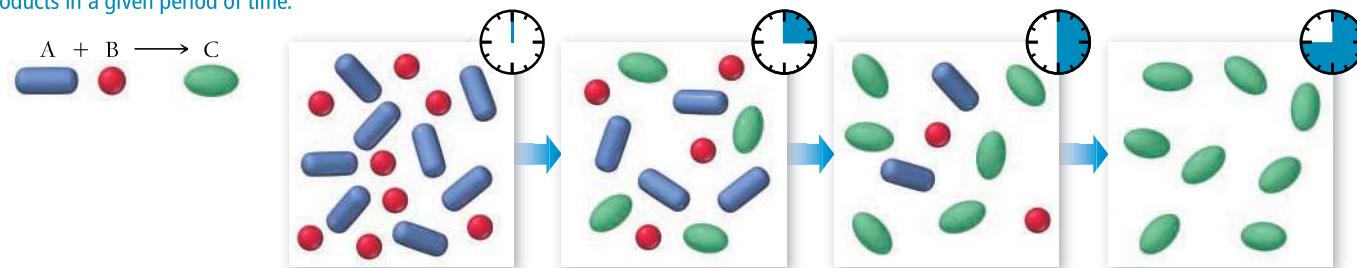


We can define the rate of this reaction in the time interval t_1 to t_2 as follows:

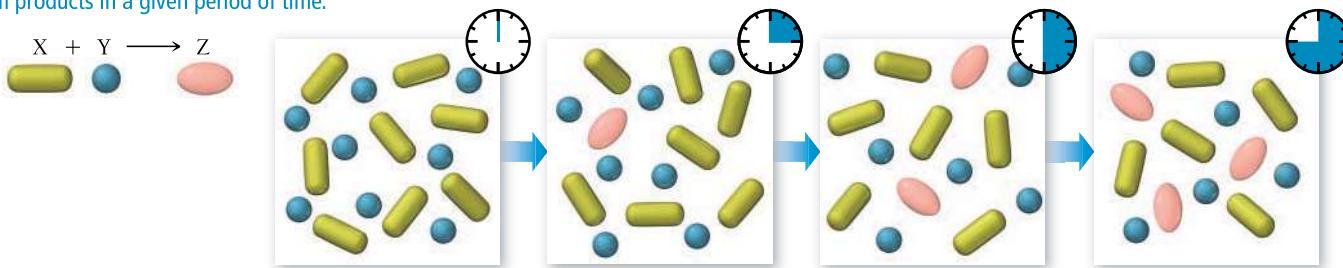
$$\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{[\text{H}_2]_{t_2} - [\text{H}_2]_{t_1}}{t_2 - t_1} \quad [15.1]$$

Recall that $[A]$ means the concentration of A in M (mol/L).

A reaction with a fast rate
A large fraction of molecules react to form products in a given period of time.



A reaction with a slow rate
Only a small fraction of molecules react to form products in a given period of time.



In this expression, $[H_2]_{t_2}$ is the hydrogen concentration at time t_2 and $[H_2]_{t_1}$ is the hydrogen concentration at time t_1 . The reaction rate is defined as *the negative* of the change in concentration of a reactant divided by the change in time. The negative sign is part of the definition when we define the reaction rate with respect to a reactant because reactant concentrations decrease as a reaction proceeds; therefore, *the change in the concentration of a reactant is negative*. The negative sign thus makes the overall *rate* positive. (By convention, we report reaction rates as positive quantities.)

Similarly, we can define the reaction rate with respect to the other reactant:

$$\text{Rate} = -\frac{\Delta[I_2]}{\Delta t} \quad [15.2]$$

Since 1 mol of H_2 reacts with 1 mol of I_2 , we define the rate in the same way. We can also define the rate with respect to the *product* of the reaction:

$$\text{Rate} = +\frac{1}{2} \frac{\Delta[HI]}{\Delta t} \quad [15.3]$$

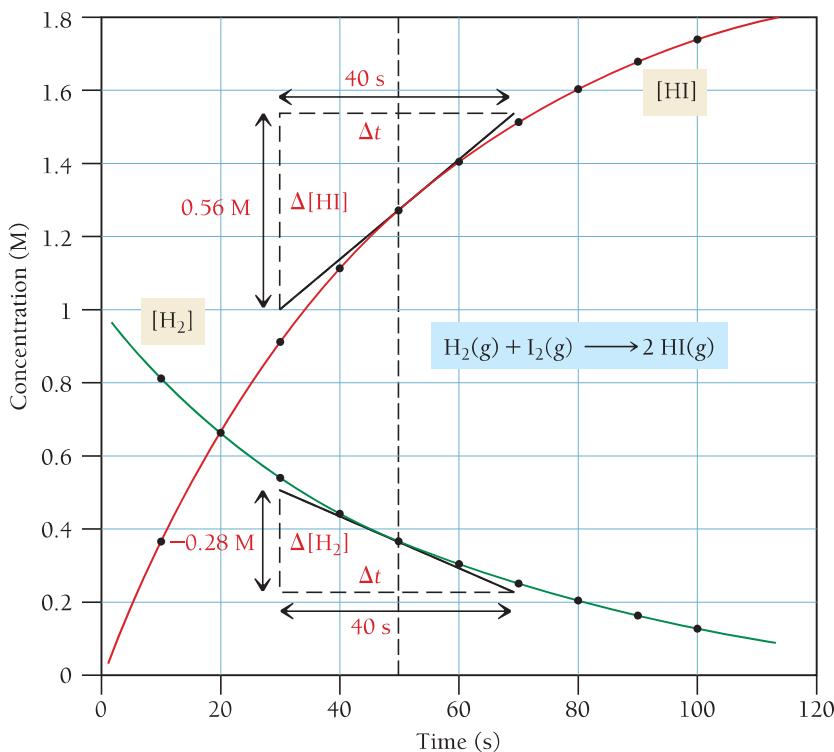
Because product concentrations *increase* as the reaction proceeds, the change in concentration of a product is positive. Therefore, when we define the rate with respect to a product, we do not include a negative sign in the definition—the rate is naturally positive. The factor of $\frac{1}{2}$ in this definition is related to the stoichiometry of the reaction. In order to have a single rate for the entire reaction, the definition of the rate with respect to each reactant and product must reflect the stoichiometric coefficients of the reaction. For this particular reaction, 2 mol of HI is produced from 1 mol of H_2 and 1 mol of I_2 :



The concentration of HI increases at twice the rate that the concentration of H_2 or I_2 decreases. In other words, if 100 I_2 molecules react per second, then 200 HI molecules form per second. In order for the overall rate to have the same value when defined with respect to any of the reactants or products, we must multiply the change in HI concentration by a factor of one-half.

Consider the graph in Figure 15.2►, which represents the changes in concentration for H_2 (one of the reactants) and HI (the product) versus time. Let's examine several features of this graph individually.

▲ FIGURE 15.1 The Rate of a Chemical Reaction

**▲ FIGURE 15.2** Reactant and Product Concentrations as a Function of Time

The graph shows the concentration of one of the reactants (H_2) and the product (HI) as a function of time. The other reactant (I_2) is omitted for clarity.

Change in Reactant and Product Concentrations

The reactant concentration, as expected, *decreases* with time because reactants are consumed in a reaction. The product concentration *increases* with time because products are formed in a reaction. The increase in HI concentration occurs at exactly twice the rate of the decrease in H_2 concentration because of the stoichiometry of the reaction: 2 mol of HI form for every 1 mol of H_2 consumed.

The Average Rate of the Reaction

We can calculate the average rate of the reaction for any time interval using Equation 15.1 for H_2 . The following table lists H_2 concentration ($[\text{H}_2]$) at various times, the change in H_2 concentration for each interval ($\Delta[\text{H}_2]$), the change in time for each interval (Δt), and the rate for each interval ($-\Delta[\text{H}_2]/\Delta t$). The rate is the average rate within the given time interval. For example, the average rate of

the reaction in the time interval between 10 and 20 seconds is 0.0149 M/s , whereas the average rate in the time interval between 20 and 30 seconds is 0.0121 M/s .

Time (s)	$[\text{H}_2] (\text{M})$	$\Delta[\text{H}_2] (\text{M})$	$\Delta t (\text{s})$	$\text{Rate} = -\Delta[\text{H}_2]/\Delta t (\text{M/s})$
0.000	1.000			
10.000	0.819	-0.181	10.000	0.0181
20.000	0.670	-0.149	10.000	0.0149
30.000	0.549	-0.121	10.000	0.0121
40.000	0.449	-0.100	10.000	0.0100
50.000	0.368	-0.081	10.000	0.0081
60.000	0.301	-0.067	10.000	0.0067
70.000	0.247	-0.054	10.000	0.0054
80.000	0.202	-0.045	10.000	0.0045
90.000	0.165	-0.037	10.000	0.0037
100.000	0.135	-0.030	10.000	0.0030

Notice that the average rate *decreases* as the reaction progresses. In other words, the reaction slows down as it proceeds. We discuss this further in the next section, where we will see that, for most reactions, the rate depends on the concentrations of the reactants. As the reactants transform to products, their concentrations decrease, and the reaction slows down.

The Instantaneous Rate of the Reaction

The instantaneous rate of the reaction is the rate at any one point in time and is represented by the instantaneous slope of the curve at that point. We can determine the instantaneous rate by calculating the slope of the tangent to the curve at the point of interest. In Figure 15.2, we have drawn the tangent lines for both $[\text{H}_2]$ and $[\text{HI}]$ at 50 seconds. We calculate the instantaneous rate at 50 seconds as follows:

Using $[\text{H}_2]$

$$\text{Instantaneous rate (at 50 s)} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{-0.28 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

Using $[HI]$

$$\text{Instantaneous rate (at 50 s)} = +\frac{1}{2} \frac{\Delta [HI]}{\Delta t} = +\frac{1}{2} \frac{0.56 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

As we would expect, the rate is the same whether we use one of the reactants or the product for the calculation. Notice that the instantaneous rate at 50 seconds (0.0070 M/s) is between the average rates calculated for the 10-second intervals just before and just after 50 seconds.

We can generalize our definition of reaction rate for the generic reaction:



where A and B are reactants, C and D are products, and a , b , c , and d are the stoichiometric coefficients. We define the rate of the reaction as follows:

$$\text{Rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = +\frac{1}{c} \frac{\Delta [C]}{\Delta t} = +\frac{1}{d} \frac{\Delta [D]}{\Delta t} \quad [15.5]$$

From the definition, we can see that knowing the rate of change in the concentration of any one reactant or product at a point in time allows us to determine the rate of change in the concentration of any other reactant or product at that point in time (from the balanced equation). *However, predicting the rate at some future time is not possible from just the balanced equation.*

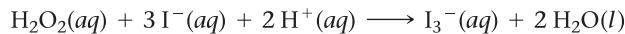
WATCH NOW!

INTERACTIVE WORKED EXAMPLE 15.1

EXAMPLE 15.1 Expressing Reaction Rates



Consider this balanced chemical equation:



In the first 10.0 seconds of the reaction, the concentration of I^- drops from 1.000 M to 0.868 M.

(a) Calculate the average rate of this reaction in this time interval.

(b) Determine the rate of change in the concentration of H^+ (that is, $\Delta[\text{H}^+]/\Delta t$) during this time interval.

SOLUTION

(a) Use Equation 15.5 to calculate the average rate of the reaction.

$$\begin{aligned} \text{Rate} &= -\frac{1}{3} \frac{\Delta [\text{I}^-]}{\Delta t} \\ &= -\frac{1}{3} \frac{(0.868 \text{ M} - 1.000 \text{ M})}{10.0 \text{ s}} \\ &= 4.40 \times 10^{-3} \text{ M/s} \end{aligned}$$

(b) Use Equation 15.5 again for the relationship between the rate of the reaction and $\Delta[\text{H}^+]/\Delta t$. After solving for $\Delta[\text{H}^+]/\Delta t$, substitute the calculated rate from part (a) and calculate $\Delta[\text{H}^+]/\Delta t$.

$$\begin{aligned} \text{Rate} &= -\frac{1}{2} \frac{\Delta [\text{H}^+]}{\Delta t} \\ \frac{\Delta [\text{H}^+]}{\Delta t} &= -2(\text{rate}) \\ &= -2(4.40 \times 10^{-3} \text{ M/s}) \\ &= -8.80 \times 10^{-3} \text{ M/s} \end{aligned}$$

FOR PRACTICE 15.1 For the reaction shown in Example 15.1, predict the rate of change in concentration of H_2O_2 ($\Delta[\text{H}_2\text{O}_2]/\Delta t$) and I_3^- ($\Delta[\text{I}_3^-]/\Delta t$) during this time interval.

REACTION RATES For the reaction $A + 2B \longrightarrow C$ under a given set of conditions, the initial rate is 0.100 M/s. What is $\Delta[B]/\Delta t$ under the same conditions?

- (a)** -0.0500 M/s **(b)** -0.100 M/s **(c)** -0.200 M/s **(d)** +0.200 M/s



ANSWER NOW!



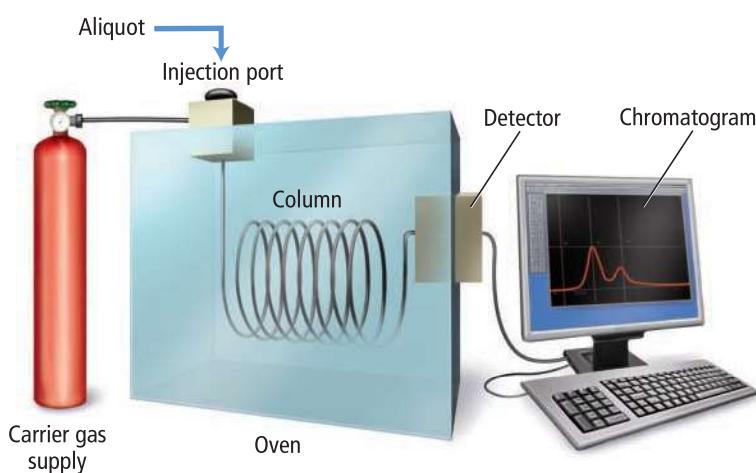
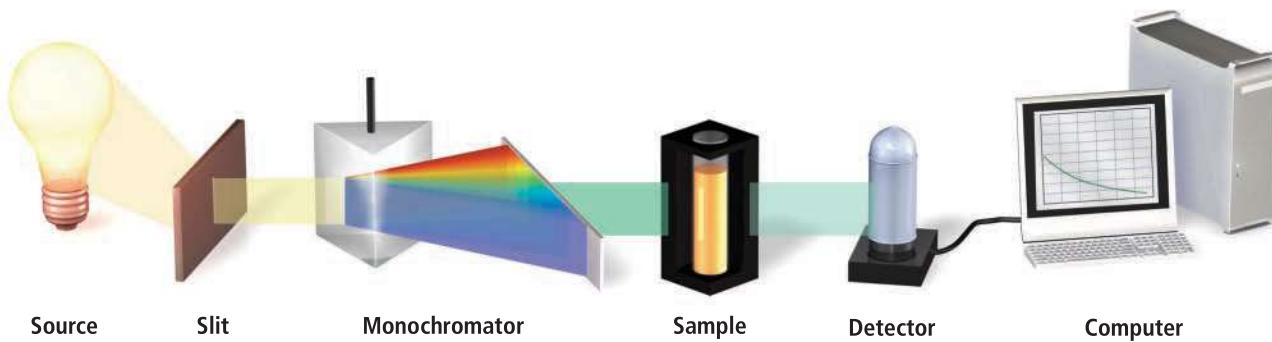
Measuring Reaction Rates

In order to study the kinetics of a reaction, we must have an experimental way to measure the concentration of at least one of the reactants or products as a function of time. For example, Ludwig Wilhelmy, whose experiment on the rate of the conversion of sucrose to glucose and fructose we discussed briefly in Section 15.1, took advantage of sucrose's ability to rotate polarized light. (Polarized light is light with an electric field oriented along one plane.) When a beam of polarized light is passed through a sucrose solution, the polarization of the light is rotated clockwise. In contrast, the products of the reaction (glucose and fructose) rotate polarized light counterclockwise. By measuring the degree of polarization of light passing through a reacting solution—a technique known as polarimetry—Wilhelmy was able to determine the relative concentrations of the reactants and products as a function of time.

Perhaps the most common way to study the kinetics of a reaction is through spectroscopy (see Section 8.3). For example, the reaction of H₂ and I₂ to form HI can be followed spectroscopically because I₂ is violet and H₂ and HI are colorless. As I₂ reacts with H₂ to form HI, the violet color of the reaction mixture fades. We can monitor the fading color with a spectrometer, a device that passes light through a sample and measures how strongly the light is absorbed (Figure 15.3▼). If the sample contains the reacting mixture, the intensity of the light absorption will decrease as the reaction proceeds, providing a direct measure of the concentration of I₂ as a function of time. Because light travels so fast and because experimental techniques can produce very short pulses of light, spectroscopy can be used to measure reactions that happen on time scales as short as several femtoseconds.

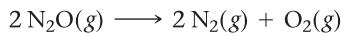
▼ FIGURE 15.3 The Spectrometer

In a spectrometer, light of a specific wavelength is passed through the sample, and the intensity of the transmitted light—which depends on how much light is absorbed by the sample—is measured and recorded.



▲ FIGURE 15.4 The Gas Chromatograph In a gas chromatograph (GC), a sample of the reaction mixture, or aliquot, is injected into a specially constructed column. Because of their characteristic physical and chemical properties, different components of the mixture pass through the column at different rates and thus exit at different times. As each component leaves the column, it is detected electronically and a chromatogram is recorded. The area under each peak in the chromatogram is proportional to the amount of one particular component in the sample mixture.

By measuring changes in pressure, we can also monitor reactions in which the number of moles of gaseous reactants and products changes as the reaction proceeds. Consider the reaction in which dinitrogen monoxide reacts to form nitrogen and oxygen gas:



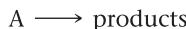
For every 2 mol of N₂O that reacts, the reaction vessel contains one additional mole of gas. As the reaction proceeds and the amount of gas increases, the pressure steadily rises. We can use the rise in pressure to determine the relative concentrations of reactants and products as a function of time.

We can use all of the three techniques mentioned here—polarimetry, spectroscopy, and pressure measurement—to monitor a reaction as it occurs in a reaction vessel. Some reactions occur slowly enough that samples, or *aliquots*, can be periodically withdrawn from the reaction vessel and analyzed to determine the progress of the reaction. We can use instrumental techniques such as gas chromatography (Figure 15.4◀) or mass spectrometry, as well as wet chemical techniques such as titration, to measure the relative amounts of reactants or products in the aliquot. By taking aliquots at regular time intervals, we can determine the relative amounts of reactants and products as a function of time.

15.3

The Rate Law: The Effect of Concentration on Reaction Rate

The rate of a reaction often depends on the concentration of one or more of the reactants. As we have already seen, Ludwig Wilhelmy noticed this effect for the hydrolysis of sucrose. For simplicity, let's consider a reaction in which a single reactant, A, decomposes into products:



As long as the rate of the reverse reaction (in which the products return to reactants) is negligibly slow, we can express the relationship between the rate of the reaction and the concentration of the reactant—called the **rate law**—as follows:

$$\text{Rate} = k[A]^n$$

[15.6]

where k is a constant of proportionality called the **rate constant** and n is the **reaction order**. The value of n (usually an integer) determines how the rate depends on the concentration of the reactant:

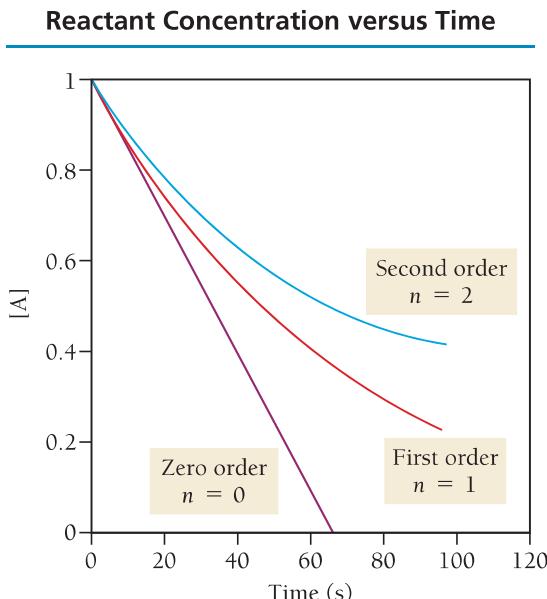
- If $n = 0$, the reaction is *zero order* and the rate is independent of the concentration of A.
- If $n = 1$, the reaction is *first order* and the rate is directly proportional to the concentration of A.
- If $n = 2$, the reaction is *second order* and the rate is proportional to the square of the concentration of A.

By definition, $[A]^0 = 1$, so the rate is equal to k regardless of [A].

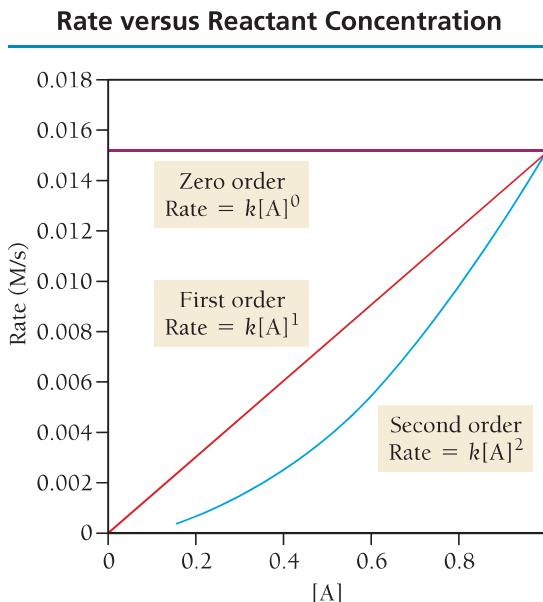
Although other orders are possible, including noninteger (or fractional) orders, these three are the most common.

The Three Common Reaction Orders ($n = 0, 1$, and 2)

Figure 15.5▼ shows three plots illustrating how the *concentration of A changes with time* for the three common reaction orders with identical numerical values for the rate constant (k) and identical initial concentrations. Figure 15.6▼ has three plots showing the *rate of the reaction* (the slope of the lines in Figure 15.5) as a function of the reactant concentration for each reaction order.



▲ FIGURE 15.5 Reactant Concentration as a Function of Time for Different Reaction Orders



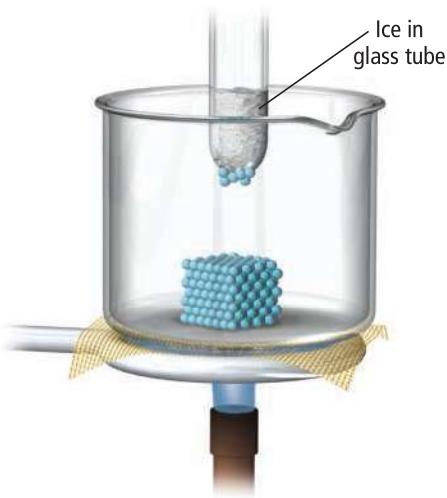
▲ FIGURE 15.6 Reaction Rate as a Function of Reactant Concentration for Different Reaction Orders

WATCH NOW!**KEY CONCEPT VIDEO 15.3**

The Rate Law for a Chemical Reaction

Sublimation Is Zero Order

When one layer of particles sublimes, the next layer is exposed. The number of particles available to sublime remains constant.



▲ FIGURE 15.7 Sublimation

When a layer of particles sublimes, another identical layer is just below it. Consequently, the number of particles available to sublime at any one time does not change with the total number of particles in the sample, and the process is zero order.

Zero-Order Reaction

In a zero-order reaction, the rate of the reaction is independent of the concentration of the reactant:

$$\text{Rate} = k[A]^0 = k \quad [15.7]$$

Consequently, for a zero-order reaction, the concentration of the reactant decreases linearly with time, as shown in Figure 15.5. The slope of the line is constant, indicating a constant rate. The rate is constant because the reaction does not slow down as the concentration of A decreases. The graph in Figure 15.6 shows that the rate of a zero-order reaction is the same at any concentration of A.

Zero-order reactions occur under conditions where the amount of reactant actually *available for reaction* is unaffected by changes in the *overall quantity of reactant*. For example, sublimation is normally zero order because only molecules at the surface of a substance can sublime, and the concentration of the surface molecules does not change as the amount of subliming substance decreases (Figure 15.7 ▲).

First-Order Reaction

In a first-order reaction, the rate of the reaction is directly proportional to the concentration of the reactant:

$$\text{Rate} = k[A]^1 \quad [15.8]$$

For a first-order reaction, the rate slows down as the reaction proceeds because the concentration of the reactant decreases. We can see this in Figure 15.5—the slope of the curve (the rate) becomes less steep (slower) with time. Figure 15.6 shows the rate as a function of the concentration of A. Notice the linear relationship—the rate is directly proportional to the concentration.

Second-Order Reaction

In a second-order reaction, the rate of the reaction is proportional to the square of the concentration of the reactant:

$$\text{Rate} = k[A]^2 \quad [15.9]$$

Consequently, for a second-order reaction, the rate is even more sensitive to the reactant concentration. We can see this in Figure 15.5—the slope of the curve (the rate) flattens out more quickly than it does for a first-order reaction. Figure 15.6 shows the rate as a function of the concentration of A. Notice the quadratic relationship—the rate is proportional to the square of the concentration.

ANSWER NOW!



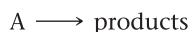
15.2
Cc
Conceptual Connection

REACTION ORDER For a particular reaction in which $A \rightarrow \text{products}$, a doubling of the concentration of A causes the reaction rate to double. What is the order of the reaction?

- (a) 0 (b) 1 (c) 2

Determining the Order of a Reaction

The *order of a reaction can be determined only by experiment*. A common way to determine reaction order is the *method of initial rates*. In this method, the initial rate—the rate for a short period of time at the beginning of the reaction—is measured by running the reaction several times with different initial reactant concentrations to determine the effect of the concentration on the rate. For example, let's return to our simple reaction in which a single reactant, A, decomposes into products:



In an experiment, the initial rate is measured at several different initial concentrations with the results shown in the table in the margin.

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.030
0.40	0.060

In this data set, when the concentration of A doubles, the rate doubles—the initial rate is directly proportional to the initial concentration. The reaction is therefore first order in A, and the rate law takes the first-order form:

$$\text{Rate} = k[A]^1$$

We can determine the value of the rate constant, k , by solving the rate law for k and substituting the concentration and the initial rate from any one of the three measurements. Here we use the first measurement:

$$\begin{aligned}\text{Rate} &= k[A]^1 \\ k &= \frac{\text{rate}}{[A]} = \frac{0.015 \text{ M/s}}{0.10 \text{ M}} = 0.15 \text{ s}^{-1}\end{aligned}$$

Notice that the rate constant for a first-order reaction has units of s^{-1} .

The following two data sets show how measured initial rates are different for zero-order and for second-order reactions having the same initial rate at $[A] = 0.10 \text{ M}$:

Zero Order ($n = 0$)		Second Order ($n = 2$)	
[A] (M)	Initial Rate (M/s)	[A] (M)	Initial Rate (M/s)
0.10	0.015	0.10	0.015
0.20	0.015	0.20	0.060
0.40	0.015	0.40	0.240

For a zero-order reaction, the initial rate is independent of the reactant concentration—the rate is the same at all measured initial concentrations. For a second-order reaction, the initial rate quadruples for a doubling of the reactant concentration—the relationship between concentration and rate is quadratic. If we are unsure about how the initial rate is changing with the initial reactant concentration, or if the numbers are not as obvious as they are in these examples, we can substitute any two initial concentrations and the corresponding initial rates into a ratio of the rate laws to determine the order (n):

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^n}{k[A]_1^n}$$

For example, we can substitute the last two measurements in the data set just given for the second-order reaction as follows:

$$\begin{aligned}\frac{0.240 \text{ M/s}}{0.060 \text{ M/s}} &= \frac{k(0.40 \text{ M})^n}{k(0.20 \text{ M})^n} \\ 4.0 &= \left(\frac{0.40}{0.20}\right)^n = 2^n \\ \log 4.0 &= \log(2^n) \\ &= n \log 2 \\ n &= \frac{\log 4}{\log 2} \\ &= 2\end{aligned}$$

The rate constants for zero- and second-order reactions have different units than for first-order reactions. The rate constant for a zero-order reaction has units of $\text{M} \cdot \text{s}^{-1}$, and the rate constant for a second-order reaction has units of $\text{M}^{-1} \cdot \text{s}^{-1}$.

Remember that $\frac{x^n}{y^n} = \left(\frac{x}{y}\right)^n$.

Remember that $\log x^n = n \log x$.

The general expression for the units of the rate constant for an n th-order reaction is $\text{M}^{(1-n)} \text{ s}^{-1}$.

RATE AND CONCENTRATION I The reaction $A \longrightarrow B$ has been experimentally determined to be second order. The initial rate is 0.0100 M/s at an initial concentration of A of 0.100 M . What is the initial rate at $[A] = 0.500 \text{ M}$?

- (a) 0.00200 M/s (b) 0.0100 M/s (c) 0.0500 M/s (d) 0.250 M/s

ANSWER NOW!



Reaction Order for Multiple Reactants

So far, we have considered a simple reaction with only one reactant. How do we define the rate law for reactions with more than one reactant? Consider the generic reaction:



As long as the reverse reaction is negligibly slow, the rate law is proportional to the concentration of [A] raised to the m power multiplied by the concentration of [B] raised to the n power:

$$\text{Rate} = k[A]^m[B]^n \quad [15.10]$$

where m is the reaction order with respect to A and n is the reaction order with respect to B. The **overall order** is the sum of the exponents ($m + n$). For example, the reaction between hydrogen and iodine has been experimentally determined to be first order with respect to hydrogen, first order with respect to iodine, and thus second order overall:¹



Similarly, the reaction between hydrogen and nitrogen monoxide has been experimentally determined to be first order with respect to hydrogen, second order with respect to nitrogen monoxide, and thus third order overall:



The rate law for any reaction must always be determined by experiment, often by the method of initial rates described previously. We can't simply look at a chemical equation and determine the rate law for the reaction. When the reaction has two or more reactants, the concentration of each reactant is usually varied independently of the others to determine the dependence of the rate on the concentration of that reactant. Example 15.2 demonstrates how to use the method of initial rates to determine the order of a reaction with multiple reactants.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 15.2

EXAMPLE 15.2 Determining the Order and Rate Constant of a Reaction

Consider the reaction between nitrogen dioxide and carbon monoxide:



The initial rate of the reaction is measured at several different concentrations of the reactants, and the tabulated results are shown here.

From the data, determine:

- (a) the rate law for the reaction
- (b) the rate constant (k) for the reaction

SOLUTION

(a) Begin by examining how the rate changes for each change in concentration. Between the first two experiments, the concentration of NO_2 doubles, the concentration of CO stays constant, and the rate quadruples, suggesting that the reaction is second order in NO_2 .

Between the second and third experiments, the concentration of NO_2 stays constant, the concentration of CO doubles, and the rate remains constant (the small change in the least significant figure is simply experimental error), suggesting that the reaction is zero order in CO.

Between the third and fourth experiments, the concentration of NO_2 again doubles and the concentration of CO halves, yet the rate quadruples again, confirming that the reaction is second order in NO_2 and zero order in CO.

$[\text{NO}_2]$ (M)	$[\text{CO}]$ (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

$[\text{NO}_2]$ (M)	$[\text{CO}]$ (M)	Initial Rate (M/s)
0.10	0.10	0.0021
$\downarrow \times 2$	\downarrow constant	$\downarrow \times 4$
0.20	0.10	0.0082
\downarrow constant	$\downarrow \times 2$	$\downarrow \times 1$
0.20	0.20	0.0083
$\downarrow \times 2$	$\downarrow \times \frac{1}{2}$	$\downarrow \times 4$
0.40	0.10	0.033

Write the overall rate expression.

$$\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

(a) ALTERNATIVE APPROACH

If the relationship between the changes in concentrations and the changes in initial rates is not immediately obvious, you can determine the reaction order for any reactant by substituting any two initial rates and the corresponding initial concentrations into a ratio of the rate laws to determine the order (n).

For NO_2 use the first and second concentrations and rates (because $[\text{NO}_2]$ changes here, but $[\text{CO}]$ is constant). Substitute the rates and concentrations into the expression for the ratio of the rate constants.

Take the log of both sides of the equation and solve for n .

For CO , use the second and third concentrations and rates (because $[\text{CO}]$ changes here, but $[\text{NO}_2]$ is constant).

Substitute the rates and concentrations into the expression for the ratio of the rate laws.

Take the log of both sides of the equation and solve for n .

Write the overall rate expression from the order of each reactant.

- (b)** To determine the rate constant for the reaction, solve the rate law for k and substitute the concentration and the initial rate from any one of the four measurements. In this case, we use the first measurement.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k[\text{A}]_2^n}{k[\text{A}]_1^n}$$

$$\begin{aligned} \text{For } \text{NO}_2 \quad \frac{\text{rate 2}}{\text{rate 1}} &= \frac{k[\text{NO}_2]_2^n}{k[\text{NO}_2]_1^n} \\ \frac{0.0082 \text{ M/s}}{0.0021 \text{ M/s}} &= \frac{k(0.20 \text{ M})^n}{k(0.10 \text{ M})^n} \\ 3.9 &= \left(\frac{0.20}{0.10}\right)^n = 2^n \end{aligned}$$

$$\begin{aligned} \log 3.9 &= \log 2^n \\ &= n \log 2 \\ n &= \frac{\log 3.9}{\log 2} \\ &= 1.96 = 2 \end{aligned}$$

$$\begin{aligned} \text{For CO} \quad \frac{\text{rate 3}}{\text{rate 2}} &= \frac{k[\text{CO}]_3^n}{k[\text{CO}]_2^n} \\ \frac{0.0083 \text{ M/s}}{0.0082 \text{ M/s}} &= \frac{k(0.20 \text{ M})^n}{k(0.10 \text{ M})^n} \\ 1.01 &= \left(\frac{0.20}{0.10}\right)^n = 2^n \end{aligned}$$

$$\begin{aligned} \log 1.01 &= \log 2^n \\ &= n \log 2 \\ n &= \frac{\log 1.01}{\log 2} \\ &= 0.01 = 0 \end{aligned}$$

$$\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

$$\text{Rate} = k[\text{NO}_2]^2$$

$$k = \frac{\text{rate}}{[\text{NO}_2]^2} = \frac{0.0021 \text{ M/s}}{(0.10 \text{ M})^2} = 0.21 \text{ M}^{-1} \cdot \text{s}^{-1}$$

FOR PRACTICE 15.2 Consider the equation:



The initial rate of reaction is measured at several different concentrations of the reactants with the tabulated results shown here.

$[\text{CHCl}_3](\text{M})$	$[\text{Cl}_2](\text{M})$	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

From the data, determine:

- (a)** the rate law for the reaction

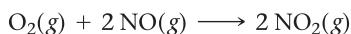
- (b)** the rate constant (k) for the reaction

ANSWER NOW!

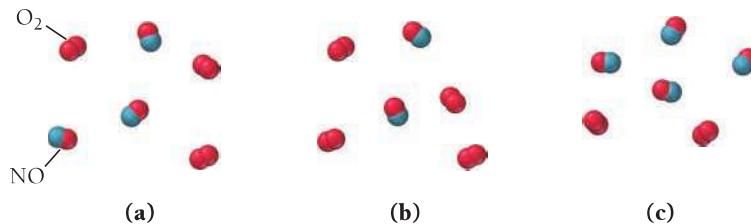


15.4 Cc Conceptual Connection

RATE AND CONCENTRATION II This reaction was experimentally determined to be first order with respect to O_2 and second order with respect to NO:



The diagrams shown here represent reaction mixtures in which the number of each type of molecule represents its relative initial concentration. Which mixture has the fastest initial rate?



WATCH NOW!

KEY CONCEPT VIDEO 15.4
The Integrated Rate Law

15.4

The Integrated Rate Law: The Dependence of Concentration on Time

The rate laws we have examined so far show the relationship between *the rate of a reaction and the concentration of a reactant*. But we often want to know the relationship between *the concentration of a reactant and time*. For example, the presence of chlorofluorocarbons (CFCs) in the atmosphere threatens the ozone layer. One of the reasons that CFCs pose such a significant threat is that the reactions that consume them are so slow (Table 15.1). Legislation has significantly reduced CFC emissions, but even if humans were to completely stop adding CFCs to the atmosphere, their concentration would decrease only very slowly. Nonetheless, we would like to know how their concentration changes with time. How much will be left in 20 years? In 50 years?

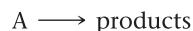
TABLE 15.1 Atmospheric Lifetimes of Several CFCs

CFC Name	Structure	Atmospheric Lifetime*
CFC-11 (CCl_3F) Trichlorofluoromethane		45 years
CFC-12 (CCl_2F_2) Dichlorodifluoromethane		100 years
CFC-113 ($C_2F_3Cl_3$) 1,1,2-Trichloro-1,2,2-trifluoroethane		85 years
CFC-114 ($C_2F_4Cl_2$) 1,2-Dichlorotetrafluoroethane		300 years
CFC-115 (C_2F_5Cl) Monochloropentafluoroethane		1700 years

*Data taken from EPA site (under section 602 of Clean Air Act).

The Integrated Rate Law

The **integrated rate law** for a chemical reaction is a relationship between the concentrations of the reactants and time. For simplicity, we return to a single reactant decomposing into products:



The integrated rate law for this reaction depends on the order of the reaction; let's examine each of the common reaction orders individually.

First-Order Integrated Rate Law

If our simple reaction is first order, the rate is directly proportional to the concentration of A:

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

Since Rate = $-\Delta[A]/\Delta t$, we can write:

$$-\frac{\Delta[A]}{\Delta t} = k[A] \quad [15.11]$$

In this form, the rate law is also known as the *differential rate law*.

We can use calculus (see margin) to integrate the differential rate law and obtain the first-order *integrated rate law*:

$$\ln[A]_t = -kt + \ln[A]_0 \quad [15.12]$$

We can also rearrange the integrated rate law by subtracting $\ln[A]_0$ from both sides of Equation 15.12:

$$\begin{aligned} \ln[A]_t &= -kt + \ln[A]_0 \\ \ln[A]_t - \ln[A]_0 &= -kt \end{aligned}$$

Since $\ln A - \ln B = \ln(A/B)$, we can rearrange this equation to get:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad [15.13]$$

where $[A]_t$ is the concentration of A at any time t , k is the rate constant, and $[A]_0$ is the initial concentration of A.

Notice that the integrated rate law shown in Equation 15.12 has the form of an equation for a straight line:

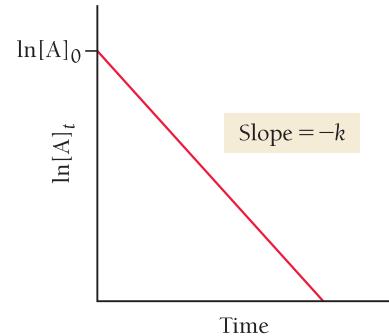
$$\begin{aligned} \ln[A]_t &= -kt + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

For a first-order reaction, a plot of the natural logarithm of the reactant concentration as a function of time yields a straight line with a slope of $-k$ and a y -intercept of $\ln[A]_0$, as shown in Figure 15.8►. (Note that the slope is negative but that the rate constant is always positive.)

$$\begin{aligned} -\frac{d[A]}{dt} &= k[A] \\ \frac{d[A]}{[A]} &= -kdt \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= - \int_0^t kdt \\ [\ln[A]]_{[A]_0}^{[A]} &= -kt \\ \ln[A] - \ln[A]_0 &= -kt \\ \ln[A] &= -kt + \ln[A]_0 \end{aligned}$$

First-Order Integrated Rate Law

A plot of the natural log of the reactant concentration as a function of time yields a straight line.

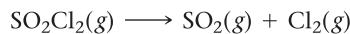


▲ FIGURE 15.8 First-Order Integrated Rate Law The slope of the line is equal to $-k$ and the y -intercept is $\ln[A]_0$.

EXAMPLE 15.3

The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Consider the equation for the decomposition of SO_2Cl_2 :



The concentration of SO_2Cl_2 is monitored at a fixed temperature as a function of time during the decomposition reaction, and the following data are tabulated:

Time (s)	$[\text{SO}_2\text{Cl}_2]$ (M)	Time (s)	$[\text{SO}_2\text{Cl}_2]$ (M)
0	0.100	800	0.0793
100	0.0971	900	0.0770
200	0.0944	1000	0.0748
300	0.0917	1100	0.0727
400	0.0890	1200	0.0706
500	0.0865	1300	0.0686
600	0.0840	1400	0.0666
700	0.0816	1500	0.0647

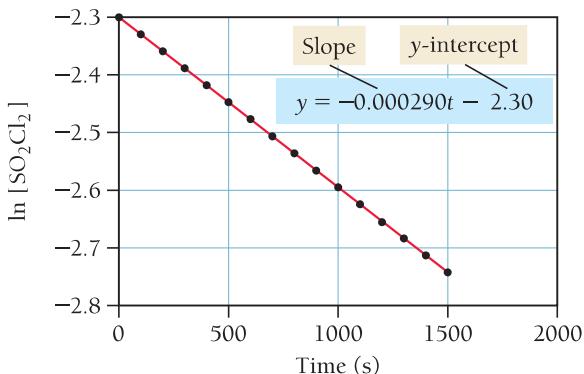
Show that the reaction is first order, and determine the rate constant for the reaction.

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SOLUTION

In order to show that the reaction is first order, prepare a graph of the natural logarithm of $[SO_2Cl_2]$ versus time as shown:



The plot is linear, confirming that the reaction is indeed first order. To obtain the rate constant, fit the data to a line. The slope of the line is equal to $-k$. Since the slope of the best-fitting line (which is most easily determined on a graphing calculator or with spreadsheet software such as Microsoft Excel) is $-2.90 \times 10^{-4} s^{-1}$, the rate constant is $+2.90 \times 10^{-4} s^{-1}$.

FOR PRACTICE 15.3 Use the graph and the best-fitting line in Example 15.3 to predict the concentration of SO_2Cl_2 at 1900 s.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 15.4

EXAMPLE 15.4

The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time



In Example 15.3, you determined that the decomposition of SO_2Cl_2 (under the given reaction conditions) is first order and has a rate constant of $+2.90 \times 10^{-4} s^{-1}$. If the reaction is carried out at the same temperature and the initial concentration of SO_2Cl_2 is 0.0225 M, what is the SO_2Cl_2 concentration after 865 s?

SORT You are given the rate constant of a first-order reaction and the initial concentration of the reactant and asked to find the concentration at 865 seconds.

GIVEN: $k = +2.90 \times 10^{-4} s^{-1}$

$[SO_2Cl_2]_0 = 0.0225 \text{ M}$

FIND: $[SO_2Cl_2]$ at $t = 865 \text{ s}$

STRATEGIZE Refer to the first-order integrated rate law to determine the SO_2Cl_2 concentration at $t = 865 \text{ s}$.

EQUATION $\ln[A]_t = -kt + \ln[A]_0$

SOLVE Substitute the rate constant, the initial concentration, and the time into the integrated rate law.

Solve the integrated rate law for the concentration of $[SO_2Cl_2]_t$.

SOLUTION

$$\ln[SO_2Cl_2]_t = -kt + \ln[SO_2Cl_2]_0$$

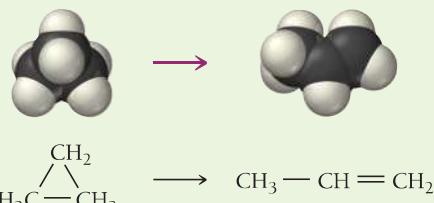
$$\ln[SO_2Cl_2]_t = -(2.90 \times 10^{-4} \text{ s}^{-1})865 \text{ s} + \ln(0.0225)$$

$$\ln[SO_2Cl_2]_t = -0.251 - 3.79$$

$$[SO_2Cl_2]_t = e^{-4.04} \\ = 0.0176 \text{ M}$$

CHECK The concentration is smaller than the original concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right-hand side of the equation.

FOR PRACTICE 15.4 Cyclopropane rearranges to form propene in the gas phase.



The reaction is first order in cyclopropane and has a measured rate constant of $3.36 \times 10^{-5} \text{ s}^{-1}$ at 720 K. If the initial cyclopropane concentration is 0.0445 M, what is the cyclopropane concentration after 235.0 minutes?

Second-Order Integrated Rate Law

If our simple reaction ($A \longrightarrow \text{products}$) is second order, the rate is proportional to the square of the concentration of A:

$$\text{Rate} = k[A]^2$$

Since $\text{Rate} = -\Delta[A]/\Delta t$, we can write the differential rate law:

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2 \quad [15.14]$$

Again, we can use calculus to integrate the second-order differential rate law. We leave this derivation to an exercise (see Exercise 115 at the end of this chapter). The derivation results in the *second-order integrated rate law*:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad [15.15]$$

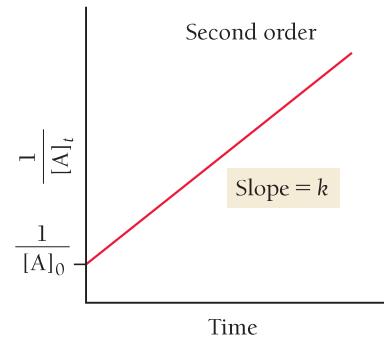
The second-order integrated rate law is also in the form of an equation for a straight line:

$$\begin{aligned} \frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\ y &= mx + b \end{aligned}$$

However, you must plot the inverse of the concentration of the reactant as a function of time. The plot yields a straight line with a slope of k and an intercept of $1/[A]_0$, as shown in Figure 15.9.

Second-Order Integrated Rate Law

A plot of the inverse of the reactant concentration as a function of time yields a straight line.



▲ FIGURE 15.9 Second-Order Integrated Rate Law The slope of the line is equal to k , and the y -intercept is $1/[A]_0$.

EXAMPLE 15.5

The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

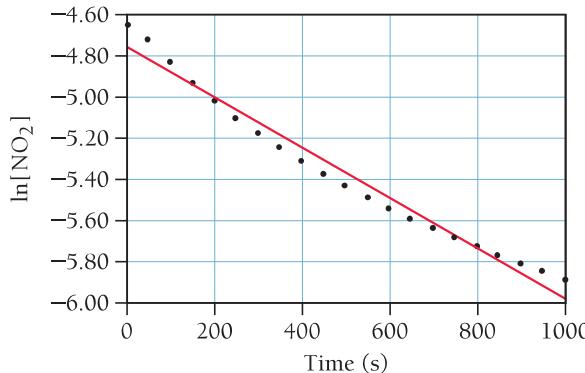
Consider the equation for the decomposition of NO_2 :



The concentration of NO_2 is monitored at a fixed temperature as a function of time during the decomposition reaction and the data tabulated in the margin at right. Show by graphical analysis that the reaction is not first order and that it is second order. Determine the rate constant for the reaction.

SOLUTION

In order to show that the reaction is *not* first order, prepare a graph of $\ln[\text{NO}_2]$ versus time as shown:

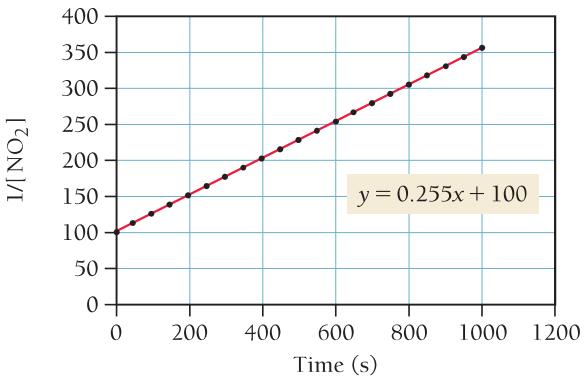


The plot is *not* linear (the straight line does not fit the data points), confirming that the reaction is not first order. In order to show that the reaction is second order, prepare a graph of $1/[\text{NO}_2]$ versus time as shown:

Time (s)	$[\text{NO}_2]$ (M)
0	0.01000
50	0.00887
100	0.00797
150	0.00723
200	0.00662
250	0.00611
300	0.00567
350	0.00528
400	0.00495
450	0.00466
500	0.00440
550	0.00416
600	0.00395
650	0.00376
700	0.00359
750	0.00343
800	0.00329
850	0.00316
900	0.00303
950	0.00292
1000	0.00282

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Continued—



This graph is linear (the data points fit well to a straight line), confirming that the reaction is indeed second order. To obtain the rate constant, determine the slope of the best-fitting line. The slope is $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$; therefore, the rate constant is $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$.

FOR PRACTICE 15.5 Use the graph and the best-fitting line in Example 15.5 to predict the concentration of NO₂ at 2000 s.

$$\begin{aligned}-\frac{d[A]}{dt} &= k[A]^0 \\ -\frac{d[A]}{dt} &= k \\ \int_{[A_0]}^{[A]} d[A] &= -k \int_0^t dt \\ [[A]]_{[A_0]} &= -kt \\ [A] - [A_0] &= -kt \\ [A] &= -kt + [A_0]\end{aligned}$$

Zero-Order Integrated Rate Law

If our simple reaction is zero order, the rate is proportional to a constant:

$$\text{Rate} = k[A]^0 = k$$

Since Rate = $-\Delta[A]/\Delta t$, we can write:

$$-\frac{\Delta[A]}{\Delta t} = k \quad [15.16]$$

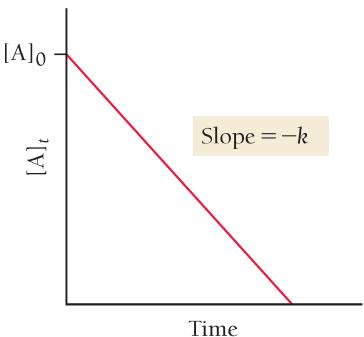
We can integrate the zero-order differential rate law (see margin) to obtain the *zero-order integrated rate law*:

$$[A]_t = -kt + [A]_0 \quad [15.17]$$

The zero-order integrated rate law in Equation 15.17 is also in the form of an equation for a straight line. A plot of the concentration of the reactant as a function of time yields a straight line with a slope of $-k$ and an intercept of $[A]_0$, shown in Figure 15.10.

Zero-Order Integrated Rate Law

A plot of the reactant concentration as a function of time yields a straight line.



▲ FIGURE 15.10 Zero-Order Integrated Rate Law The slope of the line is equal to $-k$ and the y -intercept is $[A]_0$.

The Half-Life of a Reaction

The **half-life ($t_{1/2}$)** of a reaction is the time required for the concentration of a reactant to fall to one-half of its initial value. For example, if a reaction has a half-life of 100 seconds, and if the initial concentration of the reactant is 1.0 M, the concentration will fall to 0.50 M in 100 s. The half-life expression—which defines the dependence of half-life on the rate constant and the initial concentration—is different for different reaction orders.

First-Order Reaction Half-Life

From the definition of half-life and from the integrated rate law, we can derive an expression for the half-life. For a first-order reaction, the integrated rate law is:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

At a time equal to the half-life ($t = t_{1/2}$), the concentration is exactly half of the initial concentration: $([A]_{t_{1/2}} = \frac{1}{2}[A]_0)$. Therefore, when $t = t_{1/2}$ we can write the following expression:

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -kt_{1/2} \quad [15.18]$$

Solving for $t_{1/2}$, and substituting -0.693 for $\ln \frac{1}{2}$, we arrive at the expression for the half-life of a first-order reaction:

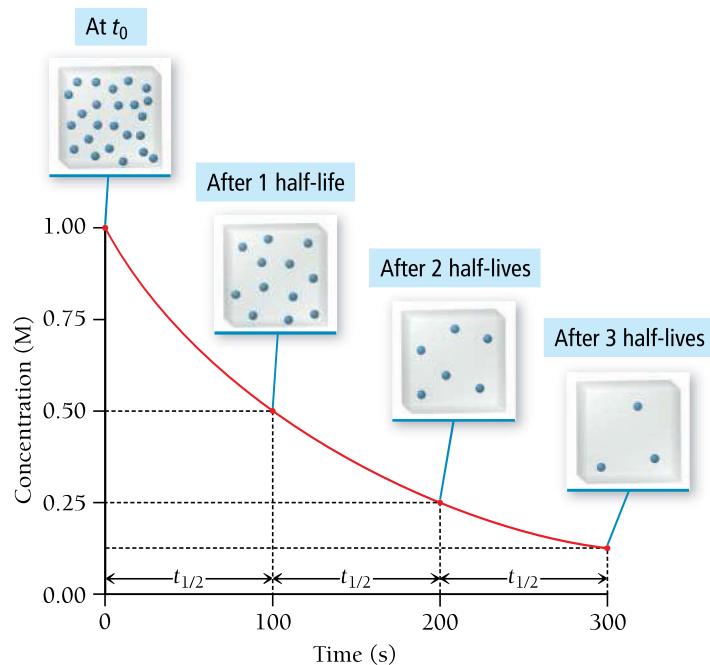
$$t_{1/2} = \frac{0.693}{k} \quad [15.19]$$

Notice that, for a first-order reaction, $t_{1/2}$ is independent of the initial concentration. For example, if $t_{1/2}$ is 100 s, and if the initial concentration is 1.0 M, the concentration falls to 0.50 M in 100 s, to 0.25 M in another 100 s, to 0.125 M in another 100 s, and so on (Figure 15.11►). Even though the concentration is changing as the reaction proceeds, the half-life (how long it takes for the concentration to halve) is constant. A constant half-life is unique to first-order reactions, making the concept of half-life particularly useful for first-order reactions.

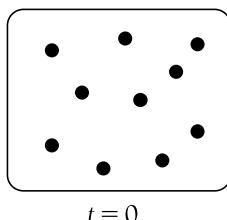
► **FIGURE 15.11** Half-Life: Concentration versus Time for a First-Order Reaction For this reaction, the concentration decreases by one-half every 100 seconds ($t_{1/2} = 100$ s). The blue spheres represent reactant molecules (the products are omitted for clarity).

Half-Life for a First-Order Reaction

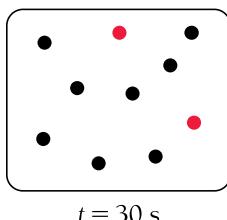
For a first-order reaction, the half-life is constant and independent of concentration.



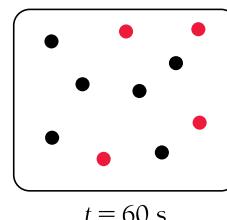
HALF-LIFE I The images shown here depict the first-order reaction $A \longrightarrow B$ at various times during the reaction process. The black circles represent reactant A, and the red circles represent product B. What is the half-life of the reaction?



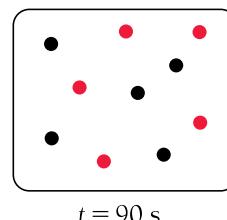
(a) 30 s



(b) 60 s



(c) 90 s



(d) 120 s

15.5
Cc
Conceptual Connection

ANSWER NOW!



HALF-LIFE II A first-order reaction ($A \longrightarrow B$) has a half-life of 25 minutes. If the initial concentration of A is 0.300 M, what is the concentration of B after 50 minutes? (Do not use a calculator to solve this problem.)

- (a)** 0.300 M **(b)** 0.225 M **(c)** 0.150 M **(d)** 0.100 M

15.6
Cc
Conceptual Connection

ANSWER NOW!



EXAMPLE 15.6 Half-Life

Molecular iodine dissociates at 625 K with a first-order rate constant of 0.271 s^{-1} . What is the half-life of this reaction?

SOLUTION

Because the reaction is first order, the half-life is given by Equation 15.19. Substitute the value of k into the expression and calculate $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{0.271 \text{ s}^{-1}} = 2.56 \text{ s}$$

FOR PRACTICE 15.6 A first-order reaction has a half-life of 26.4 seconds. How long does it take for the concentration of the reactant in the reaction to fall to one-eighth of its initial value?

Second-Order Reaction Half-Life

For a second-order reaction, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

At a time equal to the half-life ($t = t_{1/2}$), the concentration is exactly one-half of the initial concentration ($[A]_t = \frac{1}{2}[A]_0$). We can therefore write the following expression at $t = t_{1/2}$:

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0} \quad [15.20]$$

And then solve for $t_{1/2}$:

$$kt_{1/2} = \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0} \quad [15.21]$$

Notice that, for a second-order reaction, the half-life depends on the initial concentration. So if the initial concentration of a reactant in a second-order reaction is 1.0 M and the half-life is 100 s, the concentration falls to 0.50 M in 100 s. However, the time it takes for the concentration to fall to 0.25 M is now *longer than 100 s* because the initial concentration has decreased. Thus, the half-life continues to get longer as the concentration decreases.

Zero-Order Reaction Half-Life

For a zero-order reaction, the integrated rate law is:

$$[A]_t = -kt + [A]_0$$

Making the substitutions ($t = t_{1/2}$; $[A]_t = \frac{1}{2}[A]_0$), we can write the expression at $t = t_{1/2}$:

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0 \quad [15.22]$$

We then solve for $t_{1/2}$:

$$t_{1/2} = \frac{[A]_0}{2k} \quad [15.23]$$

Notice that, for a zero-order reaction, the half-life also depends on the initial concentration; however, unlike in the second-order case, the two are directly proportional—the half-life gets shorter as the concentration decreases.

Summarizing Basic Kinetic Relationships (see Table 15.2):

- The reaction order and rate law must be determined experimentally.
- The rate law relates the *rate* of the reaction to the *concentration* of the reactant(s).
- The integrated rate law (which is mathematically derived from the rate law) relates the *concentration* of the reactant(s) to *time*.
- The half-life is the time it takes for the concentration of a reactant to fall to one-half of its initial value.
- The half-life of a first-order reaction is independent of the initial concentration.
- The half-lives of zero-order and second-order reactions depend on the initial concentrations.

RATE LAW AND INTEGRATED RATE LAW A decomposition reaction, with a rate that is observed to slow down as the reaction proceeds, has a half-life that depends on the initial concentration of the reactant. Which statement is most likely true for this reaction?

- A plot of the natural log of the concentration of the reactant as a function of time is linear.
- The half-life of the reaction increases as the initial concentration increases.
- A doubling of the initial concentration of the reactant results in a quadrupling of the rate.

ANSWER NOW!

**TABLE 15.2** ■ Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	$\text{Rate} = k[A]^0$	$\text{M} \cdot \text{s}^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	$\text{Rate} = k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	$\text{Rate} = k[A]^2$	$\text{M}^{-1} \cdot \text{s}^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

WATCH NOW!**KEY CONCEPT VIDEO 15.5**
 The Effect of Temperature on Reaction Rate
15.5**The Effect of Temperature on Reaction Rate**

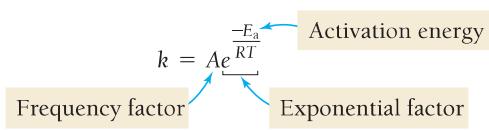
In the opening section of this chapter, we discussed how lizards become lethargic when their body temperature drops and the chemical reactions that control their muscle movement slow. The rates of chemical reactions are, in general, highly sensitive to temperature. For example, at around room temperature, a 10 °C increase in temperature increases the rate of a typical biological reaction by two or three times. How do we explain this highly sensitive temperature dependence?

The Arrhenius Equation

Recall that the rate law for a reaction is $\text{Rate} = k[\text{A}]^n$. The temperature dependence of the reaction rate is contained in the rate constant, k (which is actually a constant only when the temperature remains constant). An increase in temperature generally results in an increase in k , which results in a faster rate. In 1889, Swedish chemist Svante Arrhenius (1859–1927) wrote a paper quantifying the temperature dependence of the rate constant.

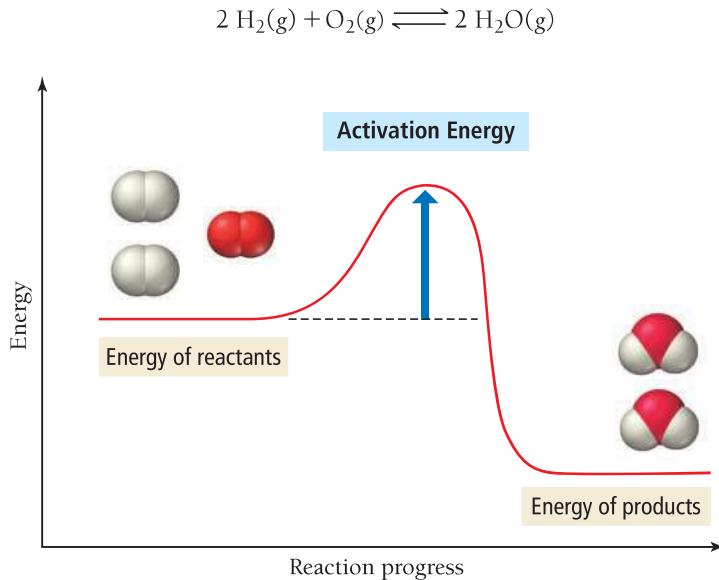
The modern form of the **Arrhenius equation** shows the relationship between the rate constant (k) and the temperature in kelvin (T):

$$k = A e^{-\frac{E_a}{RT}}$$


Activation energy
Frequency factor
Exponential factor

[15.24]

In this equation, R is the gas constant (8.314 J/mol · K), A is a constant called the *frequency factor* (or the *pre-exponential factor*), and E_a is the *activation energy* (or *activation barrier*).

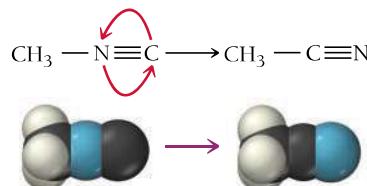
Activation Energy

▲ FIGURE 15.12 The Activation Energy Barrier Even though the reaction is energetically favorable (the energy of the products is lower than that of the reactants), an input of energy is needed for the reaction to take place.

The **activation energy** (E_a) is an energy barrier or hump that must be surmounted in order for the reactants to transform into products (Figure 15.12▲). We examine the frequency factor more closely in the next section; for now, we can think of the **frequency factor** (A) as the number of times that the reactants approach the activation barrier per unit time.

The Activation Energy, Frequency Factor, and Exponential Factor

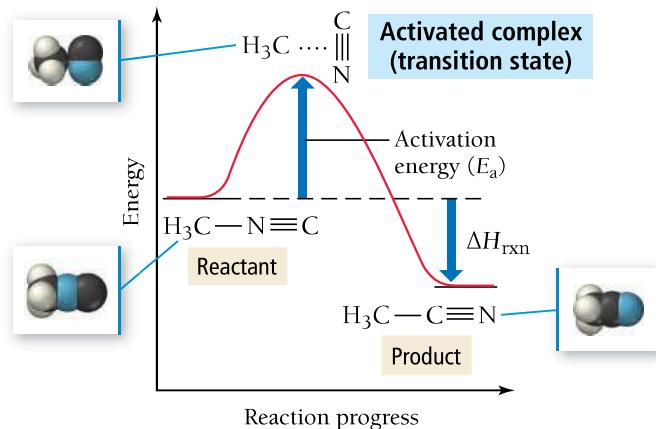
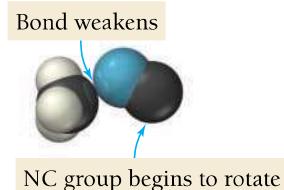
To understand each of these quantities better, consider the simple reaction in which CH₃NC (methyl isonitrile) rearranges to form CH₃CN (acetonitrile):



Let's examine the physical meaning of the activation energy, frequency factor, and exponential factor for this reaction.

The Activation Energy

Figure 15.13▶ shows the energy of a molecule as the reaction proceeds. The *x*-axis represents the progress of the reaction from left (reactant) to right (product). To get from the reactant to the product, the molecule must go through a high-energy state called the **activated complex** or **transition state**. Even though the overall reaction is energetically downhill (exothermic), it must first go uphill to reach the activated complex because energy is required to initially weaken the H₃C—N bond and allow the NC group to begin to rotate:



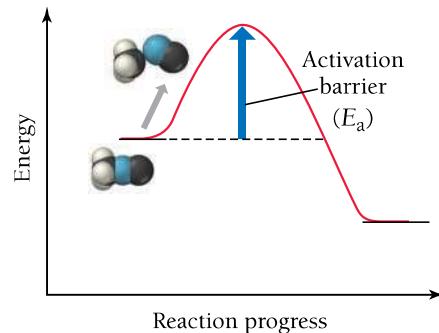
▲ **FIGURE 15.13 The Activated Complex** The reaction pathway includes a transitional state—the activated complex—that has a higher energy than either the reactant or the product.

The energy required to reach the activated complex is the *activation energy*. *The higher the activation energy, the slower the reaction rate (at a given temperature).*

The Frequency Factor

Recall that the frequency factor represents the number of approaches to the activation barrier per unit time. Any time that the NC group begins to rotate, it approaches the activation barrier. For this reaction, the frequency factor represents the rate at which the NC part of the molecule wags (vibrates side to side). With each wag, the reactant approaches the activation barrier:

Each wag is an approach to the activation barrier.



However, approaching the activation barrier is not equivalent to surmounting it. Most of the approaches do not have enough total energy to make it over the activation barrier.

The Exponential Factor

The **exponential factor** is a number between 0 and 1 that represents the fraction of molecules that have enough energy to make it over the activation barrier on a given approach. The exponential factor is the fraction of approaches that are actually successful and result in the product. For example, if the frequency factor is $10^9/\text{s}$ and the exponential factor is 10^{-7} at a certain temperature, then the overall rate constant at that temperature is $10^9/\text{s} \times 10^{-7} = 10^2/\text{s}$. In this case, the CN group wags at a rate of $10^9/\text{s}$. With each wag, the activation barrier is approached. However, for a given wag, only 1 in 10^7 molecules has sufficient energy to actually make it over the activation barrier.

The exponential factor depends on both the temperature (T) and the activation energy (E_a) of the reaction:

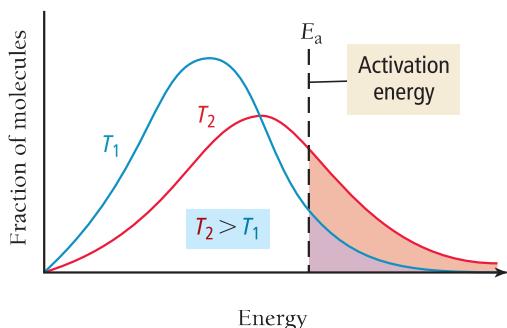
$$\text{Exponential factor} = e^{-E_a/RT}$$

A low activation energy and a high temperature make the negative exponent small, so the exponential factor approaches one. For example, if the activation energy is zero, then the exponent is zero, and the exponential factor is exactly one ($e^{-0} = 1$)—every approach to the activation barrier is successful. By contrast, a large activation energy and a low temperature make the exponent a very large negative number, so the exponential factor becomes very small. For example, as the temperature approaches 0 K, the exponent approaches an infinitely large negative number, and the exponential factor approaches zero ($e^{-\infty} = 0$).

As the temperature increases, the number of molecules having enough thermal energy to surmount the activation barrier increases. At any given temperature, a sample of molecules has a distribution of energies, as shown in Figure 15.14. Under common circumstances, only a small fraction of the molecules has enough energy to make it over the activation barrier. Because of the shape of the energy distribution curve, however, a small change in temperature results in a large difference in the number of molecules having enough energy to surmount the activation barrier. This explains the sensitivity of reaction rates to temperature.

▲ FIGURE 15.14 Thermal Energy Distribution

At any given temperature, the atoms or molecules in a gas sample have a range of energies. The higher the temperature, the wider the energy distribution and the greater the average energy. The fraction of molecules with enough energy to surmount the activation energy barrier and react (shaded regions) increases sharply as the temperature rises.



Summarizing Temperature and Reaction Rate:

- The frequency factor is the number of times that the reactants approach the activation barrier per unit time.
- The exponential factor is the fraction of the approaches that are successful in surmounting the activation barrier and forming products.
- The exponential factor increases with increasing temperature but decreases with increasing activation energy.

ANSWER NOW!



15.8

Cc
Conceptual Connection

REACTION RATE AND TEMPERATURE

Which statement best explains why reaction rates generally increase with increasing temperature?

- Reaction rates increase with increasing temperature because, as temperature increases, a greater fraction of molecules have enough thermal energy to surmount the activation barrier.
- Reaction rates increase with increasing temperature because, as temperature increases, the pre-exponential factor of the rate constant increases.
- Reaction rates increase with increasing temperature because, as temperature increases, molecules decompose into their constituent atoms, which can then form new bonds to form the products.

Arrhenius Plots: Experimental Measurements of the Frequency Factor and the Activation Energy

The frequency factor and activation energy are important quantities in understanding the kinetics of any reaction. To see how we measure these factors in the laboratory,

consider again Equation 15.24: $k = Ae^{-E_a/RT}$. Taking the natural logarithm of both sides of this equation, we get the following result:

$$\begin{aligned}\ln k &= \ln(Ae^{-E_a/RT}) \\ \ln k &= \ln A + \ln e^{-E_a/RT} \\ \ln k &= \ln A - \frac{E_a}{RT}\end{aligned}\quad [15.25]$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \quad [15.26]$$

$$y = mx + b$$

Equation 15.26 is in the form of a straight line. A plot of the natural logarithm of the rate constant ($\ln k$) versus the inverse of the temperature in kelvins ($1/T$) yields a straight line with a slope of $-E_a/R$ and a y -intercept of $\ln A$. Such a plot is called an **Arrhenius plot** and is commonly used in the analysis of kinetic data, as shown in Example 15.7.

Remember that
 $\ln(AB) = \ln A + \ln B$.

Remember that $\ln e^x = x$.

In an Arrhenius analysis, the pre-exponential factor (A) is assumed to be independent of temperature. Although the pre-exponential factor does depend on temperature to some degree, its temperature dependence is much less than that of the exponential factor and is often ignored.

EXAMPLE 15.7 Using an Arrhenius Plot to Determine Kinetic Parameters

The decomposition of ozone shown here is important to many atmospheric reactions:



A study of the kinetics of the reaction results in the following data:

Temperature (K)	Rate Constant ($\text{M}^{-1} \cdot \text{s}^{-1}$)	Temperature (K)	Rate Constant ($\text{M}^{-1} \cdot \text{s}^{-1}$)
600	3.37×10^3	1300	7.83×10^7
700	4.85×10^4	1400	1.45×10^8
800	3.58×10^5	1500	2.46×10^8
900	1.70×10^6	1600	3.93×10^8
1000	5.90×10^6	1700	5.93×10^8
1100	1.63×10^7	1800	8.55×10^8
1200	3.81×10^7	1900	1.19×10^9

Determine the value of the frequency factor and activation energy for the reaction.

SOLUTION

To determine the frequency factor and activation energy, prepare a graph of the natural log of the rate constant ($\ln k$) versus the inverse of the temperature ($1/T$).

The plot is linear, as expected for Arrhenius behavior. The line that fits best has a slope of $-1.12 \times 10^4 \text{ K}$ and a y -intercept of 26.8. Calculate the activation energy from the slope by setting the slope equal to $-E_a/R$ and solving for E_a :

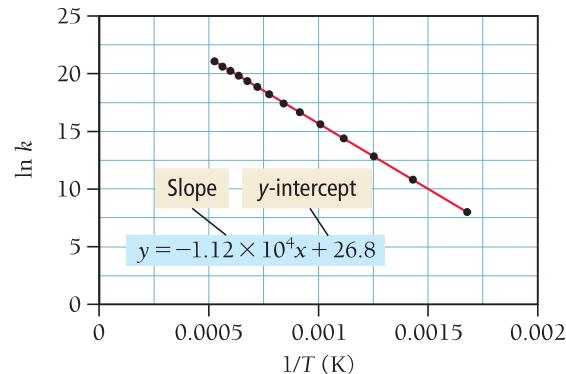
$$\begin{aligned}-1.12 \times 10^4 \text{ K} &= \frac{-E_a}{R} \\ E_a &= 1.12 \times 10^4 \text{ K} \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \\ &= 9.31 \times 10^4 \text{ J/mol} \\ &= 93.1 \text{ kJ/mol}\end{aligned}$$

Calculate the frequency factor (A) by setting the intercept equal to $\ln A$.

$$\begin{aligned}26.8 &= \ln A \\ A &= e^{26.8} \\ &= 4.36 \times 10^{11}\end{aligned}$$

Since the rate constants are measured in units of $\text{M}^{-1} \cdot \text{s}^{-1}$, the frequency factor is in the same units. Consequently, you can conclude that the reaction has an activation energy of 93.1 kJ/mol and a frequency factor of $4.36 \times 10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$.

FOR PRACTICE 15.7 For the decomposition of ozone reaction in Example 15.7, use the results of the Arrhenius analysis to predict the rate constant at 298 K.



In some cases, when either data are limited or plotting capabilities are absent, we can calculate the activation energy if we know the rate constant at just two different temperatures. We can apply the Arrhenius expression in Equation 15.26 to the two different temperatures as follows:

$$\ln k_2 = -\frac{E_a}{R} \left(\frac{1}{T_2} \right) + \ln A$$

$$\ln k_1 = -\frac{E_a}{R} \left(\frac{1}{T_1} \right) + \ln A$$

We can then subtract $\ln k_1$ from $\ln k_2$:

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

Rearranging, we get the two-point form of the Arrhenius equation:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad [15.27]$$

Example 15.8 demonstrates how to use this equation to calculate the activation energy from experimental measurements of the rate constant at two different temperatures.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 15.8

EXAMPLE 15.8 Using the Two-Point Form of the Arrhenius Equation



Consider the reaction between nitrogen dioxide and carbon monoxide:



The rate constant at 701 K is measured as $2.57 \text{ M}^{-1} \cdot \text{s}^{-1}$ and that at 895 K is measured as $567 \text{ M}^{-1} \cdot \text{s}^{-1}$. Find the activation energy for the reaction in kJ/mol.

SORT You are given the rate constant of a reaction at two different temperatures and asked to find the activation energy.

STRATEGIZE Use the two-point form of the Arrhenius equation, which relates the activation energy to the given information and R (a constant).

SOLVE Substitute the two rate constants and the two temperatures into the equation.

Solve the equation for E_a , the activation energy, and convert to kJ/mol.

GIVEN: $T_1 = 701 \text{ K}$, $k_1 = 2.57 \text{ M}^{-1} \cdot \text{s}^{-1}$
 $T_2 = 895 \text{ K}$, $k_2 = 567 \text{ M}^{-1} \cdot \text{s}^{-1}$

FIND: E_a

$$\text{EQUATION } \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

SOLUTION

$$\begin{aligned} \ln \frac{567 \text{ M}^{-1} \cdot \text{s}^{-1}}{2.57 \text{ M}^{-1} \cdot \text{s}^{-1}} &= \frac{E_a}{R} \left(\frac{1}{701 \text{ K}} - \frac{1}{895 \text{ K}} \right) \\ 5.40 &= \frac{E_a}{R} \left(\frac{3.09 \times 10^{-4}}{\text{K}} \right) \end{aligned}$$

$$\begin{aligned} E_a &= 5.40 \left(\frac{\text{K}}{3.09 \times 10^{-4}} \right) R \\ &= 5.40 \left(\frac{\text{K}}{3.09 \times 10^{-4}} \right) 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \\ &= 1.45 \times 10^5 \text{ J/mol} \\ &= 1.5 \times 10^2 \text{ kJ/mol} \end{aligned}$$

CHECK The magnitude of the answer is reasonable. Activation energies for most reactions range from tens to hundreds of kilojoules per mole.

FOR PRACTICE 15.8 Use the results from Example 15.8 and the given rate constant of the reaction at either of the two temperatures to predict the rate constant for this reaction at 525 K.

REACTION RATE AND ACTIVATION ENERGY Reaction A and reaction B have identical frequency factors. However, reaction B has a higher activation energy than reaction A. Which reaction has a greater rate constant at room temperature?

- (a) Reaction A
- (b) Reaction B

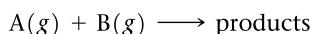


ANSWER NOW!



The Collision Model: A Closer Look at the Frequency Factor

Recall that the frequency factor in the Arrhenius equation represents the number of approaches to the activation barrier per unit time. Let's refine that idea for a reaction involving two gas-phase reactants:



In the **collision model**, a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules (Figure 15.15►). In collision theory, therefore, each approach to the activation barrier is a collision between the reactant molecules. Consequently, the value of the frequency factor should simply be the number of collisions that occur per second. However, the frequency factors of most (though not all) gas-phase chemical reactions tend to be smaller than the number of collisions that occur per second. Why?

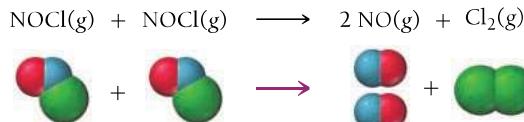
In the collision model, we can separate the frequency factor into two distinct parts, as shown in the following equations:

$$\begin{aligned} k &= Ae^{\frac{-E_a}{RT}} \\ &= pze^{\frac{-E_a}{RT}} \end{aligned}$$

Orientation factor Collision frequency

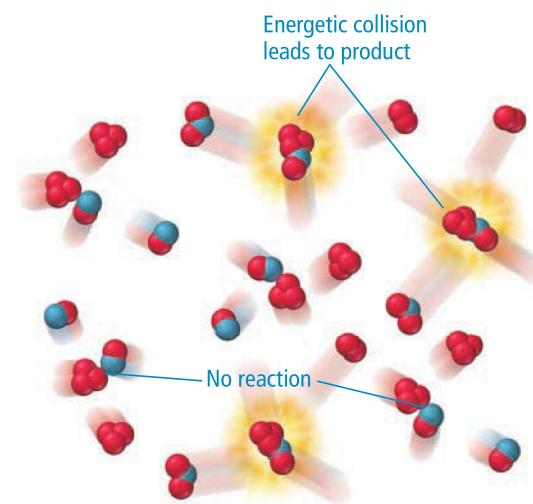
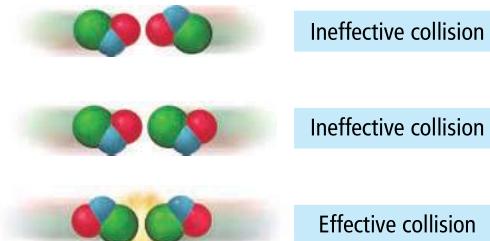
where p is the **orientation factor** and z is the **collision frequency**. The collision frequency is the number of collisions that occur per unit time, which we calculate for a gas-phase reaction from the pressure of the gases and the temperature of the reaction mixture. Under typical conditions, a single molecule undergoes on the order of 10^9 collisions every second. The orientation factor is a number, usually between 0 and 1, which represents the fraction of collisions with an orientation that allows the reaction to occur.

To better understand the orientation factor, consider the reaction represented by the following equation:



In order for the reaction to occur, two NOCl molecules must collide with sufficient energy. However, not all collisions with sufficient energy lead to products because the reactant molecules must also be properly oriented.

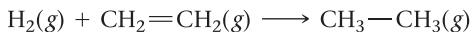
Consider the three possible collision orientations of the reactant molecules shown here:



▲ **FIGURE 15.15 The Collision Model** In the collision model, two molecules react after a sufficiently energetic collision with the correct orientation brings the reacting groups together.

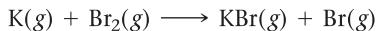
The first two collisions, even if they occur with sufficient energy, do not result in a reaction because the reactant molecules are not oriented in a way that allows the chlorine atoms to bond. In other words, if two molecules are to react with each other, they must collide in such a way that allows the necessary bonds to break and form. For the reaction of $\text{NOCl}(g)$, the orientation factor is $p = 0.16$. This means that only 16 out of 100 sufficiently energetic collisions are successful in forming the products.

Some reactions have orientation factors that are much smaller than one. Consider the reaction between hydrogen and ethene:



The orientation factor for this reaction is 1.7×10^{-6} , which means that fewer than two out of each million sufficiently energetic collisions actually form products. The small orientation factor indicates that the orientational requirements for this reaction are very stringent—the molecules must be aligned in a *very specific way* for the reaction to occur.

Reactions between *individual atoms* usually have orientation factors of approximately one because atoms are spherically symmetrical; thus any orientation can lead to the formation of products. A few reactions have orientation factors greater than one. Consider the reaction between potassium and bromine:



This reaction has an orientation factor of $p = 4.8$. In other words, there are more reactions than collisions—the reactants do not even have to collide to react! Apparently, through a process dubbed *the harpoon mechanism*, a potassium atom can actually transfer an electron to a bromine molecule without a collision. The resulting positive charge on the potassium and the negative charge on the bromine cause the two species to attract each other and form a bond. The potassium atom essentially *harpoons* a passing bromine molecule with an electron and *reels it in* through the coulombic attraction between opposite charges.

We can picture a sample of reactive gases as a frenzy of collisions between the reacting atoms or molecules. At normal temperatures, the vast majority of these collisions do not have sufficient energy to overcome the activation barrier, and the atoms or molecules simply bounce off one another. Of the collisions having sufficient energy to overcome the activation barrier, most do not have the proper orientation for the reaction to occur (for the majority of common reactions). When two molecules with sufficient energy *and* the correct orientation collide, something extraordinary happens. The electrons on one of the atoms or molecules are attracted to the nuclei of the other; some bonds begin to weaken while other bonds begin to form, and, if all goes well, the reactants go through the transition state and are transformed into the products. This is how a chemical reaction occurs.

ANSWER NOW!



15.10 Cc

Conceptual Connection

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KEY CONCEPT VIDEO 15.6



15.6

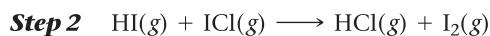
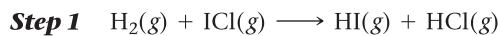
Reaction Mechanisms

Most chemical reactions do not occur in a single step but rather over the course of several steps. When we write a chemical equation to represent a chemical reaction, we *usually represent the overall reaction, not the series of individual steps by which the reaction occurs*. Consider the reaction in which hydrogen gas reacts with iodine monochloride:



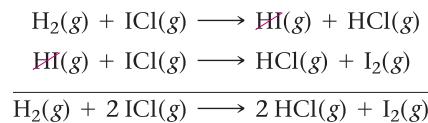
The overall equation shows only the substances present at the beginning of the reaction and the substances formed by the reaction—it does not show the intermediate steps. The **reaction mechanism** is the series of individual chemical steps by which an

overall chemical reaction occurs. For example, the proposed mechanism for the reaction between hydrogen and iodine monochloride contains two steps:



In the first step, an H_2 molecule collides with an ICl molecule and forms an HI molecule and an HCl molecule. In the second step, the HI molecule formed in the first step collides with a second ICl molecule to form another HCl molecule and an I_2 molecule. Each step in a reaction mechanism is an **elementary step**. Elementary steps cannot be broken down into simpler steps—they occur as written (they represent the exact species that are colliding in the reaction).

One of the requirements for a valid reaction mechanism is that the individual steps in the mechanism add to the overall reaction. For example, the mechanism just shown sums to the overall reaction as shown here:



Notice that the HI molecule appears in the reaction mechanism but not in the overall reaction equation. We call species such as HI *reaction intermediates*. A **reaction intermediate** forms in one elementary step and is consumed in another. The reaction mechanism is a complete, detailed description of the reaction at the molecular level—it specifies the individual collisions and reactions that result in the overall reaction. As such, reaction mechanisms are highly sought-after pieces of chemical knowledge.

How do we determine reaction mechanisms? Recall from the opening section of this chapter that chemical kinetics are not only practically important (because they allow us to control the rate of a particular reaction), but they are also theoretically important because they can help us determine the mechanism of the reaction. We can piece together possible reaction mechanisms by measuring the kinetics of the overall reaction and working backward to write a mechanism consistent with the measured kinetics.

Rate Laws for Elementary Steps

We characterize elementary steps by their **molecularity**, the number of reactant particles involved in the step. The most common molecularities are **unimolecular** and **bimolecular**:

$\text{A} \longrightarrow \text{products}$	Unimolecular
$\text{A} + \text{A} \longrightarrow \text{products}$	Bimolecular
$\text{A} + \text{B} \longrightarrow \text{products}$	Bimolecular

Elementary steps in which three reactant particles collide, called **termolecular** steps, are very rare because the probability of three particles simultaneously colliding is small.

Although we cannot deduce the rate law for an *overall chemical reaction* from the balanced chemical equation, we can deduce the rate law for an *elementary step* from its equation. Since we know that an elementary step occurs through the collision of the reactant particles, the rate is proportional to the product of the concentrations of those particles. For example, the rate for the bimolecular elementary step in which A reacts with B is proportional to the concentration of A multiplied by the concentration of B :



Similarly, the rate law for the bimolecular step in which A reacts with A is proportional to the square of the concentration of A :



Table 15.3 summarizes the rate laws for the common elementary steps, as well as those for the rare termolecular step. Notice that the molecularity of the elementary step is equal to the overall order of the step.

An elementary step represents an actual interaction between the reactant molecules in the step. An overall reaction equation shows only the starting substances and the ending substances, not the path between them.

TABLE 15.3 ■ Rate Laws for Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

ANSWER NOW!

15.11 Cc

Conceptual Connection

**ELEMENTARY STEPS**

What is the rate law for the elementary step



- (a) Rate = $k[\text{Cl}]$
 (b) Rate = $k[\text{CO}]$
 (c) Rate = $k[\text{ClCO}]$
 (d) Rate = $k[\text{Cl}][\text{CO}]$

Rate-Determining Steps and Overall Reaction Rate Laws

In most chemical reactions, one of the elementary steps—called the **rate-determining step**—is much slower than the others. The rate-determining step in a chemical reaction is analogous to the narrowest section on a freeway. If a section of a freeway narrows from four lanes to two lanes, for even a short distance, the rate at which cars travel along the freeway is limited by the rate at which they can travel through the narrow section (even though the rate might be much faster along the four-lane section). Similarly, the rate-determining step in a reaction mechanism limits the overall rate of the reaction (even though the other steps occur much faster) and therefore determines *the rate law for the overall reaction*.

► The rate-limiting step in a reaction mechanism limits the overall rate of the reaction just as the narrowest section of a highway limits the rate at which traffic can pass.



As an example, consider the reaction between nitrogen dioxide gas and carbon monoxide gas:



The experimentally determined rate law for this reaction is $\text{Rate} = k[\text{NO}_2]^2$. We can see from this rate law that the reaction must not be a single-step reaction—otherwise the rate law would be $\text{Rate} = k[\text{NO}_2][\text{CO}]$. A possible mechanism for this reaction involves two steps:

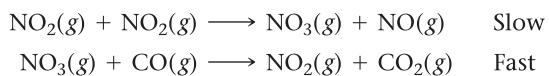
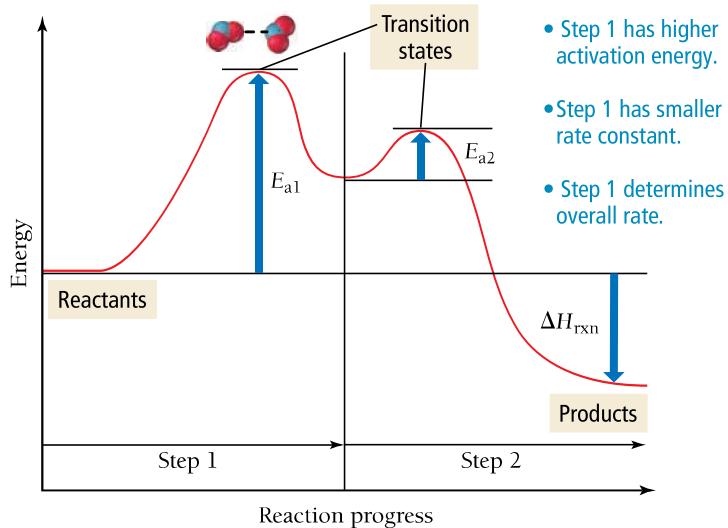


Figure 15.16► shows the energy diagram for this mechanism. The first step has a much larger activation energy than the second step. This greater activation energy results in a much smaller rate constant for the first step compared to the second step. The first step determines the overall rate of the reaction, and the predicted *overall* rate law is therefore $\text{Rate} = k[\text{NO}_2]^2$, which is consistent with the observed experimental rate law.

Energy Diagram for a Two-Step Mechanism

Because E_a for Step 1 > E_a for Step 2, Step 1 has the smaller rate constant and is rate limiting.

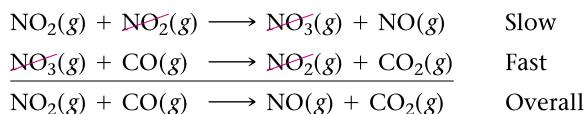


◀ FIGURE 15.16 Energy Diagram for a Two-Step Mechanism

For a proposed reaction mechanism, such as the one shown here for NO_2 and CO, to be *valid* (mechanisms can only be validated, not proven), two conditions must be met:

1. **The elementary steps in the mechanism must sum to the overall reaction.**
2. **The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.**

We have already seen that the rate law predicted by the earlier mechanism is consistent with the experimentally observed rate law. We can check whether the elementary steps sum to the overall reaction by adding them together:



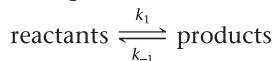
The mechanism fulfills both of the given requirements and is therefore valid. A valid mechanism is not a *proven* mechanism (because other mechanisms may also fulfill both of the given requirements). We can only say that a given mechanism is consistent with kinetic observations of the reaction and is therefore possible. Other types of data—such as the experimental evidence for a proposed intermediate—are necessary to further strengthen the validity of a proposed mechanism.

Mechanisms with a Fast Initial Step

When the proposed mechanism for a reaction has a slow initial step—such as the one shown previously for the reaction between NO_2 and CO—the rate law predicted by the mechanism normally contains only reactants involved in the overall reaction. However, when a mechanism begins with a fast initial step, some other subsequent step in the mechanism is the rate-limiting step. In these cases, the rate law predicted by the rate-limiting step may contain reaction intermediates. Because reaction intermediates do not appear in the overall reaction equation, a rate law containing intermediates cannot generally correspond to the experimental rate law. Fortunately, however, we can often express the concentration of intermediates in terms of the concentrations of the reactants of the overall reaction.

In a multistep mechanism where the first step is fast, the products of the first step may build up because the rate at which they are consumed is limited by some slower step further down the line. As those products build up, they can begin to react with one another to

re-form the reactants. As long as the first step is fast enough compared to the rate-limiting step, the first-step reaction will reach equilibrium. We indicate equilibrium as follows:

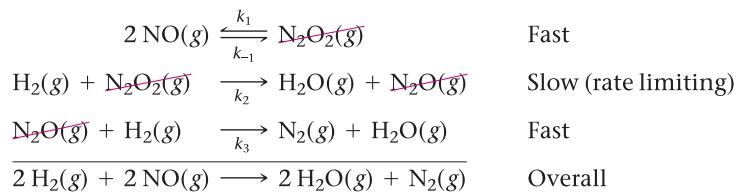


The double arrows indicate that both the forward reaction and the reverse reaction occur. If equilibrium is reached, then the rate of the forward reaction equals the rate of the reverse reaction.

As an example, consider the reaction by which hydrogen reacts with nitrogen monoxide to form water and nitrogen gas:



The experimentally observed rate law is Rate = $k[\text{H}_2][\text{NO}]^2$. The reaction is first order in hydrogen and second order in nitrogen monoxide. The proposed mechanism has a slow second step:



To determine whether the mechanism is valid, we must find whether the two conditions described previously are met. As we can see, the steps do indeed sum to the overall reaction, so the first condition is met.

The second condition is that the rate law predicted by the mechanism must be consistent with the experimentally observed rate law. Because the second step is rate limiting, we write the following expression for the rate law:

$$\text{Rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2] \quad [15.28]$$

This rate law contains an intermediate (N_2O_2) and therefore cannot be consistent with the experimentally observed rate law (which does not contain intermediates). Because of the equilibrium in the first step, however, *we can express the concentration of the intermediate in terms of the reactants of the overall equation*. Since the first step reaches equilibrium, the rate of the forward reaction in the first step equals the rate of the reverse reaction:

$$\text{Rate (forward)} = \text{Rate (reverse)}$$

The rate of the forward reaction is given by the rate law:

$$\text{Rate} = k_1[\text{NO}]^2$$

The rate of the reverse reaction is given by the rate law:

$$\text{Rate} = k_{-1}[\text{N}_2\text{O}_2]$$

Since these two rates are equal at equilibrium, we write the expression:

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Rearranging, we get:

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}}[\text{NO}]^2$$

We can now substitute this expression into Equation 15.28, the rate law obtained from the slow step:

$$\begin{aligned} \text{Rate} &= k_2[\text{H}_2][\text{N}_2\text{O}_2] \\ &= k_2[\text{H}_2] \frac{k_1}{k_{-1}}[\text{NO}]^2 \\ &= \frac{k_2 k_1}{k_{-1}} [\text{H}_2][\text{NO}]^2 \end{aligned}$$

If we combine the individual rate constants into one overall rate constant, we get the predicted rate law:

$$\text{Rate} = k[\text{H}_2][\text{NO}]^2$$

Since this rate law is consistent with the experimentally observed rate law, condition 2 is met and the proposed mechanism is valid.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 15.9

EXAMPLE 15.9 Reaction Mechanisms

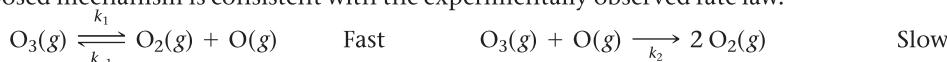
Ozone naturally decomposes to oxygen by this reaction:



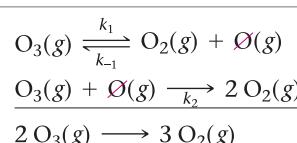
The experimentally observed rate law for this reaction is:

$$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Show that this proposed mechanism is consistent with the experimentally observed rate law.

**SOLUTION**

To determine whether the mechanism is valid, you must first determine whether the steps sum to the overall reaction. The steps do indeed sum to the overall reaction, so the first condition is met.



The second condition is that the rate law predicted by the mechanism is consistent with the experimentally observed rate law. Because the second step is rate limiting, write the rate law based on the second step.

$$\text{Rate} = k_2[\text{O}_3][\text{O}]$$

Because the rate law contains an intermediate (O), you must express the concentration of the intermediate in terms of the concentrations of the reactants of the overall reaction. To do this, set the rates of the forward reaction and the reverse reaction of the first step equal to each other. Solve the expression from the previous step for [O], the concentration of the intermediate.

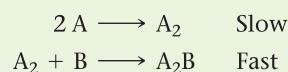
$$\begin{aligned} \text{Rate (forward)} &= \text{Rate (backward)} \\ k_1[\text{O}_3] &= k_{-1}[\text{O}_2][\text{O}] \\ [\text{O}] &= \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} \end{aligned}$$

Finally, substitute [O] into the rate law predicted by the slow step.

$$\begin{aligned} \text{Rate} &= k_2[\text{O}_3][\text{O}] \\ &= k_2[\text{O}_3] \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} \\ &= k_2 \frac{k_1}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k[\text{O}_3]^2[\text{O}_2]^{-1} \end{aligned}$$

CHECK Because the two steps in the proposed mechanism sum to the overall reaction, and because the rate law obtained from the proposed mechanism is consistent with the experimentally observed rate law, the proposed mechanism is valid. The -1 reaction order with respect to $[\text{O}_2]$ indicates that the rate slows down as the concentration of oxygen increases—oxygen inhibits, or slows down, the reaction.

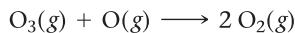
FOR PRACTICE 15.9 Predict the overall reaction and rate law that results from the following two-step mechanism:

**15.7****Catalysis**

Throughout this chapter, we have learned about ways to control the rates of chemical reactions. We can speed up the rate of a reaction by increasing the concentration of the reactants or by increasing the temperature. However, these approaches are not always feasible. There are limits to how concentrated we can make a reaction mixture, and increases in temperature may allow unwanted reactions—such as the decomposition of a reactant—to occur.

Alternatively, we can increase reaction rates by using a **catalyst**, a substance that increases the rate of a chemical reaction but is not consumed by the reaction. A catalyst works by providing an alternative mechanism for the reaction—one in which the rate-determining step has a lower activation energy.

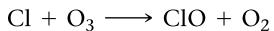
For example, consider the noncatalytic destruction of ozone in the upper atmosphere, discussed in Section 7.10, which happens according to this reaction:



In this reaction, an ozone molecule collides with an oxygen atom to form two oxygen molecules in a single elementary step.

Photodissociation means *light-induced* dissociation. The energy from a photon of light can break chemical bonds and therefore dissociate, or break apart, a molecule.

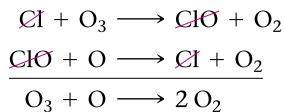
Earth has a protective ozone layer in the upper atmosphere because the activation energy for this reaction is fairly high; the reaction, therefore, proceeds at a fairly slow rate, and the ozone layer does not rapidly decompose into O₂. However, the addition of Cl atoms (which come from the photodissociation of human-made chlorofluorocarbons) to the upper atmosphere makes available another pathway by which O₃ can be destroyed. The first step in this pathway—called the catalytic destruction of ozone—is the reaction of Cl with O₃ to form ClO and O₂:



This is followed by a second step in which ClO reacts with O, regenerating Cl:

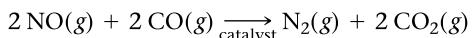


If we add the two reactions, the overall reaction is identical to the noncatalytic reaction:

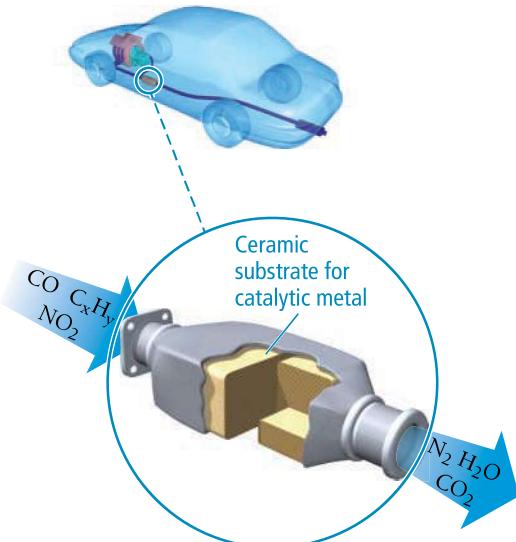
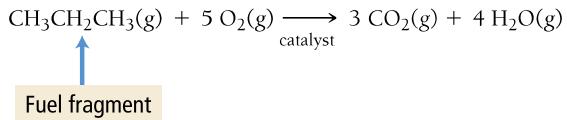


However, the activation energy for the rate-limiting step in this pathway is much smaller than that for the first, uncatalyzed pathway (as shown in Figure 15.17), and therefore the reaction occurs at a much faster rate. Note that the Cl is not consumed in the overall reaction—this is characteristic of a catalyst.

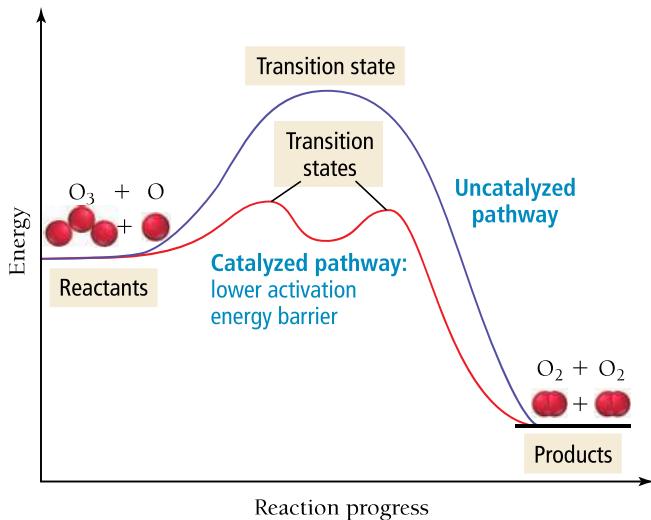
In the case of the catalytic destruction of ozone, the catalyst speeds up a reaction that we *do not* want to happen. Most of the time, however, catalysts are used to speed up reactions that we *do* want to happen. For example, your car most likely has a catalytic converter in its exhaust system. The catalytic converter contains solid catalysts, such as platinum, rhodium, or palladium, dispersed on an underlying high-surface-area ceramic structure. These catalysts convert exhaust pollutants such as nitrogen monoxide and carbon monoxide into less harmful substances:



The catalytic converter also promotes the complete combustion of any fuel fragments present in the exhaust:



► The catalytic converter in the exhaust system of a car helps eliminate pollutants in the exhaust.



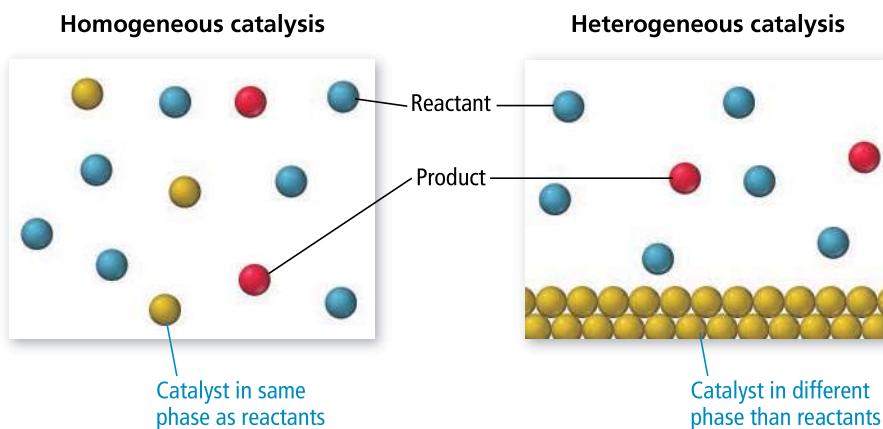
▲ FIGURE 15.17 Catalyzed and Uncatalyzed

Decomposition of Ozone In the catalytic destruction of ozone (red), the activation barrier for the rate-limiting step is much lower than that in the uncatalyzed process (blue).

Fuel fragments in exhaust are harmful because they lead to the formation of ozone. Recall from Section 7.10 that although ozone is a natural part of our *upper* atmosphere that protects us from excess exposure to ultraviolet light, it is a pollutant in the *lower* atmosphere, interfering with cardiovascular function and acting as an eye and lung irritant. The use of catalytic converters in motor vehicles has resulted in lower levels of these pollutants over most U.S. cities in the last 30 years, even though the number of cars on the roadways has dramatically increased (see Table 15.4).

Homogeneous and Heterogeneous Catalysis

We categorize catalysts into two types: homogeneous and heterogeneous (Figure 15.18▼). In **homogeneous catalysis**, the catalyst exists in the same phase (or state) as the reactants. The catalytic destruction of ozone by Cl is an example of homogeneous catalysis—the chlorine atoms exist in the gas phase with the gas-phase reactants. In **heterogeneous catalysis**, the catalyst exists in a different phase than the reactants. The solid catalysts used in catalytic converters are examples of heterogeneous catalysts—they are solids while the reactants are gases. The use of solid catalysts with gas-phase or solution-phase reactants is the most common type of heterogeneous catalysis.



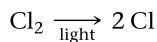
▲ **FIGURE 15.18 Homogeneous and Heterogeneous Catalysis** A homogeneous catalyst exists in the same phase as the reactants. A heterogeneous catalyst exists in a different phase than the reactants. Often, a heterogeneous catalyst provides a solid surface on which the reaction can take place.

Research has shown that heterogeneous catalysis is most likely responsible for the annual formation of an ozone hole over Antarctica. After the discovery of the Antarctic ozone hole in 1985, scientists wondered why there was such a dramatic drop in ozone over Antarctica but not over the rest of the planet. After all, the chlorine from chlorofluorocarbons that catalyzes ozone destruction is evenly distributed throughout the entire atmosphere.

As it turns out, most of the chlorine that enters the atmosphere from chlorofluorocarbons gets bound up in chlorine *reservoirs*, which are substances such as ClONO₂ that hold chlorine and prevent it from catalyzing ozone destruction. The unique conditions over Antarctica—especially the cold, isolated air mass that exists during the long dark winter—result in clouds that contain solid ice particles. These unique clouds are called polar stratospheric clouds (or PSCs), and the surfaces of the ice particles within these clouds appear to catalyze the release of chlorine from their reservoirs:



When the sun rises in the Antarctic spring, the sunlight dissociates the chlorine molecules into chlorine atoms:



The chlorine atoms then catalyze the destruction of ozone by the mechanism discussed previously. This continues until the sun melts the stratospheric clouds, allowing chlorine

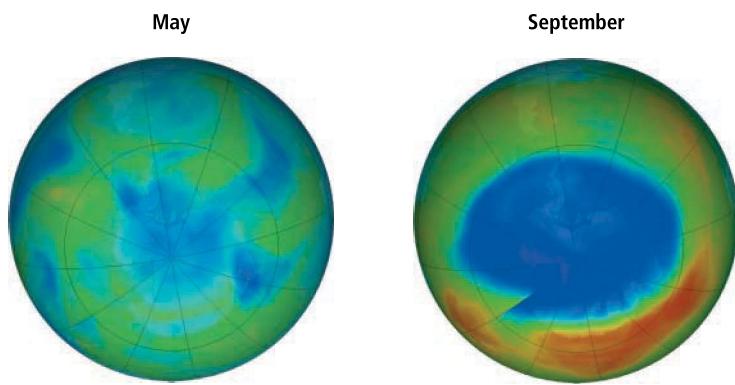
TABLE 15.4 □ Change in Pollutant Levels

Pollutant	Change 1980–2013
NO ₂	-60%
O ₃	-33%
CO	-84%

Source: EPA's National Air Trends.



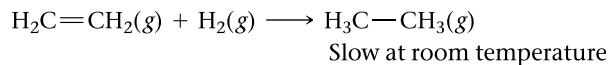
▲ Polar stratospheric clouds contain ice particles that catalyze reactions by which chlorine is released from its atmospheric chemical reservoirs.



▲ FIGURE 15.19 Ozone Depletion in the Antarctic Spring The concentration of ozone over Antarctica drops sharply during the months of September and October due to the catalyzed destruction of ozone by chlorine. The image on the left shows the average ozone levels in May 2017, and the image on the right shows the average levels from September 2017. (The lowest ozone levels are represented in blue.) Source: NASA Ozone Watch, OMI instrument (KNMI/NASA) onboard the Aura satellite.

atoms to be reincorporated into their reservoirs. The result is an ozone hole that forms every spring and lasts about six to eight weeks (Figure 15.19▲).

A second example of heterogeneous catalysis involves the **hydrogenation** of double bonds within alkenes. Consider the reaction between ethene and hydrogen, which is relatively slow at normal temperatures:

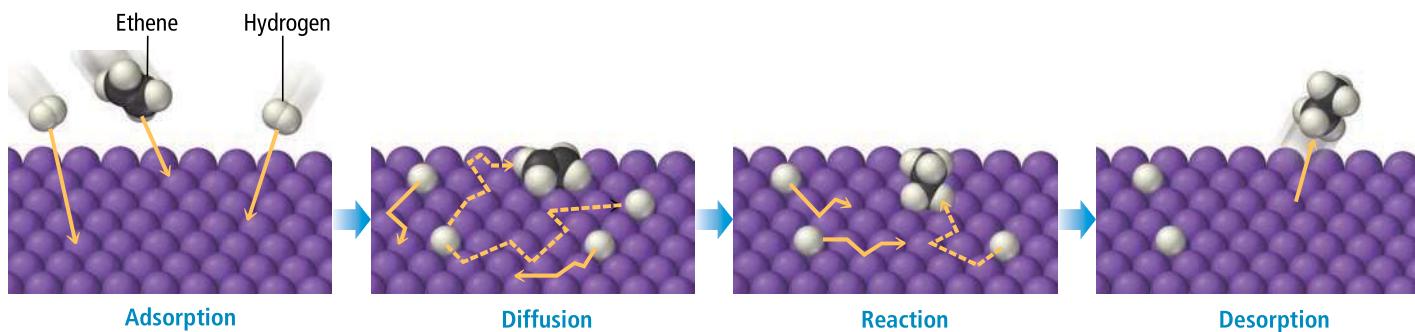


However, in the presence of finely divided platinum, palladium, or nickel, the reaction happens rapidly. The catalysis occurs by the four-step process depicted in Figure 15.20▼:

1. Adsorption: the reactants are adsorbed onto the metal surface.
2. Diffusion: the reactants diffuse on the surface until they approach each other.
3. Reaction: the reactants react to form the products.
4. Desorption: the products desorb from the surface into the gas phase.

The large activation energy of the hydrogenation reaction—due primarily to the strength of the hydrogen-hydrogen bond in H_2 —is greatly lowered when the reactants adsorb onto the surface.

Heterogeneous Catalysis

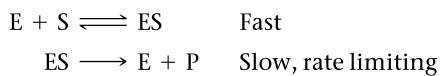


▲ FIGURE 15.20 Catalytic Hydrogenation of Ethene

Enzymes: Biological Catalysts

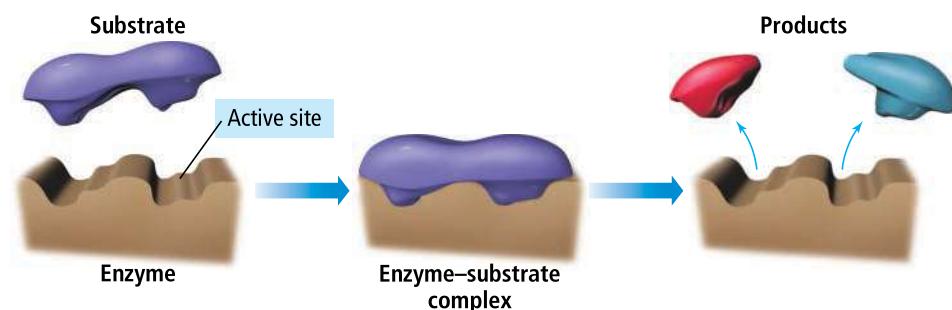
The strategies used to speed up chemical reactions in the laboratory—high temperatures, high pressures, strongly acidic or alkaline conditions—are not available to living organisms, since they would be fatal to cells.

We find perhaps the best example of chemical catalysis in living organisms. Most of the thousands of reactions that must occur for an organism to survive are too slow at normal temperatures. So living organisms rely on **enzymes**, biological catalysts that increase the rates of biochemical reactions. Enzymes are usually large protein molecules with complex three-dimensional structures. Within each enzyme's structure is a specific area called the **active site**. The properties and shape of the active site are just right to bind the reactant molecule, usually called the **substrate**. The substrate fits into the active site in a manner that is analogous to a key fitting into a lock (Figure 15.21►). When the substrate binds to the active site of the enzyme—through intermolecular forces such as hydrogen bonding and dispersion forces, or even covalent bonds—the activation energy of the reaction is greatly lowered, allowing the reaction to occur at a much faster rate. The general mechanism by which an enzyme (E) binds a substrate (S) and then reacts to form the products (P) is:



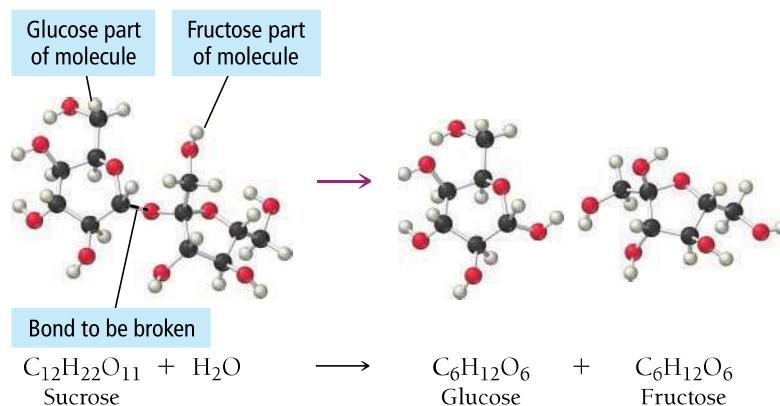
Enzyme–Substrate Binding

A substrate (or reactant) fits into the active site of an enzyme much as a key fits into a lock.



▲ FIGURE 15.21 Enzyme–Substrate Binding Intermolecular forces hold the substrate in place and form an enzyme–substrate complex. (Sometimes temporary covalent bonding may also be involved.) After the reaction occurs, the products are released from the active site.

Sucrase, for example, is an enzyme that catalyzes the breaking up of sucrose (table sugar) into glucose and fructose within the body. At body temperature, sucrose does not

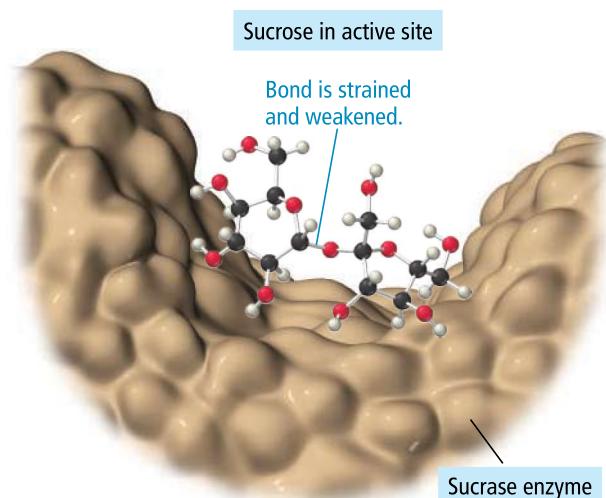


▲ Sucrose breaks up into glucose and fructose during digestion.

break into glucose and fructose because the activation energy is high, resulting in a slow reaction rate. However, when a sucrose molecule binds to the active site within sucrase, the bond between the glucose and fructose units weakens because glucose is forced into a geometry that stresses the bond (Figure 15.22►). Weakening of this bond lowers the activation energy for the reaction, increasing the reaction rate. The reaction can then proceed toward equilibrium—which favors the products—at a much lower temperature.

By allowing otherwise slow reactions to occur at reasonable rates, enzymes give living organisms tremendous control over which reactions occur and when they occur. Enzymes are extremely specific (each enzyme catalyzes only a single reaction) and efficient, speeding up reaction rates by factors of as much as a billion. (and sometimes even more).

To turn a particular reaction on, a living organism produces or activates the correct enzyme to catalyze that reaction. Because organisms are so dependent on the reactions enzymes catalyze, many substances that inhibit the action of enzymes are highly toxic. Locking up a single enzyme molecule can stop the reaction



▲ FIGURE 15.22 An Enzyme-Catalyzed Reaction Sucrase catalyzes the conversion of sucrose into glucose and fructose by weakening the bond that joins the two rings.

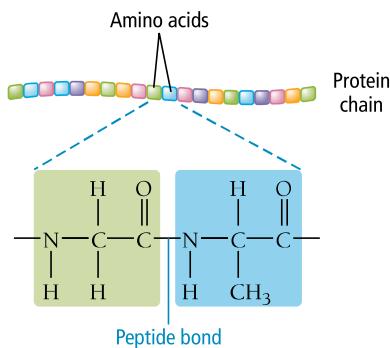
of billions of substrates, much as one motorist stalled at a tollbooth can paralyze an entire highway full of cars. (For another example of enzyme action, see the *Chemistry and Medicine* box on the role of chymotrypsin in digestion.)



CHEMISTRY AND MEDICINE

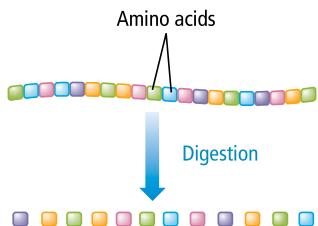
Enzyme Catalysis and the Role of Chymotrypsin in Digestion

When we eat foods containing proteins—such as meats, eggs, beans, and nuts—the proteins must be digested. Proteins are large biological molecules composed of individual units called amino acids. (We discuss the structure of proteins and other biologically important molecules more fully in Chapter 23.) The amino acids in proteins are linked together via peptide bonds, as shown in Figure 15.23▼.



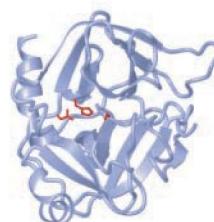
▲ FIGURE 15.23 The Structure of a Protein Proteins are chains of amino acids linked together by peptide bonds.

During digestion, the protein must be broken up into individual amino acids (Figure 15.24▼), which can pass through the walls of the small intestine and into the bloodstream. However, the peptide bonds that link amino acids together are relatively stable, and under ordinary conditions the reaction is slow.

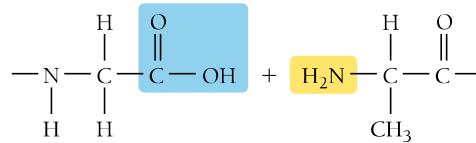
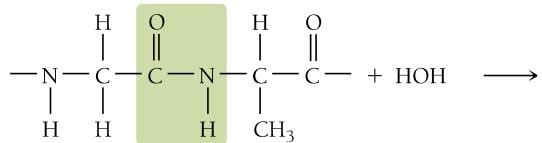


▲ FIGURE 15.24 Protein Digestion During digestion, a protein is broken down into its component amino acids.

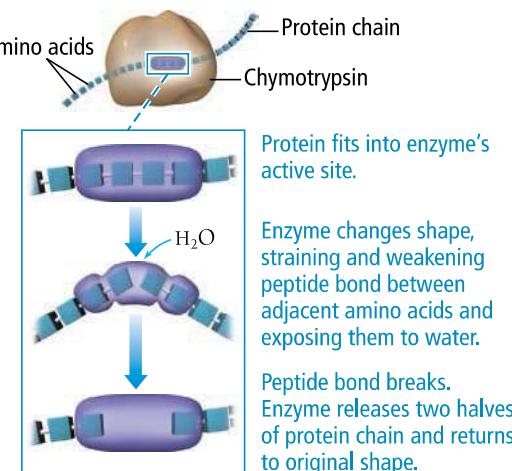
The pancreas secretes an enzyme called chymotrypsin (Figure 15.25►) into the small intestine. Like many enzymes, chymotrypsin is highly selective in its action—it operates only on peptide bonds between certain kinds of amino acids. When a protein molecule containing such a pair of amino acids is attached to the active site of chymotrypsin, the peptide bond between them is weakened as the chymotrypsin forms a covalent bond with the carbon in the peptide bond. A water molecule can then come in and cleave the bond, with an —OH from the water binding to the carbon atom and the remaining —H bonding to the nitrogen (Figure 15.26►).



▲ FIGURE 15.25 Chymotrypsin, a Digestive Enzyme This model of chymotrypsin shows a section of a protein substrate (red) in the active site.



The amino acid chain is thus clipped at the peptide bond. The products of the reaction leave the active site, another protein binds to the chymotrypsin, and the process is repeated. Other digestive enzymes cleave protein chains between other pairs of amino acids. Together, these enzymes eventually reduce the entire protein to its constituent amino acids.



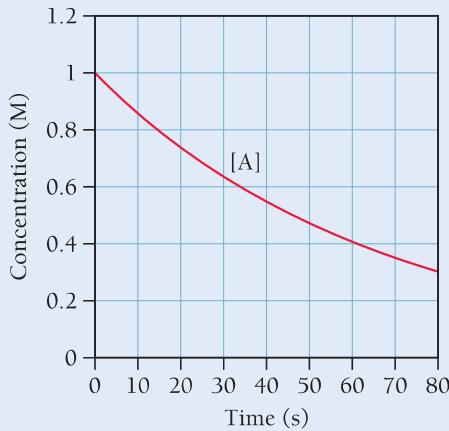
▲ FIGURE 15.26 The Action of Chymotrypsin

Self-Assessment Quiz



- Q1.** This graph shows the concentration of the reactant A in the reaction $A \rightarrow B$. Determine the average rate of the reaction between 0 and 10 seconds.

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



- a) 0.07 M/s b) 0.007 M/s c) 0.86 M/s d) 0.014 M/s

- Q2.** Dinitrogen monoxide decomposes into nitrogen and oxygen when heated. The initial rate of the reaction is 0.022 M/s. What is the initial rate of change of the concentration of N_2O (that is, $\Delta[\text{N}_2\text{O}]/\Delta t$)?

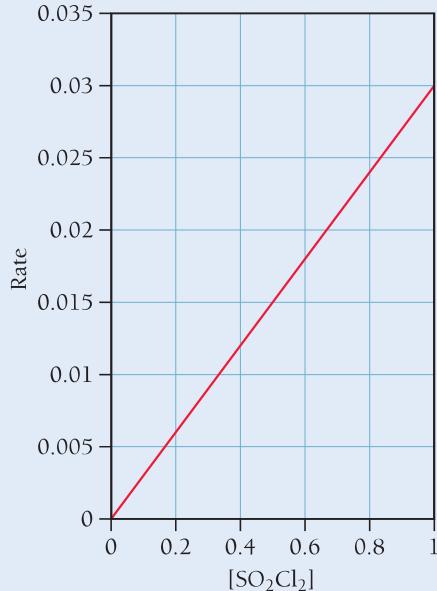
MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



- a) -0.022 M/s b) -0.011 M/s
c) -0.044 M/s d) $+0.022 \text{ M/s}$

- Q3.** This plot shows the rate of the decomposition of SO_2Cl_2 into SO_2 and Cl_2 as a function of the concentration of SO_2Cl_2 . What is the order of the reaction?

MISSED THIS? Read Section 15.3; Watch KCV 15.3



- a) first order b) second order c) zero order
d) Order cannot be determined without more information.

- Q4.** For the reaction $2 \text{A} + \text{B} \rightarrow \text{C}$, the initial rate is measured at several different reactant concentrations. From the resulting tabulated data, determine the rate law for the reaction.

MISSED THIS? Read Section 15.3; Watch KCV 15.3, IWE 15.2

[A] (M)	[B] (M)	Initial Rate (M/s)
0.05	0.05	0.035
0.10	0.05	0.070
0.20	0.10	0.56

- a) Rate = $k[\text{A}][\text{B}]$ b) Rate = $k[\text{A}]^2[\text{B}]$
c) Rate = $k[\text{A}][\text{B}]^2$ d) Rate = $k[\text{A}]^2[\text{B}]^2$

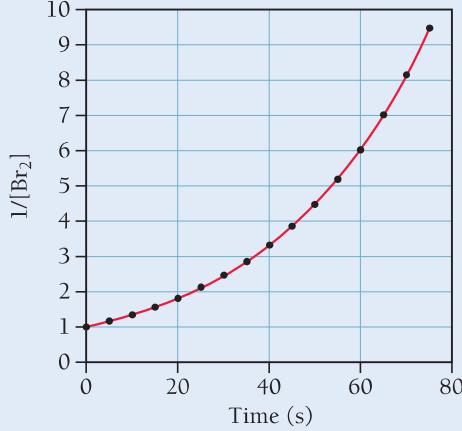
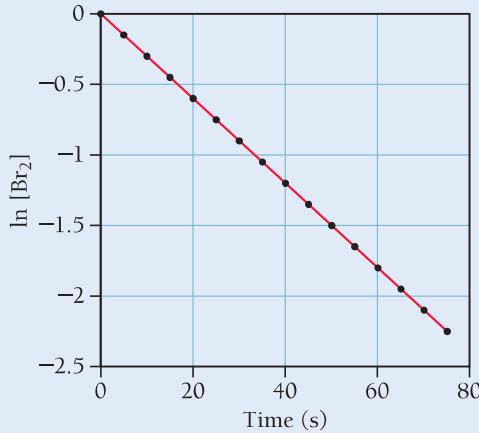
- Q5.** What is the rate constant for the reaction in Question 4?

MISSED THIS? Read Section 15.3; Watch KCV 15.3, IWE 15.2

- a) $2.8 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1}$ b) $14 \text{ M}^{-2} \cdot \text{s}^{-1}$
c) $1.4 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1}$ d) $1.4 \times 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$

- Q6.** The decomposition of Br_2 is followed as a function of time; two different plots of the data are shown. Determine the order and rate constant for the reaction.

MISSED THIS? Read Section 15.4; Watch KCV 15.4



- a) first order; 0.030 s^{-1} b) first order; 33.3 s^{-1}
c) second order; $0.045 \text{ M}^{-1} \cdot \text{s}^{-1}$ d) second order; $22.2 \text{ M}^{-1} \cdot \text{s}^{-1}$

—Continued on the next page

Continued—

- Q7.** The reaction $X \longrightarrow$ products is second order in X and has a rate constant of $0.035 \text{ M}^{-1}\text{s}^{-1}$. If a reaction mixture is initially 0.45 M in X, what is the concentration of X after 155 seconds?

MISSED THIS? Read Section 15.4; Watch KCV 15.4, IWE 15.4

- 7.6 M
- $2.0 \times 10^{-3} \text{ M}$
- 0.13 M
- 0.00 M

- Q8.** A decomposition reaction has a half-life that does not depend on the initial concentration of the reactant. What is the order of the reaction? **MISSED THIS? Read Section 15.4**

- zero order
- first order
- second order
- Order cannot be determined without more information.

- Q9.** The rate constant of a reaction is measured at different temperatures. A plot of the natural log of the rate constant as a function of the inverse of the temperature (in kelvins) yields a straight line with a slope of $-8.55 \times 10^3 \text{ K}^{-1}$.

What is the activation energy (E_a) for the reaction?

MISSED THIS? Read Section 15.5

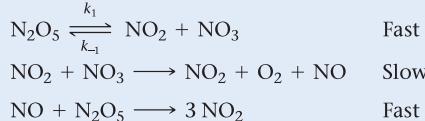
- -71 kJ/mol
- 71 kJ/mol
- 1.0 kJ/mol
- -1.0 kJ/mol

- Q10.** The rate constant for a reaction at 25.0°C is 0.010 s^{-1} , and its activation energy is 35.8 kJ . Find the rate constant at 50.0°C .

MISSED THIS? Read Section 15.5; Watch IWE 15.8

- 0.021 s^{-1}
- 0.010 s^{-1}
- 0.0033 s^{-1}
- 0.031 s^{-1}

- Q11.** The mechanism shown is proposed for the gas-phase reaction, $2 \text{N}_2\text{O}_5 \longrightarrow 4 \text{NO}_2 + \text{O}_2$. What rate law does the mechanism predict?



MISSED THIS? Read Section 15.6; Watch KCV 15.6, IWE 15.9

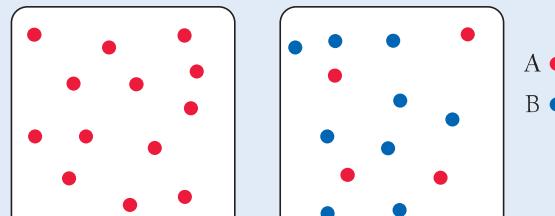
- $\text{Rate} = k[\text{N}_2\text{O}_5]$
- $\text{Rate} = k[\text{N}_2\text{O}_5]^2$
- $\text{Rate} = k[\text{N}_2\text{O}_5]^6$
- $\text{Rate} = k[\text{NO}_2][\text{NO}_3]$

- Q12.** Which statement is true regarding the function of a catalyst in a chemical reaction? **MISSED THIS? Read Section 15.7**

- A catalyst increases the rate of a reaction.
- A catalyst provides an alternate mechanism for the reaction.
- A catalyst is not consumed by the reaction.
- All of the above are true.

- Q13.** These images represent the first-order reaction $\text{A} \longrightarrow \text{B}$ initially and at some later time. The rate law for the reaction is $\text{Rate} = 0.010 \text{ s}^{-1} [\text{A}]$. How much time has passed between the two images?

MISSED THIS? Read Section 15.4; Watch KCV 15.4, IWE 15.4



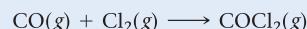
- 69 s
- 139 s
- 60 s
- 12.5 s

- Q14.** Use collision theory to determine which single-step reaction has the smallest orientation factor.

MISSED THIS? Read Section 15.5

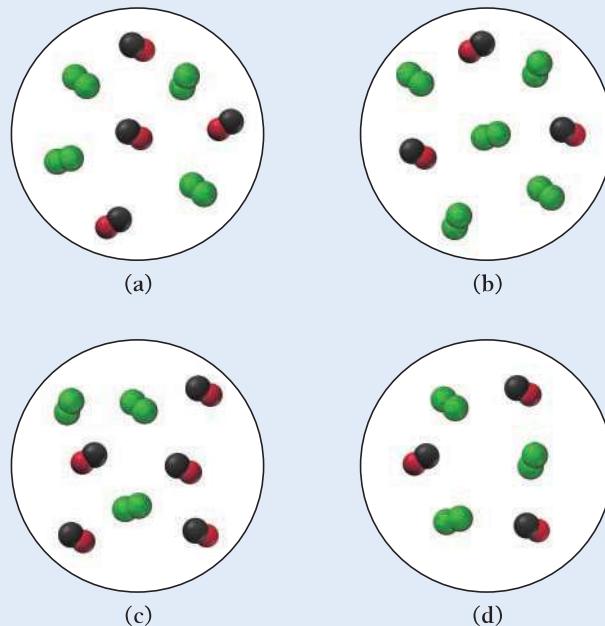
- $\text{H} + \text{H} \longrightarrow \text{H}_2$
- $\text{I} + \text{HI} \longrightarrow \text{I}_2 + \text{H}$
- $\text{H}_2 + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_3\text{C}-\text{CH}_3$
- All of these reactions have the same orientation factor.

- Q15.** Carbon monoxide and chlorine gas react to form phosgene (COCl_2) according to the equation:



The rate law for the reaction is $\text{Rate} = k[\text{Cl}_2]^{3/2}[\text{CO}]$. Which representation of a mixture of chlorine gas and carbon monoxide gas has the fastest initial rate?

MISSED THIS? Read Section 15.3; Watch KCV 15.3



CHAPTER 15 IN REVIEW

TERMS

Section 15.3

rate law (637)
rate constant (k) (637)
reaction order (n) (637)
overall order (640)

Section 15.4

integrated rate law (642)
half-life ($t_{1/2}$) (646)

Section 15.5

Arrhenius equation (650)
activation energy (E_a) (650)
frequency factor (A) (650)
activated complex
(transition state) (651)
exponential factor (652)
Arrhenius plot (653)
collision model (655)
orientation factor (655)
collision frequency (655)

Section 15.6

reaction mechanism (656)
elementary step (657)
reaction intermediate (657)
molecularity (657)
unimolecular (657)
bimolecular (657)
termolecular (657)
rate-determining step (658)

Section 15.7

catalyst (661)
homogeneous catalysis (663)
heterogeneous catalysis (663)
hydrogenation (664)
enzyme (664)
active site (664)
substrate (664)

CONCEPTS

Reaction Rates, Orders, and Rate Laws

(15.1–15.3)

- The rate of a chemical reaction is a measure of how fast a reaction occurs. The rate reflects the change in the concentration of a reactant or product per unit time and is usually reported in units of M/s.
- Reaction rates generally depend on the concentration of the reactants. The rate of a first-order reaction is directly proportional to the concentration of the reactant, the rate of a second-order reaction is proportional to the square of the concentration of the reactant, and the rate of a zero-order reaction is independent of the concentration of the reactant.
- For a reaction with more than one reactant, the order with respect to each reactant is, in general, independent of the order with respect to other reactants. The rate law shows the relationship between the rate and the concentrations of each reactant and must be determined experimentally.

Integrated Rate Laws and Half-Life (15.4)

- The rate law for a reaction describes the relationship between the rate of the reaction and the concentrations of the reactants.
- The integrated rate law for a reaction describes the relationship between the concentration of a reactant and time.
- The integrated rate law for a zero-order reaction shows that the concentration of the reactant varies linearly with time. For a first-order reaction, the *natural log* of the concentration of the reactant varies linearly with time, and for a second-order reaction, the *inverse* of the concentration of the reactant varies linearly with time.
- The half-life of a reaction can be derived from the integrated rate law and represents the time required for the concentration of a reactant to fall to one-half of its initial value. The half-life of a first-order reaction is *independent* of initial concentration of the reactant. The half-life of a zero-order or second-order reaction *depends* on the initial concentration of reactant.

The Effect of Temperature on Reaction Rate (15.5)

- The rate constant of a reaction generally depends on temperature and can be expressed by the Arrhenius equation, which consists of a frequency factor and an exponential factor.
- The frequency factor represents the number of times that the reactants approach the activation barrier per unit time. The exponential factor is the fraction of approaches that are successful in surmounting the activation barrier and forming products.

- The exponential factor depends on both the temperature and the activation energy, a barrier that the reactants must overcome to become products. The exponential factor increases with increasing temperature but decreases with increasing activation energy.
- We can determine the frequency factor and activation energy for a reaction by measuring the rate constant at different temperatures and constructing an Arrhenius plot.
- For reactions in the gas phase, Arrhenius behavior can be modeled with the collision model. In this model, reactions occur as a result of sufficiently energetic collisions. The colliding molecules must be oriented in such a way that the reaction can occur. The frequency factor contains two terms: p , which represents the fraction of collisions that have the proper orientation, and z , which represents the number of collisions per unit time.

Reaction Mechanisms (15.6)

- Most chemical reactions occur not in a single step, but in several steps. The series of individual steps by which a reaction occurs is the reaction mechanism.
- In order for a proposed reaction mechanism to be valid, it must fulfill two conditions: (a) the steps must sum to the overall reaction, and (b) the mechanism must predict the experimentally observed rate law.
- For mechanisms with a slow initial step, we derive the rate law from the slow step.
- For mechanisms with a fast initial step, we first write the rate law based on the slow step but then assume that the fast steps reach equilibrium, so we can write concentrations of intermediates in terms of the reactants.

Catalysis (15.7)

- A catalyst is a substance that increases the rate of a chemical reaction by providing an alternative mechanism that has a lower activation energy for the rate-determining step.
- Catalysts can be homogeneous or heterogeneous. A homogeneous catalyst exists in the same phase as the reactants and forms a homogeneous mixture with them. A heterogeneous catalyst exists in a different phase than the reactants.
- Enzymes are biological catalysts capable of increasing the rate of specific biochemical reactions by many orders of magnitude.

EQUATIONS AND RELATIONSHIPS

The Rate of Reaction (15.2)

For a reaction, $aA + bB \rightarrow cC + dD$, the rate is defined as:

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

The Rate Law (15.3)

$$\text{Rate} = k[A]^n \quad (\text{single reactant})$$

$$\text{Rate} = k[A]^m [B]^n \quad (\text{multiple reactants})$$

Integrated Rate Laws and Half-Life (15.4)

Reaction Order	Integrated Rate Law	Units of k	Half-Life Expression
0	$[A]_t = -kt + [A]_0$	$\text{M} \cdot \text{s}^{-1}$	$t_{1/2} = \frac{[A]_0}{2k}$
1	$\ln [A]_t = -kt + \ln [A]_0$	s^{-1}	$t_{1/2} = \frac{0.693}{k}$
2	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\text{M}^{-1} \cdot \text{s}^{-1}$	$t_{1/2} = \frac{1}{k[A]_0}$

Arrhenius Equation (15.5)

$$k = Ae^{-E_a/RT}$$

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (\text{linearized form})$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{two-point form})$$

$$k = pze^{-E_a/RT} \quad (\text{collision theory})$$

Rate Laws for Elementary Steps (15.6)

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	1	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$	2	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	2	$\text{Rate} = k[A][B]$
$A + A + A \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^3$
$A + A + B \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	3 (rare)	$\text{Rate} = k[A][B][C]$

LEARNING OUTCOMES

Chapter Objectives	Assessment
Express reaction rates (15.2)	Example 15.1 For Practice 15.1 Exercises 25–34
Analyze reactions in terms of the rate law (rate constant and reaction order) (15.3)	Example 15.2 For Practice 15.2 Exercises 35–46
Analyze graphical reaction data using the integrated rate law to determine the reaction order and the rate constant (15.4)	Examples 15.3–15.5 For Practice 15.3–15.5 Exercises 47–52
Perform half-life calculations (15.4)	Example 15.6 For Practice 15.6 Exercises 53–58
Perform rate calculations involving the Arrhenius equation (15.5)	Examples 15.7, 15.8 For Practice 15.7, 15.8 Exercises 59–74
Determine whether a reaction mechanism is valid (15.6)	Exercises 75–78
Describe the affects of catalysts on rates of reaction (15.7)	Exercises 79–82

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- Explain why lizards become sluggish in cold weather. How is this phenomenon related to chemistry?
- Why are reaction rates important (both practically and theoretically)?
- What units are typically used to express the rate of a reaction?
- Why is the reaction rate for reactants defined as the *negative* of the change in reactant concentration with respect to time, whereas for products it is defined as the change in reactant concentration with respect to time (with a positive sign)?
- Explain the difference between the average rate of reaction and the instantaneous rate of reaction.
- Consider a simple reaction in which reactant A forms products: $A \rightarrow \text{products}$. What is the rate law if the reaction is zero order with respect to A? First order? Second order? For each case, explain how a doubling of the concentration of A would affect the rate of reaction.
- How is the order of a reaction generally determined?

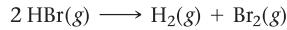
8. For a reaction with multiple reactants, how is the overall order of the reaction defined?
9. Explain the difference between the rate law for a reaction and the integrated rate law for a reaction. What relationship does each kind of rate law express?
10. Write integrated rate laws for zero-order, first-order, and second-order reactions of the form A → products.
11. What does the term *half-life* mean? Write the expressions for the half-lives of zero-order, first-order, and second-order reactions.
12. How do reaction rates typically depend on temperature? What part of the rate law is temperature dependent?
13. Explain the meaning of each term within the Arrhenius equation: activation energy, frequency factor, and exponential factor. Use these terms and the Arrhenius equation to explain why small changes in temperature can result in large changes in reaction rates.
14. What is an Arrhenius plot? Explain the significance of the slope and intercept of an Arrhenius plot.
15. Explain how a chemical reaction occurs according to the collision model. Explain the meaning of the orientation factor in this model.
16. Explain the difference between a normal chemical equation for a chemical reaction and the mechanism of that reaction.
17. In a reaction mechanism, what is an elementary step? Write down the three most common elementary steps and the corresponding rate law for each one.
18. What are the two requirements for a proposed mechanism to be valid for a given reaction?
19. What is an intermediate within a reaction mechanism?
20. What is a catalyst? How does a catalyst increase the rate of a chemical reaction?
21. Explain the difference between homogeneous catalysis and heterogeneous catalysis.
22. What are the four basic steps involved in heterogeneous catalysis?
23. What are enzymes? What is the active site of an enzyme? What is a substrate?
24. What is the general two-step mechanism by which most enzymes work?

PROBLEMS BY TOPIC

Reaction Rates

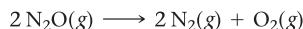
25. Consider the reaction:

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



- Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- In the first 25.0 s of this reaction, the concentration of HBr dropped from 0.600 M to 0.512 M. Calculate the average rate of the reaction during this time interval.
- If the volume of the reaction vessel in part b was 1.50 L, what amount of Br₂ (in moles) was formed during the first 15.0 s of the reaction?

26. Consider the reaction:



- Express the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- In the first 15.0 s of the reaction, 0.015 mol of O₂ is produced in a reaction vessel with a volume of 0.500 L. What is the average rate of the reaction during this time interval?
- Predict the rate of change in the concentration of N₂O during this time interval. In other words, what is Δ[N₂O]/Δt?

27. For the reaction 2 A(g) + B(g) → 3 C(g),

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1

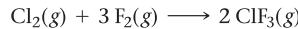
- determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- when A is decreasing at a rate of 0.100 M/s, how fast is B decreasing? How fast is C increasing?

28. For the reaction A(g) + $\frac{1}{2}$ B(g) → 2 C(g),

- determine the expression for the rate of the reaction in terms of the change in concentration of each of the reactants and products.
- when C is increasing at a rate of 0.025 M/s, how fast is B decreasing? How fast is A decreasing?

29. Consider the reaction:

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



Complete the table.

$\Delta[\text{Cl}_2]/\Delta t$	$\Delta[\text{F}_2]/\Delta t$	$\Delta[\text{ClF}_3]/\Delta t$	Rate
-0.012 M/s			

30. Consider the reaction:



Complete the table.

$\Delta[\text{H}_2\text{S}]/\Delta t$	$\Delta[\text{O}_2]/\Delta t$	$\Delta[\text{H}_2\text{O}]/\Delta t$	$\Delta[\text{S}_8]/\Delta t$	Rate
-0.080 M/s				

31. Consider the reaction:

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



The tabulated data were collected for the concentration of C₄H₈ as a function of time:

Time (s)	[C ₄ H ₈] (M)
0	1.000
10	0.913
20	0.835
30	0.763
40	0.697
50	0.637

- What is the average rate of the reaction between 0 and 10 s? Between 40 and 50 s?
- What is the rate of formation of C₂H₄ between 20 and 30 s?

32. Consider the reaction:



The tabulated data were collected for the concentration of NO_2 as a function of time:

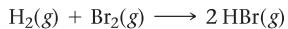
Time (s)	$[\text{NO}_2]$ (M)
0	1.000
10	0.951
20	0.904
30	0.860
40	0.818
50	0.778
60	0.740
70	0.704
80	0.670
90	0.637
100	0.606

- a. What is the average rate of the reaction between 10 and 20 s?
Between 50 and 60 s?

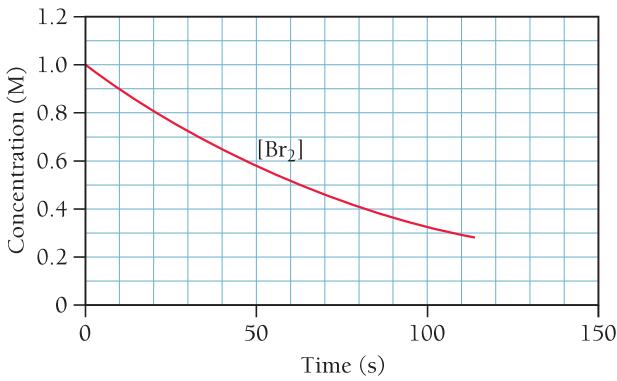
- b. What is the rate of formation of O_2 between 50 and 60 s?

33. Consider the reaction:

MISSED THIS? Read Section 15.2; Watch KCV 15.2, IWE 15.1



The graph shows the concentration of Br_2 as a function of time.

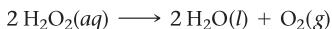


- a. Use the graph to calculate each quantity:

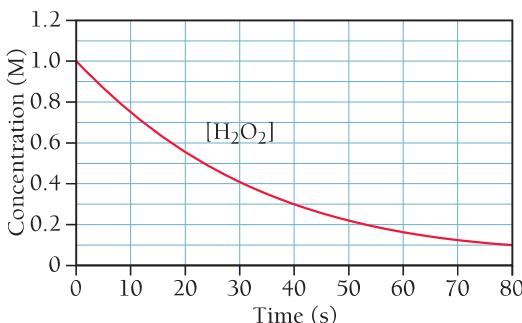
- i. the average rate of the reaction between 0 and 25 s
- ii. the instantaneous rate of the reaction at 25 s
- iii. the instantaneous rate of formation of HBr at 50 s

- b. Make a rough sketch of a curve representing the concentration of HBr as a function of time. Assume that the initial concentration of HBr is zero.

34. Consider the reaction:



The graph shows the concentration of H_2O_2 as a function of time.



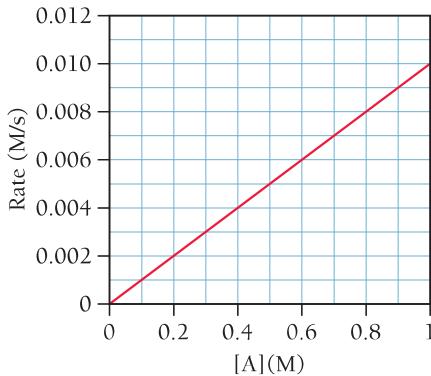
Use the graph to calculate each quantity:

- a. the average rate of the reaction between 10 and 20 s
- b. the instantaneous rate of the reaction at 30 s
- c. the instantaneous rate of formation of O_2 at 50 s
- d. If the initial volume of the H_2O_2 is 1.5 L, what total amount of O_2 (in moles) is formed in the first 50 s of reaction?

The Rate Law and Reaction Orders

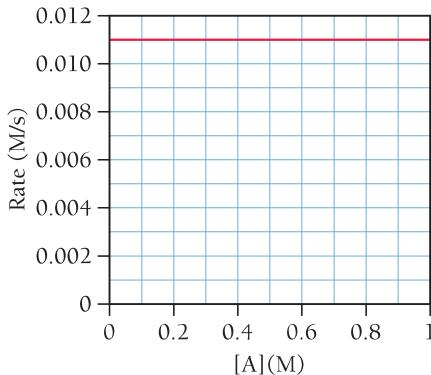
35. This graph shows a plot of the rate of a reaction versus the concentration of the reactant A for the reaction $\text{A} \longrightarrow \text{products}$.

MISSED THIS? Read Section 15.3; Watch KCV 15.3



- a. What is the order of the reaction with respect to A?
- b. Make a rough sketch of a plot of [A] versus time.
- c. Write a rate law for the reaction including an estimate for the value of k.

36. This graph shows a plot of the rate of a reaction versus the concentration of the reactant.



- a. What is the order of the reaction with respect to A?
- b. Make a rough sketch of a plot of [A] versus time.
- c. Write a rate law for the reaction including the value of k.

37. What are the units of k for each type of reaction?

MISSED THIS? Read Section 15.3

- a. first-order reaction
- b. second-order reaction
- c. zero-order reaction

38. This reaction is first order in N_2O_5 :



The rate constant for the reaction at a certain temperature is 0.053/s.

- a. Calculate the rate of the reaction when $[\text{N}_2\text{O}_5] = 0.055 \text{ M}$.
- b. What would the rate of the reaction be at the concentration indicated in part a if the reaction were second order? Zero order? (Assume the same numerical value for the rate constant with the appropriate units.)

39. A reaction in which A, B, and C react to form products is first order in A, second order in B, and zero order in C.

MISSED THIS? Read Section 15.3; Watch KCV 15.3

- Write a rate law for the reaction.
- What is the overall order of the reaction?
- By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

40. A reaction in which A, B, and C react to form products is zero order in A, one-half order in B, and second order in C.

- Write a rate law for the reaction.
- What is the overall order of the reaction?
- By what factor does the reaction rate change if [A] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [B] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if [C] is doubled (and the other reactant concentrations are held constant)?
- By what factor does the reaction rate change if the concentrations of all three reactants are doubled?

41. Consider the data showing the initial rate of a reaction ($A \rightarrow$ products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction, including the value of the rate constant, k .

MISSED THIS? Read Section 15.3; Watch KCV 15.3, IWE 15.2

[A] (M)	Initial Rate (M/s)
0.100	0.053
0.200	0.210
0.300	0.473

42. Consider the data showing the initial rate of a reaction ($A \rightarrow$ products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction, including the value of the rate constant, k .

[A] (M)	Initial Rate (M/s)
0.15	0.008
0.30	0.016
0.60	0.032

43. Consider the tabulated data showing the initial rate of a reaction ($A \rightarrow$ products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction, including the value of the rate constant, k .

MISSED THIS? Read Section 15.3; Watch KCV 15.3, IWE 15.2

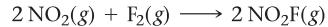
[A] (M)	Initial Rate (M/s)
0.12	0.0078
0.16	0.0104
0.20	0.0130

44. Consider the tabulated data showing the initial rate of a reaction ($A \rightarrow$ products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction, including the value of the rate constant, k .

[A] (M)	Initial Rate (M/s)
0.12	3.89×10^{-4}
0.18	8.75×10^{-4}
0.28	2.12×10^{-3}

45. The tabulated data were collected for this reaction:

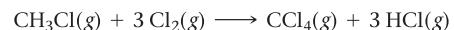
MISSED THIS? Read Section 15.3; Watch KCV 15.3, IWE 15.2



[NO ₂]	[F ₂] (M)	Initial Rate (M/s)
0.100	0.100	0.026
0.200	0.100	0.051
0.200	0.200	0.103
0.400	0.400	0.411

Write an expression for the reaction rate law and calculate the value of the rate constant, k . What is the overall order of the reaction?

46. The tabulated data were collected for this reaction:



[CH ₃ Cl] (M)	[Cl ₂] (M)	Initial Rate (M/s)
0.050	0.050	0.014
0.100	0.050	0.029
0.100	0.100	0.041
0.200	0.200	0.115

Write an expression for the reaction rate law and calculate the value of the rate constant, k . What is the overall order of the reaction?

The Integrated Rate Law and Half-Life

47. Indicate the order of reaction consistent with each observation.

MISSED THIS? Read Section 15.4; Watch KCV 15.4

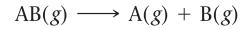
- A plot of the concentration of the reactant versus time yields a straight line.
- The reaction has a half-life that is independent of initial concentration.
- A plot of the inverse of the concentration versus time yields a straight line.

48. Indicate the order of reaction consistent with each observation.

- The half-life of the reaction gets shorter as the initial concentration is increased.
- A plot of the natural log of the concentration of the reactant versus time yields a straight line.
- The half-life of the reaction gets longer as the initial concentration is increased.

49. The tabulated data show the concentration of AB versus time for this reaction:

MISSED THIS? Read Section 15.4; Watch KCV 15.4



Time (s)	[AB] (M)
0	0.950
50	0.459
100	0.302
150	0.225
200	0.180
250	0.149
300	0.128
350	0.112
400	0.0994
450	0.0894
500	0.0812

Determine the order of the reaction and the value of the rate constant. Predict the concentration of AB at 25 s.

50. The tabulated data show the concentration of N_2O_5 versus time for this reaction:



Time (s)	$[\text{N}_2\text{O}_5]$ (M)
0	1.000
25	0.822
50	0.677
75	0.557
100	0.458
125	0.377
150	0.310
175	0.255
200	0.210

Determine the order of the reaction and the value of the rate constant. Predict the concentration of N_2O_5 at 250 s.

51. The tabulated data show the concentration of cyclobutane (C_4H_8) versus time for this reaction:

MISSED THIS? Read Section 15.4; Watch KCV 15.4



Time (s)	$[\text{C}_4\text{H}_8]$ (M)
0	1.000
10	0.894
20	0.799
30	0.714
40	0.638
50	0.571
60	0.510
70	0.456
80	0.408
90	0.364
100	0.326

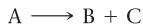
Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when $[\text{C}_4\text{H}_8] = 0.25$ M?

52. The reaction $\text{A} \longrightarrow \text{products}$ was monitored as a function of time. The results are shown here.

Time (s)	[A] (M)
0	1.000
25	0.914
50	0.829
75	0.744
100	0.659
125	0.573
150	0.488
175	0.403
200	0.318

Determine the order of the reaction and the value of the rate constant. What is the rate of reaction when $[A] = 0.10$ M?

53. This reaction was monitored as a function of time:
MISSED THIS? Read Section 15.4; Watch KCV 15.4, IWE 15.4



A plot of $\ln[\text{A}]$ versus time yields a straight line with slope $-0.0045/\text{s}$.

- What is the value of the rate constant (k) for this reaction at this temperature?
- Write the rate law for the reaction.
- What is the half-life?
- If the initial concentration of A is 0.250 M, what is the concentration after 225 s?

54. This reaction was monitored as a function of time:



A plot of $1/[\text{AB}]$ versus time yields a straight line with a slope of $+0.55/\text{M} \cdot \text{s}$.

- What is the value of the rate constant (k) for this reaction at this temperature?
- Write the rate law for the reaction.
- What is the half-life when the initial concentration is 0.55 M?
- If the initial concentration of AB is 0.250 M and the reaction mixture initially contains no products, what are the concentrations of A and B after 75 s?

55. The decomposition of SO_2Cl_2 is first order in SO_2Cl_2 and has a rate constant of $1.42 \times 10^{-4}\text{s}^{-1}$ at a certain temperature.

MISSED THIS? Read Section 15.4; Watch KCV 15.4, IWE 15.4

- What is the half-life for this reaction?
- How long will it take for the concentration of SO_2Cl_2 to decrease to 25% of its initial concentration?
- If the initial concentration of SO_2Cl_2 is 1.00 M, how long will it take for the concentration to decrease to 0.78 M?
- If the initial concentration of SO_2Cl_2 is 0.150 M, what is the concentration of SO_2Cl_2 after 2.00×10^2 s? After 5.00×10^2 s?

56. The decomposition of XY is second order in XY and has a rate constant of $7.02 \times 10^{-3}\text{M}^{-1} \cdot \text{s}^{-1}$ at a certain temperature.

- What is the half-life for this reaction at an initial concentration of 0.100 M?
- How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.100 M? When the initial concentration is 0.200 M?
- If the initial concentration of XY is 0.150 M, how long will it take for the concentration to decrease to 0.062 M?
- If the initial concentration of XY is 0.050 M, what is the concentration of XY after 5.0×10^1 s? After 5.50×10^2 s?

57. The half-life for the radioactive decay of U-238 is 4.5 billion years and is independent of initial concentration. How long will it take for 10% of the U-238 atoms in a sample of U-238 to decay? If a sample of U-238 initially contained 1.5×10^{18} atoms when the universe was formed 13.8 billion years ago, how many U-238 atoms does it contain today?

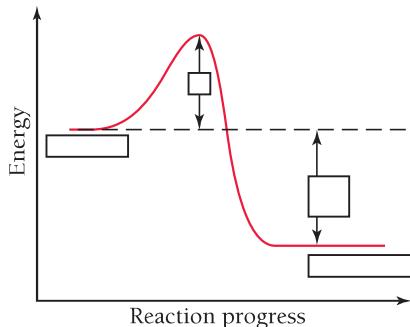
MISSED THIS? Read Section 15.4; Watch KCV 15.4, IWE 15.4

58. The half-life for the radioactive decay of C-14 is 5730 years and is independent of the initial concentration. How long does it take for 25% of the C-14 atoms in a sample of C-14 to decay? If a sample of C-14 initially contains 1.5 mmol of C-14, how many millimoles are left after 2255 years?

The Effect of Temperature and the Collision Model

59. The diagram shows the energy of a reaction as the reaction progresses. Label each blank box in the diagram.

MISSED THIS? Read Section 15.5; Watch KCV 15.5



- a. reactants
- b. products
- c. activation energy (E_a)
- d. enthalpy of reaction (ΔH_{rxn})

60. A chemical reaction is endothermic and has an activation energy that is twice the value of the enthalpy change of the reaction. Draw a diagram depicting the energy of the reaction as it progresses. Label the position of the reactants and products and indicate the activation energy and enthalpy of reaction.

61. The activation energy of a reaction is 56.8 kJ/mol, and the frequency factor is $1.5 \times 10^{11}/\text{s}$. Calculate the rate constant of the reaction at 25 °C.

MISSED THIS? Read Section 15.5; Watch KCV 15.5

62. The rate constant of a reaction at 32 °C is 0.055/s. If the frequency factor is $1.2 \times 10^{13}/\text{s}$, what is the activation barrier?

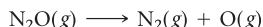
63. The rate constant (k) for a reaction was measured as a function of temperature. A plot of $\ln k$ versus $1/T$ (in K) is linear and has a slope of -7445 K . Calculate the activation energy for the reaction.

MISSED THIS? Read Section 15.5

64. The rate constant (k) for a reaction was measured as a function of temperature. A plot of $\ln k$ versus $1/T$ (in K) is linear and has a slope of $-1.01 \times 10^4 \text{ K}$. Calculate the activation energy for the reaction.

65. The data shown here were collected for the first-order reaction:

MISSED THIS? Read Section 15.5



Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (1/s)
800	3.24×10^{-5}
900	0.00214
1000	0.0614
1100	0.955

66. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (1/s)
300	0.0134
310	0.0407
320	0.114
330	0.303
340	0.757

67. The tabulated data were collected for the second-order reaction:

MISSED THIS? Read Section 15.5



Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (L/mol · s)
90	0.00357
100	0.0773
110	0.956
120	7.781

68. The tabulated data show the rate constant of a reaction measured at several different temperatures. Use an Arrhenius plot to determine the activation barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (1/s)
310	0.00434
320	0.0140
330	0.0421
340	0.118
350	0.316

69. A reaction has a rate constant of $0.0117/\text{s}$ at 400.0 K and $0.689/\text{s}$ at 450.0 K .

MISSED THIS? Read Section 15.5; Watch IWE 15.8

- a. Determine the activation barrier for the reaction.
- b. What is the value of the rate constant at 425 K ?

70. A reaction has a rate constant of $0.000122/\text{s}$ at 27°C and $0.228/\text{s}$ at 77°C .

- a. Determine the activation barrier for the reaction.
- b. What is the value of the rate constant at 17°C ?

71. If a temperature increase from 10.0°C to 20.0°C doubles the rate constant for a reaction, what is the value of the activation barrier for the reaction?

MISSED THIS? Read Section 15.5; Watch IWE 15.8

72. If a temperature increase from 20.0°C to 35.0°C triples the rate constant for a reaction, what is the value of the activation barrier for the reaction?

73. Consider these two gas-phase reactions:

MISSED THIS? Read Section 15.5

- a. $\text{AA}(g) + \text{BB}(g) \longrightarrow 2 \text{AB}(g)$
- b. $\text{AB}(g) + \text{CD}(g) \longrightarrow \text{AC}(g) + \text{BD}(g)$

If the reactions have identical activation barriers and are carried out under the same conditions, which one would you expect to have the faster rate?

74. Which of these two reactions would you expect to have the smaller orientation factor? Explain.

- a. $\text{O}(g) + \text{N}_2(g) \longrightarrow \text{NO}(g) + \text{N}(g)$
- b. $\text{NO}(g) + \text{Cl}_2(g) \longrightarrow \text{NOCl}(g) + \text{Cl}(g)$

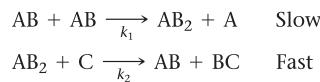
Reaction Mechanisms

75. Consider this overall reaction, which is experimentally observed to be second order in AB and zero order in C:

MISSED THIS? Read Section 15.6; Watch KCV 15.6, IWE 15.9



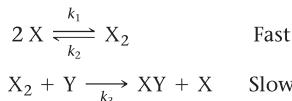
Is the following mechanism valid for this reaction?



76. Consider this overall reaction, which is experimentally observed to be second order in X and first order in Y:

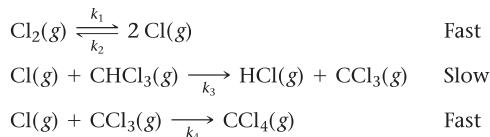


- a. Does the reaction occur in a single step in which X and Y collide?
b. Is this two-step mechanism valid?



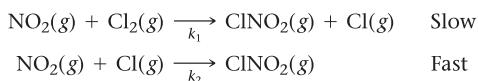
77. Consider this three-step mechanism for a reaction:

MISSED THIS? Read Section 15.6; Watch KCV 15.6, IWE 15.9



- a. What is the overall reaction?
b. Identify the intermediates in the mechanism.
c. What is the predicted rate law?

78. Consider this two-step mechanism for a reaction:



CUMULATIVE PROBLEMS

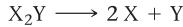
83. The tabulated data were collected for this reaction at 500 °C:



Time (h)	[CH ₃ CN] (M)
0.0	1.000
5.0	0.794
10.0	0.631
15.0	0.501
20.0	0.398
25.0	0.316

- a. Determine the order of the reaction and the value of the rate constant at this temperature.
b. What is the half-life for this reaction (at the initial concentration)?
c. How long will it take for 90% of the CH₃CN to convert to CH₃NC?

84. The tabulated data were collected for this reaction at a certain temperature:



Time (h)	[X ₂ Y] (M)
0.0	0.100
1.0	0.0856
2.0	0.0748
3.0	0.0664
4.0	0.0598
5.0	0.0543

- a. Determine the order of the reaction and the value of the rate constant at this temperature.

- a. What is the overall reaction?
b. Identify the intermediates in the mechanism.
c. What is the predicted rate law?

Catalysis

79. Many heterogeneous catalysts are deposited on high-surface-area supports. Why? **MISSED THIS?** Read Section 15.7

80. Suppose that the reaction A → products is exothermic and has an activation barrier of 75 kJ/mol. Sketch an energy diagram showing the energy of the reaction as a function of the progress of the reaction. Draw a second energy curve showing the effect of a catalyst.

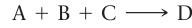
81. Suppose that a catalyst lowers the activation barrier of a reaction from 125 kJ/mol to 55 kJ/mol. By what factor would you expect the reaction rate to increase at 25 °C? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical.) **MISSED THIS?** Read Sections 15.5, 15.7

82. The activation barrier for the hydrolysis of sucrose into glucose and fructose is 108 kJ/mol. If an enzyme increases the rate of the hydrolysis reaction by a factor of 1 million, how much lower must the activation barrier be when sucrose is in the active site of the enzyme? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical and a temperature of 25 °C.)

- b. What is the half-life for this reaction (at the initial concentration)?

- c. What is the concentration of X after 10.0 hours?

85. Consider the reaction:



The rate law for this reaction is:

$$\text{Rate} = k \frac{[A][C]^2}{[B]^{1/2}}$$

Suppose the rate of the reaction at certain initial concentrations of A, B, and C is 0.0115 M/s. What is the rate of the reaction if the concentrations of A and C are doubled and the concentration of B is tripled?

86. Consider the reaction:



The rate law for this reaction is:

$$\text{Rate} = k \frac{[O_3]^2}{[O_2]}$$

Suppose that a 1.0-L reaction vessel initially contains 1.0 mol of O₃ and 1.0 mol of O₂. What fraction of the O₃ will have reacted when the rate falls to one-half of its initial value?

87. At 700 K, acetaldehyde decomposes in the gas phase to methane and carbon monoxide. The reaction is:



A sample of CH₃CHO is heated to 700 K, and the pressure is measured as 0.22 atm before any reaction takes place. The kinetics of the reaction are followed by measurements of total pressure, and these data are obtained:

t (s)	0	1000	3000	7000
P _{Total} (atm)	0.22	0.24	0.27	0.31

Find the rate law, the rate constant, and the total pressure after 2.00 × 10⁴ s.

88. At 400 K, oxalic acid decomposes according to the reaction:



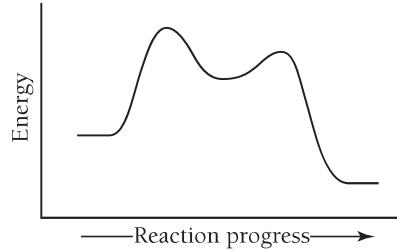
In three separate experiments, the initial pressure of oxalic acid and final total pressure after 20,000 s are measured.

Experiment	1	2	3
$P_{\text{H}_2\text{C}_2\text{O}_4}$ at $t = 0$	65.8	92.1	111
P_{Total} at $t = 20,000$ s	94.6	132	160

Find the rate law of the reaction and its rate constant.

89. Dinitrogen pentoxide decomposes in the gas phase to form nitrogen dioxide and oxygen gas. The reaction is first order in dinitrogen pentoxide and has a half-life of 2.81 h at 25 °C. If a 1.5-L reaction vessel initially contains 745 torr of N_2O_5 at 25 °C, what partial pressure of O_2 is present in the vessel after 215 minutes?
90. Cyclopropane (C_3H_6) reacts to form propene (C_3H_6) in the gas phase. The reaction is first order in cyclopropane and has a rate constant of $5.87 \times 10^{-4}/\text{s}$ at 485 °C. If a 2.5-L reaction vessel initially contains 722 torr of cyclopropane at 485 °C, how long will it take for the partial pressure of cyclopropane to drop to below 1.00×10^2 torr?
91. Iodine atoms combine to form I_2 in liquid hexane solvent with a rate constant of $1.5 \times 10^{10} \text{ L/mol} \cdot \text{s}$. The reaction is second order in I. Since the reaction occurs so quickly, the only way to study the reaction is to create iodine atoms almost instantaneously, usually by photochemical decomposition of I_2 . Suppose a flash of light creates an initial [I] concentration of 0.0100 M. How long will it take for 95% of the newly created iodine atoms to recombine to form I_2 ?
92. The hydrolysis of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) into glucose and fructose in acidic water has a rate constant of $1.8 \times 10^{-4} \text{ s}^{-1}$ at 25 °C. Assuming the reaction is first order in sucrose, determine the mass of sucrose that is hydrolyzed when 2.55 L of a 0.150 M sucrose solution is allowed to react for 195 minutes.
93. The reaction $\text{AB}(aq) \longrightarrow \text{A}(g) + \text{B}(g)$ is second order in AB and has a rate constant of $0.0118 \text{ M}^{-1} \cdot \text{s}^{-1}$ at 25.0 °C. A reaction vessel initially contains 250.0 mL of 0.100 M AB that is allowed to react to form the gaseous product. The product is collected over water at 25.0 °C. How much time is required to produce 200.0 mL of the products at a barometric pressure of 755.1 mmHg? (The vapor pressure of water at this temperature is 23.8 mmHg.)
94. The reaction $2 \text{H}_2\text{O}_2(aq) \longrightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$ is first order in H_2O_2 and under certain conditions has a rate constant of 0.00752 s^{-1} at 20.0 °C. A reaction vessel initially contains 150.0 mL of 30.0% H_2O_2 by mass solution (the density of the solution is 1.11 g/mL). The gaseous oxygen is collected over water at 20.0 °C as it forms. What volume of O_2 forms in 85.0 seconds at a barometric pressure of 742.5 mmHg? (The vapor pressure of water at this temperature is 17.5 mmHg.)

95. Consider this energy diagram:

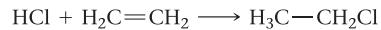


- a. How many elementary steps are involved in this reaction?
b. Label the reactants, products, and intermediates.

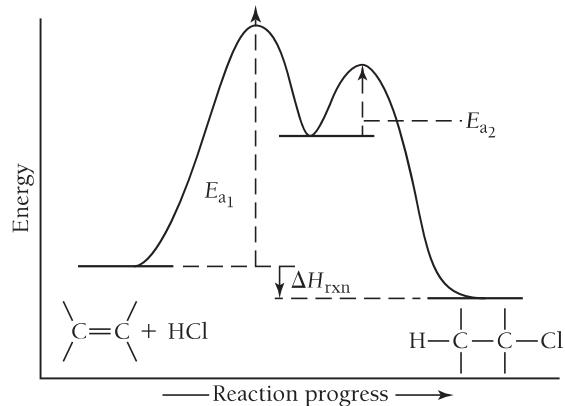
- c. Which step is rate limiting?

- d. Is the overall reaction endothermic or exothermic?

96. Consider the reaction in which HCl adds across the double bond of ethene:



The following mechanism, with the accompanying energy diagram, has been suggested for this reaction:



- a. Based on the energy diagram, determine which step is rate limiting.

- b. What is the expected order of the reaction based on the proposed mechanism?

- c. Is the overall reaction exothermic or endothermic?

97. The desorption (leaving of the surface) of a single molecular layer of *n*-butane from a single crystal of aluminum oxide is found to be first order with a rate constant of $0.128/\text{s}$ at 150 K.

- a. What is the half-life of the desorption reaction?
b. If the surface is initially completely covered with *n*-butane at 150 K, how long will it take for 25% of the molecules to desorb (leave the surface)? For 50% to desorb?
c. If the surface is initially completely covered, what fraction will remain covered after 10 s? After 20 s?

98. The evaporation of a 120-nm film of *n*-pentane from a single crystal of aluminum oxide is zero order with a rate constant of $1.92 \times 10^{13} \text{ molecules/cm}^2 \cdot \text{s}$ at 120 K.

- a. If the initial surface coverage is $8.9 \times 10^{16} \text{ molecules/cm}^2$, how long will it take for one-half of the film to evaporate?
b. What fraction of the film is left after 10 s? Assume the same initial coverage as in part a.

99. The kinetics of this reaction were studied as a function of temperature. (The reaction is first order in each reactant and second order overall.)

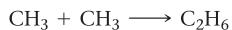


Temperature (°C)	$k (\text{L/mol} \cdot \text{s})$
25	8.81×10^{-5}
35	0.000285
45	0.000854
55	0.00239
65	0.00633

- a. Determine the activation energy and frequency factor for the reaction.
b. Determine the rate constant at 15 °C.
c. If a reaction mixture is 0.155 M in $\text{C}_2\text{H}_5\text{Br}$ and 0.250 M in OH^- , what is the initial rate of the reaction at 75 °C?

- 100.** The reaction $2 \text{N}_2\text{O}_5 \longrightarrow 2 \text{N}_2\text{O}_4 + \text{O}_2$ takes place at around room temperature in solvents such as CCl_4 . The rate constant at 293 K is found to be $2.35 \times 10^{-4} \text{ s}^{-1}$, and at 303 K the rate constant is found to be $9.15 \times 10^{-4} \text{ s}^{-1}$. Calculate the frequency factor for the reaction.

- 101.** This reaction has an activation energy of zero in the gas phase:



- Would you expect the rate of this reaction to change very much with temperature?
- Why might the activation energy be zero?
- What other types of reactions would you expect to have little or no activation energy?

- 102.** Consider the two reactions:

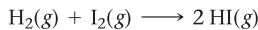


- Why is the activation barrier for the first reaction so much higher than that for the second?
- The frequency factors for these two reactions are very close to each other in value. Assuming that they are the same, calculate the ratio of the reaction rate constants for these two reactions at 25 °C.

- 103.** Anthropologists can estimate the age of a bone or other sample of organic matter by its carbon-14 content. The carbon-14 in a living organism is constant until the organism dies, after which carbon-14 decays with first-order kinetics and a half-life of 5730 years. Suppose a bone from an ancient human contains 19.5% of the C-14 found in living organisms. How old is the bone?

- 104.** Geologists can estimate the age of rocks by their uranium-238 content. The uranium is incorporated in the rock as it hardens and then decays with first-order kinetics and a half-life of 4.5 billion years. A rock contains 83.2% of the amount of uranium-238 that it contained when it was formed. (The amount that the rock contained when it was formed can be deduced from the presence of the decay products of U-238.) How old is the rock?

- 105.** Consider the gas-phase reaction:

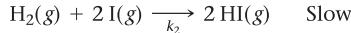
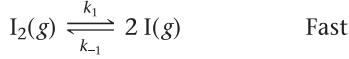


The reaction was experimentally determined to be first order in H_2 and first order in I_2 . Consider the proposed mechanisms.

Proposed mechanism I:



Proposed mechanism II:



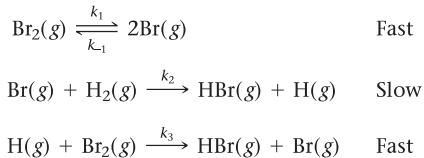
- Show that both of the proposed mechanisms are valid.
- What kind of experimental evidence might lead you to favor mechanism II over mechanism I?

- 106.** Phosgene (Cl_2CO), a poison gas used in World War I, is formed by the reaction of Cl_2 and CO. The proposed mechanism for the reaction is:



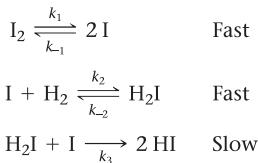
What rate law is consistent with this mechanism?

- 107.** The proposed mechanism for the formation of hydrogen bromide can be written in a simplified form as:



What rate law corresponds to this mechanism?

- 108.** A proposed mechanism for the formation of hydrogen iodide can be written in simplified form as



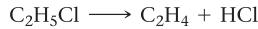
What rate law corresponds to this mechanism?

- 109.** A certain substance X decomposes. Fifty percent of X remains after 100 minutes. How much X remains after 200 minutes if the reaction order with respect to X is (a) zero order, (b) first order, (c) second order?

- 110.** The half-life for radioactive decay (a first-order process) of plutonium-239 is 24,000 years. How many years does it take for one mole of this radioactive material to decay until just one atom remains?

- 111.** The energy of activation for the decomposition of 2 mol of HI to H_2 and I_2 in the gas phase is 185 kJ. The heat of formation of $\text{HI}(g)$ from $\text{H}_2(g)$ and $\text{I}_2(g)$ is -5.65 kJ/mol . Find the energy of activation for the reaction of 1 mol of H_2 and 1 mol of I_2 to form 2 mol of HI in the gas phase.

- 112.** Ethyl chloride vapor decomposes by the first-order reaction:



The activation energy is 249 kJ/mol, and the frequency factor is $1.6 \times 10^{14} \text{ s}^{-1}$. Find the value of the rate constant at 710 K. What fraction of the ethyl chloride decomposes in 15 minutes at this temperature? Find the temperature at which the rate of the reaction would be twice as fast.

CHALLENGE PROBLEMS

- 113.** In this chapter, we have seen a number of reactions in which a single reactant forms products. For example, consider the following first-order reaction:



However, we also learned that gas-phase reactions occur through collisions.

- One possible explanation for how this reaction occurs is that two molecules of CH_3NC collide with each other and form two molecules of the product in a single elementary

step. If that were the case, what reaction order would you expect?

- Another possibility is that the reaction occurs through more than one step. For example, a possible mechanism involves one step in which the two CH_3NC molecules collide, resulting in the “activation” of one of them. In a second step, the activated molecule goes on to form the product. Write down this mechanism and determine which step must be rate determining in order for the kinetics of the reaction to be first order. Show explicitly how the mechanism predicts first-order kinetics.

- 114.** The first-order *integrated* rate law for the reaction $A \longrightarrow \text{products}$ is derived from the rate law using calculus:

$$\text{Rate} = k[A] \text{ (first-order rate law)}$$

$$\text{Rate} = -\frac{d[A]}{dt}$$

$$\frac{d[A]}{dt} = -k[A]$$

The equation just given is a first-order, separable differential equation that can be solved by separating the variables and integrating:

$$\frac{d[A]}{[A]} = -kdt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = - \int_0^t kdt$$

In the integral just given, $[A]_0$ is the initial concentration of A. We then evaluate the integral:

$$[\ln[A]] \Big|_{[A]_0}^{[A]} = -k[t] \Big|_0^t$$

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

$$\ln[A] = -kt + \ln[A]_0 \text{ (integrated rate law)}$$

- Use a procedure similar to the one just shown to derive an integrated rate law for a reaction $A \longrightarrow \text{products}$, which is one-half order in the concentration of A (that is, Rate = $k[A]^{1/2}$).
- Use the result from part a to derive an expression for the half-life of a one-half-order reaction.

- 115.** The previous exercise shows how the first-order integrated rate law is derived from the first-order differential rate law. Begin

with the second-order differential rate law and derive the second-order integrated rate law.

- 116.** The rate constant for the first-order decomposition of $\text{N}_2\text{O}_5(g)$ to $\text{NO}_2(g)$ and $\text{O}_2(g)$ is $7.48 \times 10^{-3} \text{ s}^{-1}$ at a given temperature.

- Find the length of time required for the total pressure in a system containing N_2O_5 at an initial pressure of 0.100 atm to rise to 0.145 atm.

- To 0.200 atm.

- Find the total pressure after 100 s of reaction.

- 117.** The rate of decomposition of $\text{N}_2\text{O}_3(g)$ to $\text{NO}_2(g)$ and $\text{NO}(g)$ is followed by measuring $[\text{NO}_2]$ at different times. The following data are obtained.

$[\text{NO}_2](\text{mol/L})$	0	0.193	0.316	0.427	0.784
t (s)	0	884	1610	2460	50,000

The reaction follows a first-order rate law. Calculate the rate constant. Assume that after 50,000 s all $\text{N}_2\text{O}_3(g)$ had decomposed.

- 118.** At 473 K, for the elementary reaction $2 \text{NOCl}(g) \xrightleftharpoons[k_{-1}]{k_1} 2 \text{NO}(g) + \text{Cl}_2(g)$

$$k_1 = 7.8 \times 10^{-2} \text{ L/mol s} \quad \text{and}$$

$$k_{-1} = 4.7 \times 10^2 \text{ L}^2/\text{mol}^2 \text{ s}$$

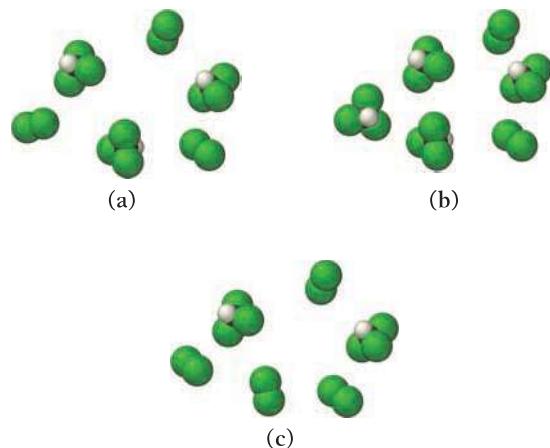
A sample of NOCl is placed in a container and heated to 473 K. When the system comes to equilibrium, $[\text{NOCl}]$ is found to be 0.12 mol/L. What are the concentrations of NO and Cl_2 ?

CONCEPTUAL PROBLEMS

- 119.** Consider the reaction:



The reaction is first order in CHCl_3 and one-half order in Cl_2 . Which reaction mixture would you expect to have the fastest initial rate?



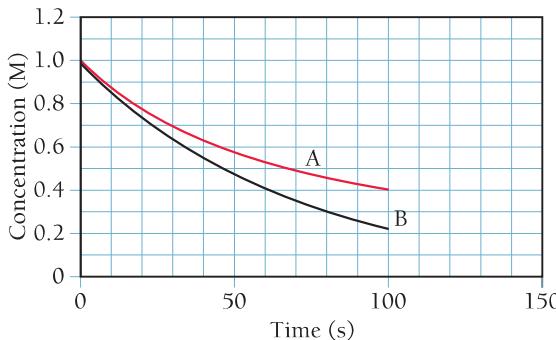
- 120.** Three different reactions involve a single reactant converting to products. Reaction A has a half-life that is independent of the initial concentration of the reactant, reaction B has a half-life that doubles when the initial concentration of the reactant doubles, and reaction C has a half-life that doubles when the initial concentration of the reactant is halved. Which statement is most consistent with these observations?

- Reaction A is first order; reaction B is second order; and reaction C is zero order.
- Reaction A is first order; reaction B is zero order; and reaction C is zero order.

- Reaction A is zero order; reaction B is first order; and reaction C is second order.

- Reaction A is second order; reaction B is first order; and reaction C is zero order.

- 121.** The accompanying graph shows the concentration of a reactant as a function of time for two different reactions. One of the reactions is first order, and the other is second order. Which of the two reactions is first order? Second order? How would you change each plot to make it linear?



- 122.** A particular reaction, $A \longrightarrow \text{products}$, has a rate that slows down as the reaction proceeds. The half-life of the reaction is found to depend on the initial concentration of A. Determine whether each statement is likely to be true or false for this reaction.

- A doubling of the concentration of A doubles the rate of the reaction.
- A plot of $1/[A]$ versus time is linear.
- The half-life of the reaction gets longer as the initial concentration of A increases.
- A plot of the concentration of A versus time has a constant slope.

QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 123.** A student says, “The initial concentration of a reactant was doubled, and the rate doubled. Therefore the reaction is second order in that reactant.” Why might the student say that? What is wrong with the statement? What is the actual order with respect to the reactant? Explain your reasoning clearly.
- 124.** A certain compound, A, reacts to form products according to the reaction $A \rightarrow P$. The amount of A is measured as a function of time under a variety of different conditions, and the tabulated results are shown here:

Time (s)	25.0 °C [A] (M)	35.0 °C [A] (M)	45.0 °C [A] (M)
0	1.000	1.000	1.000
10	0.779	0.662	0.561
20	0.591	0.461	0.312
30	0.453	0.306	0.177
40	0.338	0.208	0.100
50	0.259	0.136	0.057
60	0.200	0.093	0.032

Have one group member make a graph of $[A]$ versus t , one group member make a graph of $\ln[A]$ versus t , and one group member

Active Classroom Learning

make a graph of $1/[A]$ versus t using the data for 25 °C. Additional group members can make similar graphs for the other temperatures. What is the order of the reaction with respect to A? Explain your answer.

- Use the data to determine the rate constant at each temperature.
- What is the activation energy for this reaction?
- The same reaction is conducted in the presence of a catalyst, and the following data are obtained:

Time (s)	25.0 °C [A] (M)	35.0 °C [A] (M)	45.0 °C [A] (M)
0	1.000	1.000	1.000
0.1	0.724	0.668	0.598
0.2	0.511	0.433	0.341
0.3	0.375	0.291	0.202
0.4	0.275	0.190	0.119
0.5	0.198	0.122	0.071
0.6	0.141	0.080	0.043

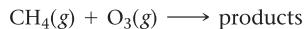
What effect does a catalyst have on the rate of the reaction? What is the activation energy for this reaction in the presence of the catalyst? How does it compare with the activation energy for the reaction when the catalyst isn't present?



DATA INTERPRETATION AND ANALYSIS

Atmospheric Methane Degradation

- 125.** Methane (CH_4) is a greenhouse gas emitted by industry, agriculture, and waste systems. Methane is the second most prevalent greenhouse gas (after carbon dioxide). Methane plays an important role in climate change because it absorbs infrared radiation more efficiently than carbon dioxide. Methane is broken down in the atmosphere by ozone (O_3), making its atmospheric lifetime shorter than that of carbon dioxide.



A research group studied the rate of the reaction by which methane reacts with ozone; the data are shown in the following tables. Study the data and answer the questions that follow.

Initial Rate vs. Initial Concentrations

[CH_4]	[O_3]	Initial Rate (M/s)
0.010	0.010	3.94×10^{-7}
0.020	0.010	7.88×10^{-7}
0.020	0.020	1.58×10^{-6}

Rate Constant vs. Temperature

Temperature (K)	$k(\text{M}^{-1} \cdot \text{s}^{-1})$
260	2.26×10^{-5}
265	3.95×10^{-5}
270	6.76×10^{-5}
275	0.000114
280	0.000187
285	0.000303
290	0.000483
295	0.000758
300	0.001171
305	0.001783

- Use the data in the first table to determine the order of the reaction with respect to each reactant.
- Use the data in the second table to determine the activation barrier and pre-exponential factor for the reaction.
- Atmospheric concentrations of methane and ozone can vary depending on the location and altitude. Calculate the rate of the reaction at 273 K for a methane concentration of 1.8 ppm (by volume) and an ozone concentration of 5.0 ppm (by volume). Note that 1 ppm of CH_4 by volume means $1 \text{ L CH}_4 / 10^6 \text{ L air}$. Assume STP (standard temperature and pressure) so that 1 mol gas occupies 22.4 L.
- What is the half-life of methane in the atmosphere in years at 323 K? (Assume that $[\text{CH}_4] = [\text{O}_3] = [\text{A}]_0 = 5.0 \times 10^{-7} \text{ M}$.)

Cc**ANSWERS TO CONCEPTUAL CONNECTIONS****Reaction Rates**

- 15.1** (c) The rate at which B changes is twice the rate of the reaction because its coefficient is 2, and it is negative because B is a reactant.

Reaction Order

- 15.2** (b) For a first-order reaction, a doubling of the reactant concentration doubles the reaction rate.

Rate and Concentration I

- 15.3** (d) Since the reaction is second order, increasing the concentration of A by a factor of 5 causes the rate to increase by 5^2 or 25.

Rate and Concentration II

- 15.4** (c) All three mixtures have the same total number of molecules, but mixture (c) has the greatest number of NO molecules. Since the reaction is second order in NO and only first order in O₂, mixture (c) has the fastest initial rate.

Half-Life I

- 15.5** (c) The half-life is 90 s because it takes 90 s for the reactant to fall to one-half of its initial concentration.

Half-Life II

- 15.6** (b) The concentration of B after 50 seconds (two half-lives) is 0.225 M as you can see from this table.

Time (min)	[A] (M)	[B] (M)
0	0.300	0.0
25	0.150	0.150
50	0.075	0.225

Rate Law and Integrated Rate Law

- 15.7** (c) The reaction is most likely second order because its rate depends on the concentration (therefore it cannot be zero order), and its half-life depends on the initial concentration (therefore it cannot be first order). For a second-order reaction, a doubling of the initial concentration results in the quadrupling of the rate.

Reaction Rate and Temperature

- 15.8** (a) As temperature increases, a greater fraction of molecules have enough thermal energy to surmount the activation barrier.

Reaction Rate and Activation Energy

- 15.9** (a) Reaction A has a faster rate because it has a lower activation energy; therefore, the exponential factor is larger at a given temperature, making the rate constant larger. (With a larger rate constant and the same initial concentration, the rate is faster.)

Collision Theory

- 15.10** (c) Since the reactants in part (a) are atoms, the orientation factor should be about one. The reactants in parts (b) and (c) are both molecules, so we expect orientation factors of less than one. Since the reactants in (b) are symmetrical, we would not expect the collision to have as specific an orientation requirement as in (c), where the reactants are asymmetrical and must therefore collide in such way that a hydrogen atom is in close proximity to another hydrogen atom. Therefore, we expect (c) to have the smallest orientation factor.

Elementary Steps

- 15.11** (d) Since the elementary step is of the form A + B → products, the rate law is rate = $k[A][B]$.