

The Rate of a Reaction

Rate, or speed, refers to something that happens in a unit of time. A car traveling at 60 km/h, for example, covers a distance of 60 kilometers in one hour.

For chemical reactions, the rate of reaction describes how fast the concentration of a reactant or product changes with time.

There are many reasons for studying the rate of a reaction. To begin with, there is intrinsic curiosity about why reactions have such vastly different rates. Some processes, such as the initial steps in vision and photosynthesis and nuclear chain reactions, take place on a time scale as short as 10^{-12} s to 10^{-6} s. Others, like the curing of cement and the conversion of graphite to diamond, take years or millions of years to complete.

We know that any reaction can be represented by the general equation;



This equation tells us that during the course of a reaction, reactants are consumed while products are formed. As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Figure 13.1 shows the progress of a simple reaction in which A molecules are converted to B molecules:

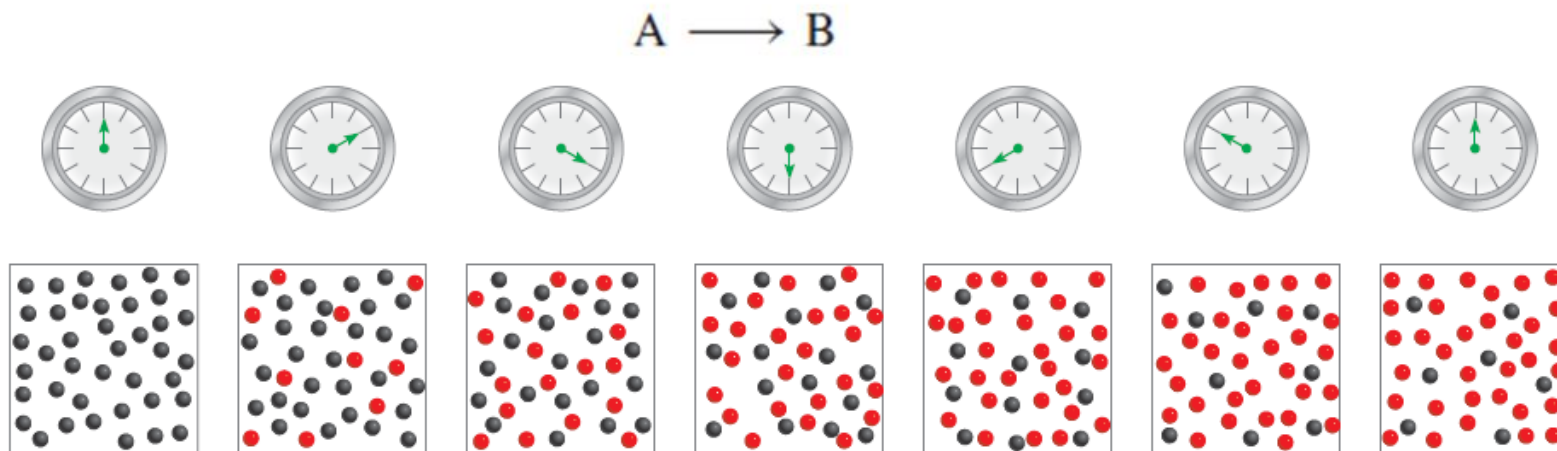


Figure 13.1 The progress of reaction $A \longrightarrow B$ at 10-s intervals over a period of 60 s. Initially, only A molecules (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.

The decrease in the number of A molecules and the increase in the number of B molecules with time are shown in Figure 13.2.

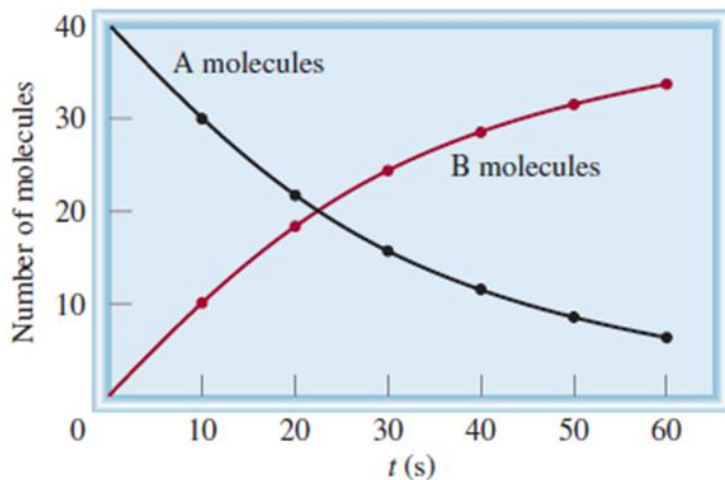


Figure 13.2 The rate of reaction $A \longrightarrow B$, represented as the decrease of A molecules with time and as the increase of B molecules with time.

In general, it is more convenient to express the reaction rate in terms of the change in concentration with time. Thus, for the reaction $A \longrightarrow B$ we can express the rate as

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

where $\Delta[A]$ and $\Delta[B]$ are the changes in concentration (molarity) over a time period Δt . Because the concentration of A *decreases* during the time interval, $\Delta[A]$ is a negative quantity. The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive.

On the other hand, the rate of product formation does not require a minus sign because $\Delta[B]$ is a positive quantity (the concentration of B *increases* with time). These rates are *average rates* because they are averaged over a certain time period Δt .

Reaction Rates and Stoichiometry

We have seen that for stoichiometrically simple reactions of the type $A \longrightarrow B$, the rate can be either expressed in terms of the decrease in reactant concentration with time, $-\Delta[A]/\Delta t$, or the increase in product concentration with time, $\Delta[B]/\Delta t$. For more complex reactions, we must be careful in writing the rate expressions. Consider, for example, the reaction



Two moles of A disappear for each mole of B that forms; that is, the rate at which B forms is one-half the rate at which A disappears. Thus, the rate can be expressed as

$$\text{rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction

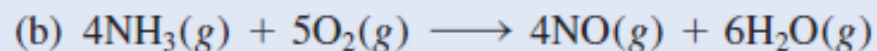
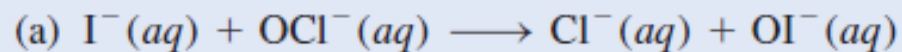


the rate is given by

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

EXAMPLE 13.1

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:



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Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:



Solution (a) Because each of the stoichiometric coefficients equals 1,

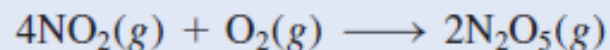
$$\text{rate} = -\frac{\Delta[\text{I}^{-}]}{\Delta t} = -\frac{\Delta[\text{OCl}^{-}]}{\Delta t} = \frac{\Delta[\text{Cl}^{-}]}{\Delta t} = \frac{\Delta[\text{OI}^{-}]}{\Delta t}$$

(b) Here the coefficients are 4, 5, 4, and 6, so

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

EXAMPLE 13.2

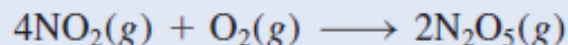
Consider the reaction



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s . (a) At what rate is N_2O_5 being formed? (b) At what rate is NO_2 reacting?

EXAMPLE 13.2

Consider the reaction



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s . (a) At what rate is N_2O_5 being formed? (b) At what rate is NO_2 reacting?

Strategy To calculate the rate of formation of N_2O_5 and disappearance of NO_2 , we need to express the rate of the reaction in terms of the stoichiometric coefficients as in Example 13.1:

$$\text{rate} = -\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

We are given

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -0.024 \text{ M/s}$$

where the minus sign shows that the concentration of O_2 is decreasing with time.

Solution (a) From the preceding rate expression we have

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Therefore,

$$\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -2(-0.024 \text{ M/s}) = 0.048 \text{ M/s}$$

(b) Here we have

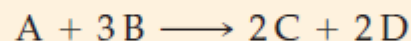
$$-\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

so

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 4(-0.024 \text{ M/s}) = -0.096 \text{ M/s}$$

EXAMPLE 20-1 Expressing the Rate of a Reaction

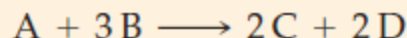
Suppose that at some point in the reaction



$[\text{B}] = 0.9986 \text{ M}$, and that 13.20 min later $[\text{B}] = 0.9746 \text{ M}$. What is the average rate of reaction during this time period, expressed in M s^{-1} ?

EXAMPLE 20-1 Expressing the Rate of a Reaction

Suppose that at some point in the reaction



$[\text{B}] = 0.9986\text{ M}$, and that 13.20 min later $[\text{B}] = 0.9746\text{ M}$. What is the average rate of reaction during this time period, expressed in M s^{-1} ?

Analyze

This is a straightforward application of the definition for rate of reaction, expression (20.2). To formulate the rate, we use $\Delta[\text{B}] = 0.9746\text{ M} - 0.9986\text{ M} = -0.0240\text{ M}$ and $\Delta t = 13.20\text{ min}$.

Solve

The solution is

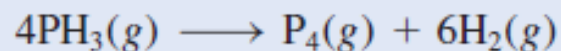
$$\text{average rate of reaction} = -\frac{1}{3} \frac{\Delta[\text{B}]}{\Delta t} = -\frac{1}{3} \times \frac{-0.0240\text{ M}}{13.20\text{ min}} = 6.06 \times 10^{-4}\text{ M min}^{-1}$$

To express the rate of reaction in moles per liter per second, we must convert from min^{-1} to s^{-1} . We can do this with the conversion factor 1 min/60 s.

$$\text{rate of reaction} = 6.06 \times 10^{-4}\text{ M min}^{-1} \times \frac{1\text{ min}}{60\text{ s}} = 1.01 \times 10^{-5}\text{ M s}^{-1}$$

Alternatively, we could have converted 13.20 min to 792 s and used $\Delta t = 792\text{ s}$ in evaluating the rate of reaction.

Practice Exercise Consider the reaction

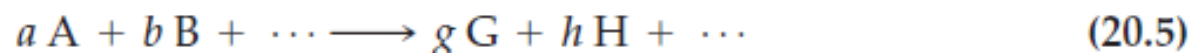


Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078 M/s . (a) At what rate is P_4 being formed? (b) At what rate is PH_3 reacting?

The Rate Law

One of the goals in a chemical kinetics study is to derive an equation that can be used to predict the relationship between the rate of reaction and the concentrations of reactants. Such an experimentally determined equation is called a **rate law**, or **rate equation**.

Consider the hypothetical reaction



where a, b, \dots stand for coefficients in the balanced equation. The rate law for reaction (20.5) can often be expressed in the following general form.*

$$\text{rate of reaction} = k[A]^m[B]^n \dots \quad (20.6)$$

The terms $[A], [B], \dots$ represent reactant molarities. The required exponents, m, n, \dots are generally small, positive whole numbers, although in some cases they may be zero, fractional, or negative. They must be determined by experiment and are generally *not* related to stoichiometric coefficients a, b, \dots . That is, often $m \neq a, n \neq b$, and so on.

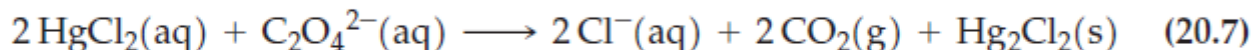
The term *order* is related to the exponents in the rate law and is used in two ways: (1) If $m = 1$, we say that the reaction is *first order in A*. If $n = 2$, the reaction is *second order in B*, and so on. (2) The **overall order of reaction** is the sum of all the exponents: $m + n + \dots$. The proportionality constant k relates the rate of reaction to reactant concentrations and is called the **rate constant** of the reaction. Its value depends on the specific reaction, the presence of a catalyst (if any), and the temperature. *The larger the value of k , the faster a reaction goes.* The order of the reaction establishes the general form of the rate law and the appropriate units of k (that is, depending on the values of the exponents).

With the rate law for a reaction, we can

- calculate rates of reaction for known concentrations of reactants
- derive an equation that expresses a reactant concentration as a function of time

Method of Initial Rates

As its name implies, this method requires us to work with *initial* rates of reaction. As an example, let's look at a specific reaction: that between mercury(II) chloride and oxalate ion.



The tentative rate law that we can write for this reaction is

$$\text{rate of reaction} = k[\text{HgCl}_2]^m[\text{C}_2\text{O}_4^{2-}]^n \quad (20.8)$$

We can follow the reaction by measuring the quantity of $\text{Hg}_2\text{Cl}_2(\text{s})$ formed as a function of time. Some representative data are given in Table 20.3, which we can assume are based on either the rate of formation of Hg_2Cl_2 or the rate of disappearance of $\text{C}_2\text{O}_4^{2-}$. In Example 20-3, we will use some of these data to illustrate the method of initial rates.

TABLE 20.3 Kinetic Data for the Reaction:
 $2 \text{HgCl}_2 + \text{C}_2\text{O}_4^{2-} \longrightarrow 2 \text{Cl}^- + 2 \text{CO}_2 + \text{Hg}_2\text{Cl}_2$

Experiment	$[\text{HgCl}_2], \text{M}$	$[\text{C}_2\text{O}_4^{2-}], \text{M}$	Initial Rate, M min^{-1}
1	$[\text{HgCl}_2]_1 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_1 = 0.15$	$R_1 = 1.8 \times 10^{-5}$
2	$[\text{HgCl}_2]_2 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_2 = 0.30$	$R_2 = 7.1 \times 10^{-5}$
3	$[\text{HgCl}_2]_3 = 0.052$	$[\text{C}_2\text{O}_4^{2-}]_3 = 0.30$	$R_3 = 3.5 \times 10^{-5}$

Experiment	[HgCl ₂], M	[C ₂ O ₄ ²⁻], M	Initial Rate, M min ⁻¹
1	[HgCl ₂] ₁ = 0.105	[C ₂ O ₄ ²⁻] ₁ = 0.15	R ₁ = 1.8 × 10 ⁻⁵
2	[HgCl ₂] ₂ = 0.105	[C ₂ O ₄ ²⁻] ₂ = 0.30	R ₂ = 7.1 × 10 ⁻⁵
3	[HgCl ₂] ₃ = 0.052	[C ₂ O ₄ ²⁻] ₃ = 0.30	R ₃ = 3.5 × 10 ⁻⁵

We begin by writing

$$R_2 = k \times [\text{HgCl}_2]_2^m \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (2 \times [\text{HgCl}_2]_3)^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$R_3 = k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$\frac{R_2}{R_3} = \frac{2 \times R_3}{R_3} = 2 = \frac{k \times 2^m \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n}{k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n} = 2^m$$

In order that $2^m = 2$, $m = 1$.

To determine the value of n , we can form the ratio R_2/R_1 . Now, [C₂O₄²⁻] is doubled and [HgCl₂] is held constant. This time, let's use actual concentrations instead of symbolic equivalents. Also, we now have the value $m = 1$.

$$R_2 = k \times [\text{HgCl}_2]_2^1 \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (0.105)^1 \times (2 \times 0.15)^n$$

$$R_1 = k \times [\text{HgCl}_2]_1^1 \times [\text{C}_2\text{O}_4^{2-}]_1^n = k \times (0.105)^1 \times (0.15)^n$$

$$\frac{R_2}{R_1} = \frac{7.1 \times 10^{-5}}{1.8 \times 10^{-5}} \approx 4 = \frac{k \times (0.105)^1 \times 2^n \times (0.15)^n}{k \times (0.105)^1 \times (0.15)^n} = 2^n$$

In order that $2^n = 4$, $n = 2$.

m+n = 3 (third order reaction)

EXAMPLE 13.3

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when $[\text{NO}] = 12.0 \times 10^{-3} M$ and $[\text{H}_2] = 6.0 \times 10^{-3} M$.

Experiment	$[\text{NO}] (M)$	$[\text{H}_2] (M)$	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Strategy We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant. We assume that the rate law takes the form

$$\text{rate} = k[\text{NO}]^x[\text{H}_2]^y$$

How do we use the data to determine x and y ? Once the orders of the reactants are known, we can calculate k from any set of rate and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of NO and H₂.

Solution (a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H₂, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \text{ M/s}}{1.3 \times 10^{-5} \text{ M/s}} \approx 4 = \frac{k(10.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}{k(5.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(10.0 \times 10^{-3} \text{ M})^x}{(5.0 \times 10^{-3} \text{ M})^x} = 2^x = 4$$

or $x = 2$, that is, the reaction is second order in NO. Experiments 2 and 3 indicate that doubling [H₂] at constant [NO] doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5} \text{ M/s}}{5.0 \times 10^{-5} \text{ M/s}} = 2 = \frac{k(10.0 \times 10^{-3} \text{ M})^x(4.0 \times 10^{-3} \text{ M})^y}{k(10.0 \times 10^{-3} \text{ M})^x(2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(4.0 \times 10^{-3} \text{ M})^y}{(2.0 \times 10^{-3} \text{ M})^y} = 2^y = 2$$

or $y = 1$, that is, the reaction is first order in H₂. Hence the rate law is given by

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

which shows that it is a (2 + 1) or third-order reaction overall.

- (b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

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

The data from experiment 2 give us

$$\begin{aligned} k &= \frac{5.0 \times 10^{-5} \text{ M/s}}{(10.0 \times 10^{-3} \text{ M})^2(2.0 \times 10^{-3} \text{ M})} \\ &= 2.5 \times 10^2/\text{M}^2 \cdot \text{s} \end{aligned}$$

- (c) Using the known rate constant and concentrations of NO and H₂, we write

$$\begin{aligned} \text{rate} &= (2.5 \times 10^2/\text{M}^2 \cdot \text{s})(12.0 \times 10^{-3} \text{ M})^2(6.0 \times 10^{-3} \text{ M}) \\ &= 2.2 \times 10^{-4} \text{ M/s} \end{aligned}$$

Practice Exercise The reaction of peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$) with iodide ion (I^-) is



From the following data collected at a certain temperature, determine the rate law and calculate the rate constant.

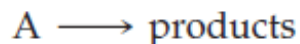
Experiment	$[\text{S}_2\text{O}_8^{2-}]$ (M)	$[\text{I}^-]$ (M)	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

The Relation Between Reactant Concentration and Time

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. The rate laws can also be used to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by first considering two of the most common rate laws—those applying to reactions that are first order overall and those applying to reactions that are second order overall.

Zero-Order Reactions

An overall **zero-order reaction** has a rate law in which the sum of the exponents, $m + n \dots$, is equal to 0. As an example, let's take a reaction in which a single reactant A decomposes to products.

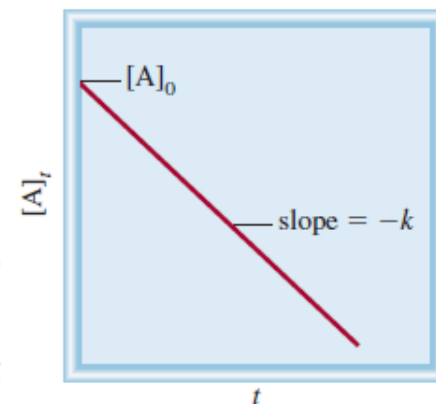


If the reaction is zero order, the rate law is

$$\text{rate of reaction} = k[A]^0 = k = \text{constant} \quad (20.9)$$

Other features of this zero-order reaction are:

- The concentration–time graph is a straight line with a *negative* slope (Fig. 20-3).
- The rate of reaction, which is equal to k and remains constant throughout the reaction, is the *negative* of the slope of this line.
- The units of k are the same as the units of the rate of a reaction: $\text{mol L}^{-1} (\text{time})^{-1}$, for example, $\text{mol L}^{-1} \text{s}^{-1}$ or M s^{-1} .

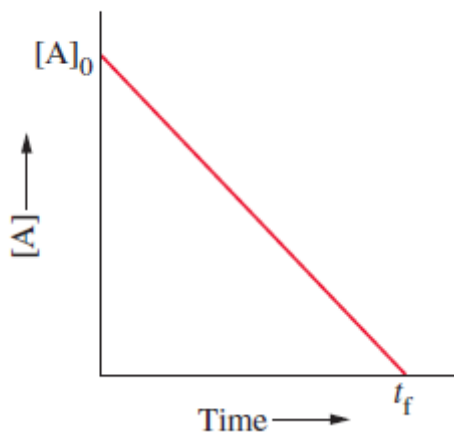


Equation (20.9) is the rate law for a zero-order reaction. Another useful equation, called an **integrated rate law**, expresses the concentration of a reactant as a function of time. This equation can be established rather easily from the graph in Figure 20-3. Let's start with the general equation for a straight line

$$y = mx + b$$

and substitute $y = [A]_t$ (the concentration of A at some time t); $x = t$ (time); $b = [A]_0$ (the initial concentration of A at time $t = 0$); and $m = -k$ (m , the slope of the straight line, is obtained as indicated in the caption to Figure 20-3).

$$[A]_t = -kt + [A]_0 \quad (20.10)$$

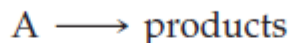


First-Order Reactions

An overall first-order reaction has a rate law in which the sum of the exponents, $m + n + \dots$, is equal to 1. A particularly common type of first-order reaction, and the only type we will consider, is one in which a single reactant decomposes into products.

An Integrated Rate Law for a First-Order Reaction

Let us begin our discussion of first-order reactions as we did zero-order reactions, by examining a hypothetical reaction



For a first-order reaction, the rate law is

$$\text{rate of reaction} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad (20.12)$$

We can obtain the *integrated* rate law for this first-order reaction by applying the calculus technique of *integration* to equation (20.12). The result of this derivation (shown in Are You Wondering 20-4) is

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \ln[A]_t = -kt + \ln[A]_0 \quad (20.13)$$

$[A]_t$ is the concentration of A at time t , $[A]_0$ is its concentration at $t = 0$, and k is the rate constant. Because the logarithms of numbers are dimensionless (have no units), the product $-k \times t$ must also be dimensionless. This means that the unit of k in a first-order reaction is $(\text{time})^{-1}$, such as s^{-1} or min^{-1} . Equation (20.13) is that of a straight line.

Equation of straight line

$$\underbrace{\ln[A]_t}_{y} = \underbrace{(-k)t}_{m \cdot x} + \underbrace{\ln[A]_0}_{b}$$

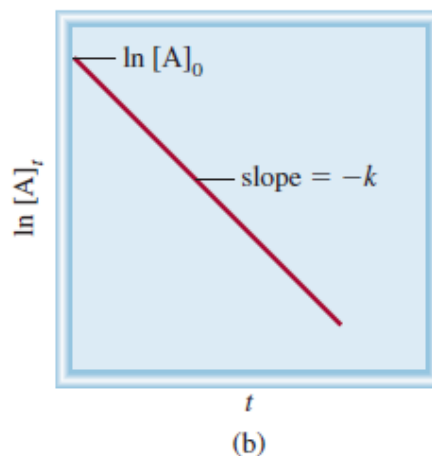
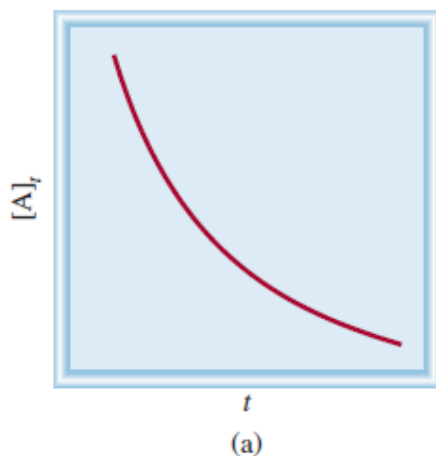


Figure 13.9 First-order reaction characteristics: (a) The exponential decrease of reactant concentration with time; (b) A plot of $\ln [A]_t$ versus t . The slope of the line is equal to $-k$.

$$\text{rate of reaction} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

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



20-4 ARE YOU WONDERING?

How do we obtain the integrated rate law for a first-order reaction?

If the reaction $A \longrightarrow$ products is first order, then the rate law is, in differential form, $d[A]/dt = -k[A]$.

Separation of the differentials leads to the expression $d[A]/[A] = -k dt$.

Integration of this expression between the limits $[A]_0$ at time $t = 0$ and $[A]_t$ at time t is indicated through the expression

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

The result of the integration is equation (20.13), the integrated rate law.

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

EXAMPLE 20-5 Using the Integrated Rate Law for a First-Order Reaction

$\text{H}_2\text{O}_2(\text{aq})$, initially at a concentration of 2.32 M, is allowed to decompose. What will $[\text{H}_2\text{O}_2]$ be at $t = 1200 \text{ s}$? Use $k = 7.30 \times 10^{-4} \text{ s}^{-1}$ for this first-order decomposition.

Analyze

We have values for three of the four quantities in equation (20.13):

$$\begin{array}{ll} k = 7.30 \times 10^{-4} \text{ s}^{-1} & t = 1200 \text{ s} \\ [\text{H}_2\text{O}_2]_0 = 2.32 \text{ M} & [\text{H}_2\text{O}_2]_t = ? \end{array}$$

Solve

We substitute into the expression

$$\begin{aligned} \ln[\text{H}_2\text{O}_2]_t &= -kt + \ln[\text{H}_2\text{O}_2]_0 \\ &= -(7.30 \times 10^{-4} \text{ s}^{-1} \times 1200 \text{ s}) + \ln(2.32) \\ &= -0.8760 + 0.8415 = -0.0345 \\ [\text{H}_2\text{O}_2]_t &= e^{-0.0345} = 0.966 \text{ M} \end{aligned}$$

EXAMPLE 20-6 **Expressing Fraction (or Percent) of Reactant Consumed
in a First-Order Reaction**

Use a value of $k = 7.30 \times 10^{-4} \text{ s}^{-1}$ for the first-order decomposition of $\text{H}_2\text{O}_2(\text{aq})$ to determine the percent H_2O_2 that has decomposed in the first 500.0 s after the reaction begins.

EXAMPLE 20-6 Expressing Fraction (or Percent) of Reactant Consumed in a First-Order Reaction

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Analyze

The ratio $[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_0$ represents the fractional part of the initial amount of H_2O_2 that remains *unreacted* at time t . Our problem is to evaluate this ratio at $t = 500.0$ s. This is done by making use of equation (20.13), which relates the concentration at $t = 0$ to the concentration at some other time.

Solve

Substituting into equation (20.13),

$$\ln \frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = -kt = -7.30 \times 10^{-4} \text{ s}^{-1} \times 500.0 \text{ s} = -0.365$$
$$\frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = e^{-0.365} = 0.694 \quad \text{and} \quad [\text{H}_2\text{O}_2]_t = 0.694[\text{H}_2\text{O}_2]_0$$

The fractional part of the H_2O_2 remaining is 0.694, or 69.4%. The percent of H_2O_2 that has decomposed is $100.0\% - 69.4\% = 30.6\%$.

The **half-life** of a reaction is the time required for one-half of a reactant to be consumed. It is the time during which the amount of reactant or its concentration decreases to one-half of its initial value. That is, at $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$. At this time, equation (20.13) takes the form

$$\ln \frac{[A]_t}{[A]_0} = \ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -\ln 2 = -k \times t_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (20.14)$$

EXAMPLE 13.6

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4} \text{ s}^{-1}$ at 700°C :



Calculate the half-life of the reaction in minutes.

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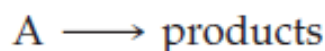
Strategy To calculate the half-life of a first-order reaction, we use Equation (13.6). A conversion is needed to express the half-life in minutes.

Solution For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (13.6)

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}} \\ &= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= \mathbf{21.5 \text{ min}} \end{aligned}$$

Second-Order Reactions

An overall second-order reaction has a rate law with the sum of the exponents, $m + n \dots$, equal to 2. As with zero- and first-order reactions, our discussion will be limited to reactions involving the decomposition of a single reactant



If the reaction is second order, then we can write

$$\text{rate of reaction} = k[A]^2 \quad (20.17)$$

Again, our primary interest will be in the integrated rate law that is derived from the rate law. For the reaction we are considering, the integrated rate law is

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (20.18)$$

Figure 20-6 is a plot of $1/[A]_t$ against time. The slope of the line is k , and the intercept is $1/[A]_0$. From the graph, we can see that the units of k must be the *reciprocal* of concentration divided by time: $M^{-1}/(\text{time})$ or $M^{-1}(\text{time})^{-1}$ —for example, $M^{-1} s^{-1}$ or $M^{-1} \text{min}^{-1}$. We can reach this same conclusion by determining the units of k that produce the required units for the rate of a reaction, that is, moles per liter per unit time. From equation (20.17):

$$\begin{array}{ll} \text{rate law:} & \text{rate of reaction} = k \times [A]^2 \\ \text{units:} & M \text{ time}^{-1} \quad M^{-1} \text{ time}^{-1} M^2 \end{array}$$

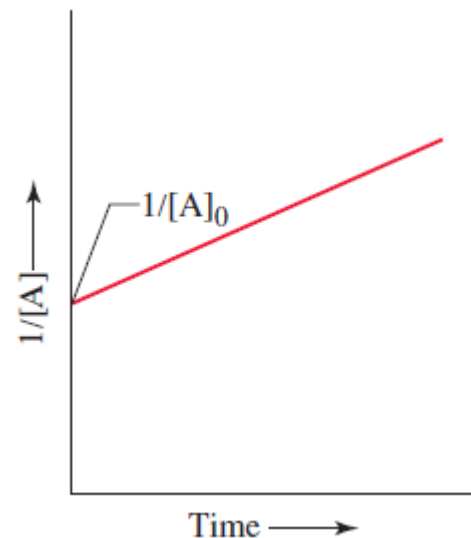
For the half-life of the second-order reaction $A \longrightarrow \text{products}$, we can substitute $t = t_{1/2}$ and $[A] = \frac{1}{2}[A]_0$ into equation (20.18).

$$\frac{1}{[A]_0/2} = kt_{1/2} + \frac{1}{[A]_0}; \quad \frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0} \quad (20.19a)$$

and

$$t_{1/2} = \frac{1}{k[A]_0} \quad (20.19b)$$

From equation (20.19a, b), we see that the half-life depends on both the rate constant *and* the initial concentration $[A]_0$. The *half-life is not constant*. Its value depends on the concentration of reactant at the start of each half-life interval. Because the starting concentration is always one-half that of the previous half-life, each successive half-life is twice as long as the one before it.



20-6 ARE YOU WONDERING?

How do we obtain the integrated rate law for the second-order reaction $A \longrightarrow \text{products}$?

In differential form, the rate law for a second-order reaction, $A \longrightarrow \text{products}$, is $d[A]/dt = -k[A]^2$.

Separation of the differentials leads to the expression $d[A]/[A]^2 = -k dt$.

Integration of this expression between the limits $[A]_0$ at time $t = 0$ and $[A]_t$ at time t is indicated through the expression

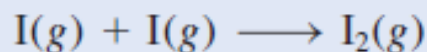
$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = - \int_0^t k dt$$

The result of the integration is equation (20.18), the integrated rate law.

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt \quad \text{or} \quad \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

EXAMPLE 13.7

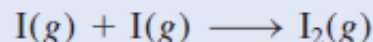
Iodine atoms combine to form molecular iodine in the gas phase



This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9 / M \cdot s$ at 23°C . (a) If the initial concentration of I was $0.086 M$, calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is $0.60 M$ and if it is $0.42 M$.

EXAMPLE 13.7

Iodine atoms combine to form molecular iodine in the gas phase



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Strategy (a) The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (13.7). (b) We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (13.8).

Solution (a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (13.7)

$$\begin{aligned}\frac{1}{[\text{A}]_t} &= kt + \frac{1}{[\text{A}]_0} \\ \frac{1}{[\text{A}]_t} &= (7.0 \times 10^9/M \cdot \text{s}) \left(2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.086 M}\end{aligned}$$

where $[\text{A}]_t$ is the concentration at $t = 2.0 \text{ min}$. Solving the equation, we get

$$[\text{A}]_t = 1.2 \times 10^{-12} M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that practically all the I atoms combine after only 2.0 min of reaction time.

(b) We need Equation (13.8) for this part.

For $[I]_0 = 0.60 M$

$$\begin{aligned}t_{\frac{1}{2}} &= \frac{1}{k[A]_0} \\&= \frac{1}{(7.0 \times 10^9 / M \cdot s)(0.60 M)} \\&= 2.4 \times 10^{-10} \text{ s}\end{aligned}$$

For $[I]_0 = 0.42 M$

$$\begin{aligned}t_{\frac{1}{2}} &= \frac{1}{(7.0 \times 10^9 / M \cdot s)(0.42 M)} \\&= 3.4 \times 10^{-10} \text{ s}\end{aligned}$$

The Effect of Temperature on Reaction Rates

From practical experience, we expect chemical reactions to go faster at higher temperatures. To speed up the biochemical reactions involved in cooking, we raise the temperature, and to slow down other reactions, we lower the temperature—as in refrigerating milk to prevent it from souring.

In 1889, Svante Arrhenius demonstrated that the rate constants of many chemical reactions vary with temperature in accordance with the expression

$$k = Ae^{-E_a/RT} \quad (20.21)$$

By taking the natural logarithm of both sides of this equation, we obtain the following expression.

$$\ln k = -\frac{E_a}{RT} + \ln A$$

We can also derive a useful variation of the equation by writing it twice—each time for a different value of k and the corresponding temperature—and then eliminating the constant $\ln A$. The result, also called the Arrhenius equation, is

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (20.22)$$

In equation (20.22)* T_2 and T_1 are two Kelvin temperatures; k_2 and k_1 are the rate constants at these temperatures; and E_a is the activation energy in joules per mole. R is the gas constant expressed as $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

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

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

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

EXAMPLE 13.9

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

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$$\begin{array}{ll} k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} & k_2 = ? \\ T_1 = 298 \text{ K} & T_2 = 350 \text{ K} \end{array}$$

Substituting in Equation (13.14),

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{298 \text{ K} - 350 \text{ K}}{(298 \text{ K})(350 \text{ K})} \right]$$

We convert E_a to units of J/mol to match the units of R . Solving the equation gives

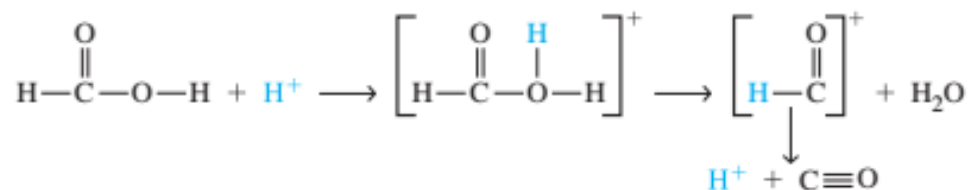
$$\begin{aligned} \ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} &= -3.01 \\ \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} &= e^{-3.01} = 0.0493 \\ k_2 &= 0.702 \text{ s}^{-1} \end{aligned}$$

Catalysis

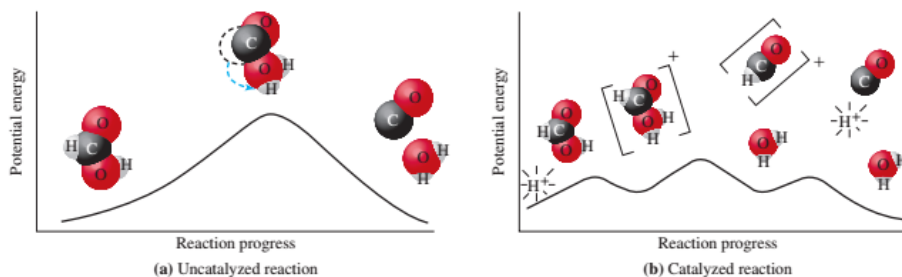
A reaction can generally be made to go faster by increasing the temperature. Another way to speed up a reaction is to use a catalyst. A catalyst provides an alternative reaction pathway of lower activation energy. The catalyst participates in a chemical reaction but does not itself undergo a permanent change. As a result, the formula of a catalyst does not appear in the overall chemical equation (its formula is generally placed over the reaction arrow).

Homogeneous Catalysis

Figure 20-17 shows reaction profiles for the decomposition of formic acid (HCOOH). In the uncatalyzed reaction, a H atom must be transferred from one part of the formic acid molecule to another, shown by the blue, dotted arrow. Then a C—O bond breaks. Because the energy requirement for this atom transfer is high, the activation energy is high and the reaction is slow. In the acid-catalyzed decomposition of formic acid, a hydrogen ion from solution attaches itself to the O atom that is singly bonded to the C atom to form $[\text{HCOOH}_2]^+$. The C—O bond breaks, and a H atom attached to a carbon atom in the intermediate species $[\text{HCO}]^+$ is released to the solution as H^+ .



This catalyzed reaction pathway does not require a H atom to be transferred within the formic acid molecule. It has a lower activation energy than does the uncatalyzed reaction and proceeds at a faster rate. Because the reactants and products of this reaction are all present throughout the solution, or homogeneous mixture, this type of catalysis is called **homogeneous catalysis**.



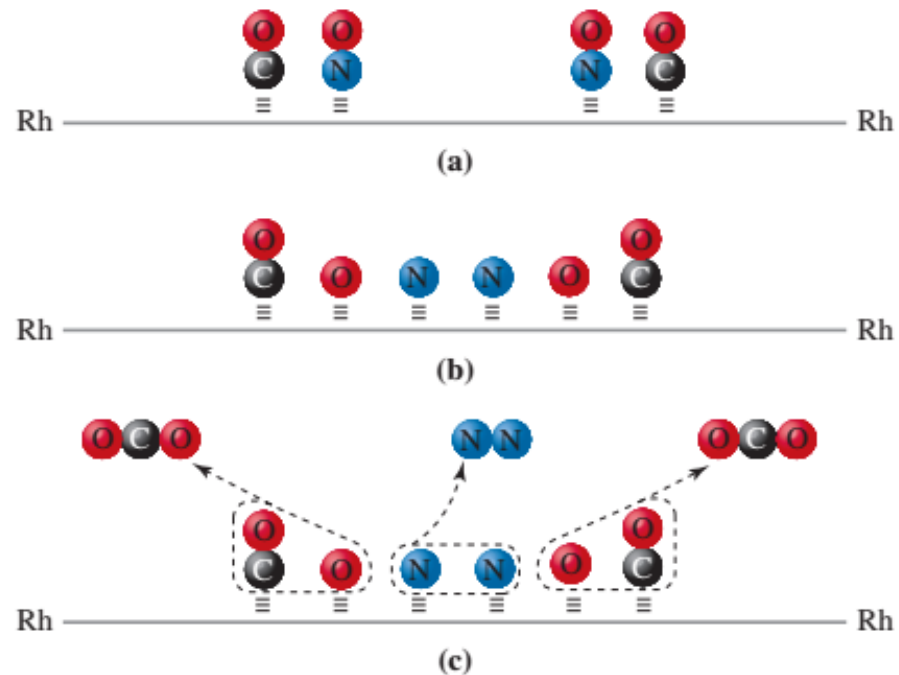
▲ FIGURE 20-17
An example of homogeneous catalysis
The activation energy is lowered in the presence of H^+ , a catalyst for the decomposition of HCOOH.

Heterogeneous Catalysis

Many reactions can be catalyzed by allowing them to occur on an appropriate solid surface. Essential reaction intermediates are found on the surface. This type of catalysis is called **heterogeneous catalysis** because the catalyst is present in a different phase of matter than are the reactants and products. Catalytic activity is associated with many transition elements and their compounds. The precise mechanism of heterogeneous catalysis is not totally understood, but in many cases the availability of electrons in *d* orbitals in surface atoms may play a role.

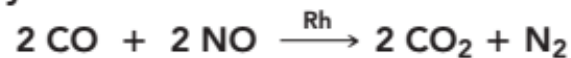
A key feature of heterogeneous catalysis is that reactants from a gaseous or solution phase are adsorbed, or attached, to the surface of the catalyst. Not all surface atoms are equally effective for catalysis; those that are effective are called **active sites**. Basically, heterogeneous catalysis involves (1) *adsorption* of reactants; (2) *diffusion* of reactants along the surface; (3) *reaction* at an active site to form adsorbed product; and (4) *desorption* of the product.

An interesting reaction is the oxidation of CO to CO₂ and the reduction of NO to N₂ in automotive exhaust gases as a smog-control measure. Figure 20-18 shows how this reaction is thought to occur on the surface of rhodium metal in a catalytic converter. In general, the reaction profile for a surface-catalyzed reaction resembles that shown in Figure 20-19.



▲ FIGURE 20-18

Heterogeneous catalysis in the reaction



(a) Molecules of CO and NO are adsorbed on the rhodium surface. (b) The adsorbed NO molecules dissociate into adsorbed N and O atoms. (c) Adsorbed CO molecules and O atoms combine to form CO₂ molecules, which desorb into the gaseous state. Two N atoms combine and are desorbed as a N₂ molecule.

Reaction Kinetics: A Summary

Let's pause briefly to review what we have learned about rates of reaction, rate constants, and reaction orders. Although a problem often can be solved in several different ways, these approaches are generally most direct.

1. To calculate a rate of reaction when the rate law is known, use this expression: rate of reaction = $k[A]^m[B]^n \dots$
2. To determine a rate of reaction when the rate law is not given, use
 - the slope of an appropriate tangent line to the graph of $[A]$ versus t
 - the expression $-\Delta[A]/\Delta t$, with a short time interval Δt
3. To determine the order of a reaction, use one of the following methods.
 - Use the method of initial rates if the experimental data are given in the form of reaction rates at different initial concentrations.
 - Find the graph of rate data that yields a straight line (Table 20.5).
 - Test for the constancy of the half-life (good only for a first-order reaction).
 - Substitute rate data into integrated rate laws to find the one that gives a constant value of k .
4. To find the rate constant k for a reaction, use one of the following methods.
 - Obtain k from the slope of a straight-line graph.
 - Substitute concentration–time data into the appropriate integrated rate law.
 - Obtain k from the half-life of the reaction (good only for a first-order reaction).
5. To relate reactant concentrations and times, use the appropriate integrated rate law after first determining k .

TABLE 20.5 Reaction Kinetics: A Summary for the Hypothetical Reaction $a A \longrightarrow \text{Products}$

Order	Rate Law ^a	Integrated Rate Equation ^b	Straight Line	$k =$	Units of k	Half-Life ^b
0	rate = k	$[A]_t = -akt + [A]_0$	$[A]$ v. time	$-\frac{1}{a} \times \text{slope}$	$\text{mol L}^{-1} \text{s}^{-1}$	$\frac{[A]_0}{2ak}$
1	rate = $k[A]$	$\ln[A]_t = -akt + \ln[A]_0$	$\ln[A]$ v. time	$-\frac{1}{a} \times \text{slope}$	s^{-1}	$\frac{0.693}{ak}$
2	rate = $k[A]^2$	$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ v. time	$\frac{1}{a} \times \text{slope}$	$\text{L mol}^{-1} \text{s}^{-1}$	$\frac{1}{ak[A]_0}$

$$^a \text{rate} = -\left(\frac{1}{a}\right) \frac{\Delta[A]}{\Delta t}$$

^bTo obtain the expressions for $a A \longrightarrow \text{products}$, we replace k with ak in the expressions given in the text for $A \longrightarrow \text{products}$.

1. Rate laws are always determined experimentally. From the concentrations of reactants and the initial reaction rates we can determine the reaction order and then the rate constant of the reaction.
2. Reaction order is always defined in terms of reactant (not product) concentrations.
3. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.