

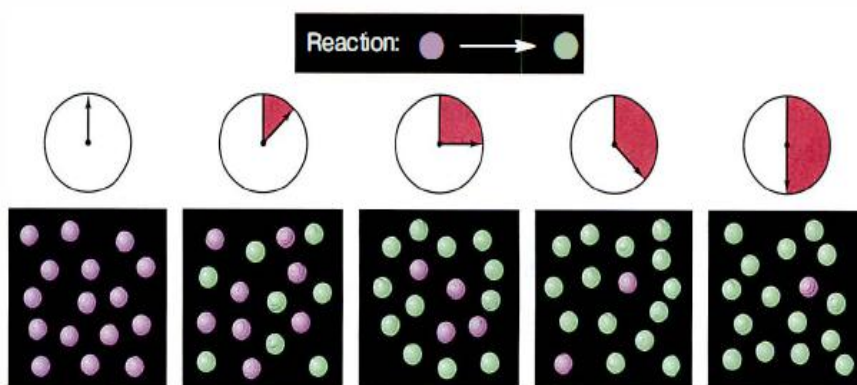
CHAPTER SIXTEEN

Kinetics: Rates and Mechanisms of Chemical Reactions

Chemical kinetics is the study of reaction rates, the changes in concentrations of reactants (or products) as a function of time (Figure 16. 1).

Figure 16. 1

Reaction rate: the central focus of chemical kinetics. The rate at which reactant becomes product is the underlying theme of chemical kinetics. As time elapses, reactant (purple) decreases and product (green) increases.



Reactions occur at a wide range of rates. Some, like a neutralization, are very fast. Others, such as the reactions involved in cooking or rusting, take a moderate length of time, from minutes to months. Still others take much longer, the reactions that make up the human aging process continue for decades, and those involved in the formation of coal from dead plants take hundreds of millions of years.

Knowing how fast a chemical change occurs can be essential. In general, the rates of these diverse processes depend on the same variables, most of which chemists can manipulate to maximize yields within a given time or to slow down an unwanted reaction.

16.1 FACTORS THAT INFLUENCE REACTION RATE

We can control four factors that affect the rate of a given reaction: the concentration of the reactants, the physical state of the reactants, the temperature of the reaction, and the use of a catalyst. We'll consider the first three factors here and discuss the fourth later in the chapter.

I. Concentration

A reaction can occur only when the reactant molecules collide. The reaction rate is proportional to the concentration of reactants:

$$\text{Rate} \propto \text{collision frequency} \propto \text{concentration}$$

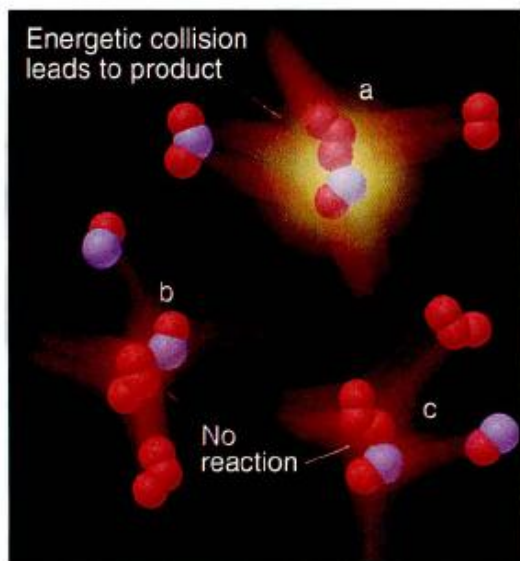
2. Physical state

- The frequency of collisions between molecules also depends on the physical states of the reactants. In an aqueous solution, random thermal motion brings reactants into contact.
- When the reactants are in different phases, vigorous stirring and grinding may be needed. *The more finely divided a solid or liquid reactant, the greater its surface area per unit volume, the more contact it makes with the other reactant, and the faster the reaction occurs.*

3. Temperature

- Molecules in a sample of gas have a range of speeds, with the most probable speed dependent on the temperature. Thus, at a higher temperature, more collisions occur in a given time.
- Temperature affects the kinetic energy of the molecules, and thus the energy of the collisions. At higher temperatures, more of the sufficiently energetic collisions occur. Thus, raising the temperature increases the reaction rate by increasing the number and, especially, the energy of the collisions Figure 16.2:

$$\text{Rate} \propto \text{collision energy} \propto \text{temperature}$$

**Figure 1 6.2**

Collision energy and reaction rate. The reaction equation is shown in the panel. Although many collisions between NO and O₃ molecules occur, relatively few have enough energy to cause reaction. At this temperature, only collision a is energetic enough to lead to product; the reactant molecules in collisions b and c just bounce off each other.

16.2 EXPRESSING THE REACTION RATE

A **rate** is a change in some variable per unit of time. In the case of a chemical change, the reaction rate refers to the changes in concentrations of reactants or products per unit time; *reactant concentrations decrease while product concentrations increase*.

Consider a general reaction, $A \rightarrow B$. If the reactant concentration changes from A_1 , (at t_1) to A_2 (at t_2), then the **average rate** is:

$$\text{Rate of reaction} = -\frac{\text{change in concentration of A}}{\text{change in time}} = -\frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = -\frac{\Delta(\text{conc A})}{\Delta t}$$

The rate has usually units of moles per liter per second ($\text{mol L}^{-1} \text{s}^{-1}$). By convention, reaction *rate is a positive number*. However the change in reactant concentration is *negative*, while the change in product concentration is *positive*. For the simple reaction $A \rightarrow B$, the rate can be expressed for A and B as:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Rate} = \frac{\Delta[B]}{\Delta t}$$

Average, Instantaneous, and Initial Reaction Rates

Not only the concentration, but the rate itself varies with time as the reaction proceeds. Consider the reversible gas-phase reaction that is involved in the formation of photochemical smog:



$$\text{Rate} = -\frac{\Delta[\text{C}_2\text{H}_4]}{\Delta t} = -\frac{\Delta[\text{O}_3]}{\Delta t}$$

Table 16.1 shows the concentration of O_3 at various times during the first minute after we introduce C_2H_4 gas. The rate over the entire 60.0 s corresponds to the **average rate**:

$$\text{Rate} = -\frac{\Delta[\text{O}_3]}{\Delta t} = -\frac{(1.10 \times 10^{-5} \text{ mol/L}) - (3.20 \times 10^{-5} \text{ mol/L})}{60.0 \text{ s} - 0.0 \text{ s}} = 3.50 \times 10^{-7} \text{ mol/L}\cdot\text{s}$$

However, the average rate tells nothing about how fast the ozone concentration is decreasing at *any given instant*. Actually, the rate decreases during the course of the reaction. This is because as O_3 molecules are used up, fewer of them are present to collide with C_2H_4 molecules, so the rate decreases.

Table 16.1 Concentration of O_3 at Various Times in Its Reaction with C_2H_4 at 303 K

Time (s)	Concentration of O_3 (mol/L)
0.0	3.20×10^{-5}
10.0	2.42×10^{-5}
20.0	1.95×10^{-5}
30.0	1.63×10^{-5}
40.0	1.40×10^{-5}
50.0	1.23×10^{-5}
60.0	1.10×10^{-5}

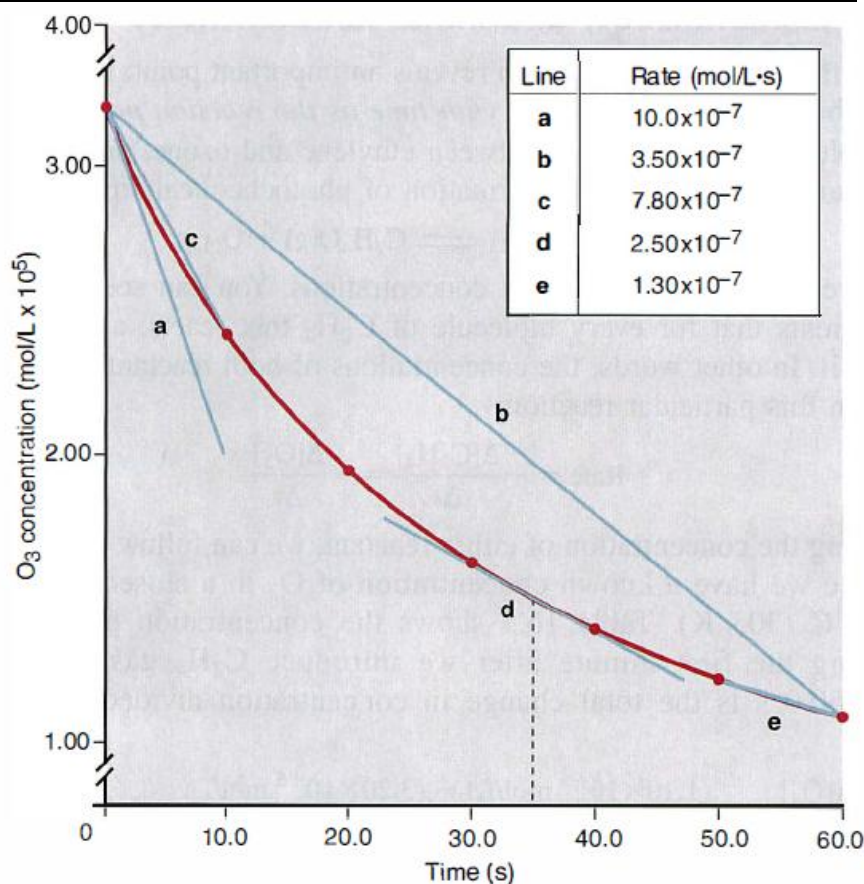
The change in rate can be seen by plotting the concentrations vs. the times at which they were measured (Figure 16.3). A curve is obtained, which means that the rate changes.

- The slope of the straight line ($\Delta[\text{O}_3]/\Delta t$) joining any two points gives the average rate over that period.
- The **instantaneous rate** is the slope of a line tangent to the curve at a given time. The reaction rate of C_2H_4 and O_3 at 35.0 s is $2.50 \times 10^{-7} \text{ mol/L}\cdot\text{s}$, which is

the slope of the line drawn tangent to the curve through the point at which $t = 35.0$ s (line d in Figure 16.3).

Figure 16.3

The concentration of O_3 vs. time during its reaction with C_2H_4 . The slope of line b is the **average rate** over the first 60.0 s of the reaction. The slopes of lines c and e give the average rate over the first and last 10.0-s intervals, respectively. Line c is steeper than line e because the average rate over the earlier period is higher. The **instantaneous rate** at 35.0 s is the slope of line d, the tangent to the curve at $t = 35.0$ s. The **initial rate** is the slope of line a, the tangent to the curve at $t = 0$ s.



As a reaction continues, the product concentrations increase, and so the reverse reaction (reactants \rightarrow products) proceeds more quickly. To find the overall (net) rate, we would have to take both **forward** and **reverse** reactions into account and calculate the difference between their rates. A common way to avoid this complication for many reactions is to measure **the initial rate**; the instantaneous rate at the moment the reactants are mixed. Under these conditions, the product concentrations are negligible, so the reverse rate is negligible.

The initial rate is measured by determining the slope of the line tangent to the curve at $t=0$ s. In Figure 16.3, the initial rate is $10.0 \times 10^{-7} \text{ mol/L} \cdot \text{s}$ (line a). Unless stated otherwise, we will use initial rate data to determine other kinetic parameters.

Expressing Rate in Terms of Reactant and Product Concentrations

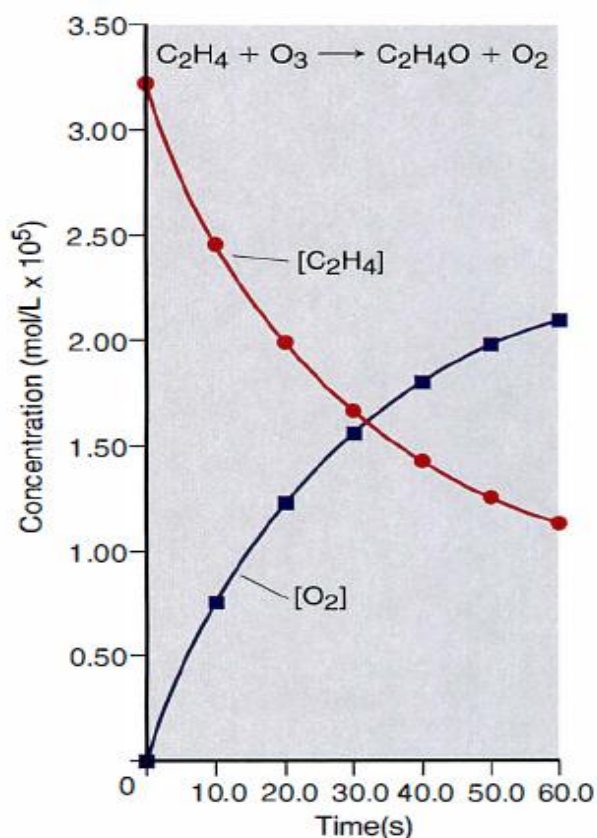
From the balanced equation of the previous reaction, we see that one molecule of C_2H_4O and one of O_2 appear for every molecule of C_2H_4 and of O_3 that disappear. We can express the rate in terms of any of the four substances involved:

$$\text{Rate} = -\frac{\Delta[C_2H_4]}{\Delta t} = -\frac{\Delta[O_3]}{\Delta t} = +\frac{\Delta[C_2H_4O]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

Note the negative values for the reactants and the positive values for the products. Figure 16.4 shows a plot of the simultaneous monitoring of one reactant and one product.

Figure 16.4

Plots of $[C_2H_4]$ and $[O_2]$ vs. time. Measuring reactant concentration, $[C_2H_4]$, and product concentration, $[O_2]$, gives curves of identical shapes but changing in opposite directions. The steep upward (positive) slope of $[O_2]$ early in the reaction mirrors the steep downward (negative) slope of $[C_2H_4]$ because the faster C_2H_4 is used up, the faster O_2 is formed. The curve shapes are identical in this case because the equation coefficients are identical.

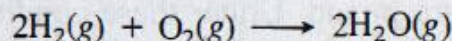


The mathematical expression for the rate of a particular reaction and the numerical value of the rate depend on which substance serves as the reference. For any reaction, $aA + bB \rightarrow cC + dD$, where a , b , c , and d are coefficients of the balanced equation, the rate is related to reactant or product concentrations as follows:

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

SAMPLE PROBLEM 16.1 Expressing Rate in Terms of Changes in Concentration with Time

Problem Because it has a nonpolluting combustion product (water vapor), hydrogen gas is used for fuel aboard the space shuttle and in prototype cars with Earth-bound engines:



(a) Express the rate in terms of changes in $[\text{H}_2]$, $[\text{O}_2]$, and $[\text{H}_2\text{O}]$ with time.

(b) When $[\text{O}_2]$ is decreasing at $0.23 \text{ mol/L}\cdot\text{s}$, at what rate is $[\text{H}_2\text{O}]$ increasing?

Plan (a) Of the three substances in the equation, let's choose O_2 as the reference because its coefficient is 1. For every molecule of O_2 that disappears, two molecules of H_2 disappear, so the rate of $[\text{O}_2]$ decrease is one-half the rate of $[\text{H}_2]$ decrease. By similar reasoning, we see that the rate of $[\text{O}_2]$ decrease is one-half the rate of $[\text{H}_2\text{O}]$ increase. (b) Because $[\text{O}_2]$ is decreasing, the change in its concentration must be negative. We substitute the negative value into the expression and solve for $\Delta[\text{H}_2\text{O}]/\Delta t$.

Solution (a) Expressing the rate in terms of each component:

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

(b) Calculating the rate of change of $[\text{H}_2\text{O}]$:

$$\begin{aligned} \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} &= -\frac{\Delta[\text{O}_2]}{\Delta t} = -(-0.23 \text{ mol/L}\cdot\text{s}) \\ \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} &= 2(0.23 \text{ mol/L}\cdot\text{s}) = 0.46 \text{ mol/L}\cdot\text{s} \end{aligned}$$

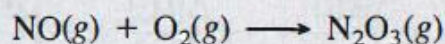
Check (a) A good check is to use the rate expression to obtain the balanced equation: $[\text{H}_2]$ changes twice as fast as $[\text{O}_2]$, so two H_2 molecules react for each O_2 . $[\text{H}_2\text{O}]$ changes twice as fast as $[\text{O}_2]$, so two H_2O molecules form from each O_2 . From this reasoning, we get $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$. The $[\text{H}_2]$ and $[\text{O}_2]$ decrease, so they take minus signs; $[\text{H}_2\text{O}]$ increases, so it takes a plus sign. Another check is to use Equation 16.2, with $A = \text{H}_2$, $a = 2$; $B = \text{O}_2$, $b = 1$; $C = \text{H}_2\text{O}$, $c = 2$. Thus,

$$\begin{aligned} \text{Rate} &= -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} \\ \text{or} \quad \text{Rate} &= -\frac{1}{2} \frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} \end{aligned}$$

(b) Given the rate expression, it makes sense that the numerical value of the rate of $[\text{H}_2\text{O}]$ increase is twice that of $[\text{O}_2]$ decrease.

Comment Thinking through this type of problem at the molecular level is the best approach, but use Equation 16.2 to confirm your answer.

FOLLOW-UP PROBLEM 16.1 (a) Balance the following equation and express the rate in terms of the change in concentration with time for each substance:

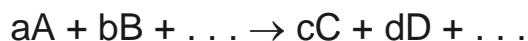


(b) How fast is $[\text{O}_2]$ decreasing when $[\text{NO}]$ is decreasing at a rate of $1.60 \times 10^{-4} \text{ mol/L}\cdot\text{s}$?

16.3 THE RATE LAW AND ITS COMPONENTS

The rate law expresses the rate as a function of reactant concentrations, product concentrations, and temperature. Any hypothesis we make about how the reaction occurs on the molecular level must conform to the rate law because it is based on experimental fact.

For a general reaction,



the rate law has the form:

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

The proportionality constant **k**, called the **rate constant**, is specific for a given reaction at a given temperature, which change with temperature. The exponents **m** and **n**, called the reaction orders, define how the rate is affected by reactant concentration.

Thus, if the rate doubles when [A] doubles, then $m = 1$. Similarly, if the rate quadruples when [B] doubles, then $n = 2$. In another reaction, the rate may not change at all when [A] doubles; in that case, the rate does not depend on [A], or $m = 0$. *Keep in mind that the coefficients a and b in the general balanced equation are not necessarily related in any way to these reaction orders m and n.*

The components of the rate law—rate, reaction orders, and rate constant *must be found by experiment*. Chemists take an experimental approach to finding these components by

1. Using concentration measurements to find the initial rate
2. Using initial rates from several experiments to find the reaction orders
3. Using these values to calculate the rate constant

Many experimental techniques have been developed to measure the concentrations in order to find initial rates. For reactions that involve a colored substance, **spectroscopic methods** can be used. For reactions that involve a change in number of moles of gas, the **change in pressure** can be monitored. A third technique monitors a **change in conductivity** (ion concentration).

Reaction Order Terminology

We speak of a reaction as having an individual order "with respect to" or "in" each reactant as well as an overall order, which is simply the sum of the individual orders.

In the simplest case, a reaction with a single reactant A, the reaction is first order overall if the rate is directly proportional to [A]:

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

It is second order overall if the rate is directly proportional to the square of [A]:

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

And it is zero order overall if the rate is not dependent on [A] at all, a common situation in metal-catalyzed and biochemical processes:

$$\text{Rate} = k[A]^0 = k(1) = k$$

Some examples are;

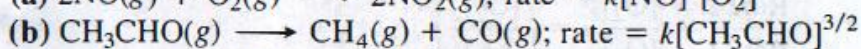
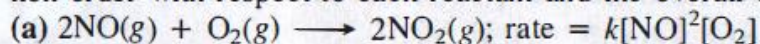
<u>Reaction</u>	<u>Rate Equation</u>
$\text{NO}(g) + \text{O}_3(g) \longrightarrow \text{NO}_2(g) + \text{O}_2(g)$	$\text{Rate} = k[\text{NO}][\text{O}_3]$
$2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$	$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$
$\text{CHCl}_3(g) + \text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{HCl}(g)$	$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$
$2\text{O}_3(g) \rightleftharpoons 3\text{O}_2(g)$	$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$

Notice that,

- Reaction orders cannot be deduced from the balanced equation.
- Reaction orders are usually positive integers or zero, but they can also be fractional or negative.
- A negative exponent means that the rate decreases when the concentration of that component increases

SAMPLE PROBLEM 16.2 Determining Reaction Order from Rate Laws

Problem For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and the overall order:



Plan We inspect the exponents in the rate law, *not* the coefficients of the balanced equation, to find the individual orders, and then take their sum to find the overall reaction order.

Solution (a) The exponent of $[\text{NO}]$ is 2, so the reaction is second order with respect to NO , first order with respect to O_2 , and third order overall.

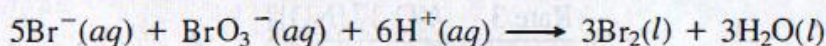
(b) The reaction is $\frac{3}{2}$ order in CH_3CHO and $\frac{3}{2}$ order overall.

(c) The reaction is first order in H_2O_2 , first order in I^- , and second order overall.

The reactant H^+ does not appear in the rate law, so the reaction is zero order in H^+ .

Check Be sure that each reactant has an order and that the sum of the individual orders gives the overall order.

FOLLOW-UP PROBLEM 16.2 Experiment shows that the reaction



obeys this rate law: rate = $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$. What are the reaction orders in each reactant and the overall reaction order?

Determining Reaction Orders Experimentally

Consider the reaction between oxygen and nitrogen monoxide, a key step in the formation of acid rain and in the industrial production of nitric acid:



To find the reaction orders, we run a series of experiments, starting each one with a different set of reactant concentrations and obtaining an initial rate in each case.

Table 16.2 Initial Rates for a Series of Experiments with the Reaction Between O_2 and NO

Experiment	Initial Reactant Concentrations (mol/L)		Initial Rate (mol/L·s)
	O_2	NO	
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}
5	1.10×10^{-2}	3.90×10^{-2}	28.8×10^{-3}

If we compare experiments 1 and 2, we see the effect of doubling $[\text{O}_2]$ on the rate. First, we take the ratio of their rate laws:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{O}_2]_2^m [\text{NO}]_2^n}{k[\text{O}_2]_1^m [\text{NO}]_1^n}$$

Because k is a constant and $[\text{NO}]$ does not change between these two experiments, these quantities cancel:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{[\text{O}_2]_2^m}{[\text{O}_2]_1^m} = \left(\frac{[\text{O}_2]_2}{[\text{O}_2]_1}\right)^m$$

Substituting the values from Table 16.2, we obtain

$$\frac{6.40 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}} = \left(\frac{2.20 \times 10^{-2} \text{ mol/L}}{1.10 \times 10^{-2} \text{ mol/L}}\right)^m$$

$m = 1$, the reaction is first order in O_2 ; when $[\text{O}_2]$ doubles, the rate doubles.

To find the order with respect to NO , we compare experiments 3 and 1, in which $[\text{O}_2]$ is held constant and $[\text{NO}]$ is doubled:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[\text{O}_2]_3^m [\text{NO}]_3^n}{k[\text{O}_2]_1^m [\text{NO}]_1^n}$$

As before, k is constant, and in this pair of experiments $[\text{O}_2]$ does not change, so:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[\text{NO}]_3}{[\text{NO}]_1}\right)^n$$

The actual values give

$$\frac{12.8 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}} = \left(\frac{2.60 \times 10^{-2} \text{ mol/L}}{1.30 \times 10^{-2} \text{ mol/L}}\right)^n$$

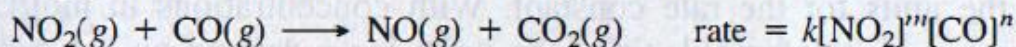
Thus, $n = 2$; the reaction is second order in NO , when $[\text{NO}]$ doubles, the rate quadruples. Based on the above, the rate law is:

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

You may want to use experiment 1 in combination with experiments 4 and 5 to check this result.

SAMPLE PROBLEM 16.3 Determining Reaction Orders from Initial Rate Data

Problem Many gaseous reactions occur in car engines and exhaust systems. One of these is



Use the following data to determine the individual and overall reaction orders:

Experiment	Initial Rate (mol/L·s)	Initial [NO ₂] (mol/L)	Initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

Plan We need to solve the general rate law for the reaction orders m and n . To solve for each exponent, we proceed as in the text, taking the ratio of the rate laws for two experiments in which only the reactant in question changes.

Solution Calculating m in $[\text{NO}_2]^m$: We take the ratio of the rate laws for experiments 1 and 2, in which $[\text{NO}_2]$ varies but $[\text{CO}]$ is constant:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{NO}_2]_2^m [\text{CO}]_2^n}{k[\text{NO}_2]_1^m [\text{CO}]_1^n} = \left(\frac{[\text{NO}_2]_2}{[\text{NO}_2]_1}\right)^m \quad \text{or} \quad \frac{0.080 \text{ mol/L}\cdot\text{s}}{0.0050 \text{ mol/L}\cdot\text{s}} = \left(\frac{0.40 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^m$$

This gives $16 = 4.0^m$, so $m = 2.0$. The reaction is second order in NO_2 .

Calculating n in $[\text{CO}]^n$: We take the ratio of the rate laws for experiments 1 and 3, in which $[\text{CO}]$ varies but $[\text{NO}_2]$ is constant:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[\text{NO}_2]_3^m [\text{CO}]_3^n}{k[\text{NO}_2]_1^m [\text{CO}]_1^n} = \left(\frac{[\text{CO}]_3}{[\text{CO}]_1}\right)^n \quad \text{or} \quad \frac{0.0050 \text{ mol/L}\cdot\text{s}}{0.0050 \text{ mol/L}\cdot\text{s}} = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^n$$

We have $1.0 = (2.0)^n$, so $n = 0$. The rate does not change when $[\text{CO}]$ varies, so the reaction is zero order in CO .

Therefore, the rate law is

$$\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2(1) = k[\text{NO}_2]^2$$

The reaction is second order overall.

Check A good check is to reason through the orders. If $m = 1$, quadrupling $[\text{NO}_2]$ would quadruple the rate; but the rate *more* than quadruples, so $m > 1$. If $m = 2$, quadrupling $[\text{NO}_2]$ would increase the rate by a factor of 16 (4^2). The ratio of rates is $0.080/0.005 = 16$, so $m = 2$. In contrast, increasing $[\text{CO}]$ has no effect on the rate, which can happen only if $[\text{CO}]^n = 1$, so $n = 0$.

FOLLOW-UP PROBLEM 16.3 Find the rate law and the overall reaction order for the reaction $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$ from the following data at 450°C :

Experiment	Initial Rate (mol/L·s)	Initial [H ₂] (mol/L)	Initial [I ₂] (mol/L)
1	1.9×10^{-23}	0.0113	0.0011
2	1.1×10^{-22}	0.0220	0.0033
3	9.3×10^{-23}	0.0550	0.0011
4	1.9×10^{-22}	0.0220	0.0056

Determining the Rate Constant

The experiments with the reaction of O₂ and NO were run at the same temperature, so we can use data from any to solve for k. From experiment 1 in Table 16.2, for instance, we obtain;

$$k = \frac{\text{rate 1}}{[\text{O}_2]_1[\text{NO}]_1^2} = \frac{3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{(1.10 \times 10^{-2} \text{ mol/L})(1.30 \times 10^{-2} \text{ mol/L})^2}$$

$$= \frac{3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{1.86 \times 10^{-6} \text{ mol}^3/\text{L}^3} = 1.73 \times 10^3 \text{ L}^2/\text{mol}^2\cdot\text{s}$$

Note the units for the rate constant. With concentrations in mol/L and the reaction rate in units of mol/L·time, the units for k depend on the order of the reaction and, of course, the time unit. The units for k in our example, L²/mol²·s, are required to give a rate with units of mol/L·s.

The rate constant will always have these units for an overall third-order reaction with the time unit in seconds. Table 16.3 shows the units of k for some common overall reaction orders, but you can always determine the units mathematically.

Table 16.3 Units of the Rate Constant *k* for Several Overall Reaction Orders

Overall Reaction Order	Units of <i>k</i> (<i>t</i> in seconds)
0	mol/L·s (or mol L ⁻¹ s ⁻¹)
1	1/s (or s ⁻¹)
2	L/mol·s (or L mol ⁻¹ s ⁻¹)
3	L ² /mol ² ·s (or L ² mol ⁻² s ⁻¹)

General formula:

$$\text{Units of } k = \frac{\left(\frac{\text{L}}{\text{mol}}\right)^{\text{order}-1}}{\text{unit of } t}$$

16.4 INTEGRATED RATE LAWS: CONCENTRATION CHANGES OVER TIME

Notice that the rate laws we've developed so far do not include time as a variable. The time dependence of the rate is expressed in different forms of the rate laws, called **integrated rate laws**.

Integrated Rate Laws for First-Order, Second-Order, and Zero-Order Reactions

For a simple first-order reaction, $A \rightarrow B$;

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t}$$

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

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

Using calculus, this expression is integrated over time to give the integrated rate law for a first-order reaction:

$$\ln \frac{[A]_0}{[A]_t} = kt \quad (\text{first-order reaction; rate} = k[A])$$

Where \ln is the natural logarithm, $[A]_0$ is the concentration of A at $t = 0$, and $[A]$ is the concentration of A at any time t during an experiment.

For a general second-order reaction, *if only one reactant is involved*, then:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

Integrating over time gives the integrated rate law for a second-order reaction involving one reactant:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \quad (\text{second-order reaction; rate} = k[A]^2)$$

For a zero-order reaction, we have

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0$$

Integrating over time gives the integrated rate law for a zero-order reaction:

$$[A]_t - [A]_0 = -kt \quad (\text{zero-order reaction; rate} = k[A]^0 = k)$$

SAMPLE PROBLEM 16.4 Determining the Reactant Concentration at a Given Time

Problem At 1000°C, cyclobutane (C_4H_8) decomposes in a first-order reaction, with the very high rate constant of 87 s^{-1} , to two molecules of ethylene (C_2H_4).

(a) If the initial C_4H_8 concentration is 2.00 M , what is the concentration after 0.010 s ?

(b) What fraction of C_4H_8 has decomposed in this time?

Plan (a) We must find the concentration of cyclobutane at time t , $[C_4H_8]_t$. The problem tells us this is a first-order reaction, so we use the integrated first-order rate law:

$$\ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt$$

We know k (87 s^{-1}), t (0.010 s), and $[C_4H_8]_0$ (2.00 M), so we can solve for $[C_4H_8]_t$.

(b) The fraction decomposed is the concentration that has decomposed divided by the initial concentration:

$$\text{Fraction decomposed} = \frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0}$$

Solution (a) Substituting the data into the integrated rate law:

$$\ln \frac{2.00\text{ mol/L}}{[C_4H_8]_t} = (87\text{ s}^{-1})(0.010\text{ s}) = 0.87$$

Taking the antilog of both sides:

$$\frac{2.00\text{ mol/L}}{[C_4H_8]_t} = e^{0.87} = 2.4$$

Solving for $[C_4H_8]_t$:

$$[C_4H_8]_t = \frac{2.00\text{ mol/L}}{2.4} = 0.83\text{ mol/L}$$

(b) Finding the fraction that has decomposed after 0.010 s :

$$\frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00\text{ mol/L} - 0.83\text{ mol/L}}{2.00\text{ mol/L}} = 0.58$$

Check The concentration remaining after 0.010 s (0.83 mol/L) is less than the starting concentration (2.00 mol/L), which makes sense. Raising e to an exponent slightly less than 1 should give a number (2.4) slightly less than the value of e (2.718). Moreover, the final result makes sense: a high rate constant indicates a fast reaction, so it's not surprising that so much decomposes in such a short time.

Comment Integrated rate laws are also used to solve for the time it takes to reach a certain reactant concentration, as in the follow-up problem.

FOLLOW-UP PROBLEM 16.4 At 25°C , hydrogen iodide breaks down very slowly to hydrogen and iodine: $\text{rate} = k[\text{HI}]^2$. The rate constant at 25°C is $2.4 \times 10^{-21}\text{ L/mol}\cdot\text{s}$. If 0.0100 mol of $\text{HI}(g)$ is placed in a 1.0-L container, how long will it take for the concentration of HI to reach 0.00900 mol/L (10.0% reacted)?

Determining the Reaction Order from the Integrated Rate Law

An integrated rate law can be rearranged into the form of an equation for a straight line, $y = mx + b$, where m is the slope and b is the y-axis intercept. For a first-order reaction, we have:

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

Therefore, a plot of $\ln [A]_t$ vs. time gives a straight line with slope = $-k$, and y intercept = $\ln [A]_0$ (Figure 16.5A).

For a simple second-order reaction, we have

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

In this case, a plot of $1/[A]_t$ vs. time gives a straight line with slope= k , y intercept = $1/[A]_0$ (Figure 16.5B).

For a zero-order reaction, we have:

$$[A]_t - [A]_0 = -kt$$
$$[A]_t = -kt + [A]_0$$
$$y = mx + b$$

Thus, a plot of $[A]$, vs. time gives a straight line with slope = $-k$ and y intercept = $[A]_0$ (Figure 16.5C).

- If you obtain a straight line when you plot \ln [reactant] vs. time, the reaction is first order with respect to that reactant.
- If you obtain a straight line when you plot $1/[$ reactant] vs. time, the reaction is second order with respect to that reactant.
- If you obtain a straight line when you plot [reactant] vs. time, the reaction is

zero order with respect to that reactant.

Figure 16.6 shows how this approach is used to determine the order for the decomposition of N_2O_5 .

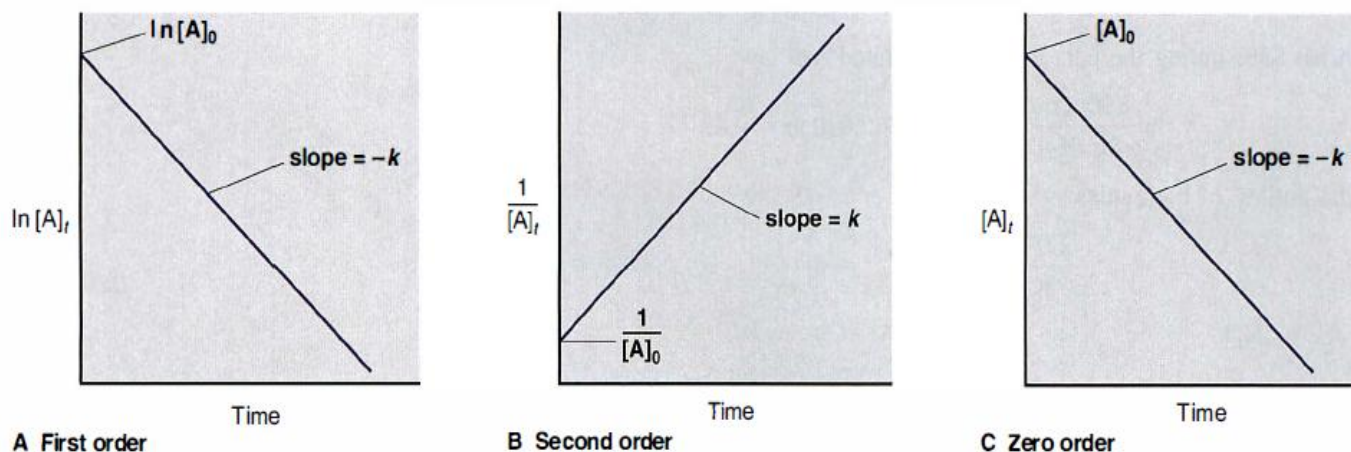
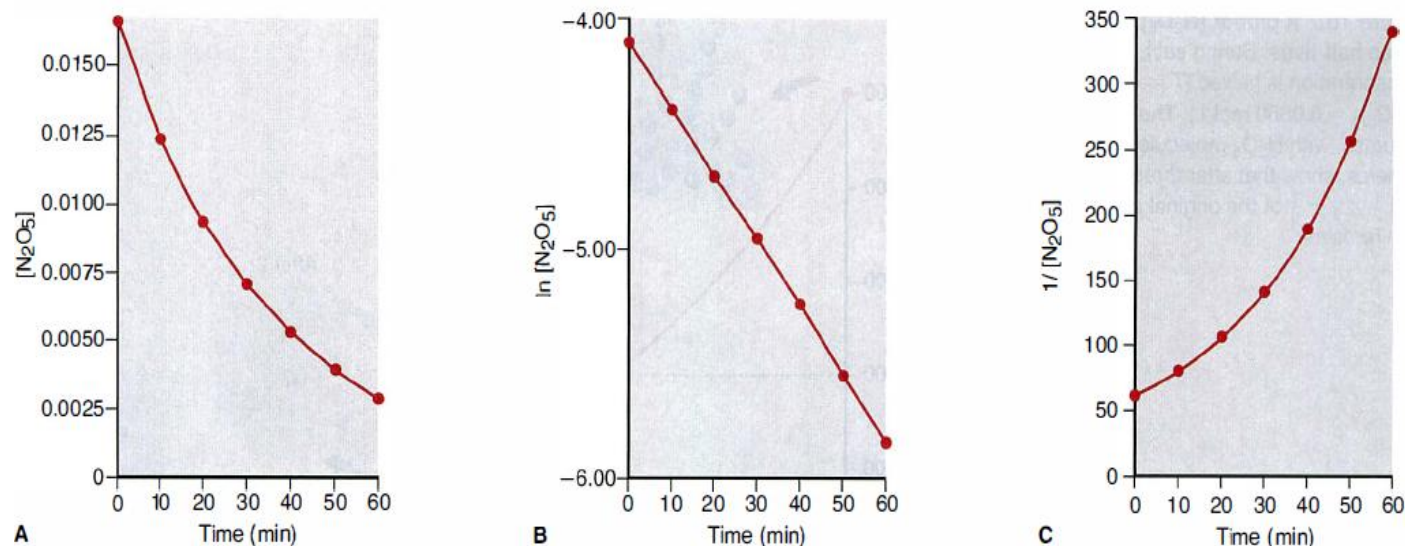


Figure 16.5 Integrated rate laws and reaction orders. A, Plot of $\ln [A]_t$ vs. time gives a straight line for a reaction that is first order in A. B, Plot of $1/[A]_t$ vs. time gives a straight line for a reaction that is second order in A. C, Plot of $[A]_t$ vs. time gives a straight line for a reaction that is zero order in A.

Figure 16.6 Graphical determination of the reaction order for the decomposition of N_2O_5 . A, a plot of $[\text{N}_2\text{O}_5]$ vs. time is curved, indicating that the reaction is not zero order in N_2O_5 . B, a plot of $\ln [\text{N}_2\text{O}_5]$ vs. time gives a straight line, indicating that the reaction is first order in N_2O_5 . C, a plot of $1/[\text{N}_2\text{O}_5]$ vs. time is curved, indicating that the reaction is not second order in $[\text{N}_2\text{O}_5]$. Plots A and C support the conclusion from plot B.

Time (min)	$[\text{N}_2\text{O}_5]$	$\ln [\text{N}_2\text{O}_5]$	$1/[\text{N}_2\text{O}_5]$
0	0.0165	-4.104	60.6
10	0.0124	-4.390	80.6
20	0.0093	-4.68	1.1×10^2
30	0.0071	-4.95	1.4×10^2
40	0.0053	-5.24	1.9×10^2
50	0.0039	-5.55	2.6×10^2
60	0.0029	-5.84	3.4×10^2



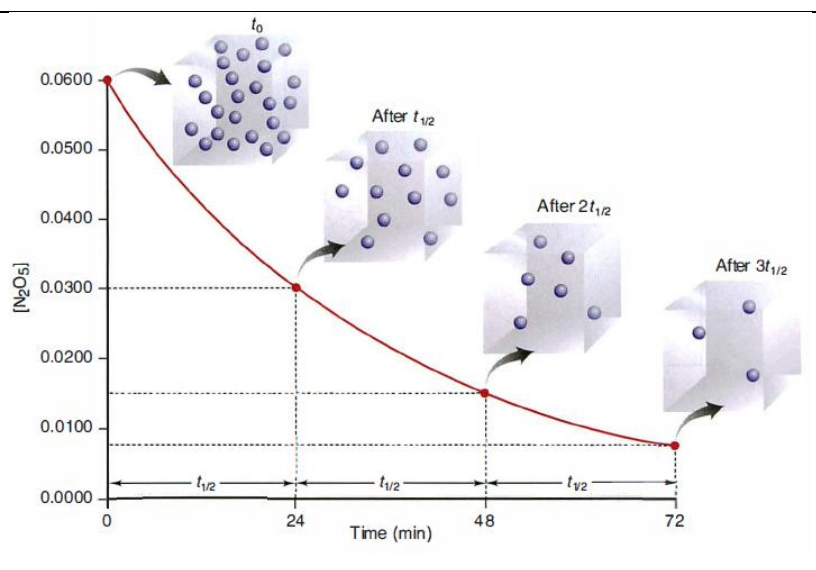
Reaction Half-Life

The half-life ($t_{1/2}$) of a reaction is the time required for the reactant concentration to reach half its initial value.

At fixed conditions, *the half-life of a first-order reaction is a constant*, independent of reactant concentration. For example, the half-life for the first-order decomposition of N_2O_5 at 45°C is 24.0 min. If we start with 0.0600 mol/L of N_2O_5 at 45°C , after 24 min (one half-life), 0.0300 mol/L has been consumed and 0.0300 mol/L remains; after 48 min (two half-lives), 0.0150 mol/L remains; after 72 min (three half-lives), 0.0075 mol/L remains, and so forth (Figure 16.7).

Figure 16.7

A plot of $[\text{N}_2\text{O}_5]$ vs. time for three half-lives. During each half-life, the concentration is halved ($T=45^\circ\text{C}$ and $[\text{N}_2\text{O}_5]_0 = 0.0600$ mol/L). The blow-up volumes, with N_2O_5 molecules as colored spheres, show that after three half-lives, $1/2 \times 1/2 \times 1/2 = 1/8$ of the original concentration remains.



We can see from the integrated rate law why the half-life of a first-order reaction is independent of concentration:

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

After one half-life, $t = t_{1/2}$, and $[\text{A}]_t = [\text{A}]_0/2$. Substituting, we obtain

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (\text{first-order process; rate} = k[\text{A}])$$

In contrast, the half-life of a second order and zero order reactions does depend on reactant concentration. For a second order reaction (one reactant);

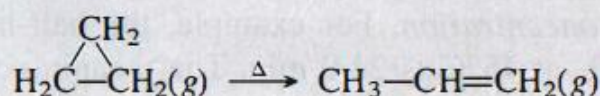
$$t_{1/2} = \frac{1}{k[A]_0}$$

For zero order reactions;

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

SAMPLE PROBLEM 16.5 Determining the Half-Life of a First-Order Reaction

Problem Cyclopropane is the smallest cyclic hydrocarbon. Because its 60° bond angles reduce orbital overlap, its bonds are weak. As a result, it is thermally unstable and rearranges to propene at 1000°C via the following first-order reaction:



The rate constant is 9.2 s^{-1} . **(a)** What is the half-life of the reaction? **(b)** How long does it take for the concentration of cyclopropane to reach one-quarter of the initial value?

Plan **(a)** The cyclopropane rearrangement is first order, so to find $t_{1/2}$ we use Equation 16.7 and substitute for k (9.2 s^{-1}). **(b)** Each half-life decreases the concentration to one-half of its initial value, so two half-lives decrease it to one-quarter.

Solution **(a)** Solving for $t_{1/2}$:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{9.2 \text{ s}^{-1}} = 0.075 \text{ s}$$

It takes 0.075 s for half the cyclopropane to form propene at this temperature.

(b) Finding the time to reach one-quarter of the initial concentration:

$$\text{Time} = 2(t_{1/2}) = 2(0.075 \text{ s}) = 0.15 \text{ s}$$

Check For **(a)**, rounding gives $0.7/9 \text{ s}^{-1} = 0.08 \text{ s}$, so the answer seems correct.

FOLLOW-UP PROBLEM 16.5 Iodine-123 is used to study thyroid gland function. This radioactive isotope breaks down in a first-order process with a half-life of 13.1 h. What is the rate constant for the process?

Table 16.4 An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

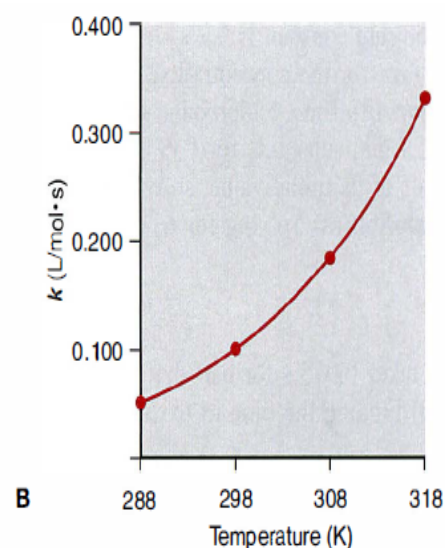
	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units for k	mol/L·s	1/s	L/mol·s
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$1/[A]_t = kt + 1/[A]_0$
Plot for straight line	$[A]_t$ vs. time	$\ln [A]_t$ vs. time	$1/[A]_t$ vs. time
Slope, y intercept	$-k, [A]_0$	$-k, \ln [A]_0$	$k, 1/[A]_0$
Half-life	$[A]_0/2k$	$(\ln 2)/k$	$1/k[A]_0$

16.5 THE EFFECT OF TEMPERATURE ON REACTION RATE

Temperature often has a major effect on reaction rate. As Figure 16.8A shows for a common organic reaction-hydrolysis, when reactant concentrations are held constant, the rate nearly doubles with each rise in temperature of 10 K (or 10°C). How does the rate law express this effect of temperature? temperature affects the rate by affecting the rate constant. A plot of k vs. T gives a curve that increases exponentially (Figure 16.8B).

Figure 16.8 Dependence of the rate constant on temperature. **A**, In the hydrolysis of the ester ethyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}$, when reactant concentrations are held constant and temperature increases, the rate and rate constant increase. Note the near doubling of k with each rise of 10 K (10°C). **B**, A plot of rate constant vs. temperature for this reaction shows an exponentially increasing curve.

Exp't	[Ester]	[H ₂ O]	T(K)	Rate (mol/L·s)	k (L/mol·s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.02×10^{-3}	0.101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332



These results are consistent with Arrhenius equation given as:

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

where k is the rate constant, e is the base of natural logarithms, T is the absolute temperature, and R is the universal gas constant. The E_a term is the **activation energy** of the reaction, considered as the minimum energy the molecules must have to react. This negative exponential relationship between T and k means that as T increases, the negative exponent becomes smaller, so the value of k becomes larger, which means that the rate increases.

The equation can be recasted into one for a straight line:

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

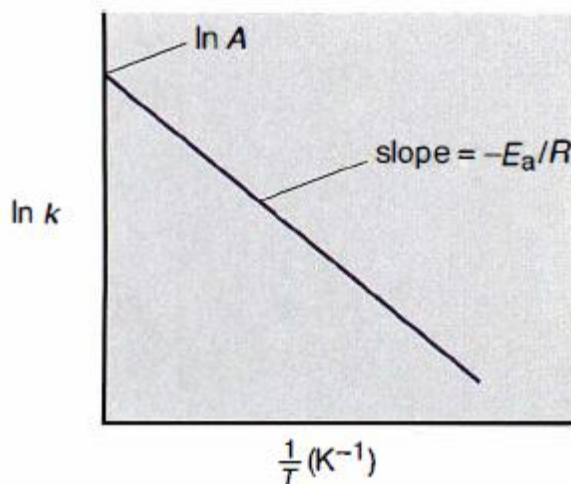
$$y = b + mx$$

Figure 16.9

Graphical determination of the activation energy.

A plot of $\ln k$ vs. $1/T$ gives a straight line with slope = $-E_a/R$.

Because the relationship between $\ln k$ and $1/T$ is linear, we can use a simpler method to find E_a if we know the rate constants at two temperatures, T_2 and T_1 :



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

SAMPLE PROBLEM 16.6 Determining the Energy of Activation

Problem The decomposition of hydrogen iodide,



has rate constants of 9.51×10^{-9} L/mol·s at 500. K and 1.10×10^{-5} L/mol·s at 600. K. Find E_a .

Plan We are given the rate constants, k_1 and k_2 , at two temperatures, T_1 and T_2 , so we substitute into Equation 16.9 and solve for E_a .

Solution Rearranging Equation 16.9 to solve for E_a :

$$\begin{aligned} \ln \frac{k_2}{k_1} &= -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ E_a &= -R \left(\ln \frac{k_2}{k_1} \right) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)^{-1} \\ &= -(8.314 \text{ J/mol}\cdot\text{K}) \left(\ln \frac{1.10 \times 10^{-5} \text{ L/mol}\cdot\text{s}}{9.51 \times 10^{-9} \text{ L/mol}\cdot\text{s}} \right) \left(\frac{1}{600. \text{ K}} - \frac{1}{500. \text{ K}} \right)^{-1} \\ &= 1.76 \times 10^5 \text{ J/mol} = 1.76 \times 10^2 \text{ kJ/mol} \end{aligned}$$

Comment Be sure to retain the same number of significant figures in $1/T$ as you have in T , or a significant error could be introduced. Round to the correct number of significant figures only at the final answer. On most pocket calculators, the expression $(1/T_2 - 1/T_1)$ is entered as follows: $(T_2)(1/x) - (T_1)(1/x) =$

FOLLOW-UP PROBLEM 16.6 The reaction $2\text{NOCl}(g) \longrightarrow 2\text{NO}(g) + \text{Cl}_2(g)$ has an E_a of 1.00×10^2 kJ/mol and a rate constant of 0.286 L/mol·s at 500. K. What is the rate constant at 490. K?

16.6 EXPLAINING THE EFFECTS OF CONCENTRATION AND TEMPERATURE

The two major models that explain the observed effects of concentration and temperature on reaction rate highlight different aspects of the reaction process but are completely compatible.

- Collision theory views the reaction rate as the result of particles colliding with a certain frequency and minimum energy.
- Transition state theory offers a close-up view of how the energy of a collision converts reactant to product.

Collision Theory: Basis of the Rate Law

The basic tenet of collision theory is that reactant particles-atoms, molecules, and ions-must collide with each other to react. Therefore, the number of collisions per unit time provides an upper limit on how fast a reaction can take place.

The model restricts itself to simple one-step reactions in which two particles collide and form products: $A + B \rightarrow \text{products}$. With its emphasis on collisions between three-dimensional particles, this model explains:

- why reactant concentrations are multiplied together in the rate law,
- how temperature affects the rate, and
- what influence molecular structure has on rate.

Why Concentrations Are Multiplied in the Rate Law

The laws of probability tell us why the rate depends on the product of the reactant concentrations, not their sum. Imagine that you have only two particles of A and two of B confined in a reaction vessel. Figure 16.11 shows that four A-B collisions are possible. If you add another particle of A, there can be six A-B collisions (3×2), not just five ($3 + 2$); add another particle of B, and there can be nine A-B collisions (3×3), not just six ($3 + 3$). Thus, collision theory is consistent with the observation that concentrations are multiplied in the rate law.

Figure 16.11

The dependence of number of possible collisions on the product of reactant concentrations. Concentrations are multiplied, not added, in the rate law because the number of possible collisions is the product, not the sum, of the numbers of particles present.

How Temperature Affects Rate: The Importance of Activation Energy

Increasing the temperature of a reaction increases the *collision frequency*. But the vast majority of collisions, the molecules rebound without reacting. Arrhenius proposed that every reaction has an energy threshold that the colliding molecules must exceed in order to react.

This minimum collision energy is the activation energy (E_a). According to collision theory, *only those collisions with enough energy to exceed E_a can lead to reaction*. In fact, *the temperature rise enlarges the fraction of collisions with enough energy to exceed the activation energy*. This key point is shown in Figure 16.12.

At a given temperature, the fraction, f , of molecular collisions with energy greater than or equal to the activation energy E_a is given by:

$$f = e^{-E_a/RT}$$

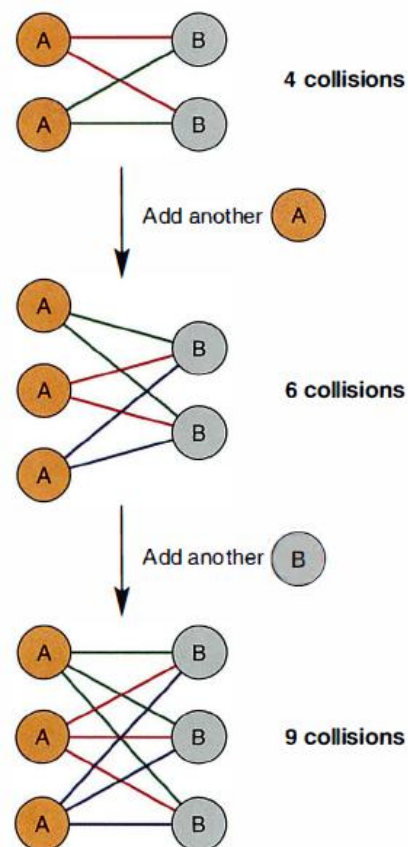
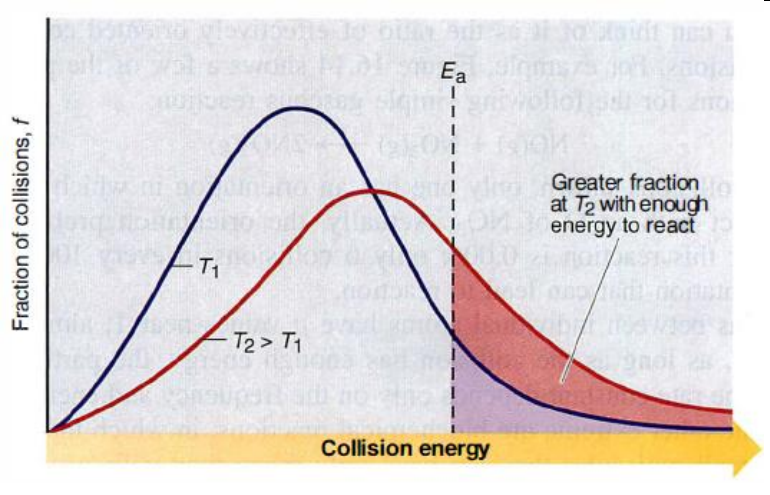


Figure 16.12 The effect of temperature on the distribution of collision energies. At the higher temperature, T_2 , a larger fraction of collisions occur with enough energy to exceed E_a .



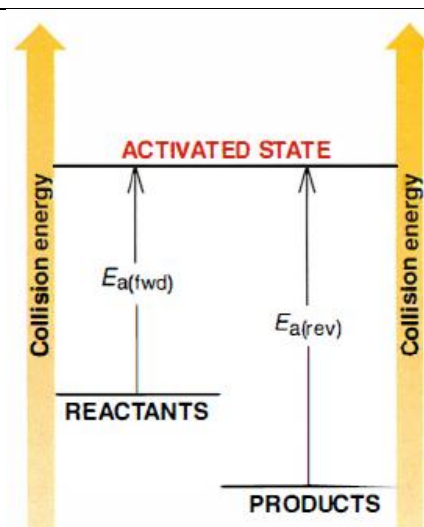
The magnitudes of both E_a and T affect the fraction of sufficiently energetic collisions (see Table 16.5). Note that the fraction nearly doubles for a 10°C increase. Doubling the fraction doubles the rate constant, which doubles the reaction rate.

Table 16.5 The Effect of E_a and T on the Fraction (f) of Collisions with Sufficient Energy to Allow Reaction

E_a (kJ/mol)	f (at $T = 298$ K)
50	1.70×10^{-9}
75	7.03×10^{-14}
100	2.90×10^{-18}
T	f (at $E_a = 50$ kJ/mol)
25°C (298 K)	1.70×10^{-9}
35°C (308 K)	3.29×10^{-9}
45°C (318 K)	6.12×10^{-9}

A reversible reaction has two activation energies (Figure 16.13). The activation energy for the forward reaction, $E_{a(\text{fwd})}$, is the energy difference between the activated state and the reactants; the activation energy for the reverse reaction, $E_{a(\text{rev})}$, is the energy difference between the activated state and the products.

Figure 16.13 Energy-level diagram for a reaction. For molecules to react, they must collide with enough energy to reach an activated state. This minimum collision energy is the energy of activation, E_a . A reaction can occur in either direction, so the diagram shows two activation energies. Here, the forward reaction is exothermic and $E_{a(\text{fwd})} < E_{a(\text{rev})}$.



How Molecular Structure Affects Rate

In order to be effective, a collision must have enough energy and a **particular molecular orientation**. In the Arrhenius equation, the effect of molecular orientation is contained in the term A :

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

This term is called the frequency factor, the product of the collision frequency Z and an **orientation probability factor, p** , which is specific for each reaction;

$$A = pz.$$

The factor p is related to the *structural complexity* of the colliding particles. You can think of it as the ratio of effectively oriented collisions to all possible collisions. For example, Figure 16.14 shows a few of the possible collision orientations for the following simple gaseous reaction:

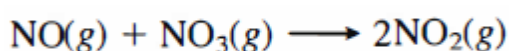
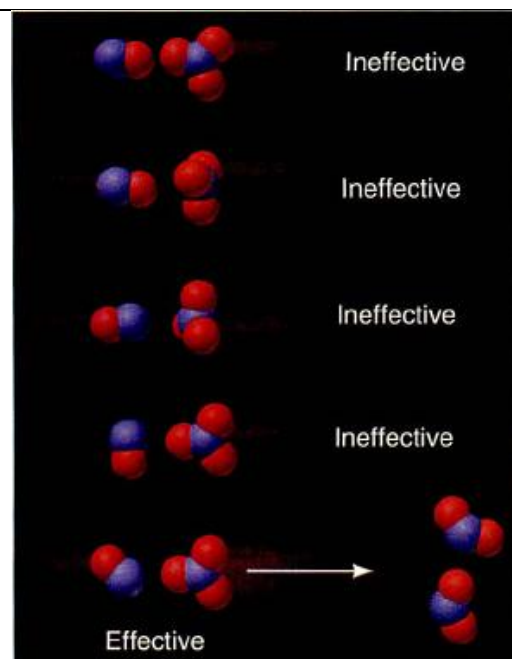


Figure 16.14 The importance of molecular orientation to an effective collision. Only one of the five orientations shown for the collision between NO and NO₃ has the correct orientation to lead to product. In the effective orientation, contact occurs between the atoms that will become bonded in the product.

Actually, the orientation probability factor (p value) for this reaction is 0.006; only 6 collisions in every 1000 have an orientation that can lead to reaction.



Transition State Theory: Molecular Nature of the Activated Complex

The transition state theory focuses on the high-energy species that forms through an effective collision and introduces the concept of activated complex.

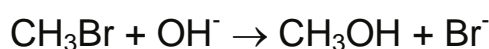
Visualizing the Transition State

Recall that the internal energy of a system is the sum of its kinetic and potential energies. When two molecules approach one another, some kinetic energy is converted to potential energy as the electron clouds repel each other.

- At the moment of a head-on collision, if this potential energy is less than the activation energy, the molecules recoil without reacting.
- The tiny fraction of molecules that are oriented effectively and moving at the highest speed overcome repulsions and react.

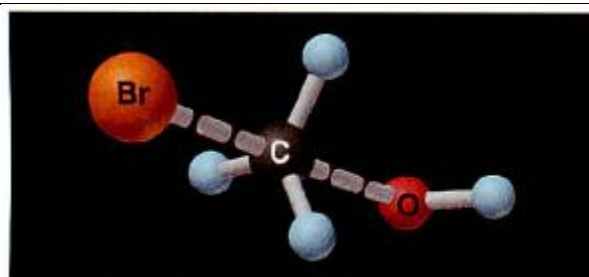
At some point during this transformation, what exists is neither reactant nor product but a transitional species with partial bonds. This extremely unstable species, which is called the **transition state**, or **activated complex**, exists only at the instant when the reacting system is highest in potential energy.

Consider the reaction between methyl bromide and hydroxide ion:



- The negatively charged oxygen in OH^- approaches the partially positive carbon with enough energy to begin forming a C-O bond, which causes the C-Br bond to weaken.
- Transition state: C is surrounded by five atoms (trigonal bipyramidal), which never occurs in its stable compounds.
- A transition state can change in either direction: if the C - O bond continues to shorten and strengthen, products form; however, if the C -Br bond becomes shorter and stronger again, the transition state reverts to reactants.

Figure 16.15 Nature of the transition state in the reaction between CH_3Br and OH^- . Note the partial (elongated) C - O and C - Br bonds and the trigonal bipyramidal shape of the transition state of this reaction.



Depicting the Change with Reaction Energy Diagrams

A useful way to depict the events we just described is with a **reaction energy diagram**, which shows the potential energy of the system during the reaction as a smooth curve. Figure 16.16 shows the reaction energy diagram for the reaction of

CH_3Br and OH^- , and also includes electron density relief maps, structural formulas, and molecular-scale views at various points during the change.

The horizontal axis, labeled "Reaction progress," means reactants change to products from left to right. This reaction is exothermic, so reactants are higher in energy than products. The diagram also shows activation energies for the forward and reverse reactions; in this case, $E_{a(\text{fwd})}$ is less than $E_{a(\text{rev})}$. This difference, which reflects the change in bond energies, equals the heat of reaction, ΔH_{rxn} :

$$\Delta H_{\text{rxn}} = E_{a(\text{fwd})} - E_{a(\text{rev})}$$

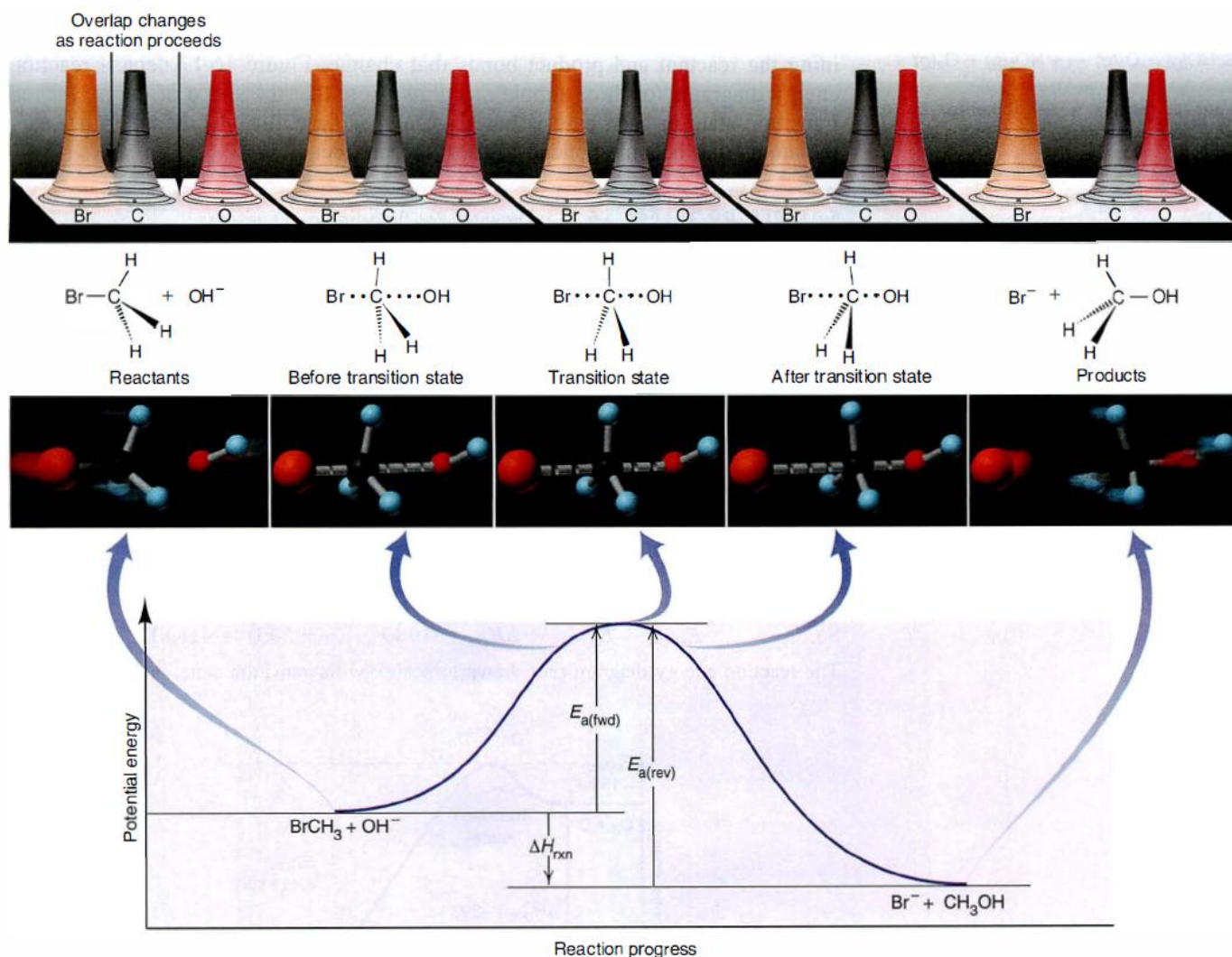


Figure 16.16 Reaction energy diagram for the reaction between CH_3Br and OH^- . A plot of potential energy vs. reaction progress shows the relative energy levels of reactants, products, and transition state joined by a curved line, as well as the activation energies of the

forward and reverse steps and the heat of reaction. The electron density relief maps, structural formulas, and molecular-scale views depict the change at five points. Note the gradual bond forming and bond breaking as the system goes through the transition state.

Transition state theory proposes that every reaction goes through its own transition state, from which it can continue in either direction. Figure 16.17 depicts reaction energy diagrams for three simple reactions.

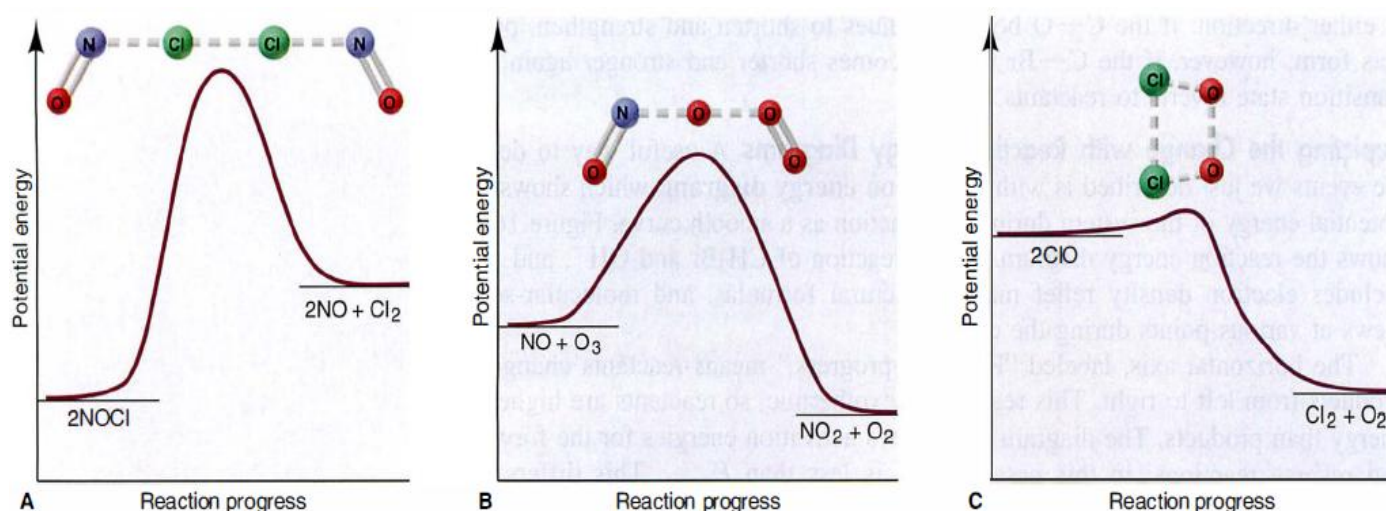
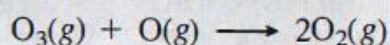


Figure 16.17 Reaction energy diagrams and possible transition states for three reactions. A, $2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$ (Despite the formula NOCl , the atom sequence is ClNO .) B, $\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)$. C, $2\text{ClO}(g) \rightarrow \text{Cl}_2(g) + \text{O}_2(g)$. Note that reaction A is endothermic, B and C are exothermic, and C has a very small $E_{a(\text{fwd})}$.

SAMPLE PROBLEM 16.7 Drawing Reaction Energy Diagrams and Transition States

Problem A key reaction in the upper atmosphere is



The $E_{a(\text{fwd})}$ is 19 kJ, and the ΔH_{rxn} for the reaction as written is -392 kJ. Draw a reaction energy diagram for this reaction, postulate a transition state, and calculate $E_{a(\text{rev})}$.

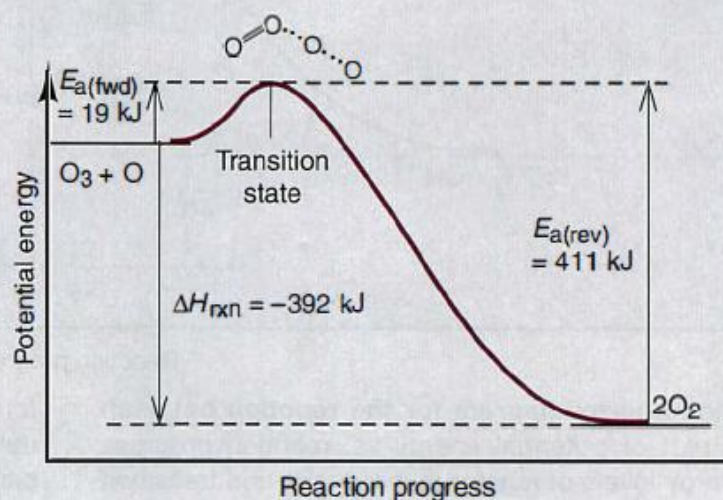
Plan The reaction is highly exothermic ($\Delta H_{\text{rxn}} = -392$ kJ), so the products are much lower in energy than the reactants. The small $E_{a(\text{fwd})}$ (19 kJ) means the energy of the reactants lies slightly below that of the transition state. We use Equation 16.10 to calculate $E_{a(\text{rev})}$. To postulate the transition state, we sketch the species and note that one of the bonds in O_3 weakens, and this partially bonded O begins forming a bond to the separate O atom.

Solution Solving for $E_{a(\text{rev})}$:

$$\Delta H_{\text{rxn}} = E_{a(\text{fwd})} - E_{a(\text{rev})}$$

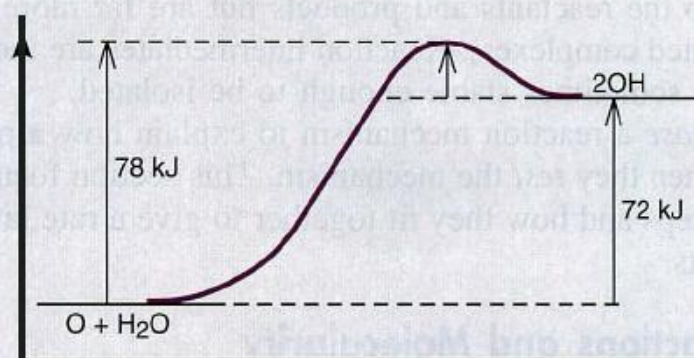
So,
$$E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H_{\text{rxn}} = 19 \text{ kJ} - (-392 \text{ kJ}) = 411 \text{ kJ}$$

The reaction energy diagram (not drawn to scale), with transition state, is



Check Rounding to find $E_{a(\text{rev})}$ gives $\sim 20 + 390 = 410$.

FOLLOW-UP PROBLEM 16.7 The following reaction energy diagram depicts another key atmospheric reaction. Label the axes, identify $E_{a(\text{fwd})}$, $E_{a(\text{rev})}$, and ΔH_{rxn} , draw and label the transition state, and calculate $E_{a(\text{rev})}$ for the reaction.

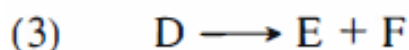
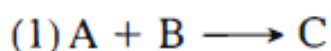


16.7 REACTION MECHANISMS: STEPS IN THE OVERALL REACTION

Most reactions occur through a **reaction mechanism**, a sequence of single reaction steps that sum to the overall reaction. For example, a possible mechanism for the overall reaction:



might involve these three simpler steps:



Adding them together we obtain the overall equation above. Note that C is a product in step 1 and a reactant in step 2, and D is a product in 2 and a reactant in 3. Each functions as a **reaction intermediate**, a substance that is formed and used up, and as a result *do not appear* in the overall balanced equation.

They are usually *unstable relative to the reactants and products but are far more stable than transition states* (activated complexes). Reaction intermediates are molecules with normal bonds and are sometimes stable enough to be isolated.

Chemists propose a reaction mechanism to explain how a particular reaction might occur, and then they test the mechanism. This section focuses on the nature of the individual steps and how they fit together to give a rate law consistent with experimental results.

Elementary Reactions and Molecularity

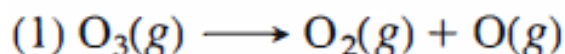
The individual steps, which together make up a proposed reaction mechanism, are called **elementary reactions** (or **elementary steps**) .

- An elementary step is not made up of simpler steps.
- An elementary step is characterized by its molecularity, the number of reactant particles involved in the step.

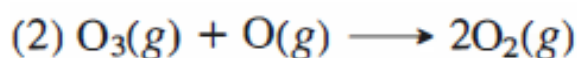
Consider overall reaction:



A two-step mechanism has been proposed for this reaction. The first elementary step is a **unimolecular** reaction, one that involves the decomposition or rearrangement of a single particle:



The second step is a **bimolecular reaction**, one in which two particles react:



Some termolecular elementary steps occur, but they are extremely rare because the probability of three particles colliding simultaneously with enough energy and with an effective orientation is very small. Higher molecularities are not known.

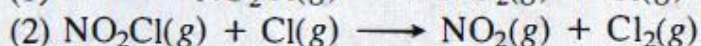
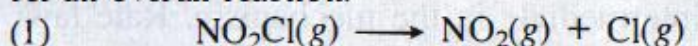
The **rate law for an elementary reaction, unlike that for an overall reaction, can be deduced from the reaction stoichiometry.** Therefore, we use the equation coefficients as the reaction orders in the rate law for an elementary step; that is, reaction order equals molecularity (Table 16.6).

Table 16.6 Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{product}$	Unimolecular	Rate = $k[A]$
$2A \longrightarrow \text{product}$	Bimolecular	Rate = $k[A]^2$
$A + B \longrightarrow \text{product}$	Bimolecular	Rate = $k[A][B]$
$2A + B \longrightarrow \text{product}$	Termolecular	Rate = $k[A]^2[B]$

SAMPLE PROBLEM 16.8 Determining Molecularity and Rate Laws for Elementary Steps

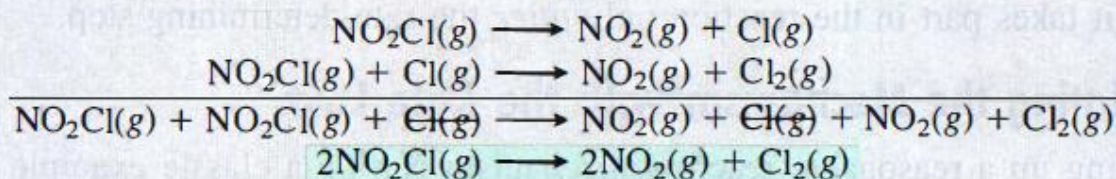
Problem The following two reactions are proposed as elementary steps in the mechanism for an overall reaction:



- (a) Write the overall balanced equation.
 (b) Determine the molecularity of each step.
 (c) Write the rate law for each step.

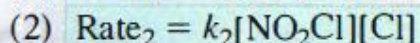
Plan We find the overall equation from the sum of the elementary steps. The molecularity of each step equals the total number of reactant particles. We write the rate law for each step using the molecularities as reaction orders.

Solution (a) Writing the overall balanced equation:



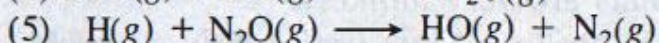
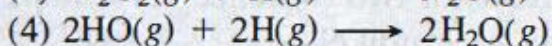
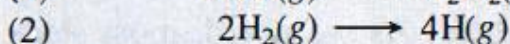
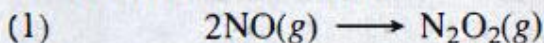
(b) Determining the molecularity of each step: The first elementary step has only one reactant, NO_2Cl , so it is **unimolecular**. The second elementary step has two reactants, NO_2Cl and Cl , so it is **bimolecular**.

(c) Writing rate laws for the elementary reactions:



Check In part (a), be sure the equation is balanced; in part (c), be sure the substances in brackets are the reactants of each elementary step.

FOLLOW-UP PROBLEM 16.8 The following elementary steps constitute a proposed mechanism for a reaction:



(a) Write the balanced equation for the overall reaction.

(b) Determine the molecularity of each step.

(c) Write the rate law for each step.

The Rate-Determining Step of a Reaction Mechanism

All the elementary steps in a mechanism do not have the same rate. Usually, one step is much *slower than the others*, so it limits how fast the overall reaction proceeds. This step is called the **rate-determining step** (or **rate-limiting step**).

Consider the reaction between nitrogen dioxide and carbon monoxide:



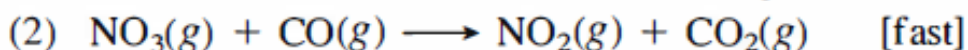
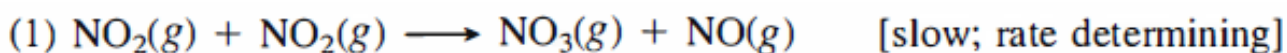
If the overall reaction were an elementary reaction, that is, if the mechanism consisted of only one step—we could immediately write the overall rate law as:

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

However, as you saw in Sample Problem 16.3, experiment shows that the actual rate law is:

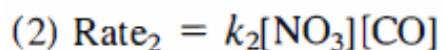
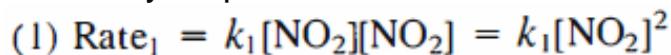
$$\text{Rate} = k[\text{NO}_2]^2$$

A proposed two-step mechanism is:



Note that NO_3 functions as a reaction intermediate in the mechanism.

Rate laws for these elementary steps are:



Note that if $k_1 = k_2$, the rate law for the rate-determining step (step 1) is identical to the experimental rate law. CO is absent from the overall rate law because it appears after the rate-determining step.

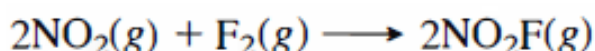
Correlating the Mechanism with the Rate Law

Regardless of the elementary steps proposed for a mechanism, they must meet three criteria:

1. The elementary steps must add up to the overall balanced equation.
2. The elementary steps must be physically reasonable. Most steps should involve one reactant particle (unimolecular) or two (bimolecular). Steps with three reactant particles (termolecular) are very unlikely.
3. The mechanism must correlate with the rate law.

Mechanisms with a Slow Initial Step

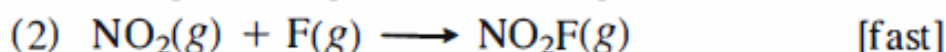
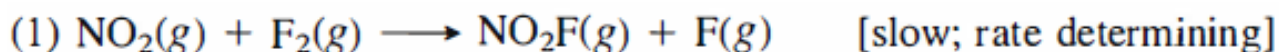
Consider the reaction between nitrogen dioxide and fluorine gas:



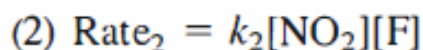
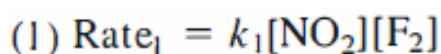
The experimental rate law is first order in NO_2 and in F_2 :

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

The accepted mechanism for the reaction is:



write the rate laws for the elementary steps:



Step 1 is the rate-determining step and therefore gives the overall rate law, with

$k_1 = k$. Because the second molecule of NO_2 appears in the step that follows the rate-determining step, it does not appear in the overall rate law.

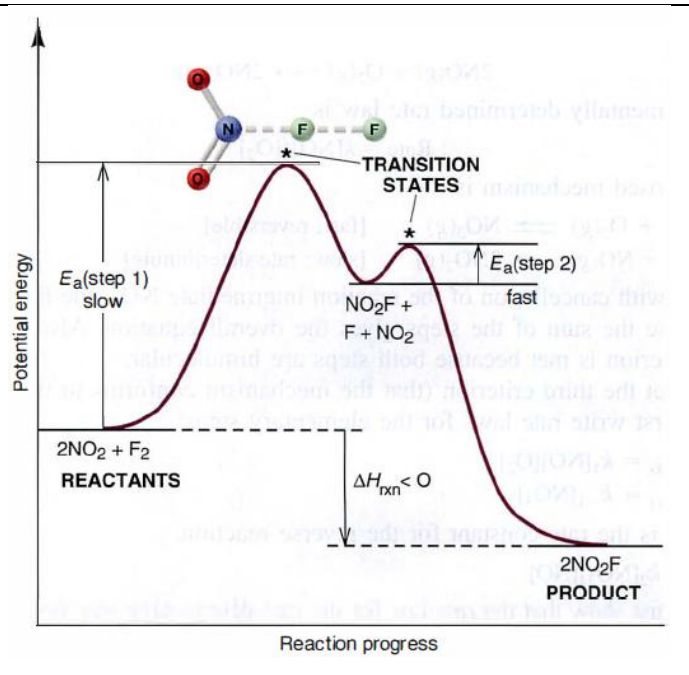
Figure 16.18 is a reaction energy diagram for the reaction of NO_2 and F_2 .

Note that:

- Each step in the mechanism has its own transition state.
- The F atom intermediate is a reactive, unstable species, so it is higher in energy than the reactants or product.
- The first step is slower (rate limiting), so its activation energy is larger than that of the second step.
- The overall reaction is exothermic, so the product is lower in energy than the reactants.

Figure 16.18

Reaction energy diagram for the two-step reaction of NO_2 and F_2 . Each step in the mechanism has its own transition state. The proposed transition state is shown for step 1. Reactants for the second step are the F atom intermediate and the second molecule of NO_2 . Note that the first step is slower (higher E_a). The overall reaction is exothermic ($\Delta H_{\text{rxn}} < 0$).

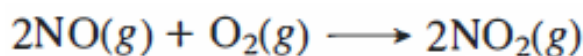


Mechanisms with a Fast Initial Step

If the rate-determining step in a mechanism is not the initial step, it acts as a bottleneck later in the reaction sequence. As a result, the product of a fast initial step builds up and starts reverting to reactant, while waiting for the slow step to remove

it. With time, the product of the initial step is changing back to reactant as fast as it is forming. In other words, the fast initial step reaches equilibrium.

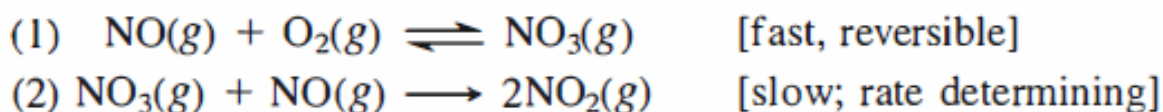
Consider once again the oxidation of nitrogen monoxide:



The experimentally determined rate law is

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

and a proposed mechanism is



We first write rate laws for the elementary steps:

$$\begin{array}{l} (1) \quad \text{Rate}_{1(\text{fwd})} = k_1[\text{NO}][\text{O}_2] \\ \quad \quad \text{Rate}_{1(\text{rev})} = k_{-1}[\text{NO}_3] \end{array}$$

where k_{-1} is the rate constant for the reverse reaction.

$$(2) \quad \text{Rate}_2 = k_2[\text{NO}_3][\text{NO}]$$

the rate-determining step (step 2) contains the intermediate NO_3 , and an overall rate law can include only reactants (and products). Therefore, we must eliminate $[\text{NO}_3]$ from the step 2 rate law. To do so, we express $[\text{NO}_3]$ in terms of reactants.

$$\text{Rate}_{1(\text{fwd})} = \text{Rate}_{1(\text{rev})} \quad \text{or} \quad k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3]$$

$$[\text{NO}_3] = \frac{k_1}{k_{-1}}[\text{NO}][\text{O}_2]$$

$$\text{Rate}_2 = k_2[\text{NO}_3][\text{NO}] = k_2 \left(\frac{k_1}{k_{-1}}[\text{NO}][\text{O}_2] \right) [\text{NO}] = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$$

This rate law is identical to the overall rate law, with $k = k_2 k_1 / k_{-1}$.

16.8 CATALYSIS: SPEEDING UP A CHEMICAL REACTION

Sometimes, we can speed up a reaction sufficiently with a higher temperature, but energy is costly and many substances are heat sensitive and easily decomposed. Alternatively, we can often employ a **catalyst**, a *substance that increases the rate without being consumed in the reaction*.

Two important points stand out in Figure 16.19 regarding catalysis:

- A catalyst speeds up the forward and reverse reactions. A reaction with a catalyst does not yield more product than one without a catalyst, but it yields the product more quickly.
- A catalyst causes a lower activation energy by providing a different mechanism for the reaction, and thus a new, lower energy pathway.

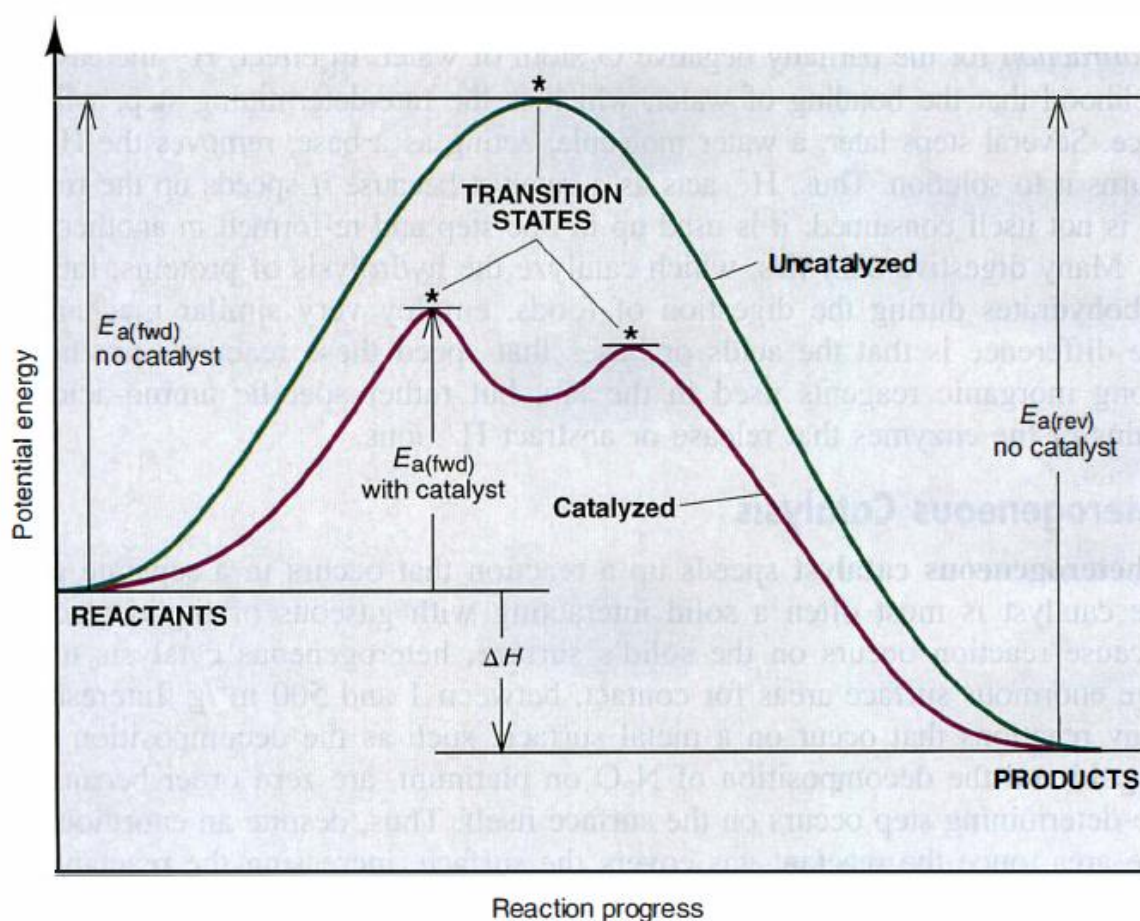
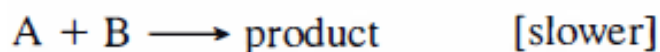
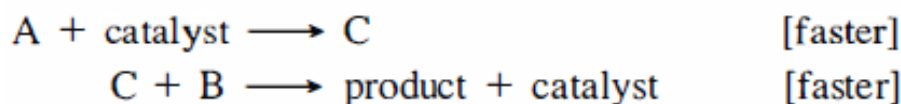


Figure 16.19 Reaction energy diagram for a catalyzed and an uncatalyzed process. A catalyst speeds a reaction by providing a new, lower energy pathway, in this case by replacing the one-step mechanism with a two-step mechanism. Both forward and reverse rates are increased to the same extent, so a catalyst does not affect the overall reaction yield. (The only activation energy shown for the catalyzed reaction is the larger one for the forward direction.)

Consider a general uncatalyzed reaction involving a bimolecular collision:



In the catalyzed reaction, a reactant molecule interacts with the catalyst, so the mechanism might involve a two-step pathway:

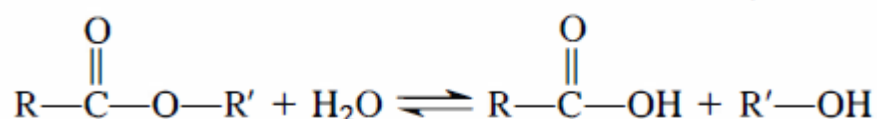


Note that the catalyst is used and then regenerated, and the activation energies of both steps are lower than the activation energy of the uncatalyzed pathway.

There are two general categories of catalyst; **homogeneous catalysts** and **heterogeneous catalysts**, based on whether the catalyst is in the same phase as the reactant and product.

Homogeneous Catalysis

A homogeneous catalyst exists in solution with the reaction mixture. All homogeneous catalysts are gases, liquids, or soluble solids. A thoroughly studied example of homogeneous catalysis is the hydrolysis of an organic ester (RCOOR'):



The reaction rate is low at room temperature but can be increased greatly by adding a small amount of strong acid, which provides H^+ ion, the catalyst in the reaction; strong bases, which supply OH^- ions, also speed ester hydrolysis, but by a slightly different mechanism. The acid-catalyzed reaction is shown in Figure 16.20.

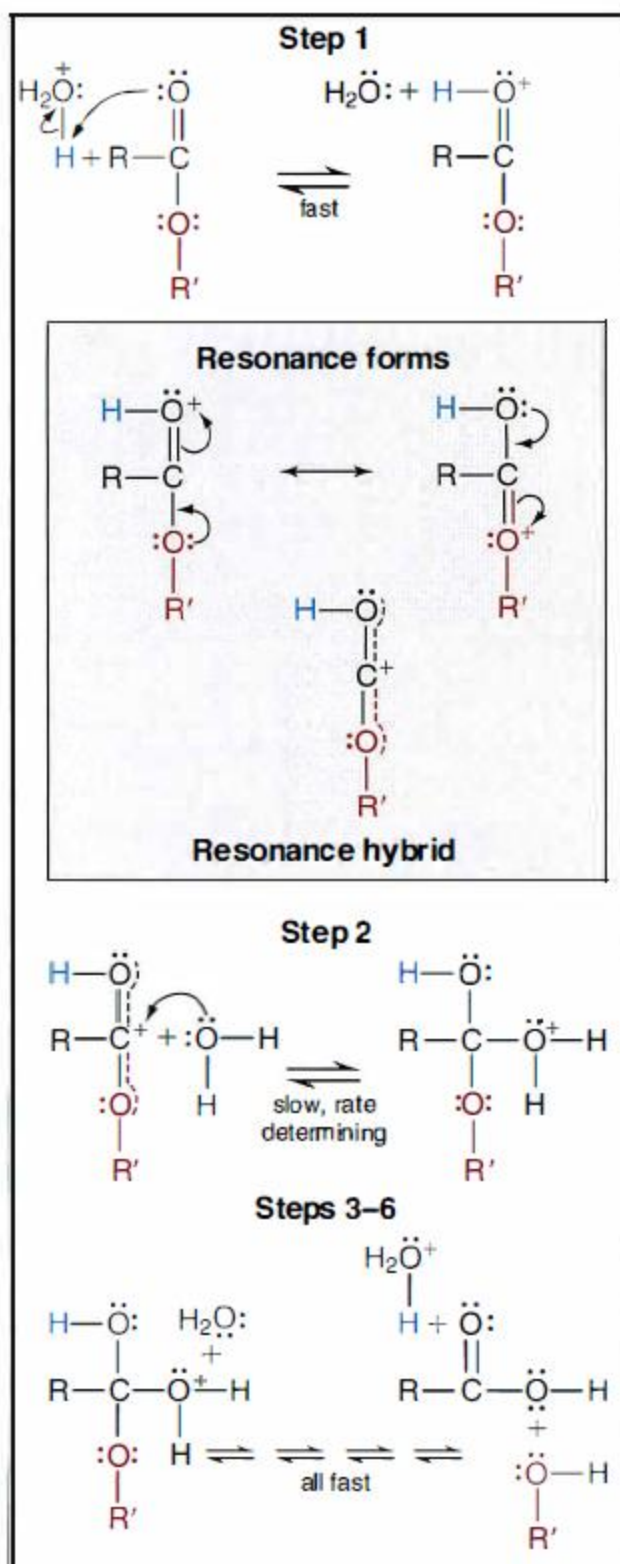
Heterogeneous Catalysis

A heterogeneous catalyst is most often a solid interacting with gaseous or liquid reactants. Because reaction occurs on the solid's surface, heterogeneous catalysts usually have enormous surface areas for contact, between 1 and 500 m^2/g . Interestingly, many reactions that occur on a metal surface, such as the

Figure 16.20

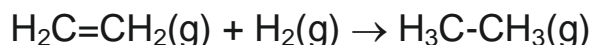
Mechanism for the catalyzed hydrolysis of an organic ester.

In step 1, the catalytic H^+ ion binds to the electron-rich oxygen. The resonance hybrid of this product (see gray panel) shows the C atom is more positive than it would ordinarily be. The enhanced charge on C attracts the partially negative O of water more strongly, increasing the fraction of effective collisions and thus speeding up step 2, the rate-determining step. Loss of $R'OH$ and removal of H^+ by water occur in a final series of fast steps.

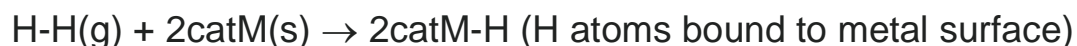


decomposition of HI on gold and the decomposition of N_2O on platinum, are *zero order* because the rate-determining step occurs on the surface itself. Thus, despite an enormous surface area, once the reactant gas covers the surface, increasing the reactant concentration cannot increase the rate.

Consider the hydrogenation of ethylene to ethane:

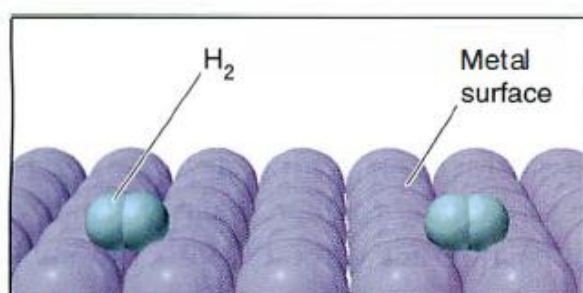


In the absence of a catalyst, the reaction occurs very slowly. At high H_2 pressure in the presence of finely divided Ni, Pd, or Pt, the reaction becomes rapid even at ordinary temperatures. These Group 8B(10) metals *catalyze by chemically adsorbing the reactants onto their surface* (Figure 16.21). The H_2 lands and splits into separate H atoms chemically bound to the solid catalyst's metal atoms (catM):

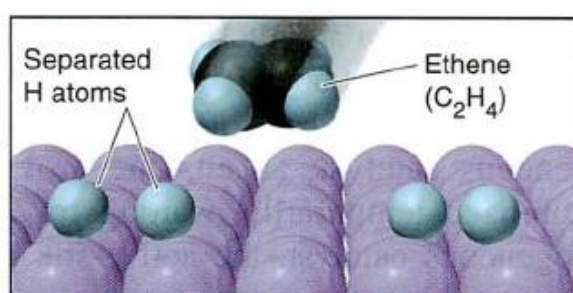


Then, C_2H_4 adsorbs and reacts with two H atoms, one at a time, to form C_2H_6 .

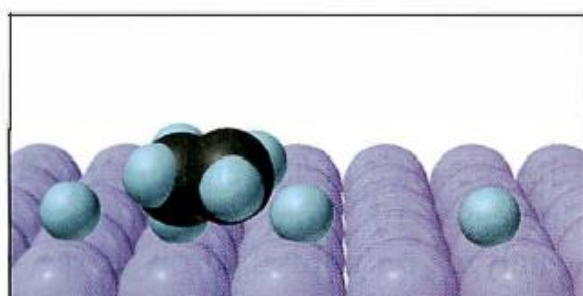
The H-H bond breakage is the rate-determining step in the overall process, and interaction with the catalyst's surface provides the low- E_a step as part of an alternative reaction mechanism.



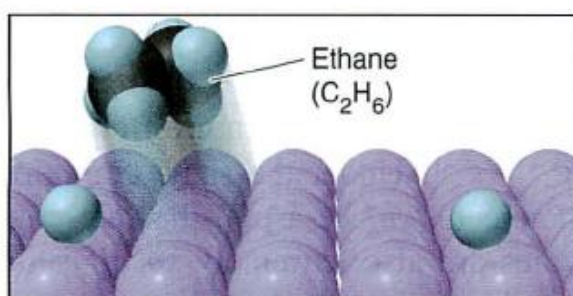
① H_2 adsorbs to metal surface



② Rate-limiting step is H-H bond breakage.



③ After C_2H_4 adsorbs, one C-H forms.



④ Another C-H bond forms; C_2H_6 leaves surface.

Figure 16.21 The metal-catalyzed hydrogenation of ethylene.

Catalysis in Nature

Catalytic processes occur in natural settings as well, and a brief description of two important systems follows.

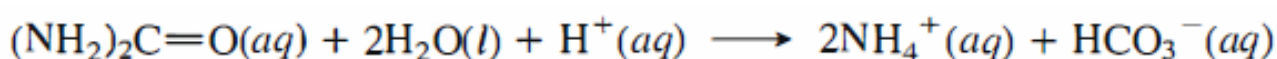
Cellular Catalysis: The Function of Enzymes

Within every living cell, thousands of individual reactions occur in dilute solution at ordinary temperatures and pressures. Virtually every cell reaction is catalyzed by its own specific **enzyme**, a protein whose complex three-dimensional shape-and thus its function-has been perfected through natural selection.

Every enzyme has an active site, a small region whose shape results from those of the side chains (R groups) of the amino acids that make it up. When reactant molecules, called the substrates, bind to an active site, usually through intermolecular forces, the chemical change begins.

With molar masses ranging from 15,000 to 1,000,000 g/mol, most enzymes are enormous relative to their substrates, and they are often embedded within membranes. Like a homogeneous catalyst, the active-site R groups interact directly with the substrates in multistep sequences.

Consider the hydrolysis of urea, a key component in amino-acid metabolism:



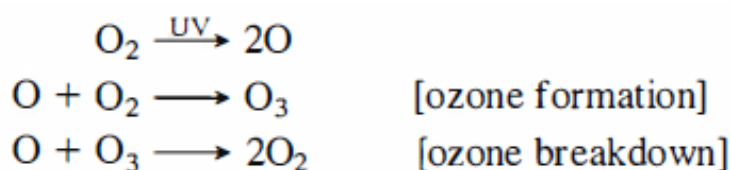
In water at room temperature, the rate constant for the uncatalyzed reaction is $3 \times 10^{-10} \text{ s}^{-1}$. Under the same conditions in the presence of the enzyme urease the rate constant increases to $3 \times 10^4 \text{ s}^{-1}$. Enzymes are extremely **effective** and **specific**: with extremely high rate, urease catalyzes only this hydrolysis reaction and no other enzyme does so.

There are two main models of enzyme action. In the **lock-and-key** model, when the "key" (substrate) fits the "lock" (active site), the chemical change begins. However, experiments show that, in many cases, the enzyme changes shape when the substrate lands at its active site. Thus, rather than a rigidly shaped lock in which a particular key fits, the **induced-fit model** pictures a "hand" (substrate) entering a "glove" (active site), causing it to attain its functional shape.

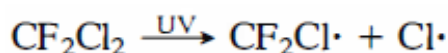
Atmospheric Catalysis: Depletion of the Ozone Layer

At Earth's surface, ozone is an air pollutant, contributing to smog and other problems. In the stratosphere, however, a natural layer of ozone absorbs UV radiation from the Sun. If this radiation reaches the surface, it can break bonds in DNA, promote skin cancer, and damage simple life forms at the base of the food chain.

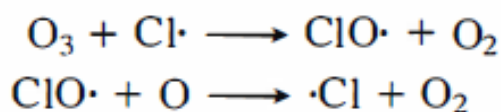
Stratospheric ozone concentrations are maintained naturally by a simple sequence of reactions:



Chlorofluorocarbons (CFCs), used as aerosol propellants and air-conditioning coolants, disrupt this sequence by catalyzing the breakdown reaction. CFCs are unreactive in the lower atmosphere, but slowly rise to the stratosphere, where UV radiation cleaves them:



Like many species with unpaired electrons (free radicals), atomic Cl is very reactive. It reacts with ozone to produce chlorine monoxide ($\text{ClO}\cdot$), which then reacts to regenerate Cl atoms :



The sum of these steps is the ozone breakdown reaction:



During its stratospheric half-life of about 2 years, each Cl atom speeds the breakdown of about 100,000 ozone molecules. High levels of chlorine monoxide over Antarctica have given rise to an ozone hole, an area of the stratosphere showing a severe reduction of ozone.