

Chapter 7 : Chemical kinetics

Chapter 15: Chemical kinetics

15.1 Reaction Rates

15.2 Rate Laws: An Introduction

**15.3 Determining the Form of
the Rate Law**

15.4 The Integrated Rate Law

15.5 Rate Laws: A Summary

**15.8 A Model for Chemical
Kinetics**

15.9 Catalysis

Chemical Kinetics is the study of the speed or rate at which chemical reactions occur.

Consider the decomposition of nitrogen dioxide to nitric oxide and oxygen:



We start with a flask containing NO_2 at room temperature and quickly heat it to 300°C . The decomposition starts.

We then measure the concentrations of NO_2 , NO , and O_2 over time as the reaction proceeds.

Table 15.1

Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(g) \longrightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

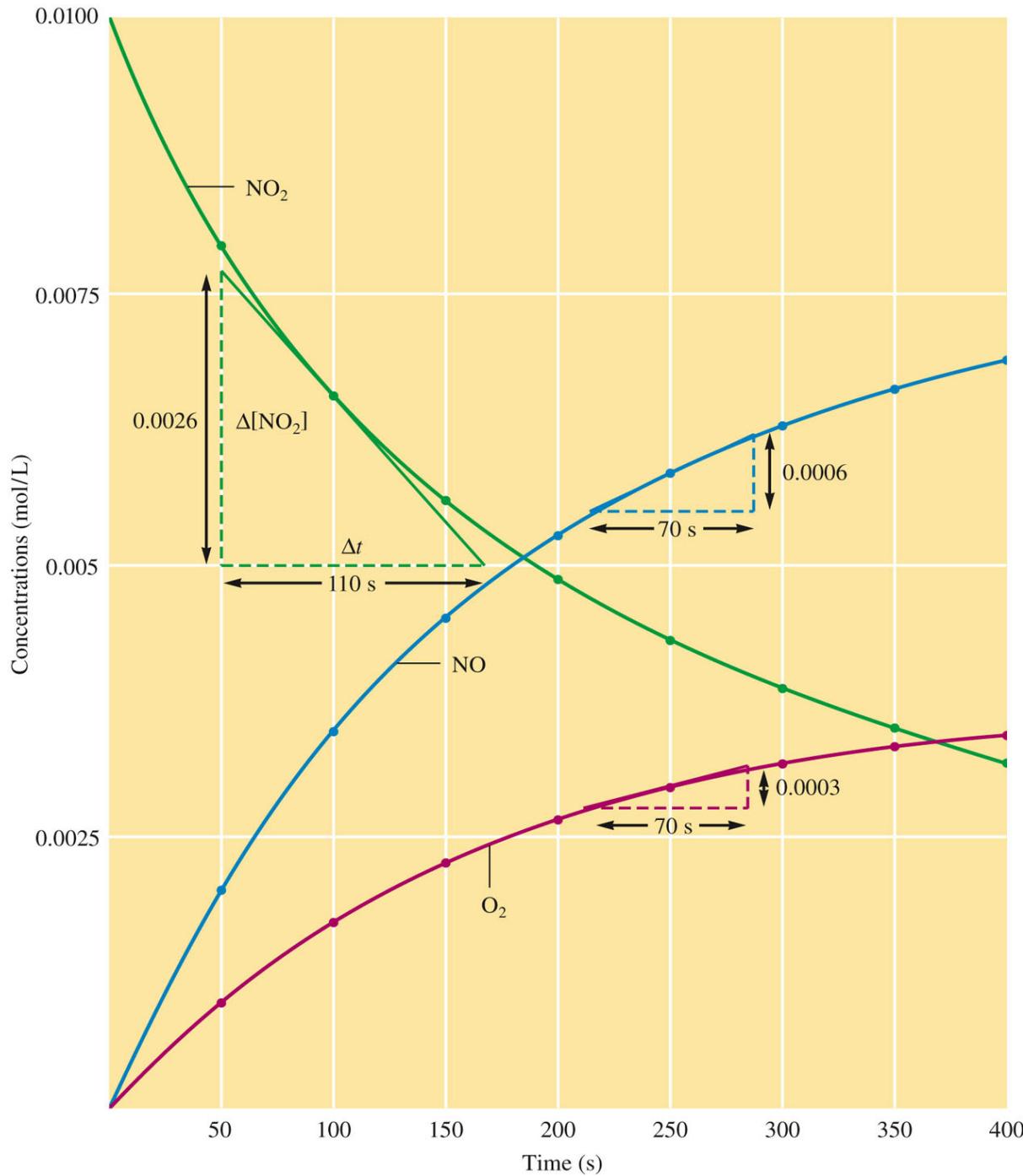


Figure 15.1
Starting with pure nitrogen dioxide at 300°C, the concentrations of nitrogen dioxide, nitric oxide, and oxygen are plotted versus time.

The **reaction rate** of a chemical reaction is the change in concentration of a reactant or product per unit time (M/s).

$$\begin{aligned}\text{Rate} &= \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1} \\ &= \frac{\Delta[A]}{\Delta t}\end{aligned}$$

Now let's calculate the average rate at which the concentration of NO_2 changes over the first 50 seconds of the reaction, using the data given in Table 15.1.

$$\begin{aligned}
 \text{Rate} &= \frac{\Delta[\text{NO}_2]}{\Delta t} \\
 &= \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50 \text{ s} - 0 \text{ s}} \\
 &= \frac{0.0079 \text{ mol/L} - 0.0100 \text{ mol/L}}{50 \text{ s}} \\
 &= -4.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}
 \end{aligned}$$

Note that since the concentration of NO_2 decreases with time, $\Delta[\text{NO}_2]$ is a negative quantity. Because it is customary to work with *positive* reaction rates, we define the rate of this particular reaction as

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Since the concentrations of reactants always decrease with time, any rate expression involving a reactant will include a negative sign. The average rate of this reaction from 0 to 50 seconds is then

$$\begin{aligned}
 \text{Rate} &= -\frac{\Delta[\text{NO}_2]}{\Delta t} \\
 &= -(-4.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}) \\
 &= 4.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}
 \end{aligned}$$

Table 15.2

Average Rate (in $\text{mol L}^{-1} \text{ s}^{-1}$)
of Decomposition of Nitrogen
Dioxide as a Function of Time

$-\frac{\Delta[\text{NO}_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

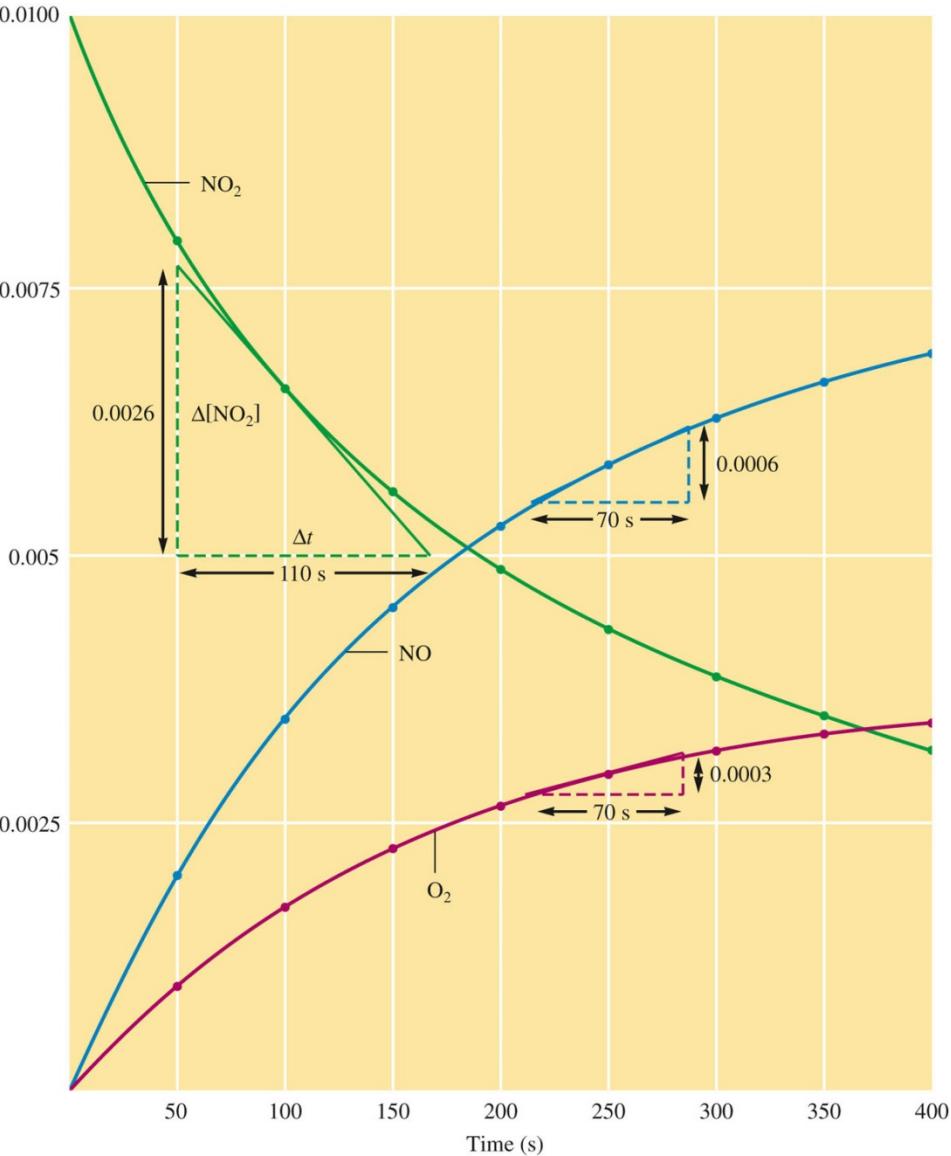
Note: The *rate* decreases with time.

Table 15.2 shows average rates over 50-second time intervals. Note that the rate is not constant but decreases with time.

The value of the rate at a particular time (the **instantaneous rate**) can be obtained by computing the slope of a line tangent to the curve at that point.

Figure 15.1 shows a tangent drawn at $t = 100$ seconds. The *slope* of this line gives the instantaneous rate at $t = 100$ seconds:

$$\begin{aligned}\text{Rate} &= -(\text{slope of the tangent line}) \\ &= 2.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$



The rate can also be defined in terms of the products.

The coefficients in the balanced equation must be taken into account, because the stoichiometry determines the relative rates of the consumption of reactants and the generation of products.



$$\boxed{\text{Rate of consumption of } \text{NO}_2} = \boxed{\text{rate of production of } \text{NO}} = \boxed{2(\text{rate of production of } \text{O}_2)}$$

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

A **rate law** is an expression which shows how the rate depends on the concentrations of reactants (under conditions that the reverse reaction can be neglected).



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

k: rate constant

n: order of the reaction

Both ***k*** and ***n*** must be determined by experiment.

The order of a reactant can be positive or negative and can be an integer or a fraction.

*Note that the value of the exponent ***n*** cannot be written from the balanced equation.*

Types of rate laws

The **differential rate law** (often simply called rate law) expresses how the rate of a reaction depends on concentration.

The **integrated rate law** expresses how the concentrations of species in the reaction depend on time.

A given differential rate law is always related to a certain type of integrated rate law, and vice versa.

15.3 | Determining the Form of the Rate Law

Method of initial rates

The initial rate of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$).

Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run.

The results are then compared to see how the initial rate depends on the initial concentrations.

Consider the following reaction:

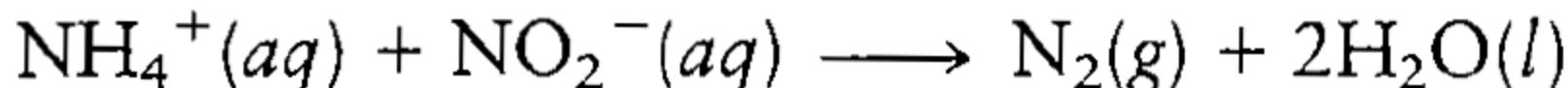


Table 15.4

Initial Rates from Three Experiments for the Reaction $\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate ($\text{mol L}^{-1} \text{s}^{-1}$)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

The general form of the rate law is:

$$\text{Rate} = -\frac{d[\text{NH}_4^+]}{dt} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

$$\text{Rate} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

we have, for Experiment 1,

$$\text{Rate} = 1.35 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m$$

and for Experiment 2,

$$\text{Rate} = 2.70 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m$$

The ratio of these rates is

$$\begin{aligned}\frac{\text{Rate 2}}{\text{Rate 1}} &= \frac{\underline{2.70 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}}{\underline{1.35 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}} = \frac{\cancel{k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m}}{\cancel{k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m}} \\ &= \frac{\underline{(0.010 \text{ mol/L})^m}}{\underline{(0.0050 \text{ mol/L})^m}} \\ &= (2.0)^m\end{aligned}$$

Thus

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 2.00 = (2.0)^m$$

which means the value of m is 1. The rate law for this reaction is first order in the reactant NO_2^- .

A similar analysis of the results for Experiments 2 and 3 yields the following ratio:

$$\begin{aligned}\frac{\text{Rate 3}}{\text{Rate 2}} &= \frac{5.40 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}{2.70 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{(0.200 \text{ mol/L})^n}{(0.100 \text{ mol/L})^n} \\ &= 2.00 = \left(\frac{0.200}{0.100}\right)^n = (2.00)^n\end{aligned}$$

The value of n is also 1.

We have shown that the values of n and m are both 1. Therefore, the rate law is

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

The **overall reaction order** is the sum of n and m . For this reaction, $n + m = 2$. The reaction is second order overall.

The value of the rate constant (k) can now be calculated by using the results of *any* of the three experiments shown in Table 15.4. From the data for Experiment 1 we know that

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

$$1.35 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.100 \text{ mol/L})(0.0050 \text{ mol/L})$$

Then

$$k = \frac{1.35 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.100 \text{ mol/L})(0.0050 \text{ mol/L})} = 2.7 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$$

Example 15.1

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the following equation:

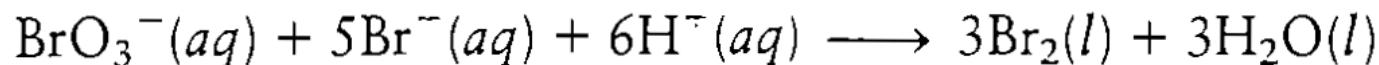
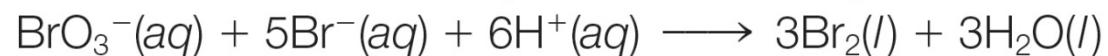


Table 15.5 gives the results of four experiments involving this reaction. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

Table 15.5

The Results from Four Experiments to Study the Reaction



Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol L ⁻¹ s ⁻¹)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Solution

The general form of the rate law for this reaction is

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

We can determine the values of n , m , and p by comparing the rates from the various experiments. To determine the value of n , we use the results from Experiments 1 and 2, in which only $[\text{BrO}_3^-]$ changes:

$$\begin{aligned}\frac{\text{Rate 2}}{\text{Rate 1}} &= \frac{1.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{8.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}} \\ &= \frac{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 2.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}} \right)^n = (2.0)^n\end{aligned}$$

Thus n is equal to 1.

To determine the value of m , we use the results from Experiments 2 and 3, in which only $[\text{Br}^-]$ changes:

$$\begin{aligned}\frac{\text{Rate 3}}{\text{Rate 2}} &= \frac{3.2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{1.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}} \\ &= \frac{k(0.20 \text{ mol/L})^n(0.20 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 2.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}} \right)^m = (2.0)^m\end{aligned}$$

Thus m is equal to 1.

To determine the value of p , we use the results from Experiments 1 and 4, in which $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ are constant but $[\text{H}^+]$ changes:

$$\begin{aligned}\frac{\text{Rate 4}}{\text{Rate 1}} &= \frac{3.2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{8.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}} \\ &= \frac{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.20 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 4.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}} \right)^p \\ 4.0 &= (2.0)^p = (2.0)^2\end{aligned}$$

Thus p is equal to 2.

The rate of this reaction is first order in BrO_3^- and Br^- and second order in H^+ . The overall reaction order is $n + m + p = 4$.

The rate law can now be written:

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

The value of the rate constant k can be calculated from the results of any of the four experiments. For Experiment 1 the initial rate is $8.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, and $[\text{BrO}_3^-] = 0.100 \text{ M}$, $[\text{Br}^-] = 0.100 \text{ M}$, and $[\text{H}^+] = 0.100 \text{ M}$. Using these values in the rate law gives

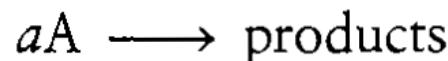
$$8.00 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2$$

$$8.00 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = k(1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4)$$

$$\begin{aligned} k &= \frac{8.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4} \\ &= 8.00 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1} \end{aligned}$$

Check: Verify that the same value of k can be obtained from the results of the other experiments.

We will proceed by first looking at reactions involving a single reactant:



all of which have a rate law of the form

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

We will develop the integrated rate laws individually for the cases $n = 1$ (first order), $n = 2$ (second order), and $n = 0$ (zero order).

First-Order Rate Laws

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

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

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

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

The reaction is first order if a plot of $\ln[A]$ versus t is a straight line.

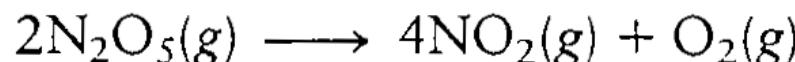
$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$[A] = [A]_0 e^{-kt}$$

$[A]$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t = 0$

Example 15.2

The decomposition of N_2O_5 in the gas phase was studied at constant temperature:



The following results were collected:

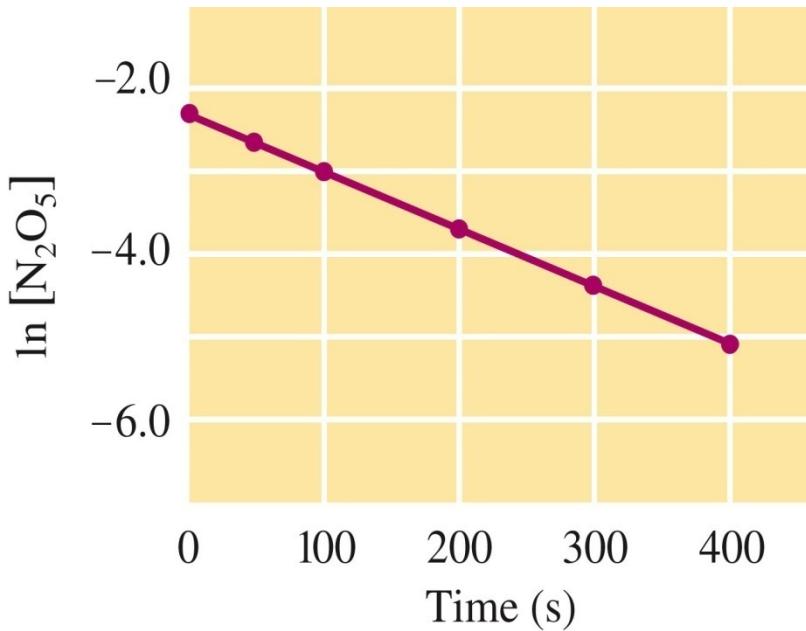
$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Using these data, verify that the rate law is first order in $[\text{N}_2\text{O}_5]$, and calculate the value of the rate constant, where the rate = $-d[\text{N}_2\text{O}_5]/dt$.

Solution

We can verify that the rate law is first order in $[N_2O_5]$ by constructing a plot of $\ln[N_2O_5]$ versus time. The values of $\ln[N_2O_5]$ at various times are given below, and the plot of $\ln[N_2O_5]$ versus time is shown in Fig. 15.3.

$\ln[N_2O_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400



The plot is a straight line, confirming that the reaction is first order in N_2O_5 , since it follows the equation $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$.

Since the reaction is first order, the slope of the line equals $-k$. In this case

$$k = -(\text{slope}) = 6.93 \times 10^{-3} \text{ s}^{-1}$$

Example 15.3

Using the data given in Example 15.2, calculate $[N_2O_5]$ 150. s after the start of the reaction.

Solution

We know from Example 15.2 that $[N_2O_5] = 0.0500 \text{ mol/L}$ at 100 s and $[N_2O_5] = 0.0250 \text{ mol/L}$ at 200 s. Since 150 s is halfway between 100 s and 200 s, it is tempting to assume that we can use a simple average to obtain $[N_2O_5]$ at that time. This is incorrect, because it is $\ln[N_2O_5]$, not $[N_2O_5]$, that depends directly on t . To calculate $[N_2O_5]$ after 150 s, we must use Equation (15.2):

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

where $t = 150. \text{ s}$, $k = 6.93 \times 10^{-3} \text{ s}^{-1}$ (as determined in Example 15.2), and $[N_2O_5]_0 = 0.100 \text{ mol/L}$.

$$\begin{aligned}\ln([N_2O_5])_{t=150} &= -(6.93 \times 10^{-3} \text{ s}^{-1})(150. \text{ s}) + \ln(0.100) \\ &= -1.040 - 2.303 = -3.343\end{aligned}$$

$$[N_2O_5]_{t=150} = \text{antilog}(-3.343) = 0.0353 \text{ mol/L}$$

Note that this value of $[N_2O_5]$ is *not* halfway between 0.0500 mol/L and 0.0250 mol/L.

Half-Life of a first order reaction

The time required for a reactant to reach half of its original concentration is called the half-life of a reaction and is designated by $t_{1/2}$.

If the reaction is first order in $[A]$,

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

By definition, when $t = t_{1/2}$, $[A] = \frac{[A]_0}{2}$

Then for $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

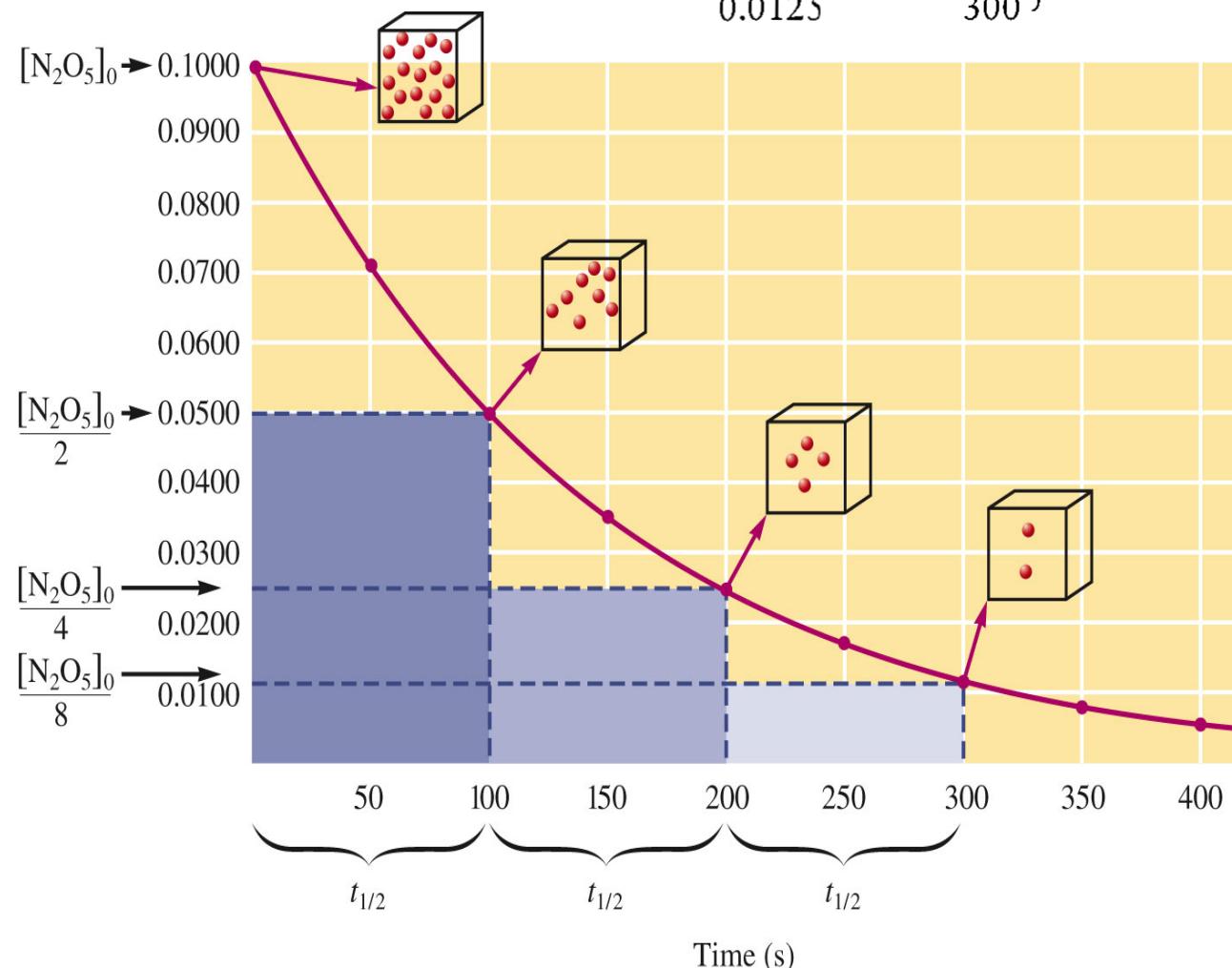
or

$$\ln(2) = kt_{1/2}$$

Substituting the value of $\ln(2)$ and solving for $t_{1/2}$ gives

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

$[N_2O_5] \text{ (mol/L)}$	$t \text{ (s)}$
0.1000	0
0.0500	100
0.0250	200
0.0125	300



Note that for a first-order reaction the half-life does not depend on concentration.

Example 15.4

A certain first-order reaction has a half-life of 20.0 min.

- Calculate the rate constant for this reaction.
- How much time is required for this reaction to be 75% complete?

Solution

- Solving Equation (15.3) for k gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

- We use the integrated rate law in the form

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

If the reaction is 75% complete, 75% of the reactant has been consumed. This leaves 25% in the original form:

$$\frac{[A]}{[A]_0} \times 100 = 25$$

This means that

$$\frac{[A]}{[A]_0} = 0.25 \quad \text{and} \quad \frac{[A]_0}{[A]} = 4.0$$

Therefore

$$\ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

and

$$t = 40. \text{ min}$$

Thus it takes 40. min for this particular reaction to reach 75% completion.

Second-Order Rate Laws

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

$$\text{Rate} = -\frac{d[A]}{dt} = k [A]^2$$

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

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

A plot of $1/[A]$ versus t will produce a straight line with a slope equal to k .

Half life of a second order reaction

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

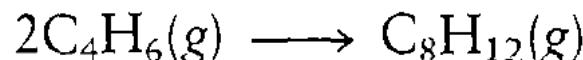
$$\frac{\frac{1}{[A]_0} - \frac{1}{[A]}}{2} = kt_{1/2} + \frac{\frac{1}{[A]_0}}{2}$$

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

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

Example 15.5

Butadiene reacts to form its dimer according to the equation



The following data were collected for this reaction at a given temperature:

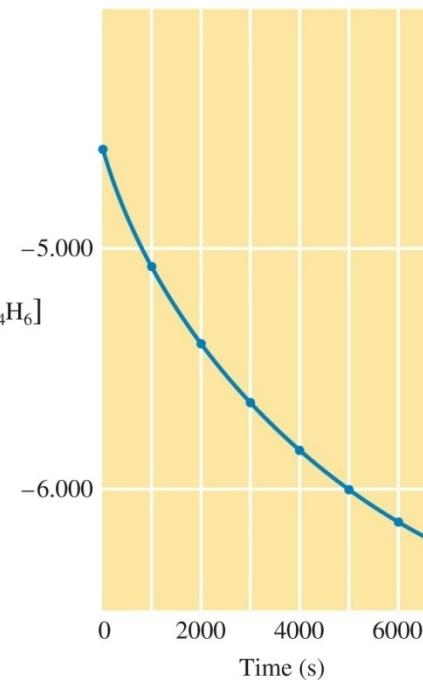
[C ₄ H ₆] (mol/L)	Time (± 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

- Is this reaction first order or second order?
- What is the value of the rate constant for the reaction?
- What is the half-life for the reaction under the conditions of this experiment?

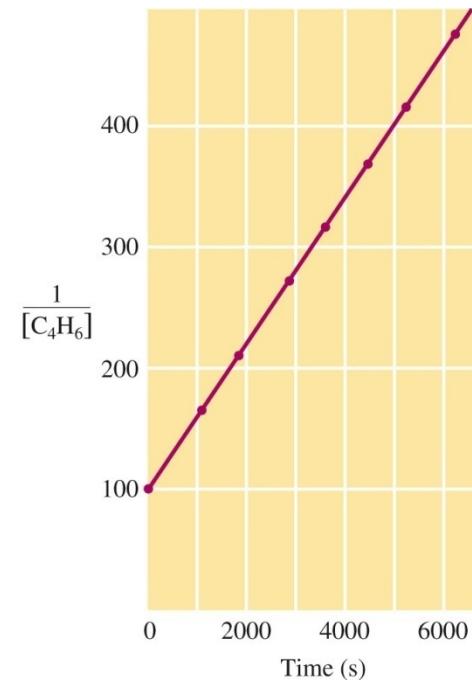
Solution

- a. To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of $\ln[C_4H_6]$ versus time is a straight line (first order) or the plot of $1/[C_4H_6]$ versus time is a straight line (second order). The data necessary to make these plots are as follows:

t (s)	$\frac{1}{[C_4H_6]}$	$\ln[C_4H_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	319	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175



(a)



(b)

The resulting plots are shown in Fig. 15.5. Since the $\ln[C_4H_6]$ versus t plot is not a straight line, the reaction is *not* first order. The reaction is, however, second order, as shown by the linearity of the $1/[C_4H_6]$ versus t plot. Thus we can now write the rate law for this second-order reaction:

- b. For a second-order reaction a plot of $1/[C_4H_6]$ versus t produces a straight line with slope k . In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[C_4H_6]$ and $x = t$. In this case,

$$k = \text{slope} = 6.14 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

- c. The expression for the half-life of a second-order reaction is

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

In this case $k = 6.14 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ (from part b) and $[A]_0 = [C_4H_6]_0 = 0.01000 \text{ M}$ (the concentration at $t = 0$). Thus

$$\begin{aligned} t_{1/2} &= \frac{1}{(6.14 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1})(1.000 \times 10^{-2} \text{ mol/L})} \\ &= 1.63 \times 10^3 \text{ s} \end{aligned}$$

The initial concentration of C_4H_6 is halved in 1630 s.

Zero-Order Rate Laws

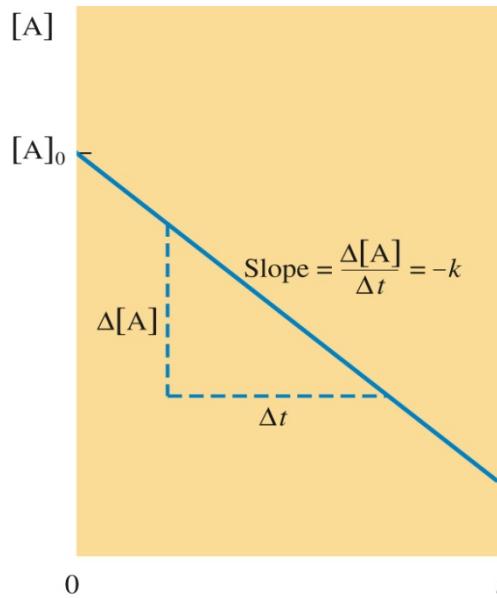
$$\text{Rate} = k[A]^0 = k$$

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

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

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

A plot of $[A]$ versus t gives a straight line of slope $-k$.



Half life of a zero order reaction

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

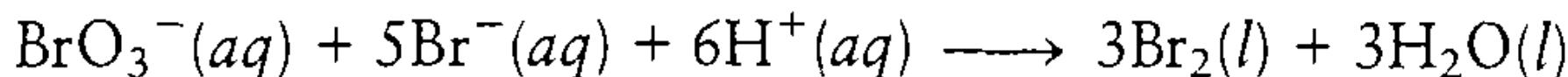
$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

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

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

Integrated Rate Laws for Reactions with More Than One Reactant

So far we have considered the integrated rate laws for simple reactions with only one reactant. Special techniques are required to deal with more complicated reactions.



From experimental evidence the rate law is

$$\text{Rate} = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Suppose we run this reaction under conditions where $[\text{BrO}_3^-]_0 = 1.0 \times 10^{-3} \text{ M}$, $[\text{Br}^-]_0 = 1.0 \text{ M}$, and $[\text{H}^+]_0 = 1.0 \text{ M}$. As the reaction proceeds, $[\text{BrO}_3^-]$ decreases significantly; but because the Br^- ion and H^+ ion concentrations are so large initially, relatively little of either of these two reactants is consumed. Thus $[\text{Br}^-]$ and $[\text{H}^+]$ remain *approximately constant*.

$$[\text{Br}^-] = [\text{Br}^-]_0 \quad \text{and} \quad [\text{H}^+] = [\text{H}^+]_0$$

This means that the rate law can be written as

$$\text{Rate} = k[\text{Br}^-]_0[\text{H}^+]_0^2[\text{BrO}_3^-] = k'[\text{BrO}_3^-]$$

where, since $[\text{Br}^-]_0$ and $[\text{H}^+]_0$ are constant,

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

The rate law

$$\text{Rate} = k'[\text{BrO}_3^-]$$

is first order. However, since this rate law was obtained by simplifying a more complicated one, it is called a **pseudo-first-order rate law**. Under the conditions of this experiment, a plot of $\ln[\text{BrO}_3^-]$ versus t gives a straight line with a slope equal to $-k'$. Since $[\text{Br}^-]_0$ and $[\text{H}^+]_0$ are known, the value of k can be calculated from the equation

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

which can be rearranged to give

$$k = \frac{k'}{[\text{Br}^-]_0[\text{H}^+]_0^2}$$

Table 15.6

Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate law	$\text{Rate} = k$	$\text{Rate} = k[A]$	$\text{Rate} = k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of the straight line	$\text{Slope} = -k$	$\text{Slope} = -k$	$\text{Slope} = k$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

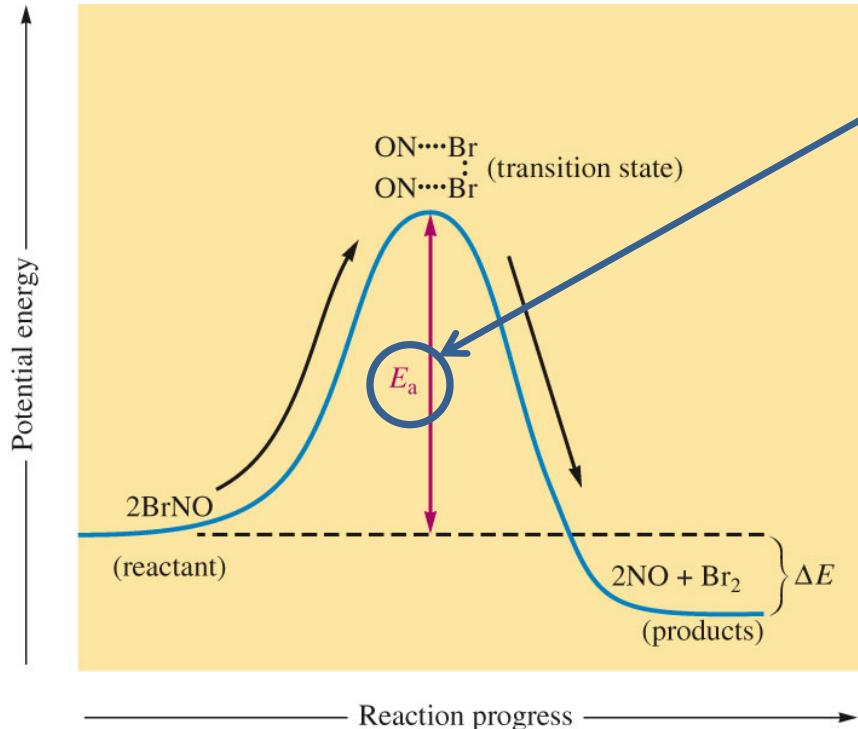
The **kinetic molecular theory** of gases predicts that an increase in temperature increases molecular velocities and so increases the frequency of intermolecular collisions.

→ reaction rates are greater at higher temperatures.

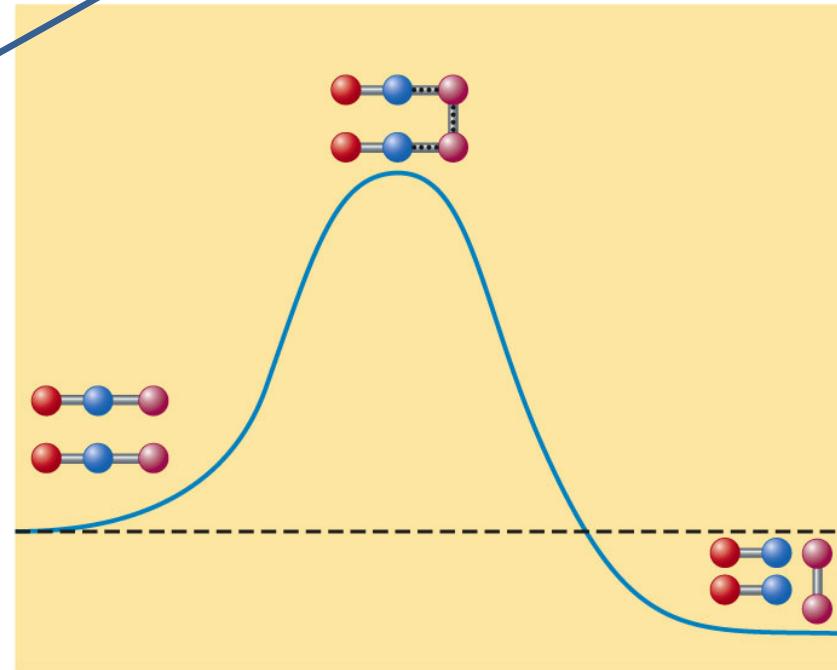
A threshold energy, called the activation energy, must be overcome to produce a chemical reaction.



Activation energy



(a)



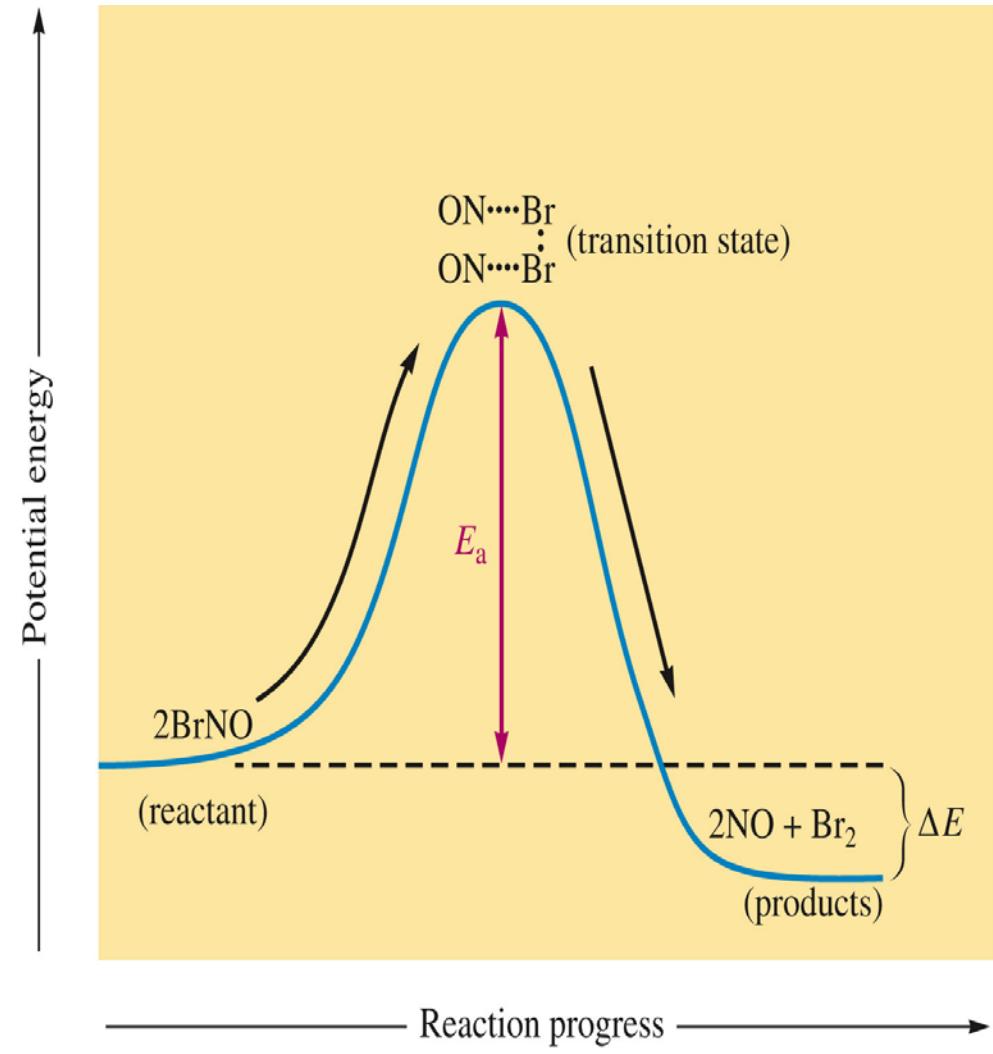
(b)

Two Br-N bonds must be broken and one Br-Br bond must be formed.

The energy required to break the bonds comes from the kinetic energies possessed by the reacting molecules before the collision.

This kinetic energy is changed into potential energy as the molecules are distorted during a collision, breaking bonds and rearranging the atoms into the product molecules.

The arrangement of atoms found at the top of the potential energy “hill”, or barrier, is called the **activated complex**, or **transition state**.



(a)

The relationship between the rate constant (k) and the activation energy (E_a) is given by the **Arrhenius equation**:

$$k = A e^{-E_a / RT}$$

A is the pre-exponential factor, or frequency factor, for the reaction.

R is the universal gas constant ($R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$).

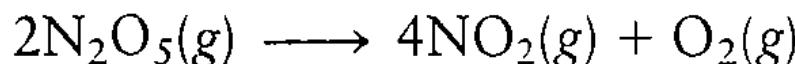
T is the Kelvin temperature.

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

A plot of $\ln(k)$ vs. $1/T$ has a slope = $-E_a/R$ and intercept = $\ln(A)$

Example 15.8

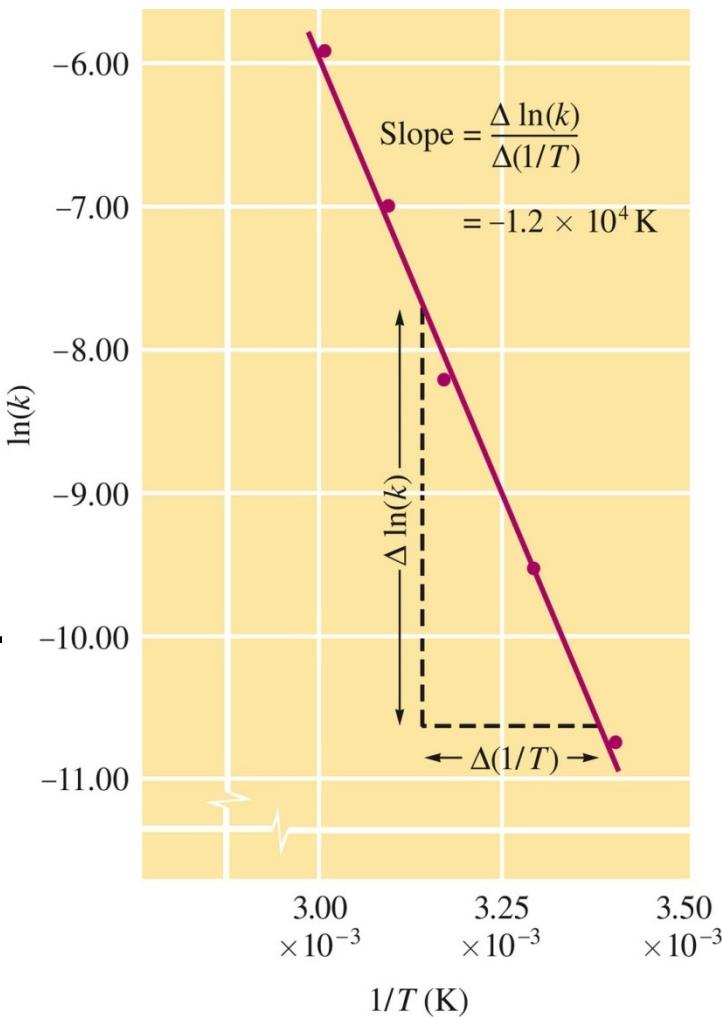
The reaction



was studied at several temperatures and the following values of k were obtained:

k (s ⁻¹)	T (°C)
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

Calculate the value of E_a for this reaction.



Solution

To obtain the value of E_a , we need to construct a plot of $\ln(k)$ versus $1/T$. First, we must calculate values of $\ln(k)$ and $1/T$:

T (°C)	T (K)	$1/T$ (K)	k (s ⁻¹)	$\ln(k)$
20	293	3.41×10^{-3}	2.0×10^{-5}	-10.82
30	303	3.30×10^{-3}	7.3×10^{-5}	-9.53
40	313	3.19×10^{-3}	2.7×10^{-4}	-8.22
50	323	3.10×10^{-3}	9.1×10^{-4}	-7.00
60	333	3.00×10^{-3}	2.9×10^{-3}	-5.84

The plot of $\ln(k)$ versus $1/T$ is shown in Fig. 15.14. The slope is found to be -1.2×10^4 K. Since

$$\text{Slope} = -\frac{E_a}{R}$$

then

$$\begin{aligned}E_a &= -R(\text{slope}) = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(-1.2 \times 10^4 \text{ K}) \\&= 1.0 \times 10^5 \text{ J/mol}\end{aligned}$$

Thus the value of the activation energy for this reaction is 1.0×10^5 J/mol.

At temperature T_1 , the rate constant is k_1 ; thus

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

At temperature T_2 , the rate constant is k_2 ; thus

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

Subtracting the first equation from the second gives

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

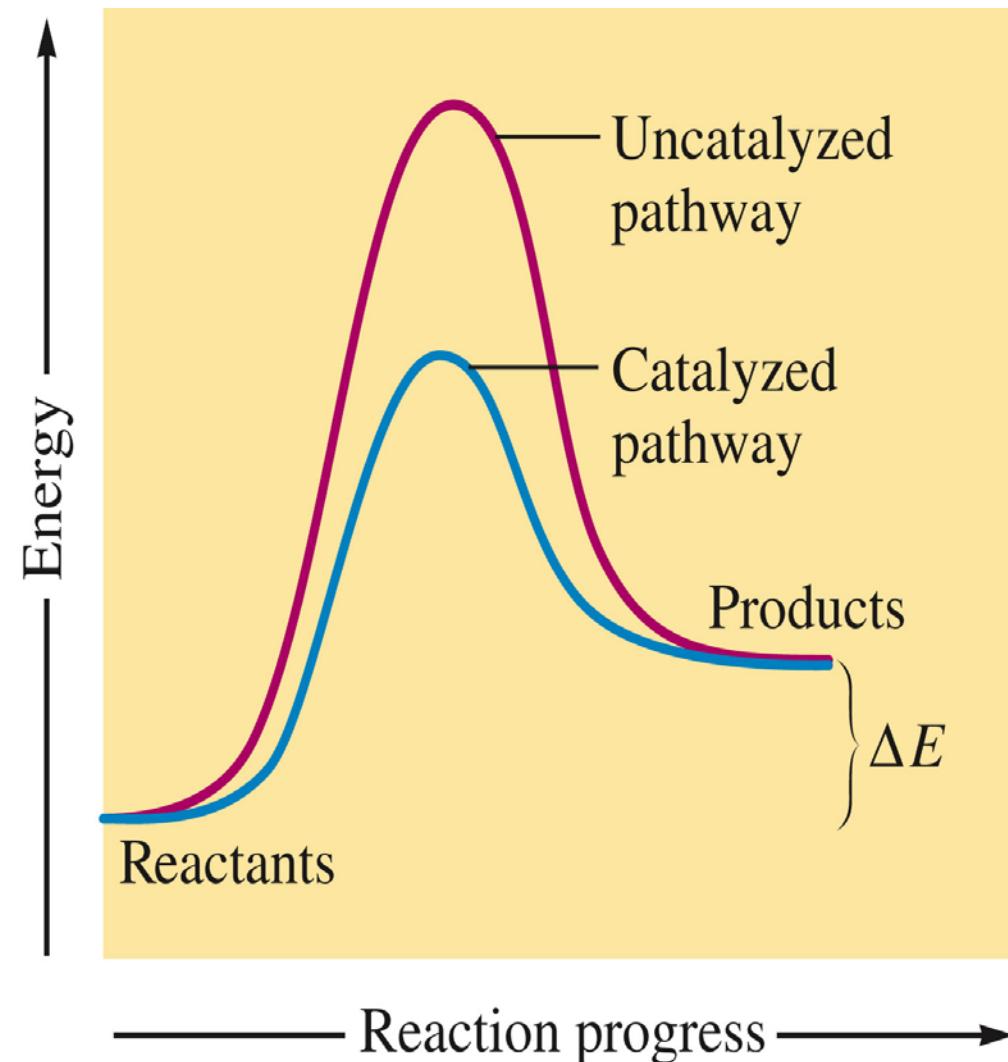
Therefore the values of k_1 and k_2 measured at temperatures T_1 and T_2 can be used to calculate E_a .

15.9 | Catalysis

A **catalyst** is a substance that speeds up a reaction *without* being consumed itself. Example: enzymes

The catalyst provides a new pathway for the reaction, with a lower activation energy (E_a).

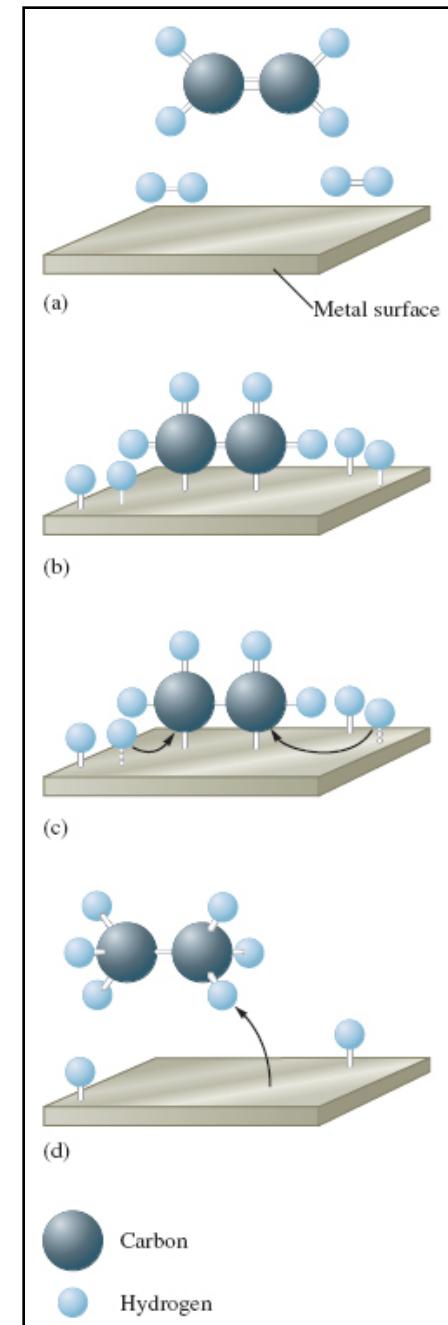
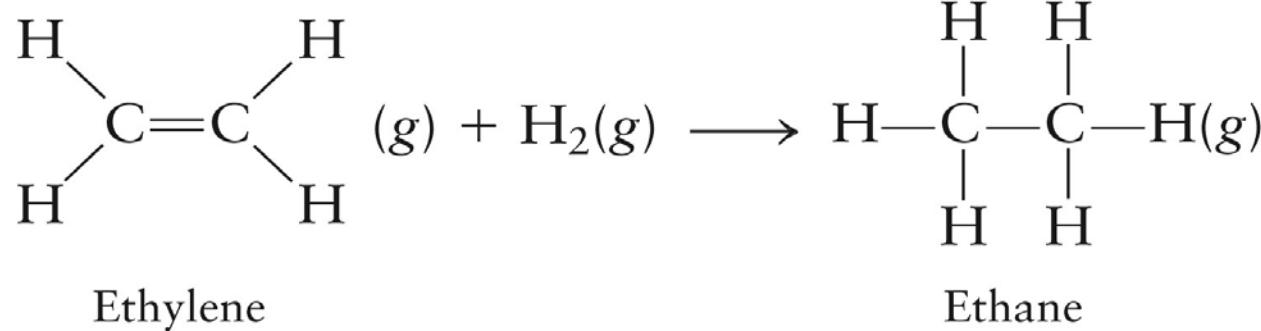
Although the catalyst lowers the activation energy for a reaction, it *does not* affect the energy difference (ΔE) between products and reactants



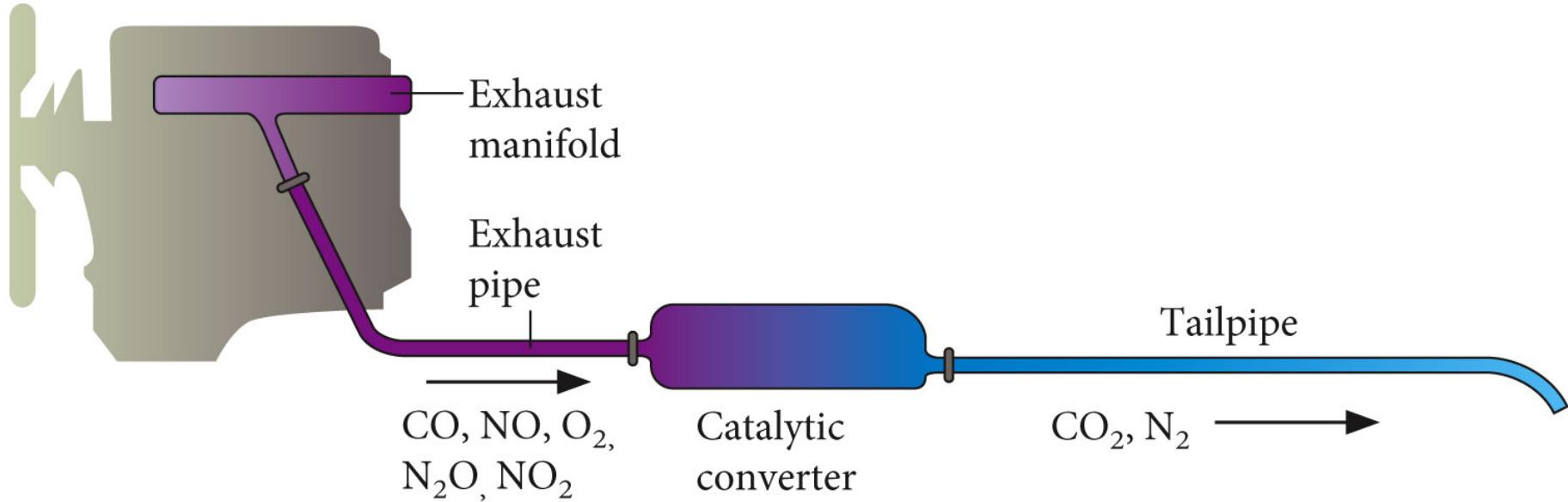
Heterogeneous Catalysis

A heterogeneous catalyst is one that is present in a different phase, usually a solid, than the reacting molecules.

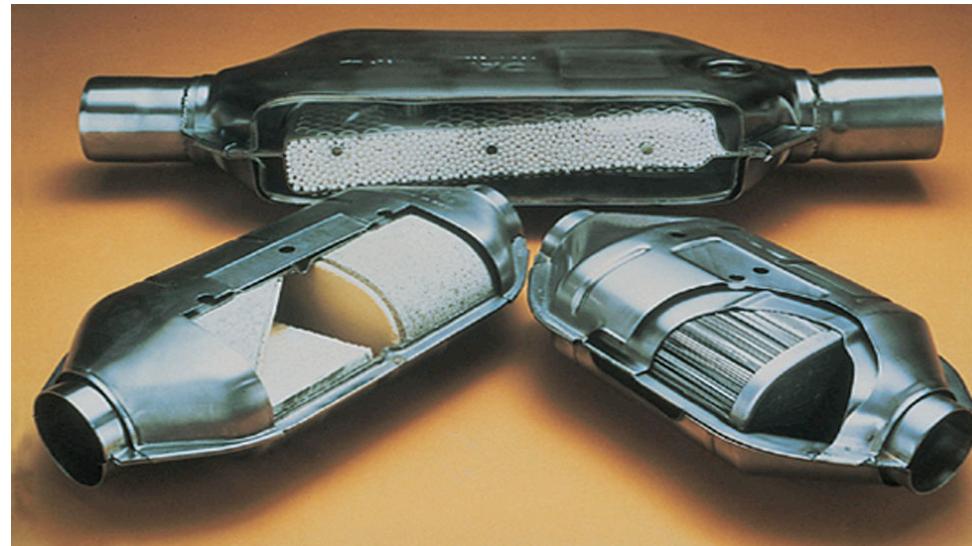
Example: Heterogeneous catalysis of the hydrogenation of ethylene.



The solid catalyst can be platinum, palladium, or nickel.



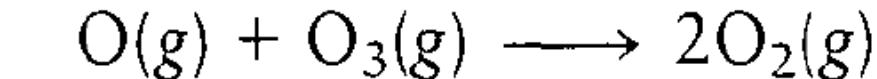
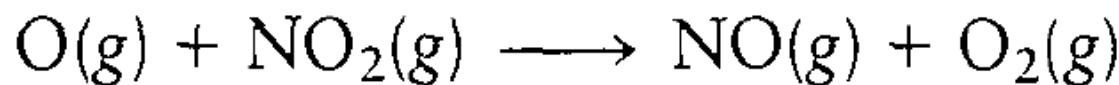
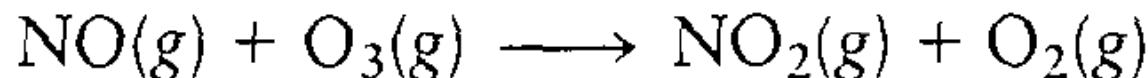
The exhaust gases from an automobile engine are passed through a catalytic converter to minimize environmental damage.



Homogeneous Catalysis

A homogeneous catalyst exists in the same phase as the reacting molecules.

Example: catalytic behavior of nitric oxide toward ozone.



HOMEWORK

Chap.15: 12, 16, 19, 28, 29, 34, 35, 46, 77, 79

12

Consider the reaction



If, in a certain experiment, over a specific time period, 0.0048 mol PH_3 is consumed in a 2.0-L container during each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

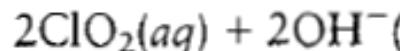
16

What are the units for each of the following if concentrations are expressed in moles per liter and time in seconds?

- a. rate of a chemical reaction
- b. rate constant for a zero-order rate law
- c. rate constant for a first-order rate law
- d. rate constant for a second-order rate law
- e. rate constant for a third-order rate law

19

The following data were obtained for the reaction



where

$$\text{Rate} = -\frac{d[\text{ClO}_2]}{dt}$$

$[\text{ClO}_2]_0$ (mol/L)	$[\text{OH}^-]_0$ (mol/L)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

- Determine the rate law and the value of the rate constant.
- What would be the initial rate for an experiment with $[\text{ClO}_2]_0 = 0.175$ mol/L and $[\text{OH}^-]_0 = 0.0844$ mol/L?

28

A certain reaction has the following general form:



At a particular temperature and $[A]_0 = 2.80 \times 10^{-3} M$, concentration versus time data were collected for this reaction, and a plot of $1/[A]$ versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. Calculate the half-life for this reaction.
- c. How much time is required for the concentration of A to decrease to $7.00 \times 10^{-4} M$?

29

A certain reaction has the following general form:



At a particular temperature and $[A]_0 = 2.00 \times 10^{-2} M$, concentration versus time data were collected for this reaction, and a plot of $\ln[A]$ versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2} \text{ min}^{-1}$.

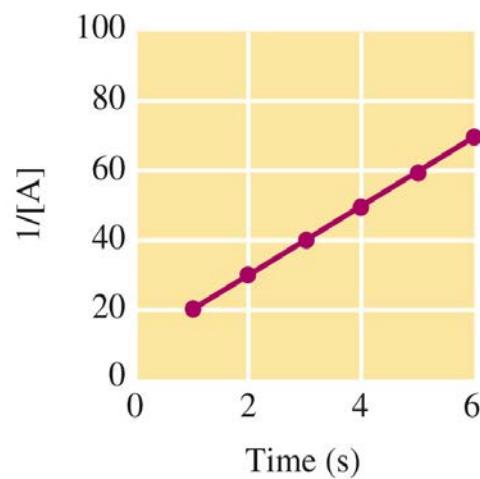
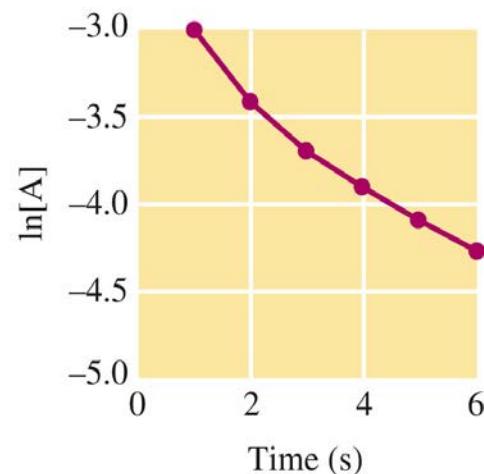
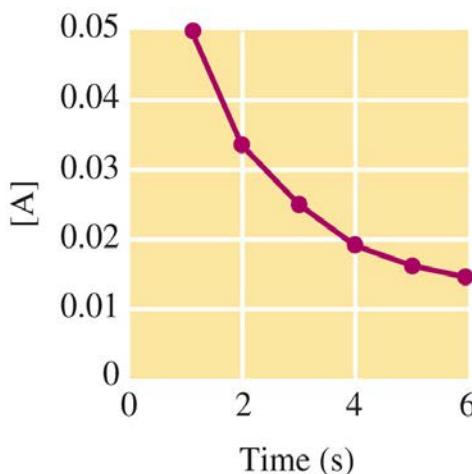
- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. Calculate the half-life for this reaction.
- c. How much time is required for the concentration of A to decrease to $2.50 \times 10^{-3} M$?

34

Experimental data for the reaction



have been plotted in the following three different ways (with concentration units in mol/L):



- What is the order of the reaction with respect to A and what is the initial concentration of A?
- What is the concentration of A after 9 s?
- What are the first three half-lives for this experiment?

35

The rate of the reaction



depends only on the concentration of nitrogen dioxide at temperatures below 225°C. At a temperature below 225°C the following data were collected:

Time (s)	[NO ₂] (mol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the integrated rate law, the differential rate law, and the value of the rate constant at this temperature. Calculate [NO₂] at 2.70×10^4 s after the start of the reaction.

46

The rate law for the reaction



at some temperature is

$$\text{Rate} = -\frac{d[\text{NOBr}]}{dt} = k[\text{NOBr}]^2$$

- a. If the half-life for this reaction is 2.00 s when $[\text{NOBr}]_0 = 0.900 \text{ M}$, calculate the value of k for this reaction.
- b. How much time is required for the concentration of NOBr to decrease to 0.100 M?

77

A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

79

Experimental values for the temperature dependence of the rate constant for the gas-phase reaction



are as follows:

T (K)	k (L mol $^{-1}$ s $^{-1}$)
195	1.08×10^9
230.	2.95×10^9
260.	5.42×10^9
298	12.0×10^9
369	35.5×10^9

Make the appropriate graph using these data, and determine the activation energy for this reaction.