

18.2: Rate Laws

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \quad (18.2.1)$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k , a positive value.

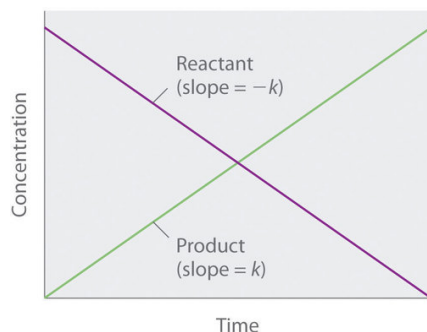


Figure 18.2.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k . The product is in green and has a slope of positive k .

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \quad (18.2.2)$$

where $[A]_0$ is the initial concentration of reactant A . Equation 18.2.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the

decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2 , which occurs at temperatures ranging from 200°C to 400°C :



Without a platinum surface, the reaction requires temperatures greater than 700°C , but between 200°C and 400°C , the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O , where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2} \left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t} \right) = \frac{1}{2} \left(\frac{\Delta[\text{N}_2]}{\Delta t} \right) = \frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{N}_2\text{O}]^0 = k \quad (18.2.4)$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 18.2.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

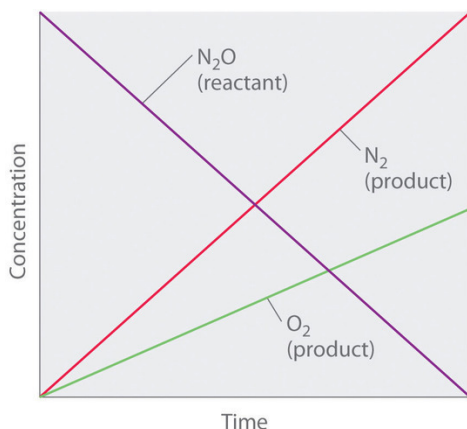


Figure 18.2.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N_2O is the reactant is graphed in purple. O_2 is one of the products and is graphed in green. The second product is N_2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is



Figure 18.2.2

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure 18.2.3a). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 18.2.3).

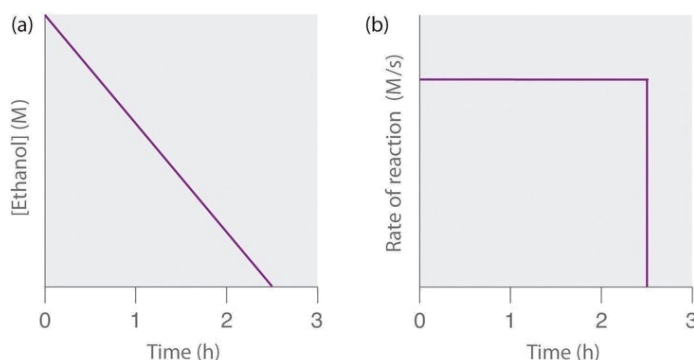


Figure 18.2.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form $A \rightarrow \text{products}$. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad (18.2.5)$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \quad (18.2.6)$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 18.2.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 18.2.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t :

$$\ln[A] = \ln[A]_0 - kt \quad (18.2.7)$$

Because Equation 18.2.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 18.2.5) or the integrated rate law (Equation 18.2.7) can be used to determine whether a particular reaction is first order.

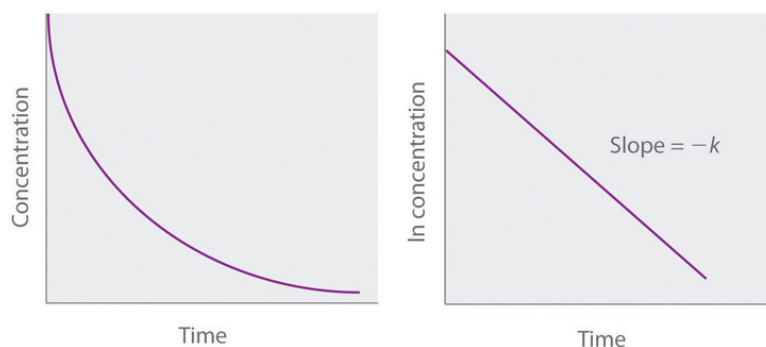


Figure 18.2.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

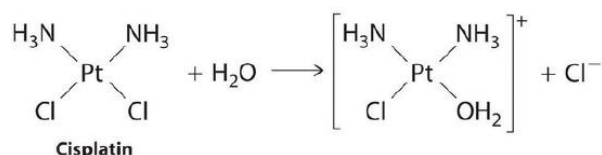


Figure 18.2.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 18.2.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 18.2.4 have been studied extensively to find ways of maximizing the concentration of the active species.

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 18.2.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 18.2.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	[Cisplatin] ₀ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 18.2.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 2.0$] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5} \text{ M/min}) \div (9.0 \times 10^{-6} \text{ M/min}) = 5.0$] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is $\text{rate} = k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 18.2.1. For example, substituting the values for Experiment 3 into Equation 18.2.5,

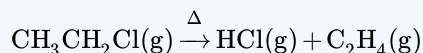
$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

✓ Example 18.2.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:



Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[\text{CH}_3\text{CH}_2\text{Cl}]_0 \text{ (M)}$	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

- Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
- Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[\text{CH}_3\text{CH}_2\text{Cl}]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[\text{CH}_3\text{CH}_2\text{Cl}]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is $\text{rate} = k[\text{CH}_3\text{CH}_2\text{Cl}]$.

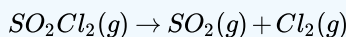
C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})$$

$$1.6 \times 10^{-6} \text{ s}^{-1} = k$$

? Exercise 18.2.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:



Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	[SO ₂ Cl ₂] ₀ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure 18.2.6a shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

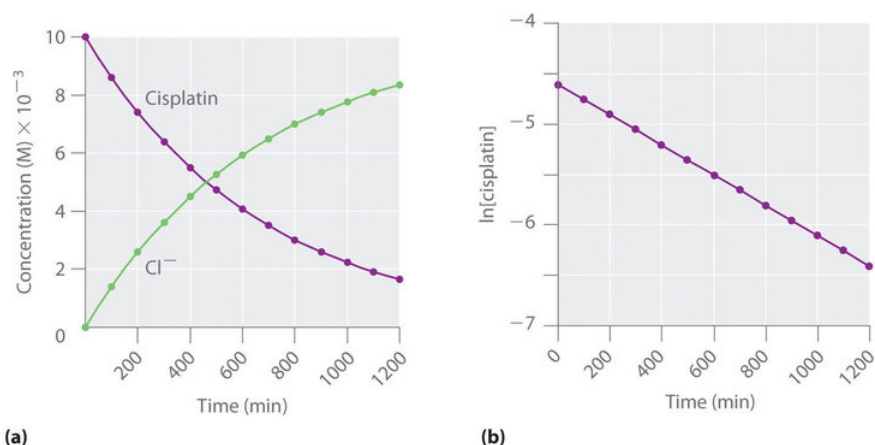


Figure 18.2.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 18.2.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 18.2.6 for $t = 100 \text{ min}$ ($[\text{cisplatin}] = 0.0086 \text{ M}$) and $t = 1000 \text{ min}$ ($[\text{cisplatin}] = 0.0022 \text{ M}$),

$$\begin{aligned} \text{slope} &= \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000 \text{ min} - 100 \text{ min}} \\ -k &= \frac{\ln 0.0022 - \ln 0.0086}{1000 \text{ min} - 100 \text{ min}} = \frac{-6.12 - (-4.76)}{900 \text{ min}} = -1.51 \times 10^{-3} \text{ min}^{-1} \\ k &= 1.5 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 18.2.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



Video Example Using the First-Order Integrated Rate Law Equation:

[Example Using the First-Order Integrated Rate Law Equation](#)(opens in new window) [youtu.be]

✓ Example 18.2.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6} \text{ s}^{-1}$) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

- Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ($[A]$) at the given time t .
- Given a concentration $[A]$, solve the integrated rate law for time t .

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 18.2.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6} \text{ s}^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time t . Substituting the known values into the integrated rate law,

$$\begin{aligned} [\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= [\text{CH}_3\text{CH}_2\text{Cl}]_0 e^{-kt} \\ &= 0.0200 \text{ M} (e^{-(1.6 \times 10^{-6} \text{ s}^{-1})(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min})}) \\ &= 0.0189 \text{ M} \end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 18.2.7):

$$\begin{aligned} \ln[\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6} \text{ s}^{-1})(10 \text{ h})(60 \text{ min/h})(60 \text{ s/min}) \\ &= -3.912 - 0.0576 = -3.970 \\ [\text{CH}_3\text{CH}_2\text{Cl}]_{10 \text{ h}} &= e^{-3.970} \text{ M} \\ &= 0.0189 \text{ M} \end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t . Equation 18.2.7 gives the following:

$$\ln[\text{CH}_3\text{CH}_2\text{Cl}]_t = \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - kt$$

$$kt = \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - \ln[\text{CH}_3\text{CH}_2\text{Cl}]_t = \ln \frac{[\text{CH}_3\text{CH}_2\text{Cl}]_0}{[\text{CH}_3\text{CH}_2\text{Cl}]_t}$$

$$t = \frac{1}{k} \left(\ln \frac{[\text{CH}_3\text{CH}_2\text{Cl}]_0}{[\text{CH}_3\text{CH}_2\text{Cl}]_t} \right) = \frac{1}{1.6 \times 10^{-6} \text{ s}^{-1}} \left(\ln \frac{0.0200 \text{ M}}{0.0050 \text{ M}} \right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6} \text{ s}^{-1}} = 8.7 \times 10^5 \text{ s} = 240 \text{ h} = 2.4 \times 10^2 \text{ h}$$

? Exercise 18.2.2

In the exercise in Example 18.2.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C .

- Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C .
- How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

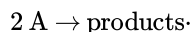
0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form



A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form $\text{A} + \text{B} \rightarrow \text{products}$. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which $2\text{A} \rightarrow \text{products}$ is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{2\Delta t} = k[\text{A}]^2 \quad (18.2.8)$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($\text{M}^{-1}\cdot\text{s}^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as $\text{L}(\text{mol}\cdot\text{s})$.

For the reaction $2\text{A} \rightarrow \text{products}$, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt \quad (18.2.9)$$

Because Equation 18.2.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[\text{A}]$ and $b = 1/[\text{A}]_0$, a plot of $1/[\text{A}]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[\text{A}]_0$.

Second-order reactions generally have the form $2\text{A} \rightarrow \text{products}$ or $\text{A} + \text{B} \rightarrow \text{products}$.



Video Discussing the Second-Order Integrated Rate Law Equation: [Second-Order Integrated Rate Law Equation](#)(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2 . Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

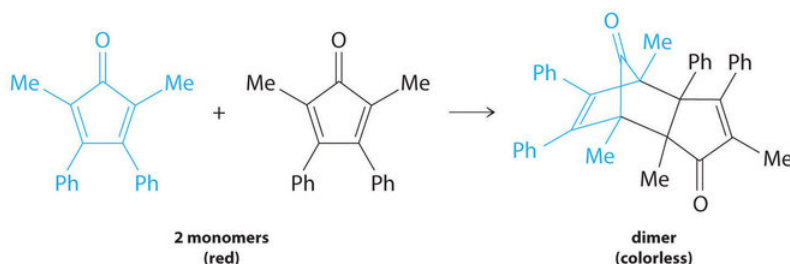


Figure 18.2.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is $2\text{A} \rightarrow \text{product}$. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 18.2.8) or the integrated rate law (Equation 18.2.9).

Table 18.2.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 18.2.2. From the data, we see that the reaction rate is not independent of the monomer

concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5} \text{ M/min}}{1.8 \times 10^{-5} \text{ M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3} \text{ M}}{2.0 \times 10^{-3} \text{ M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 18.2.8 and the data from any row in Table 18.2.2 we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \quad (18.2.10)$$

$$8.0 \times 10^{-5} \text{ M/min} = k(4.4 \times 10^{-3} \text{ M})^2 \quad (18.2.11)$$

$$4.1 \text{ M}^{-1} \cdot \text{min}^{-1} = k \quad (18.2.12)$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 18.2.8a. The measurements show that the concentration of the monomer (initially $5.4 \times 10^{-3} \text{ M}$) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of $1/[\text{monomer}]$ versus t should be a straight line, as shown in Figure 18.2.8b. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1 \text{ M}^{-1} \cdot \text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

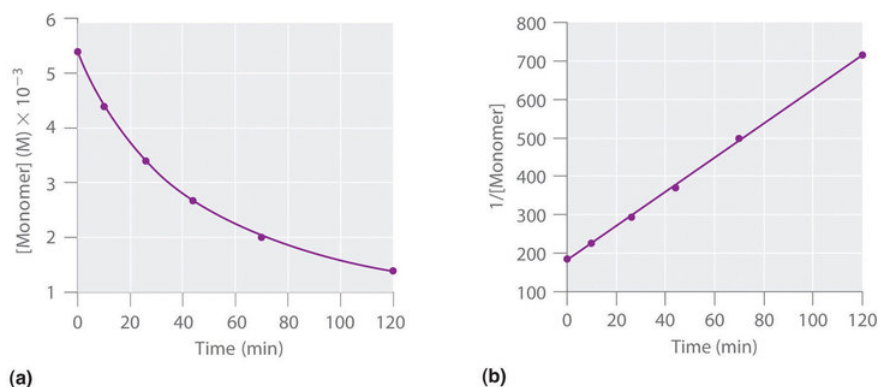
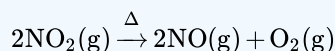


Figure 18.2.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) $1/[\text{monomer}]$ versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

✓ Example 18.2.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.



Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO_2

Experiment	$[\text{NO}_2]_0 (\text{M})$	Initial Rate (M/s)
1	0.015	1.22×10^{-4}

Experiment	[NO ₂] ₀ (M)	Initial Rate (M/s)
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

- From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
- Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

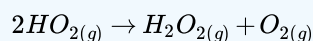
A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO₂ concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to [NO₂]². Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to [NO₂]². This behavior is characteristic of a second-order reaction.

B We have rate = $k[\text{NO}_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned}\text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5} \text{ M/s} &= k(0.010 \text{ M})^2 \\ 0.54 \text{ M}^{-1} \cdot \text{s}^{-1} &= k\end{aligned}$$

? Exercise 18.2.3

When the highly reactive species HO₂ forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:



The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	[HO ₂] ₀ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO₂; $k = 1.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of $1/(\text{reactant concentration})$ versus time is linear, then the reaction is second order.

✓ Example 18.2.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C , what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

- Given k , t , and $[\text{A}]_0$, use the integrated rate law for a second-order reaction to calculate $[\text{A}]$.
- Setting $[\text{A}]$ equal to 1/10 of $[\text{A}]_0$, use the same equation to solve for t .

Solution

A We know k and $[\text{NO}_2]_0$, and we are asked to determine $[\text{NO}_2]$ at $t = 1 \text{ h}$ (3600 s). Substituting the appropriate values into Equation 18.2.9,

$$\begin{aligned}\frac{1}{[\text{NO}_2]_{3600}} &= \frac{1}{[\text{NO}_2]_0} + kt \\ &= \frac{1}{0.056 \text{ M}} + [(0.54 \text{ M}^{-1} \cdot \text{s}^{-1})(3600 \text{ s})] \\ &= 2.0 \times 10^3 \text{ M}^{-1}\end{aligned}$$

Thus $[\text{NO}_2]_{3600} = 5.1 \times 10^{-4} \text{ M}$.

B In this case, we know k and $[\text{NO}_2]_0$, and we are asked to calculate at what time $[\text{NO}_2] = 0.1[\text{NO}_2]_0 = 0.1(0.056 \text{ M}) = 0.0056 \text{ M}$. To do this, we solve Equation 18.2.9 for t , using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[\text{NO}_2]) - (1/[\text{NO}_2]_0)}{k} \\ &= \frac{(1/0.0056 \text{ M}) - (1/0.056 \text{ M})}{0.54 \text{ M}^{-1} \cdot \text{s}^{-1}} \\ &= 3.0 \times 10^2 \text{ s} = 5.0 \text{ min}\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

? Exercise 18.2.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2 , calculate the concentration of HO_2 that remains after 1.0 h at 25°C . How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated in the exercise in Example 18.2.3

Answer

$$2.0 \times 10^{-13} \text{ M}; 6.4 \times 10^{-6} \text{ s}$$

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow \text{products}$, in which the reaction is first order in A and first order in B . The differential rate law for this reaction is as follows:

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

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k \\ [A] &= [A]_0 - kt\end{aligned}$$

- **first-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k[A] \\ [A] &= [A]_0 e^{-kt} \\ \ln[A] &= \ln[A]_0 - kt\end{aligned}$$

- **second-order reaction:**

$$\begin{aligned}\text{rate} &= -\frac{\Delta[A]}{\Delta t} = k[A]^2 \\ \frac{1}{[A]} &= \frac{1}{[A]_0} + kt\end{aligned}$$

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