

Chapter 12

Kinetics



Figure 12.1 An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

Chapter Outline

- 12.1 Chemical Reaction Rates
- 12.2 Factors Affecting Reaction Rates
- 12.3 Rate Laws
- 12.4 Integrated Rate Laws
- 12.5 Collision Theory
- 12.6 Reaction Mechanisms
- 12.7 Catalysis

Introduction

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. In this chapter, we will examine the factors that

influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur.

12.1 Chemical Reaction Rates

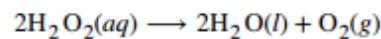
By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A **rate** is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2 , in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:



The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} \text{rate of decomposition of } \text{H}_2\text{O}_2 &= - \frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= - \frac{[\text{H}_2\text{O}_2]_{t_2} - [\text{H}_2\text{O}_2]_{t_1}}{t_2 - t_1} \\ &= - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\text{H}_2\text{O}_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1 ; likewise, $[\text{H}_2\text{O}_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2 ; and $\Delta[\text{H}_2\text{O}_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\text{H}_2\text{O}_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. **Figure 12.2** provides an example of data collected during the decomposition of H_2O_2 .

Time (h)	[H ₂ O ₂] (mol L ⁻¹)	[H ₂ O ₂] (mol L ⁻¹)	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
6.00	0.500	−0.500	6.00	−0.0833
12.00	0.250	−0.250	6.00	−0.0417
18.00	0.125	−0.125	6.00	−0.0208
24.00	0.0625	−0.062	6.00	−0.0103

Figure 12.2 The rate of decomposition of H₂O₂ in an aqueous solution decreases as the concentration of H₂O₂ decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500 \text{ mol/L} - 1.000 \text{ mol/L})}{(6.00 \text{ h} - 0.00 \text{ h})} = 0.0833 \text{ mol L}^{-1} \text{ h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625 \text{ mol/L} - 0.125 \text{ mol/L})}{(24.00 \text{ h} - 18.00 \text{ h})} = 0.0103 \text{ mol L}^{-1} \text{ h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at “time zero,” when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle’s initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1 —would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car’s average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H₂O₂ at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 12.3). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

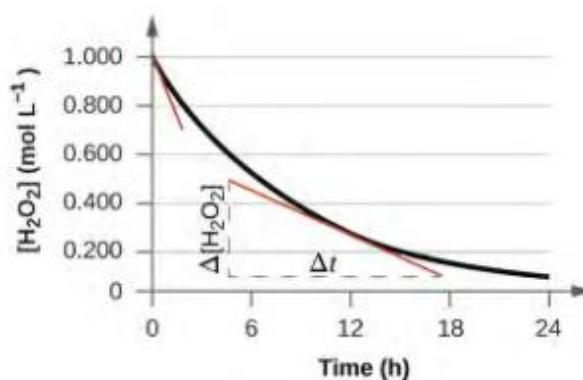


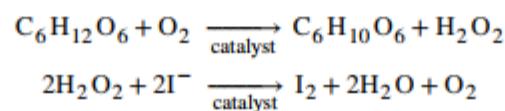
Figure 12.3 This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2 . The rate at any instant is equal to the opposite of the slope of a line tangent to this curve at that time. Tangents are shown at $t = 0$ h ("initial rate") and at $t = 10$ h ("instantaneous rate" at that particular time).

Chemistry in Everyday Life

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 12.4). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:



The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of catalysis, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

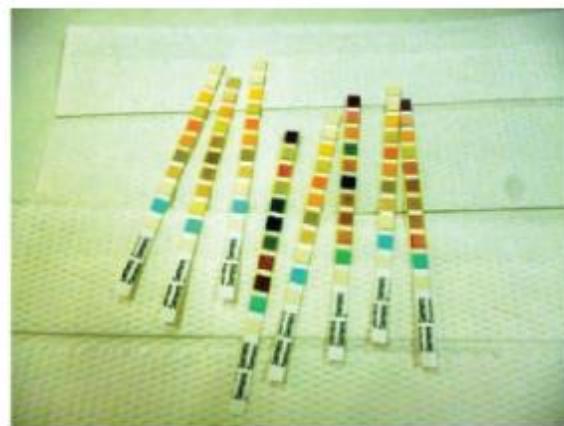
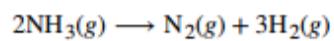


Figure 12.4 Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:



The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to relate reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2} \frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2} \frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t}$$

Similarly, the rate of formation of H₂ is three times the rate of formation of N₂ because three moles of H₂ form during the time required for the formation of one mole of N₂:

$$\frac{1}{3} \frac{\Delta [\text{H}_2]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t}$$

Figure 12.5 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at $t = 500$ seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6} \text{ M/s}}{9.71 \times 10^{-6} \text{ M/s}} \approx 3$$

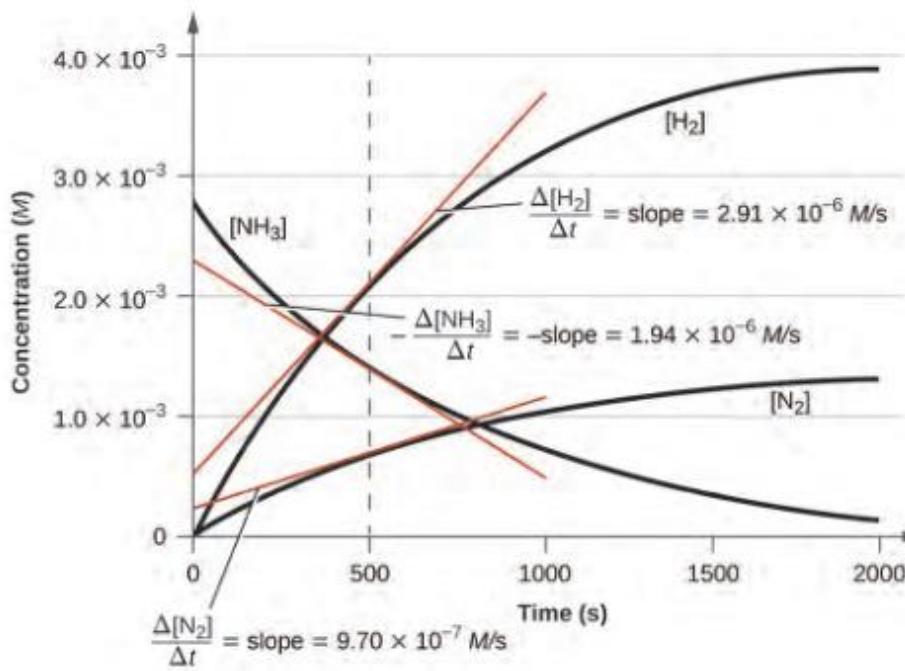


Figure 12.5 This graph shows the changes in concentrations of the reactants and products during the reaction $2\text{NH}_3 \rightarrow 3\text{N}_2 + \text{H}_2$. The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at $t = 500$ s.

Example 12.1

Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:



Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

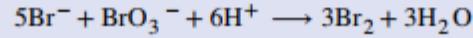
Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Check Your Learning

The rate of formation of Br_2 is 6.0×10^{-6} mol/L/s in a reaction described by the following net ionic equation:



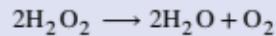
Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

$$\text{Answer: } -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Example 12.2

Reaction Rate Expressions for Decomposition of H₂O₂

The graph in [Figure 12.3](#) shows the rate of the decomposition of H₂O₂ over time:



Based on these data, the instantaneous rate of decomposition of H₂O₂ at $t = 11.1$ h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

What is the instantaneous rate of production of H₂O and O₂?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

and

$$\frac{\Delta[\text{O}_2]}{\Delta t} = 1.60 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$$

Check Your Learning

If the rate of decomposition of ammonia, NH₃, at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

$$\text{Answer: } 1.05 \times 10^{-6} \text{ mol/L/s, N}_2 \text{ and } 3.15 \times 10^{-6} \text{ mol/L/s, H}_2.$$

12.2 Factors Affecting Reaction Rates

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure 12.6). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

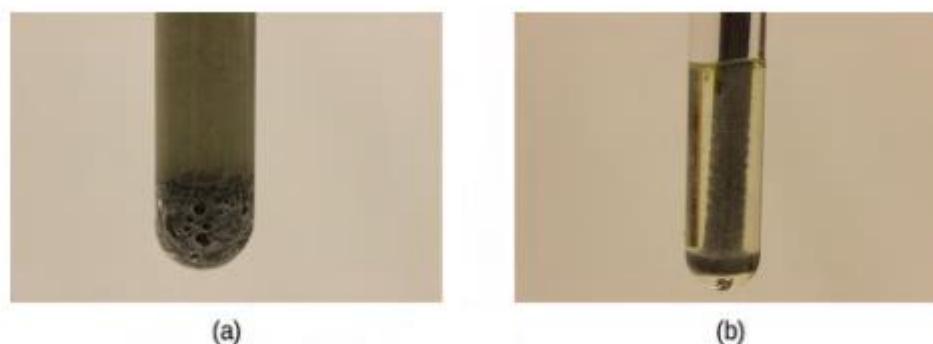


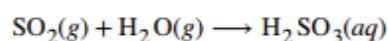
Figure 12.6 (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area: $2\text{Fe}(s) + 6\text{HCl}(aq) \longrightarrow 2\text{FeCl}_3(aq) + 3\text{H}_2(g)$. (b) An iron nail reacts more slowly.

Temperature of the Reactants

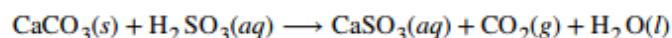
Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate (CaCO_3) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 12.7). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:



Calcium carbonate reacts with sulfurous acid as follows:



In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure 12.7 Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the

reaction to follow (Figure 12.8). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

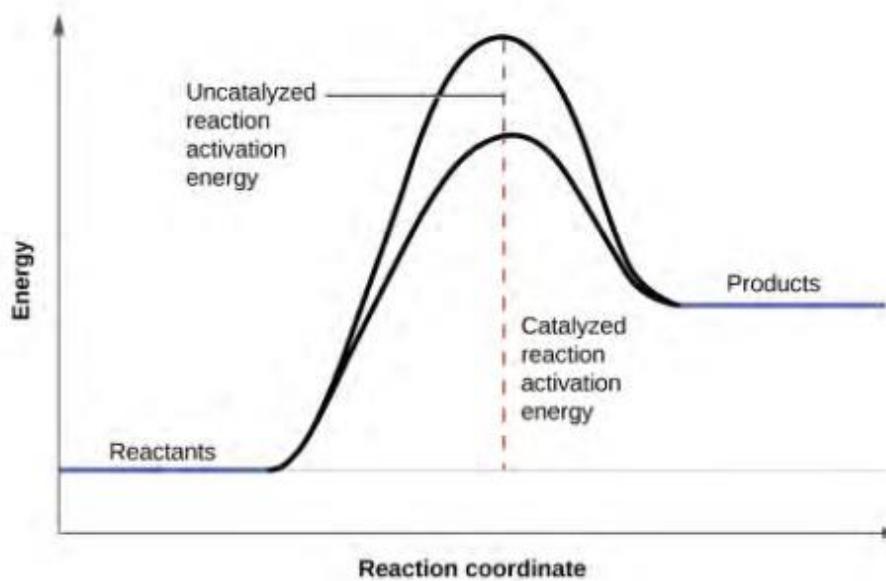


Figure 12.8 The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

12.3 Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. **Rate laws** or **rate equations** are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p\dots$$

in which $[A]$, $[B]$, and $[C]$ represent the molar concentrations of reactants, and k is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents m , n , and p are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant k and the exponents m , n , and p must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant k is independent of the concentration of A , B , or C , but it does vary with temperature and surface area.

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the **reaction order**. Consider a reaction for which the rate law is:

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

If the exponent m is 1, the reaction is first order with respect to A . If m is 2, the reaction is second order with respect to A . If n is 1, the reaction is first order in B . If n is 2, the reaction is second order in B . If m or n is zero, the reaction is zero order in A or B , respectively, and the rate of the reaction is not affected by the concentration of that reactant. The **overall reaction order** is the sum of the orders with respect to each reactant. If $m = 1$ and $n = 1$, the overall order of the reaction is second order ($m + n = 1 + 1 = 2$).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+ , first order in OH^- , and second order overall.

Example 12.3

Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:



is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

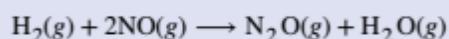
The reaction is second order in NO_2 ; thus $m = 2$. The reaction is zero order in CO ; thus $n = 0$. The rate law is:

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

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2 . When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Check Your Learning

The rate law for the reaction:

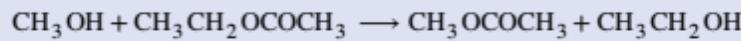


has been determined to be rate = $k[\text{NO}]^2[\text{H}_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer: order in NO = 2; order in H₂ = 1; overall order = 3

Check Your Learning

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH₃OH) and ethyl acetate (CH₃CH₂OCOCH₃) as a sample reaction before studying the chemical reactions that produce biodiesel:



The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[\text{CH}_3\text{OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer: order in CH₃OH = 1; order in CH₃CH₂OCOCH₃ = 0; overall order = 1

It is sometimes helpful to use a more explicit algebraic method, often referred to as the **method of initial rates**, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Example 12.4

Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica ([Figure 12.9](#)). One such reaction is the combination of nitric oxide, NO, with ozone, O₃:

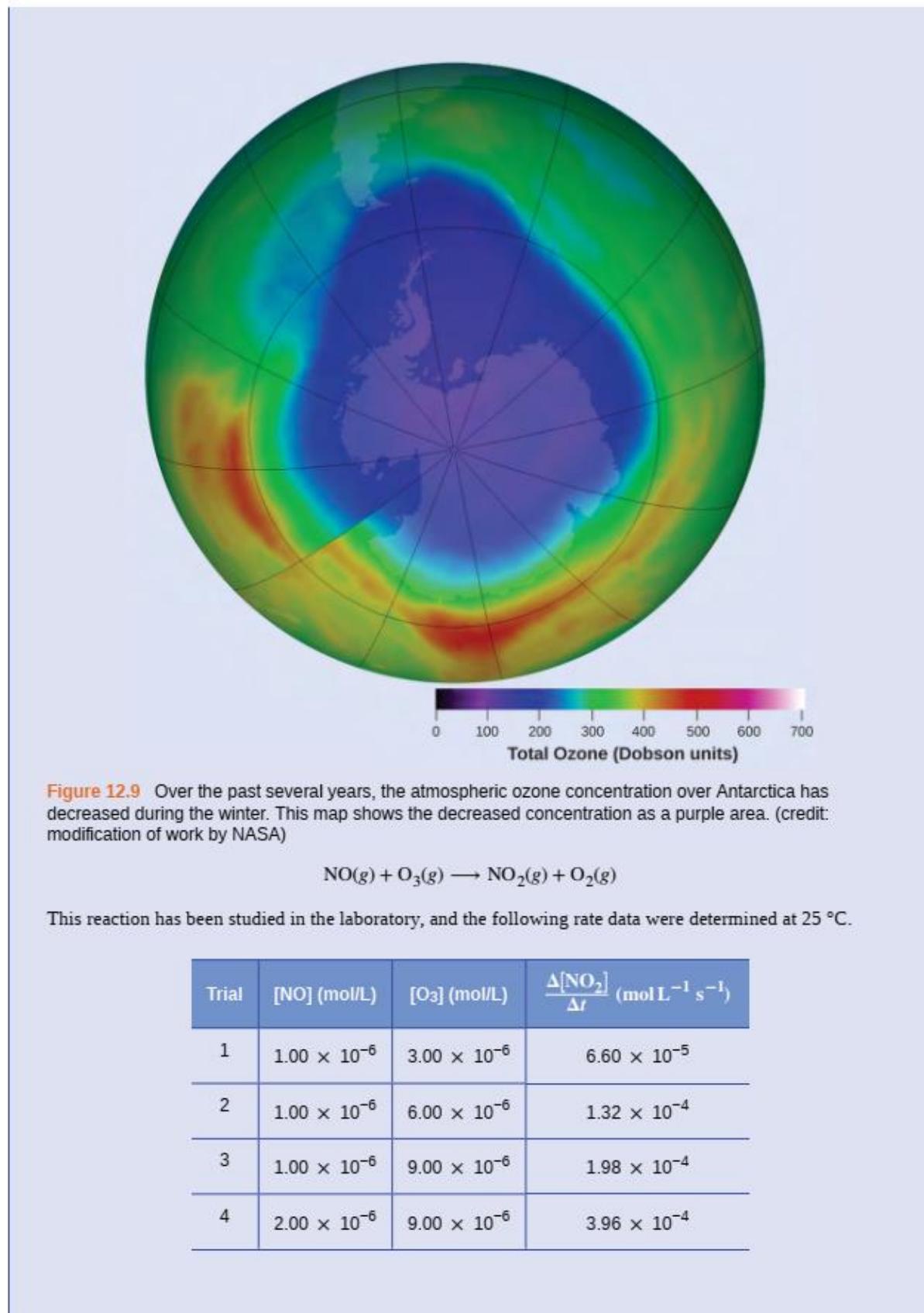


Figure 12.9 Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)



This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O ₃] (mol/L)	$\frac{\Delta[\text{NO}_2]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}

Trial	[NO] (mol/L)	[O ₃] (mol/L)	$\frac{\Delta[\text{NO}_2]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{O}_3]^n$$

We can determine the values of m , n , and k from the experimental data using the following three-part process:

Step 1. Determine the value of m from the data in which [NO] varies and [O₃] is constant. In the last three experiments, [NO] varies while [O₃] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and m in the rate law is equal to 1.

Step 2. Determine the value of n from data in which [O₃] varies and [NO] is constant. In the first three experiments, [NO] is constant and [O₃] varies. The reaction rate changes in direct proportion to the change in [O₃]. When [O₃] doubles from trial 1 to 2, the rate doubles; when [O₃] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O₃], and n is equal to 1. The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

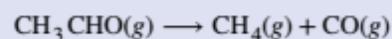
Step 3. Determine the value of k from one set of concentrations and the corresponding rate.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{0.660 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}}{(1.00 \times 10^{-6} \text{ mol L}^{-1})(3.00 \times 10^{-6} \text{ mol L}^{-1})} \\ &= 2.20 \times 10^7 \text{ L mol}^{-1}\text{s}^{-1} \end{aligned}$$

The large value of k tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Check Your Learning

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:



Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH ₃ CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L ⁻¹ s ⁻¹)
1	1.75×10^{-3}	2.06×10^{-11}

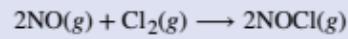
Trial	$[\text{CH}_3\text{CHO}] (\text{mol/L})$	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t} (\text{mol L}^{-1} \text{s}^{-1})$
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer: rate = $k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6} \text{ L/mol/s}$

Example 12.5

Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:



Trial	$[\text{NO}] (\text{mol/L})$	$[\text{Cl}_2] (\text{mol/L})$	$-\frac{\Delta[\text{NO}]}{\Delta t} (\text{mol L}^{-1} \text{s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in [Example 12.4](#), we can approach this problem in a stepwise fashion, determining the values of m and n from the experimental data and then using these values to determine the value of k . In this example, however, we will use a different approach to determine the values of m and n :

Step 1. Determine the value of m from the data in which $[\text{NO}]$ varies and $[\text{Cl}_2]$ is constant. We can write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m [\text{Cl}_2]_x^n}{k[\text{NO}]_y^m [\text{Cl}_2]_y^n}$$

Using the third trial and the first trial, in which $[\text{Cl}_2]$ does not vary, gives:

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

We can use natural logs to determine the value of the exponent m :

$$\begin{aligned}\ln(2.25) &= m\ln(1.5) \\ \frac{\ln(2.25)}{\ln(1.5)} &= m \\ 2 &= m\end{aligned}$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

Step 2. Determine the value of n from data in which $[Cl_2]$ varies and $[NO]$ is constant.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancellation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{Rate} = k[NO]^m[Cl_2]^n = k[NO]^2[Cl_2]$$

Step 3. Determine the numerical value of the rate constant k with appropriate units. The units for the rate of a reaction are mol/L/s. The units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol³/L³. The units for k should be mol⁻² L²/s so that the rate is in terms of mol/L/s.

To determine the value of k once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for k :

$$\begin{aligned}0.00300 \text{ mol L}^{-1} \text{ s}^{-1} &= k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1 \\ k &= 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}\end{aligned}$$

Check Your Learning

Use the provided initial rate data to derive the rate law for the reaction whose equation is:



Trial	[OCl ⁻] (mol/L)	[I ⁻] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

$$\text{Answer: } \frac{\text{rate}_2}{\text{rate}_3} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate} = k[\text{OCl}^-]^2[\text{I}^-]^1$$

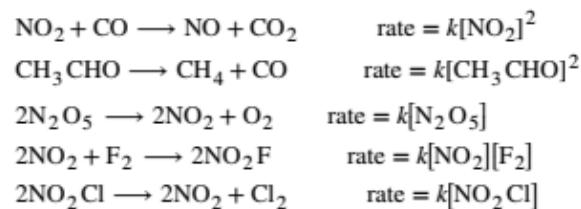
$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:



It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry*.

Reaction orders also play a role in determining the units for the rate constant k . In [Example 12.4](#), a second-order reaction, we found the units for k to be $\text{L mol}^{-4} \text{ s}^{-1}$, whereas in [Example 12.5](#), a third order reaction, we found the units for k to be $\text{mol}^{-2} \text{ L}^2/\text{s}$. More generally speaking, the units for the rate constant for a reaction of order $(m+n)$ are $\text{mol}^{1-(m+n)} \text{ L}^{(m+n)-1} \text{ s}^{-1}$. [Table 12.1](#) summarizes the rate constant units for common reaction orders.

Rate Constants for Common Reaction Orders

Reaction Order	Units of k
($m+n$)	$\text{mol}^{1-(m+n)} \text{ L}^{(m+n)-1} \text{ s}^{-1}$
zero	mol/L/s

Table 12.1

Rate Constants for Common Reaction Orders

Reaction Order	Units of k
first	s^{-1}
second	L/mol/s
third	$\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$

Table 12.1

Note that the units in the table can also be expressed in terms of molarity (M) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

12.4 Integrated Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

An equation relating the rate constant k to the initial concentration $[A]_0$ and the concentration $[A]_t$ present after any given time t can be derived for a first-order reaction and shown to be:

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

or

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

Example 12.6

The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C₄H₈ at 500 °C is 9.2 × 10⁻³ s⁻¹:



How long will it take for 80.0% of a sample of C₄H₈ to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

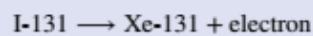
There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know [A]₀, [A], and k, and need to find t.

The initial concentration of C₄H₈, [A]₀, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or 0.200x. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln \frac{0.100 \text{ mol L}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.7 \times 10^2 \text{ s} \end{aligned}$$

Check Your Learning

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:



The decay is first-order with a rate constant of 0.138 d⁻¹. All radioactive decay is first order. How many days will it take for 90% of the iodine-131 in a 0.500 M solution of this substance to decay to Xe-131?

Answer: 16.7 days

We can use integrated rate laws with experimental data that consist of time and concentration information to determine the order and rate constant of a reaction. The integrated rate law can be rearranged to a standard linear equation format:

$$\begin{aligned} \ln[A] &= (-k)t + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of ln[A] versus t for a first-order reaction is a straight line with a slope of -k and an intercept of ln[A]₀. If a set of rate data are plotted in this fashion but do not result in a straight line, the reaction is not first order in A.

Example 12.7

Determination of Reaction Order by Graphing

Show that the data in [Figure 12.2](#) can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Solution

The data from [Figure 12.2](#) with the addition of values of $\ln[H_2O_2]$ are given in [Figure 12.10](#).

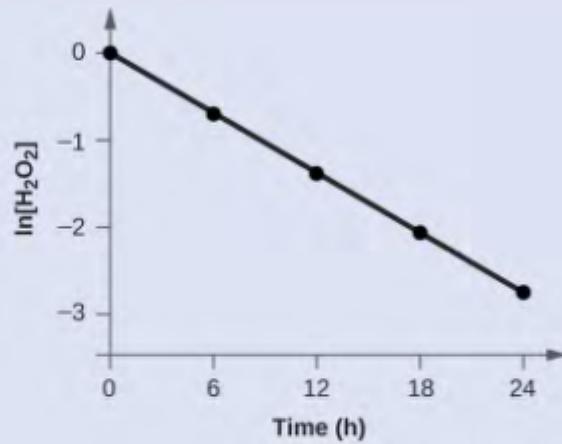


Figure 12.10 The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

Trial	Time (h)	$[H_2O_2] (M)$	$\ln[H_2O_2]$
1	0	1.000	0.0
2	6.00	0.500	-0.693
3	12.00	0.250	-1.386
4	18.00	0.125	-2.079
5	24.00	0.0625	-2.772

The plot of $\ln[H_2O_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

In order to determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 6.00 h is -0.693 ; the value when $t = 12.00$ h is -1.386 :

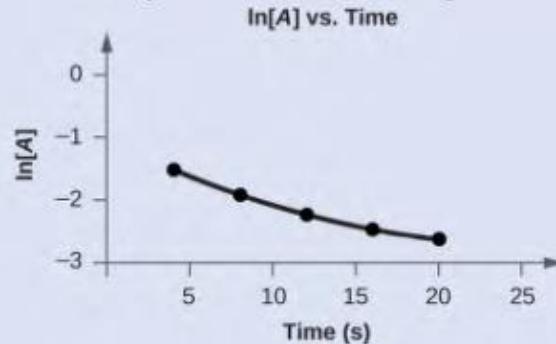
$$\begin{aligned}\text{slope} &= \frac{-1.386 - (-0.693)}{12.00 \text{ h} - 6.00 \text{ h}} \\ &= \frac{-0.693}{6.00 \text{ h}} \\ &= -1.155 \times 10^{-2} \text{ h}^{-1} \\ k &= -\text{slope} = -(-1.155 \times 10^{-2} \text{ h}^{-1}) = 1.155 \times 10^{-2} \text{ h}^{-1}\end{aligned}$$

Check Your Learning

Graph the following data to determine whether the reaction $A \rightarrow B + C$ is first order.

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer: The plot of $\ln[A]$ vs. t is not a straight line. The equation is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions are fairly complicated. We will limit ourselves to the simplest second-order reactions, namely, those with rates that are dependent upon just one reactant's concentration and described by the differential rate law:

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

For these second-order reactions, the integrated rate law is:

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

where the terms in the equation have their usual meanings as defined earlier.

Example 12.8

The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:



The reaction is second order with a rate constant equal to $5.76 \times 10^{-2} \text{ L/mol/min}$ under certain conditions.

If the initial concentration of butadiene is $0.200 M$, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

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

We know three variables in this equation: $[A]_0 = 0.200 \text{ mol/L}$, $k = 5.76 \times 10^{-2} \text{ L/mol/min}$, and $t = 10.0 \text{ min}$. Therefore, we can solve for $[A]$, the fourth variable:

$$\begin{aligned}\frac{1}{[A]} &= (5.76 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1})(10 \text{ min}) + \frac{1}{0.200 \text{ mol}^{-1}} \\ \frac{1}{[A]} &= (5.76 \times 10^{-1} \text{ L mol}^{-1}) + 5.00 \text{ L mol}^{-1} \\ \frac{1}{[A]} &= 5.58 \text{ L mol}^{-1} \\ [A] &= 1.79 \times 10^{-1} \text{ mol L}^{-1}\end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Check Your Learning

If the initial concentration of butadiene is $0.0200 M$, what is the concentration remaining after 20.0 min?

Answer: 0.0196 mol/L

The integrated rate law for our second-order reactions has the form of the equation of a straight line:

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

A plot of $\frac{1}{[A]}$ versus t for a second-order reaction is a straight line with a slope of k and an intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 12.9 Determination of Reaction Order by Graphing

Test the data given to show whether the dimerization of C₄H₆ is a first- or a second-order reaction.

Solution

Trial	Time (s)	[C ₄ H ₆] (M)
1	0	1.00 × 10 ⁻²
2	1600	5.04 × 10 ⁻³
3	3200	3.37 × 10 ⁻³
4	4800	2.53 × 10 ⁻³
5	6200	2.08 × 10 ⁻³

In order to distinguish a first-order reaction from a second-order reaction, we plot ln[C₄H₆] versus *t* and compare it with a plot of $\frac{1}{[C_4H_6]}$ versus *t*. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]} (M^{-1})$	ln[C ₄ H ₆]
0	100	-4.605
1600	198	-5.289
3200	296	-5.692
4800	395	-5.978
6200	481	-6.175

The plots are shown in [Figure 12.11](#). As you can see, the plot of ln[C₄H₆] versus *t* is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]}$ versus *t* is linear, indicating that the reaction is second order.

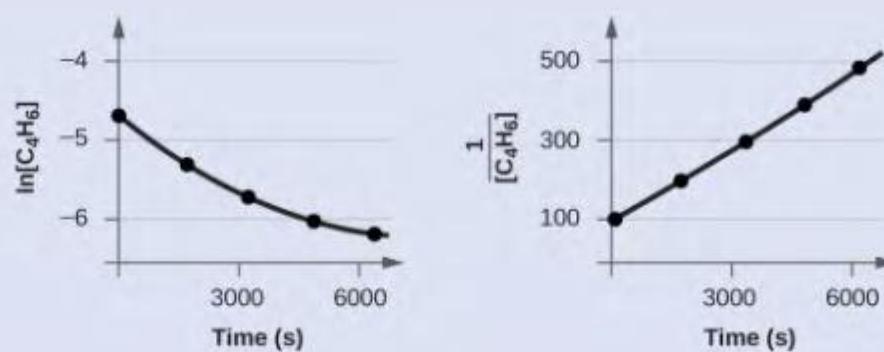


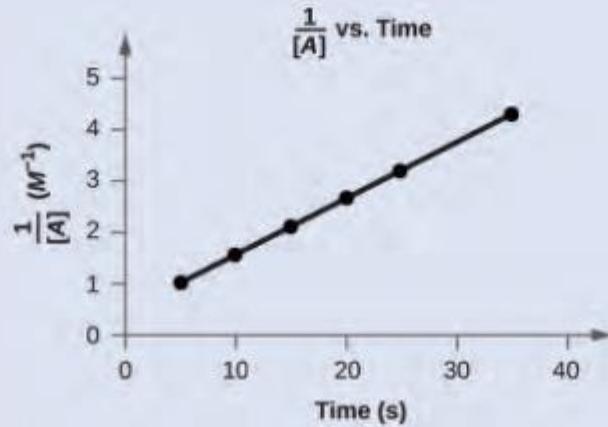
Figure 12.11 These two graphs show first- and second-order plots for the dimerization of C_4H_6 . Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

Check Your Learning

Does the following data fit a second-order rate law?

Trial	Time (s)	$[A] (M)$
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer: Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

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

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

The integrated rate law for a zero-order reaction also has the form of the equation of a straight line:

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

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$. **Figure 12.12** shows a plot of $[\text{NH}_3]$ versus t for the decomposition of ammonia on a hot tungsten wire and for the decomposition of ammonia on hot quartz (SiO_2). The decomposition of NH_3 on hot tungsten is zero order; the plot is a straight line. The decomposition of NH_3 on hot quartz is not zero order (it is first order). From the slope of the line for the zero-order decomposition, we can determine the rate constant:

$$\text{slope} = -k = 1.31 \times 10^{-6} \text{ mol/L/s}$$

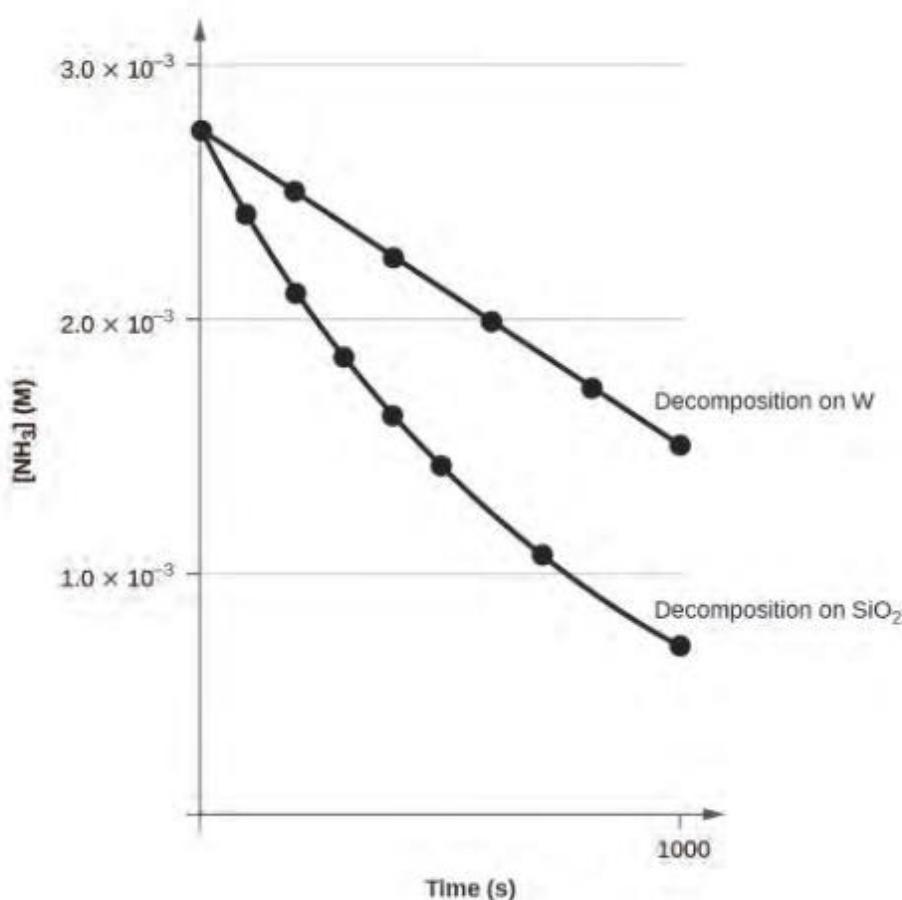


Figure 12.12 The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

The Half-Life of a Reaction

The **half-life of a reaction ($t_{1/2}$)** is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (Figure 12.2) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 M to 0.500 M. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 M to 0.250 M; during the third half-life, it decreases from 0.250 M to 0.125 M. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

$$\begin{aligned}\ln \frac{[A]_0}{[A]} &= kt \\ t &= \ln \frac{[A]_0}{[A]} \times \frac{1}{k}\end{aligned}$$

If we set the time t equal to the half-life, $t_{1/2}$, the corresponding concentration of A at this time is equal to one-half of its initial concentration. Hence, when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$.

Therefore:

$$\begin{aligned}t_{1/2} &= \ln \frac{\frac{1}{2}[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k} \\ &= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}\end{aligned}$$

Thus:

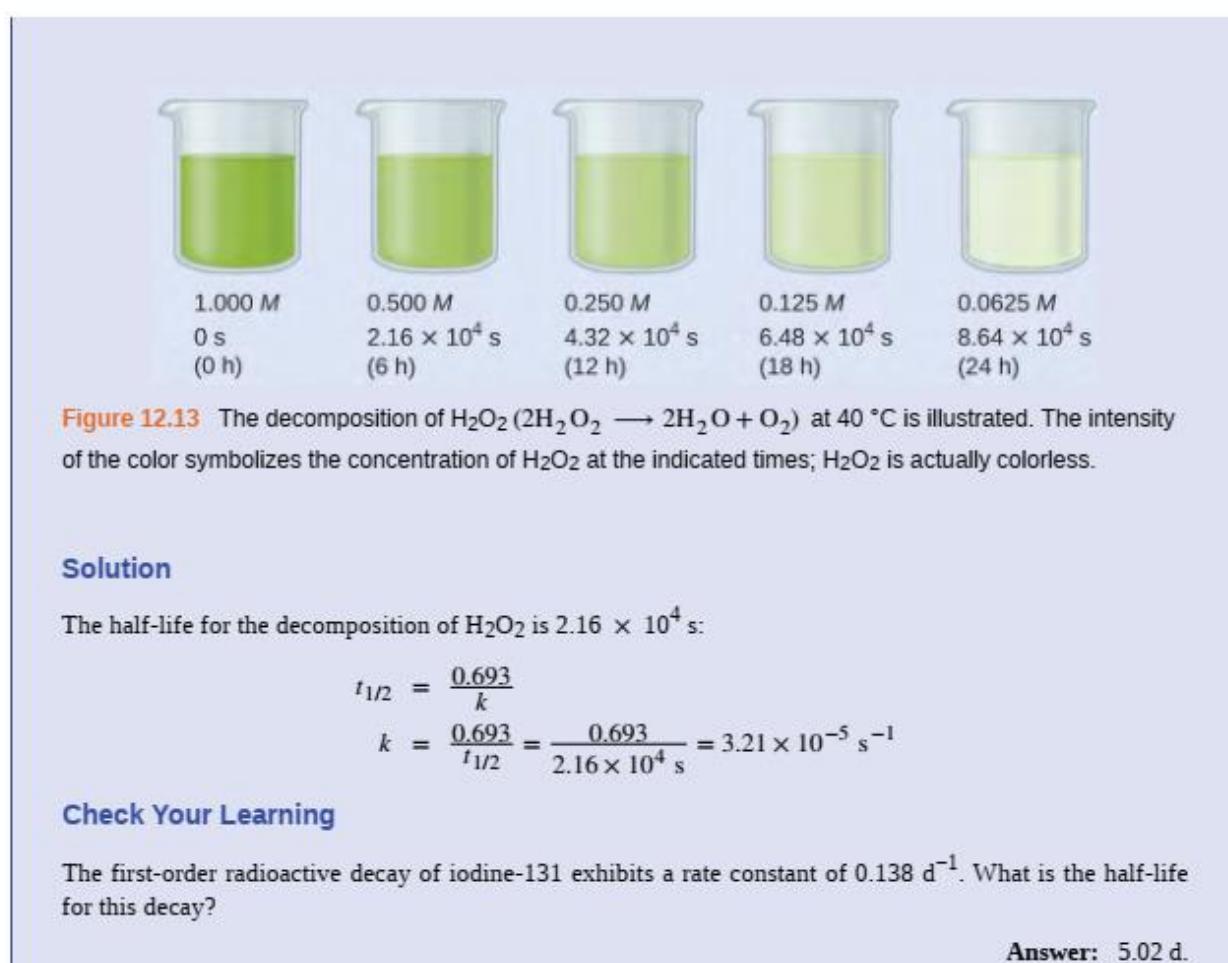
$$t_{1/2} = \frac{0.693}{k}$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant k . A fast reaction (shorter half-life) will have a larger k ; a slow reaction (longer half-life) will have a smaller k .

Example 12.10

Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 12.13.



Solution

The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

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

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 \text{ s}} = 3.21 \times 10^{-5} \text{ s}^{-1}$$

Check Your Learning

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1} . What is the half-life for this decay?

Answer: 5.02 d.

Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

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

or

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

If

$$t = t_{1/2}$$

then

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

and we can write:

$$\begin{aligned}\frac{\frac{1}{2}[A]_0 - \frac{1}{[A]_0}}{2[A]_0 - \frac{1}{[A]_0}} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2}\end{aligned}$$

Thus:

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

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero order reaction as follows:

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

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Thus:

$$\begin{aligned}\frac{[A]_0}{2} &= -kt_{1/2} + [A]_0 \\ kt_{1/2} &= \frac{[A]_0}{2}\end{aligned}$$

and

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

The half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in **Table 12.2**.

Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M s^{-1}$	s^{-1}	$M^{-1} s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t

Table 12.2

Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = +\text{slope}$
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Table 12.2

12.5 Collision Theory

By the end of this section, you will be able to:

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

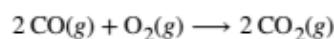
Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\# \text{ collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:



Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:



Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in **Figure 12.14**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a

central carbon atom bonded to two oxygen atoms ($\text{O} = \text{C} = \text{O}$). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

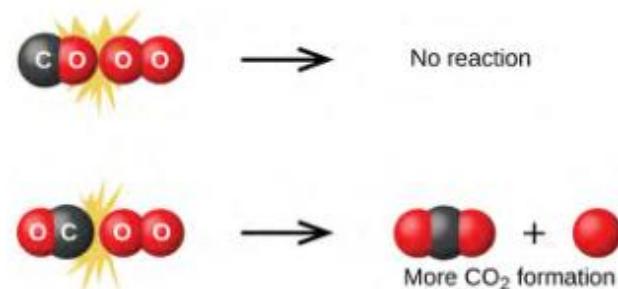


Figure 12.14 Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way. As **Figure 12.15** demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed **activated complex** or **transition state**.

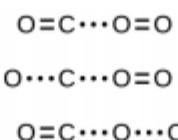


Figure 12.15 Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the $\text{O}=\text{O}$ double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy** (E_a). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic

energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure 12.16 shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:



The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a , the activation energy. Thus, the sum of the kinetic energies of A and B must be equal to or greater than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In **Figure 12.16**, ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

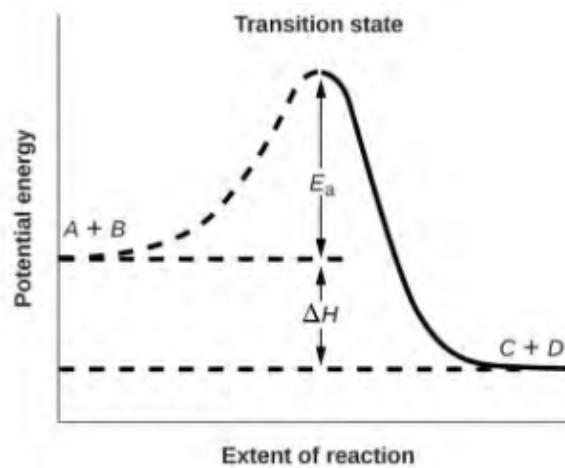


Figure 12.16 This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a . The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH . The curve's peak is represented the transition state.

We can use the **Arrhenius equation** to relate the activation energy and the rate constant, k , of a given reaction:

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

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, e is the constant 2.7183, and A is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor A is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction. An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 12.17), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A . Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k .

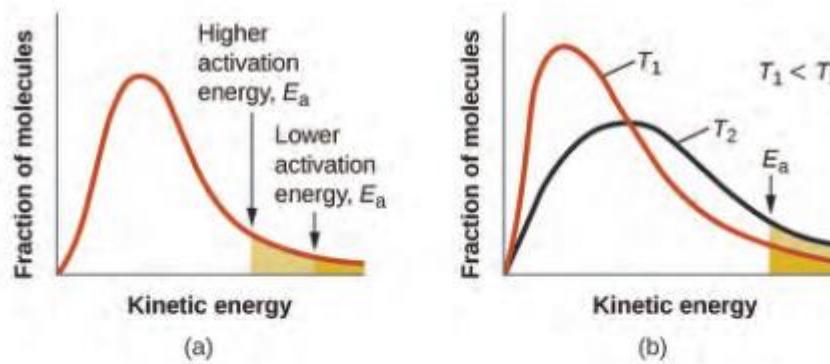


Figure 12.17 (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T_2 , more molecules have kinetic energies greater than E_a , as shown by the yellow shaded area.

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using of an alternate version of the Arrhenius equation that takes the form of linear equation:

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

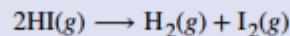
$$y = mx + b$$

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$.

Example 12.11

Determination of E_a

The variation of the rate constant with temperature for the decomposition of $\text{HI}(g)$ to $\text{H}_2(g)$ and $\text{I}_2(g)$ is given here. What is the activation energy for the reaction?



T (K)	k (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and $\ln k$ are:

$\frac{1}{T}$ (K ⁻¹)	$\ln k$
1.80×10^{-3}	-14.860
1.74×10^{-3}	-13.617
1.55×10^{-3}	-9.362
1.43×10^{-3}	-6.759
1.28×10^{-3}	-3.231

Figure 12.18 is a graph of $\ln k$ versus $\frac{1}{T}$. To determine the slope of the line, we need two values of $\ln k$, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of $\ln k$ determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is -2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is -14.447.

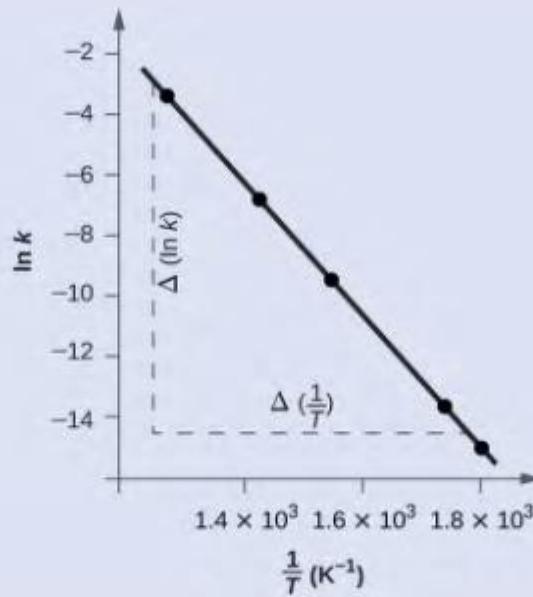


Figure 12.18 This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned}\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3} \text{ K}^{-1}) - (1.25 \times 10^{-3} \text{ K}^{-1})} \\ &= \frac{-11.854}{0.53 \times 10^{-3} \text{ K}^{-1}} = 2.2 \times 10^4 \text{ K} \\ &= -\frac{E_a}{R}\end{aligned}$$

Thus:

$$\begin{aligned}E_a &= -\text{slope} \times R = -(-2.2 \times 10^4 \text{ K} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \\ E_a &= 1.8 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

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

can be rearranged as shown to give:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$

or

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

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

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

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

T (K)	k (L/mol/s)	$\frac{1}{T}$ (K $^{-1}$)	$\ln k$
555	3.52×10^{-7}	1.80×10^{-3}	-14.860
781	3.95×10^{-2}	1.28×10^{-3}	-3.231

After calculating $\frac{1}{T}$ and $\ln k$, we can substitute into the equation:

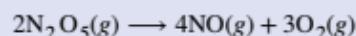
$$E_a = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} \text{ K}^{-1} - 1.80 \times 10^{-3} \text{ K}^{-1}} \right)$$

and the result is $E_a = 185,900$ J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

Check Your Learning

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:



Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer: 113,000 J/mol

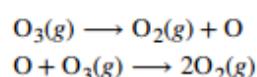
12.6 Reaction Mechanisms

By the end of this section, you will be able to:

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The **reaction mechanism** (or reaction path) is the process, or pathway, by which a reaction occurs.

A chemical reaction usually occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:



We call each step in a reaction mechanism an **elementary reaction**. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

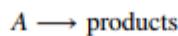


Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

Unimolecular Elementary Reactions

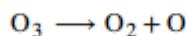
The **molecularity** of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a **unimolecular reaction** involves the rearrangement of a *single* reactant species to produce one or more molecules of product:



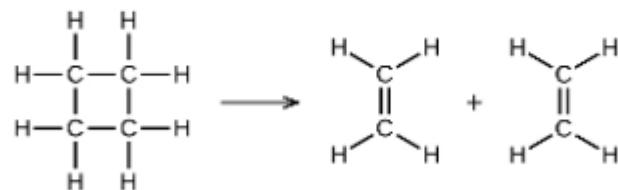
The rate equation for a unimolecular reaction is:

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

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

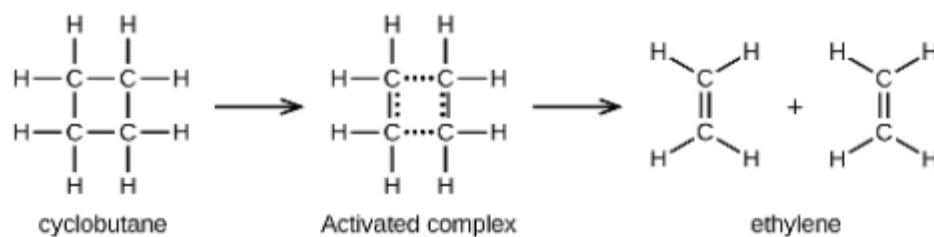


illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C₄H₈, to ethylene, C₂H₄, occurs via a unimolecular, single-step mechanism:



For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C₄H₈, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In a sample of C₄H₈, a few of the rapidly moving C₄H₈ molecules collide with other rapidly moving molecules and pick up additional energy. When the C₄H₈ molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C₄H₈ molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

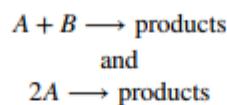
The rate of decomposition of C₄H₈ is directly proportional to its concentration. Doubling the concentration of C₄H₈ in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C₄H₈ per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\frac{\Delta[\text{C}_4\text{H}_8]}{\Delta t} = k[\text{C}_4\text{H}_8]$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a **bimolecular reaction**. There are two types of bimolecular elementary reactions:



For the first type, in which the two reactant molecules are different, the rate law is first-order in A and first order in B:

$$\text{rate} = k[A][B]$$

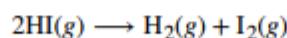
For the second type, in which two identical molecules collide and react, the rate law is second order in A:

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

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:



Another is the decomposition of two hydrogen iodide molecules to produce hydrogen, H₂, and iodine, I₂ **Figure 12.19**:



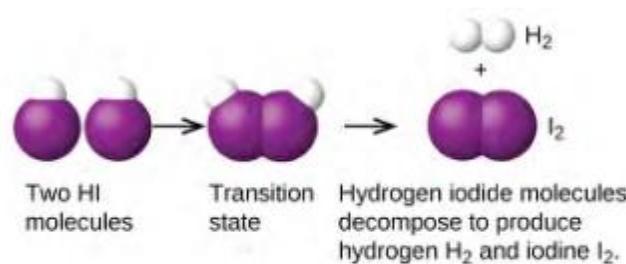


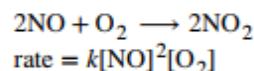
Figure 12.19 The probable mechanism for the dissociation of two HI molecules to produce one molecule of H₂ and one molecule of I₂.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

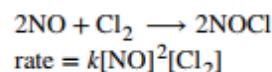


Termolecular Elementary Reactions

An elementary **termolecular reaction** involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:



Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:



Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the **rate-limiting step** (or rate-determining step) of the reaction **Figure 12.20**.



Figure 12.20 A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:



For temperatures above 225 °C, the rate law has been found to be:

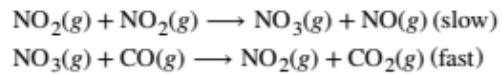
$$\text{rate} = k[\text{NO}_2][\text{CO}]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2 :

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

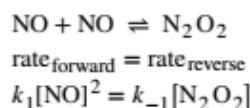
This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:



The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2 , with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:



If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

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

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. **Example 12.12** will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 12.12

Deriving the Overall Rate Law Expression for a Multistep Reaction Mechanism

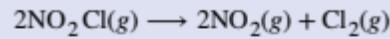
Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

1. $2\text{NO}_2\text{Cl}(g) \rightleftharpoons \text{ClO}_2(g) + \text{N}_2\text{O}(g) + \text{ClO}(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $\text{N}_2\text{O}(g) + \text{ClO}_2(g) \rightleftharpoons \text{NO}_2(g) + \text{NOCl}(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $\text{NOCl} + \text{ClO} \longrightarrow \text{NO}_2 + \text{Cl}_2$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:



Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$\begin{aligned} k_1[\text{NO}_2\text{Cl}]_2 &= k_{-1}[\text{ClO}_2][\text{N}_2\text{O}][\text{ClO}] \\ k_2[\text{N}_2\text{O}][\text{ClO}_2] &= k_{-2}[\text{NO}_2][\text{NOCl}] \\ \text{Rate} &= k_3[\text{NOCl}][\text{ClO}] \end{aligned}$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate expression could be written as $\text{Rate} = k_3[\text{NOCl}][\text{ClO}]$. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent $[\text{NOCl}]$ and $[\text{ClO}]$ such that no intermediates remain in the overall rate law expression.

$$\text{Using elementary reaction 1, } [\text{ClO}] = \frac{k_1[\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{ClO}_2][\text{N}_2\text{O}]}.$$

$$\text{Using elementary reaction 2, } [\text{NOCl}] = \frac{k_2[\text{N}_2\text{O}][\text{ClO}_2]}{k_{-2}[\text{NO}_2]}.$$

Now substitute these algebraic expressions into the overall rate law expression and simplify:

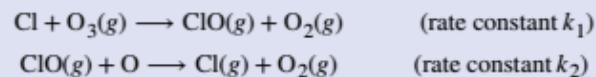
$$\text{rate} = k_3 \left(\frac{k_2 [\text{N}_2\text{O}][\text{ClO}_2]}{k_{-2}[\text{NO}_2]} \right) \left(\frac{k_1 [\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{ClO}_2]\text{N}_2\text{O}} \right)$$

$$\text{rate} = \frac{k_3 k_2 k_1 [\text{NO}_2\text{Cl}]^2}{k_{-2} k_{-1} [\text{NO}_2]}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Check Your Learning

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:



Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer: overall reaction: $\text{O}_3(g) + \text{O} \longrightarrow 2\text{O}_2(g)$

rate₁ = $k_1[\text{O}_3][\text{Cl}]$; rate₂ = $k_2[\text{ClO}][\text{O}]$

intermediate: ClO(g)

overall rate = $k_2 k_1 [\text{O}_3][\text{Cl}][\text{O}]$

12.7 Catalysis

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in [Figure 12.21](#).

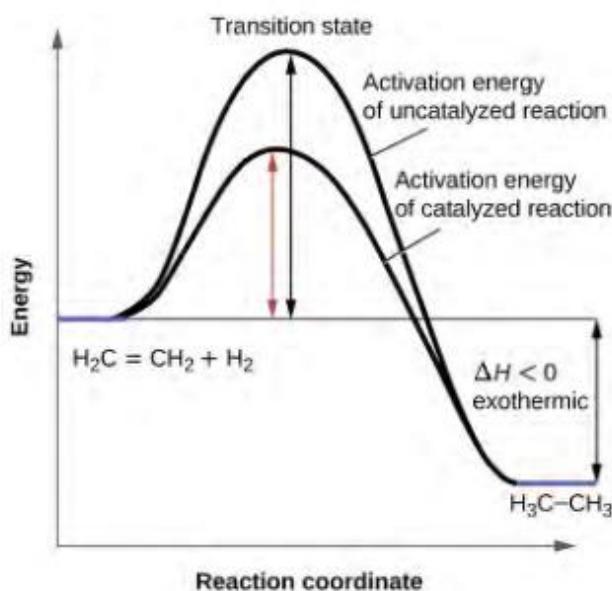


Figure 12.21 This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in **Figure 12.22**. This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).

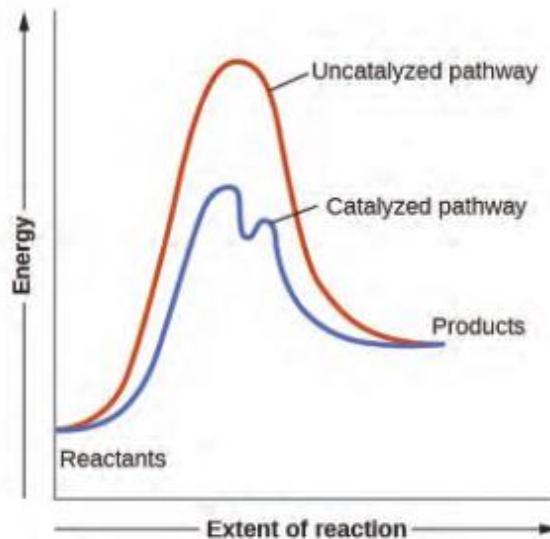
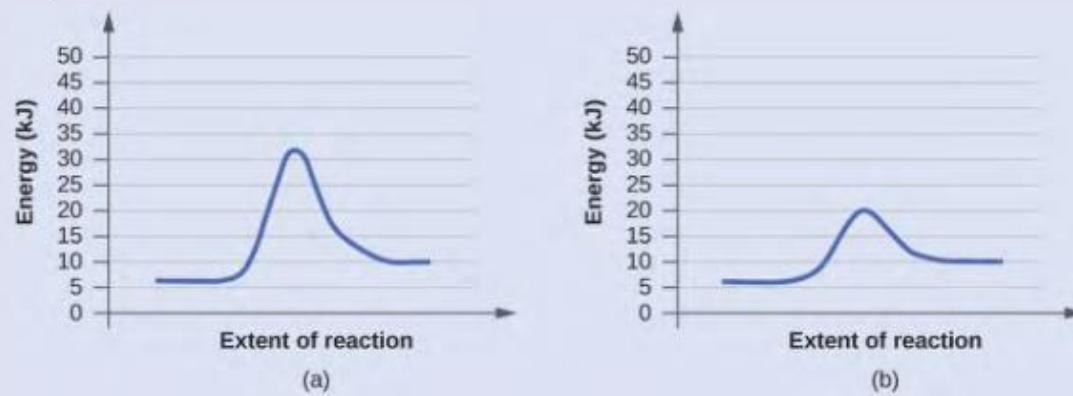


Figure 12.22 This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transition states).

Example 12.13**Using Reaction Diagrams to Compare Catalyzed Reactions**

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:

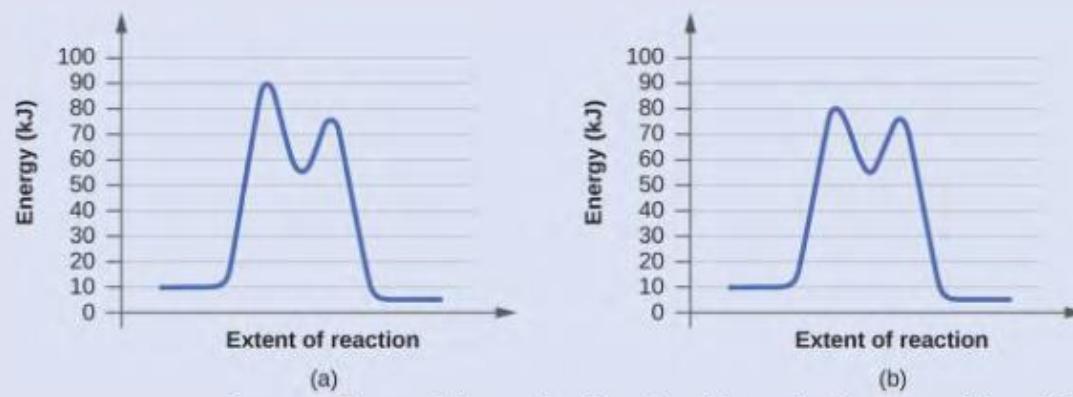
**Solution**

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20 \text{ kJ} - 6 \text{ kJ} = 14 \text{ kJ}$$

Check Your Learning

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:

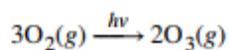


Answer: Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

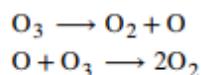
Homogeneous Catalysts

A **homogeneous catalyst** is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

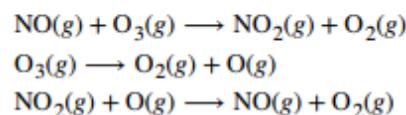
As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:



Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:



The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:



The overall chemical change for the catalyzed mechanism is the same as:



The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

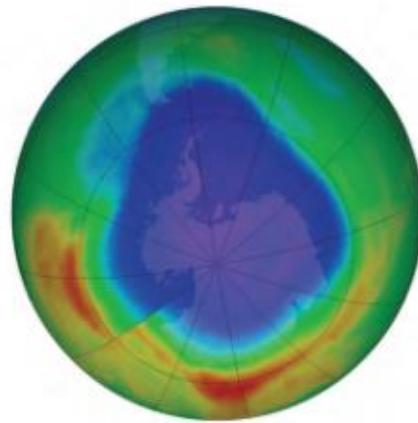
Portrait of a Chemist

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 12.23), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."^[1] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a)

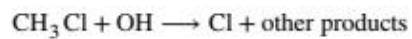


(b)

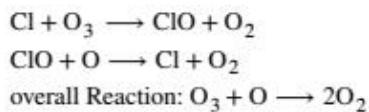
Figure 12.23 (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation—strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:



Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:



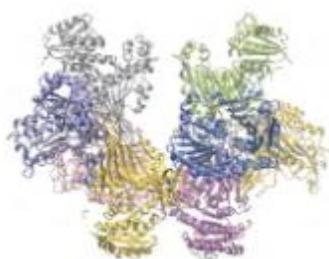
A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and ClONO_2 .

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

How Sciences Interconnect

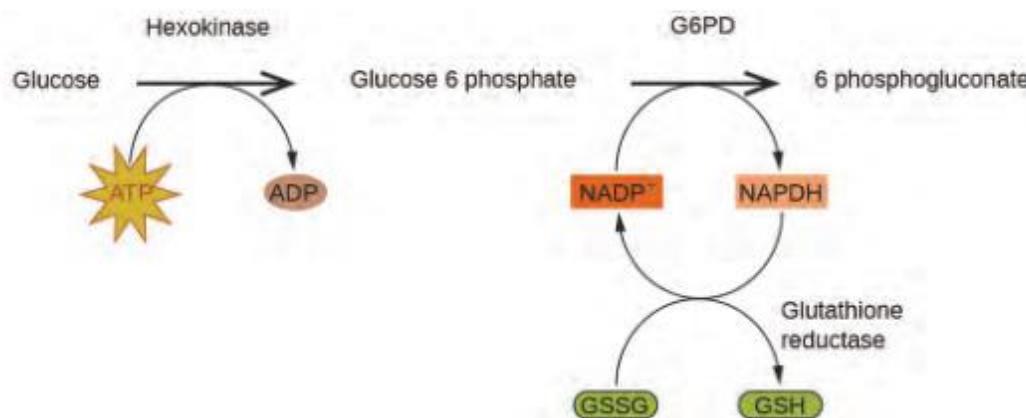
Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in [Figure 12.24](#), is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells ([Figure 12.25](#)).



[Figure 12.24](#) Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.



[Figure 12.25](#) In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A **heterogeneous catalyst** is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 12.26 illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

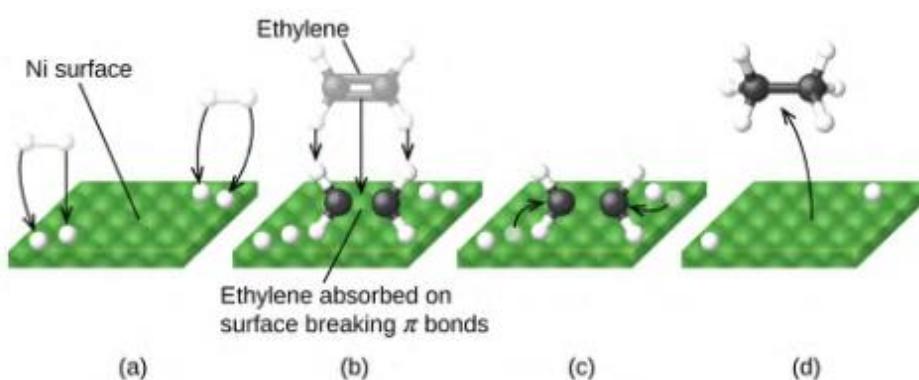


Figure 12.26 There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π -bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules escape from the nickel surface, since they are not strongly attracted to nickel.

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH . Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 12.27).

Chemistry in Everyday Life

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 12.27).

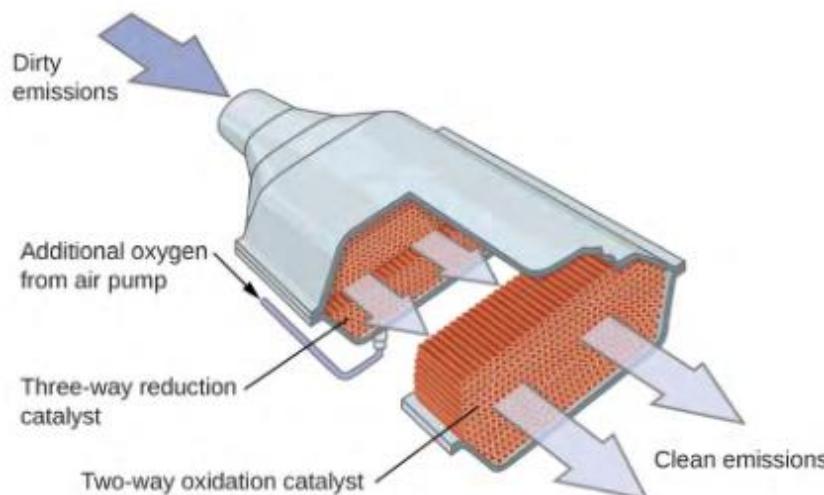
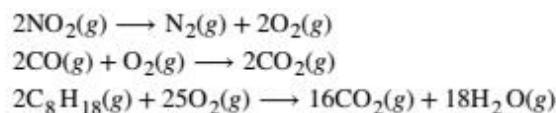


Figure 12.27 A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:



In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

How Sciences Interconnect

Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important

compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in **Table 12.3**.

Classes of Enzymes and Their Functions	
Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 12.3

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (**Figure 12.28**).

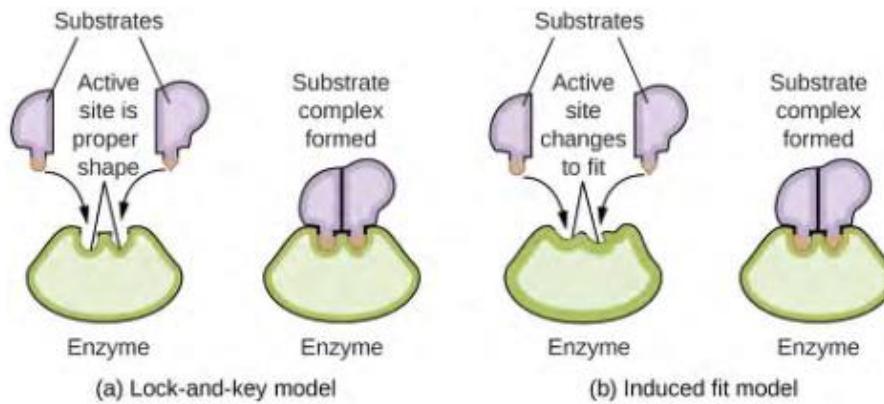


Figure 12.28 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Key Terms

activated complex (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a) energy necessary in order for a reaction to take place

Arrhenius equation mathematical relationship between the rate constant and the activation energy of a reaction

average rate rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

bimolecular reaction elementary reaction involving the collision and combination of two reactant species

catalyst substance that increases the rate of a reaction without itself being consumed by the reaction

collision theory model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

elementary reaction reaction that takes place precisely as depicted in its chemical equation

frequency factor (A) proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

half-life of a reaction ($t_{1/2}$) time required for half of a given amount of reactant to be consumed

heterogeneous catalyst catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst catalyst present in the same phase as the reactants

initial rate instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

integrated rate law equation that relates the concentration of a reactant to elapsed time of reaction

intermediate molecule or ion produced in one step of a reaction mechanism and consumed in another

method of initial rates use of a more explicit algebraic method to determine the orders in a rate law

molecularity number of reactant species (atoms, molecules or ions) involved in an elementary reaction

overall reaction order sum of the reaction orders for each substance represented in the rate law

rate constant (k) proportionality constant in the relationship between reaction rate and concentrations of reactants

rate expression mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

rate law (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

rate of reaction measure of the speed at which a chemical reaction takes place

rate-determining step (also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism stepwise sequence of elementary reactions by which a chemical change takes place

reaction order value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

termolecular reaction elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

Key Equations

- relative reaction rates for $aA \longrightarrow bB = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}$
- integrated rate law for zero-order reactions: $[A] = -kt + [A]_0, \quad t_{1/2} = \frac{[A]_0}{2k}$
- integrated rate law for first-order reactions: $\ln[A] = -kt + [A]_0, \quad t_{1/2} = \frac{0.693}{k}$
- integrated rate law for second-order reactions: $\frac{1}{[A]} = kt + \frac{1}{[A]_0}, \quad t_{1/2} = \frac{1}{[A]_0 k}$
- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Summary

12.1 Chemical Reaction Rates

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

12.2 Factors Affecting Reaction Rates

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

12.3 Rate Laws

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

12.4 Integrated Rate Laws

Differential rate laws can be determined by the method of initial rates or other methods. We measure values for the initial rates of a reaction at different concentrations of the reactants. From these measurements, we determine the order

of the reaction in each reactant. Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

12.5 Collision Theory

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

12.6 Reaction Mechanisms

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

12.7 Catalysis

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Exercises

12.1 Chemical Reaction Rates

- What is the difference between average rate, initial rate, and instantaneous rate?
- Ozone decomposes to oxygen according to the equation $2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.
- In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \longrightarrow 2\text{ClF}_3(\text{g})$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3 .
- A study of the rate of dimerization of C_4H_6 gave the data shown in the table:



Time (s)	0	1600	3200	4800	6200
$[\text{C}_4\text{H}_6] (\text{M})$	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

- (a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?

(c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5. A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

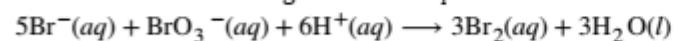
Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
$[A] (M)$	1.00	0.952	0.625	0.465	0.370	0.308	0.230

(a) Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(b) Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus $[A]$. What are the units of this rate?

(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

6. Consider the following reaction in aqueous solution:



If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4} M s^{-1}$, what is the rate of appearance of $Br_2(aq)$ at that moment?

12.2 Factors Affecting Reaction Rates

7. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

8. Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)