$$O_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O_3 + O \overset{k_2}{\to} 2\,O_2$$

Method

First, determine the rate law for the destruction of ozone, i.e., an expression for $-d[O_3]/dt$. Then use the steady-state approximation to solve for the concentration of the intermediate, O. Finally, substitute the O atom concentration into the ozone rate law and simplify.

Solution

The rate law for the destruction of ozone is

$$\frac{-d[O_3]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] + k_2[O_3][O].$$

The steady-state equation for [O] is

$$\frac{d[O]}{dt} = 0 = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O_3][O].$$

Some algebra can be avoided by subtracting these two to obtain

$$\frac{-d[O_3]}{dt} = 2k_2[O_3][O].$$

Solution of the steady-state equation gives

$$[O] = \frac{k_1[O_3][M]}{k_2[O_3] + k_{-1}[O_2][M]}.$$

Substitution of this equation into the simplified ozone destruction equation gives the final answer:

$$\frac{-d[O_3]}{dt} = \frac{2k_2 k_1[M][O_3]^2}{k_2[O_3] + k_1[O_2][M]}.$$

Comment

Note that at high values of the pressure, [M] will be large enough so that the second term in the denominator will be large compared to the first. The result will then simplify to $-d[O_3]/dt = (2k_2 k_1/k_{-1}) \cdot [O_3]^2/[O_2]$.

2.4.4 Unimolecular Decomposition: The Lindemann Mechanism

As an example of the use of the steady-state approximation, we consider in detail the mechanism of unimolecular decomposition. The overall reaction is A → products, and under high-pressure conditions the rate law is $-d[A]/dt = k_{ap}[A]$, where k_{ap} is the apparent rate constant. A question that begs an answer is how the A molecules obtain enough energy to decompose. The matter was debated vigorously in

the early 1900s.[j] It was F. A. Lindemann who first suggested in 1922[k] that the reactants obtained the necessary energy from collisions. In its simplest form, the mechanism he proposed is shown below:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M,$$

(2.68)

$$A^* \overset{k_2}{\to} P.$$
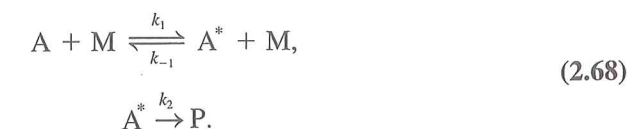
In these equations P stands for the products and M represents any molecule that can energize A by collision; M might be A itself, or it might be a nonreactive molecule in which the reactant is mixed.

The overall rate of the reaction is $-d[A]/dt$, or equivalently by $d[P]/dt$:

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k_2[A^*].$$

(2.69)

Since A^* is an intermediate in the mechanism, it will be useful to apply the steady-state approximation:

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0.$$

(2.70)

Here, the time dependence of A^* is equal to a production term, $k_1[A][M]$, and two destruction terms, $k_{-1}[A^*][M]$ and $k_2[A^*]$. We can then solve this last equation for the steady-state concentration of A^* to obtain

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}.$$

(2.71)

Substitution of this last equation into **equation 2.69** yields the solution

$$\frac{d[P]}{dt} = \frac{k_2 k_1[A][M]}{k_{-1}[M] + k_2}.$$

(2.72)

Recall that use of the steady-state approximation assumes that the concentration of the intermediate is small compared to the concentration of the starting material. This assumption is almost always valid for the system under consideration. Rearrangement of **equation 2.71** shows that $[A^*]/[A]$ is much smaller than unity when $k_1[M]/(k_{-1}[M] + k_2) \ll 1$. However, even if k_2 were zero, this last expression would still be satisfied since k_1/k_{-1} is simply the equilibrium constant for the first reaction, and this equilibrium constant must be smaller than unity because A^* has much more energy than A. In addition, for A^* of sufficiently high energy, k_2 is usually very rapid, so that the inequality $k_1[M]/(k_{-1}M + k_2) \ll 1$ is ensured.

Having convinced ourselves that the steady-state approximation is valid for the Lindemann mechanism, **equation 2.68**, it is instructive to examine the solution, **equation 2.72**, under two limiting conditions. Let us first consider the "high-pressure

[j]For an interesting discussion of the history of this problem, see J. I. Steinfeld, J. S. Francisco, and William L. Hase, *Chemical Kinetics and Dynamics*, 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1999), Section 11.3.

[k]F. A. Lindemann, *Trans. Faraday Soc.* **17**, 598 (1922).

limit," for which $k_{-1}[M] \gg k_2$. In this limit, the denominator of **equation 2.72** can be approximated by its first term, and division of numerator and denominator by $[M]$ gives $d[P]/dt = (k_2 k_1/k_{-1})[A]$. Thus, in this limit the $[M]$ cancels and the reaction is first order. Physically, in the high-pressure limit A^* is rapidly being created and destroyed, and only a small fraction goes on to form products.

In the "low-pressure" limit, when $k_{-1}[M] \ll k_2$, the second term in the denominator of **equation 2.72** dominates, and $d[P]/dt = k_1[A][M]$. In this limit the reaction is second order. Physically, in this limit most of the A^* that is formed lasts long enough to react to form P, and very little gets deactivated.

This behavior is shown in **Figure 2.13,** which plots a theoretical curve on a log-log plot for the apparent first-order rate constant, defined by $k_{ap} \equiv (1/[A]) \, d[P]/dt$, as a function of $[M]$ for the isomerization of *cis*-but-3-ene to *trans*-but-2-ene. The log-log plot is necessary to show both extremes in pressure. In the high-pressure limit, we have seen that $d[P]/dt = (k_2 k_1/k_{-1})[A]$ so that $\log(k_{ap})$ should be a constant. At high pressures, the apparent rate constant is, indeed, found to be constant, but below about 10^6 torr the apparent rate constant is linearly proportional to pressure. This is because, in the low-pressure limit $d[P]/dt = k_1[A][M]$ so that $\log(k_{ap})$ should be equal to $\log(k_1[M])$; i.e., it should vary linearly with $\log[M]$, as observed in the plot. An important practical application of the Lindemann mechanism is given in **Example 2.5.**

The high-pressure result for the Lindemann mechanism also illustrates an important point about the temperature dependence of the overall rate constant in complex reactions. In the high-pressure limit $d[P]/dt = k_{ap}[A] = (k_2 k_1/k_{-1})[A]$. Thus, the temperature dependence of the overall rate constant k_{ap} depends on how k_1, k_{-1}, and k_2 depend on temperature. Suppose that each of the rate constants for the elementary processes can be expressed in Arrhenius form: $k_i = A_i \exp(-E_i/kT)$. Simple multiplication and division of exponentials shows that
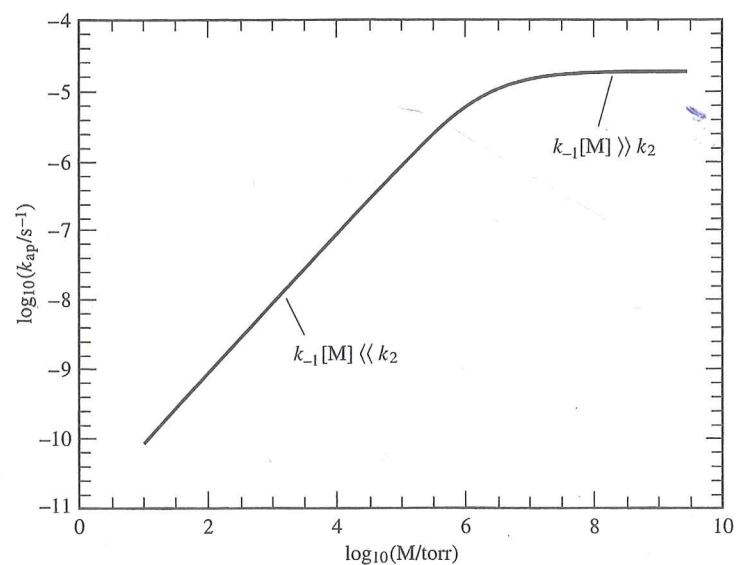
■ Figure 2.13

Theoretical dependence of the Lindemann apparent rate constant with pressure for the isomerization of *cis*-but-2-ene.

$$
\begin{aligned}
k_{ap} &= \frac{k_2 k_1}{k_{-1}} \\
&= \frac{A_2 A_1}{A_{-1}} \exp[-(E_2 + E_1 - E_{-1})/kT] \\
&= A_{ap} \exp(-E_{ap}/kT),
\end{aligned}
\tag{2.73}
$$

where $A_{ap} = A_2 A_1/A_{-1}$ and $E_{ap} = E_2 + E_1 - E_{-1}$. The general form of this result holds for very complicated reactions, even, as described in Problem 2.26, for reactions as complicated as those that control the rate of firefly flashing!

Like most good experimental or theoretical advances, the Lindemann mechanism raised more questions than it answered. For example, how do the rate constants k_1 and k_2 depend on how much energy the A^* molecule has? And what kind of energy is important in energizing A? We will defer these questions until Chapter 7; they form the basis for much of the current research in physical chemistry.

2.5   HOMOGENEOUS CATALYSIS

A catalyst, by definition, is a substance that is neither created nor consumed in the reaction but that increases the rate of the reaction. In most catalytic mechanisms, the catalyst transforms the reactants through a series of intermediates to products, but the catalyst is regenerated in the process of making the product. Since the intermediates are usually of much lower concentration than the starting material, catalytic mechanisms can usually be analyzed using the steady-state approximation. As an example, we will study in detail below the use of the steady-state approximation to analyze enzyme reactions. We will concentrate here on forms of homogeneous catalysis, while leaving the important area of heterogeneous catalysis until Chapter 6.

2.5.1   Acid-Base Catalysis

One prevalent form of catalysis is acid or base catalyzed hydrolysis. For example, an ester might be hydrolyzed by the following mechanism in the presence of an acid:
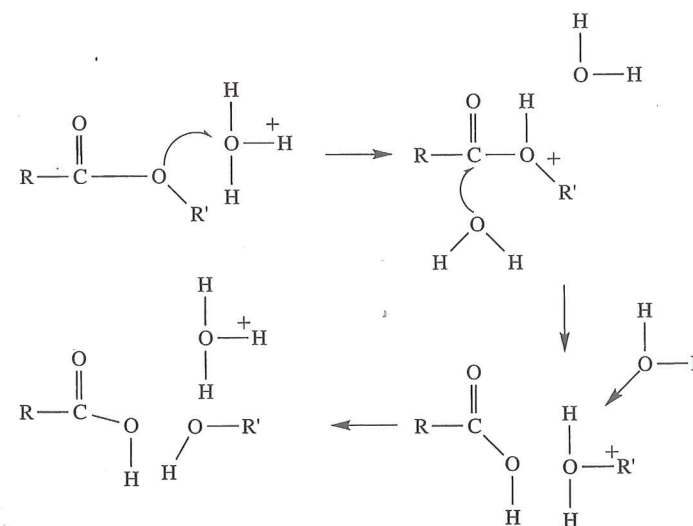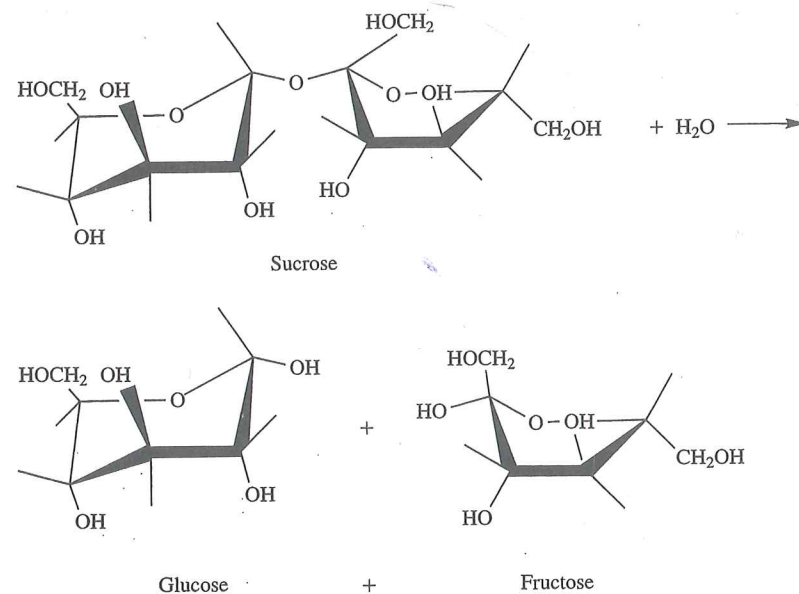
The same reaction can be base catalyzed:
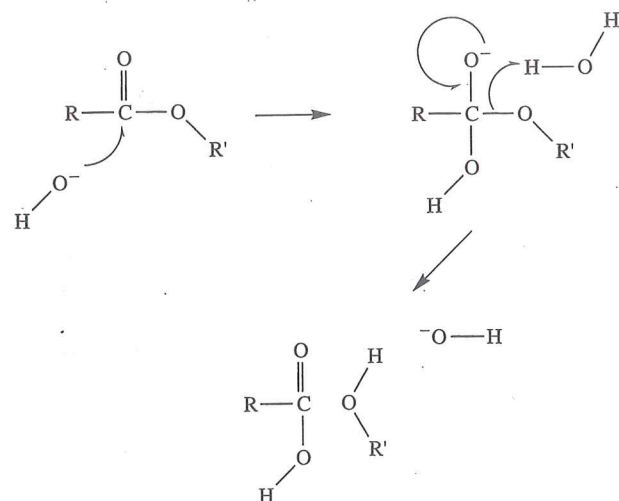
Since neither H_3O^+ nor OH^- is consumed in these processes, the overall rate law for this mechanism would be first order in each of the two reactants, the ester and water. However, because these reactions are always carried out in aqueous solution, the concentration of water can be taken as constant and incorporated into the rate constant; i.e., the system follows pseudo-first-order kinetics. The species H_3O^+ or OH^- is a catalyst in the reaction; it is neither created nor consumed but provided another, more favorable, mechanism for the reaction.

2.5.2 Enzyme Catalysis

Enzymes are macromolecules (MW = $10^4 - 10^6$) that are remarkable in their efficiency and specificity in catalyzing reactions of biological significance. For example, the enzyme invertase (β-fructofuranidase), a component of yeast, catalyzes the conversion of sucrose to fructose and glucose by the hydrolysis reaction:

While the reaction can be catalyzed simply by H^+ ions, it proceeds much faster if the yeast enzyme is present. The name for the enzyme comes from the fact that the conversion produces an inversion in the direction of rotation of plane polarized light by the sugar solution, noted in 1832 by Persoz. Michaelis and Menten used the yeast enzyme responsible for this conversion in their classic 1914 studies that resulted in the following proposed mechanism for enzymatic action, known, not surprisingly, as the Michaelis-Menten mechanism.[1]

Consider the following reaction sequence:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X,$$
$$X \overset{k_2}{\rightarrow} P + E. \tag{2.74}$$

In this mechanism, the enzyme E can reversibly bind to a substrate S to yield the intermediate X. Once bound, the enzyme can also convert the substrate to products P, which it releases while returning to its original state. The enzyme is thus available to convert more substrate. How does the rate of the reaction depend on the amount of substrate and the amount of enzyme?

We analyze the sequence using the steady-state approximation for the intermediate complex X:

$$\frac{d[X]}{dt} = k_1[E][S] - k_{-1}[X] - k_2[X] = 0. \tag{2.75}$$

Let the original concentration of enzyme be E_0. Then by mass balance $E_0 = [E] + [X]$. In a similar manner, if the initial concentration of substrate is S_0, then by mass balance $S_0 = [S] + [X] + [P]$. Substituting these into **equation 2.75,** we obtain

$$\frac{d[X]}{dt} = k_1(E_0 - [X])(S_0 - [X] - [P]) - k_{-1}[X] - k_2[X] = 0. \tag{2.76}$$

We now suppose, as is generally the case, that the initial concentration of enzyme is much smaller than the initial concentration of substrate, $E_0 << S_0$. Since [X] can never be larger than E_0, it follows that $[X] << S_0$, so that we may safely ignore it in the term $S_0 - [X] - [P]$. We now consider the initial rate of the reaction, $v_0 \equiv d[P]/dt$ as $t \rightarrow 0$, where $[P] \approx 0$. Solving **equation 2.76** for [X] gives

$$[X] = \frac{k_1 E_0 S_0}{k_1 S_0 + k_{-1} + k_2}. \tag{2.77}$$

---

[1]Jean-Francois Persoz (1805–1868) was a professor at the Sorbonne; Leonor Michaelis (1875–1949) was a German-born physician and biochemist who did research at the Rockefeller Foundation later in life. In addition to developing with Menten his famous equation, he is responsible for finding that keratin, the chief ingredient of hair, is soluble in glycolic acid, a discovery that made possible the development of the permanent. Maude Menten received her B.A. in 1904 and her M.D. in 1911 from the University of Toronto but had to leave Canada to pursue a career as a research scientist, because in those days women were not allowed to do research in Canadian universities. After study at the Rockefeller Institute and the Western Reserve University, she went to Berlin to study with Michaelis, where the two developed the Michaelis-Menten equation. Ultimately, she received a Ph.D. in biochemistry from the University of Chicago and became a professor at the University of Pittsburgh School of Medicine.
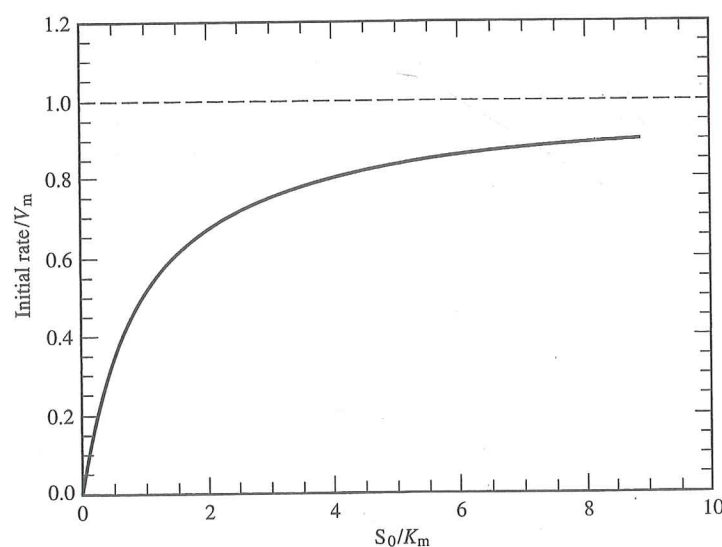
Finally, the initial rate of the reaction is

$$v_0 = \left.\frac{d[P]}{dt}\right|_{t\to 0} = k_2[X]$$

$$= \frac{k_1 k_2 E_0}{k_1 + \dfrac{k_{-1} + k_2}{S_0}} \tag{2.78}$$

$$= \frac{V_m}{1 + \dfrac{K_m}{S_0}},$$

where $V_m = k_2 E_0$ and $K_m = (k_{-1} + k_2)/k_1$. Note that the rate is proportional to the initial concentration of enzyme and to the rate constant k_2, sometimes called the *turnover number* of the enzyme. At very high initial substrate concentrations, the initial rate approaches $d[P]/dt = V_m = k_2 E_0$, or $d([P]/E_0)/dt = k_2$. The turnover number, k_2, is thus the number of molecules of product per molecule of enzyme that can be created per unit time. Typical values are 10^2–10^3 per second, but values as large as 10^6 per second have been observed.

A plot of **equation 2.78** is shown in **Figure 2.14,** in which reduced units have been used. The rate at first increases linearly with S_0 and then levels off to an asymptote equal to V_m. While **Figure 2.14** is useful in showing the behavior of the initial rate, it is not very useful for determining the rate constants. An alternate method of analysis is to take the reciprocal of both sides of **equation 2.78** to obtain the Lineweaver-Burk form

$$\frac{1}{v_0} = \frac{1}{V_m} + \frac{K_m}{V_m S_0}. \tag{2.79}$$

Figure 2.14

A plot of the initial rate, in units of V_m, as a function of the initial substrate concentration, in units of K_m, for the Michaelis-Menten mechanism.
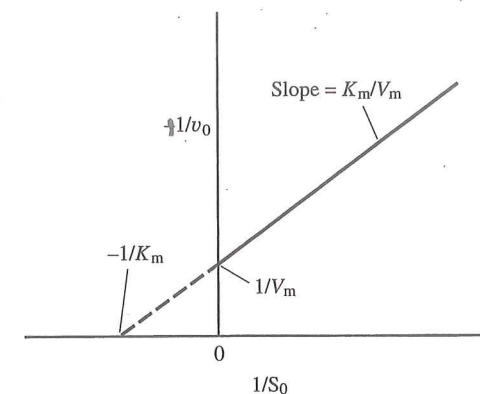
Figure 2.15

Lineweaver-Burk plot for and enzyme reaction obeying the Michaelis-Menten mechanism.

This form shows that a plot of the reciprocal of the initial rate as a function of $(S_0)^{-1}$ should yield a straight line whose intercept is V_m^{-1} and whose slope is K_m/V_m, as shown in **Figure 2.15.**

An example of an enzyme whose kinetics obey the Michaelis-Menten mechanism is lactase, the enzyme responsible for catalyzing the hydrolysis of lactose to D-glucose and D-galactose. Most adults of northern European background have sufficient enzyme to digest the milk that they consume, but many of other backgrounds do not possess this enzyme, the lack of which leads to breakdown of lactose by microbial action in the large intestine rather than by the enzyme in the small intestine. The resulting fermentation in the large intestine leads to diarrhea. One strategy to make milk more digestible for those who might otherwise suffer is to add *Lactobacillus acidophilus* to the milk. **Example 2.6** examines the enzyme kinetics of lactase in the hydrolysis of a synthetic substrate similar to lactose.[m]

example 2.6

Determination of the Michaelis-Menten Constant for the Lactase Catalyzed Hydrolysis of a Synthetic Substrate, o-nitrophenyl-β-D-galactopyranoside

Objective   Calculate the Michaelis-Menten constant, K_m, given the following data pairs for $1/v_0$, in arbitrary units, and $1/S_0$, in units of $10^3\ M^{-1}$: (2.8,0.7), (3.2,0.9), (4.2,1.3), (6.2,2.2), and (9.0,3.3).

Method   Plot $1/v_0$ as a function of $1/S_0$ and determine the slope ($= K_m/V_m$) and the intercept ($= 1/V_m$). The value of K_m is given by the ratio of the former to the latter.

Solution   A least squares fit of the data to a line gives a slope of 0.24×10^{-2} and an intercept of 1.08. The ratio is $2.2 \times 10^{-3}\ M$.

[m]S. F. Russo and L. Moothart, *J. Chem. Ed.* **63,** 242 (1986).

An important mediator in the catalytic action of enzymes is the phenomenon of enzyme inhibition. An inhibitor is a compound that decreases the enzyme-catalyzed reaction by reacting with the enzyme itself or the enzyme substrate complex.

Competitive inhibition occurs when the inhibitor competes with the substrate for binding at the active site of the enzyme. The mechanism can be represented by

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X,$$

$$X \overset{k_2}{\to} P + E \tag{2.80}$$
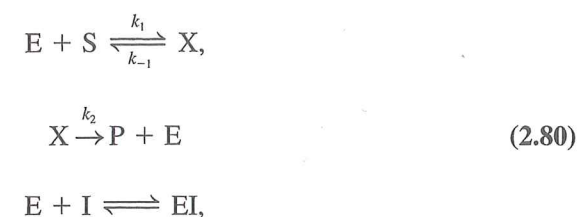
$$E + I \rightleftharpoons EI,$$

where it is assumed that the last reaction is always at equilibrium and that the complex EI cannot catalyze the reaction. Application of the steady-state approximation yields (Problem 2.20)

$$v_0 = \frac{V_m}{1 + \dfrac{K_m}{S_0}\left[1 + \dfrac{[I]}{K_I}\right]}, \tag{2.81}$$

where $K_I = [E][I]/[EI]$ is the equilibrium constant for the reverse of the last reaction in **equation 2.80.** The Lineweaver-Burk equation then becomes

$$\frac{1}{v_0} = \frac{1}{V_m} + \left[1 + \frac{[I]}{K_I}\right]\frac{K_m}{V_m S_0}, \tag{2.82}$$

so that a plot of the inverse of the initial rate as a function of the inverse of the initial substrate concentration gives the same intercept as in the absence of inhibitor, but a different slope, as shown in **Figure 2.16A.** An example of a competitive inhibitor is malonic acid, $CH_2(COOH)_2$, which resembles succinic acid, $(COOH)CH_2CH_2(COOH)$ closely enough to bind to the enzyme succinic dehydrogenase and inhibit it from converting succinic acid to fumaric acid, $(COOH)CH{=}CH(COOH)$.

Noncompetitive inhibition occurs when the inhibitor does not bind to the active site of the enzyme but still inhibits product formation:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X,$$

$$X \overset{k_2}{\to} P + E \tag{2.83}$$
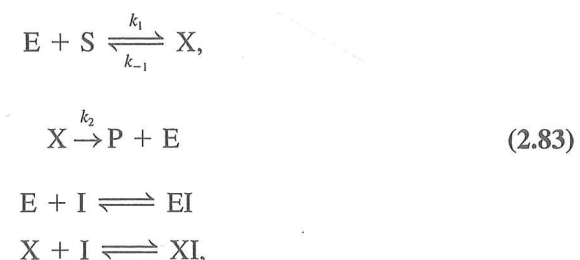
$$E + I \rightleftharpoons EI$$

$$X + I \rightleftharpoons XI,$$

where the last two reactions are assumed to be in equilibrium with the same equilibrium constant for their reverse: $K_I = [E][I]/[EI] = [X][I]/[XI]$. The initial rate of reaction is (Problem 2.21)

$$v_0 = \frac{V_m S_0}{[S_0 + K_m]\left[1 + \dfrac{[I]}{K_I}\right]}, \tag{2.84}$$
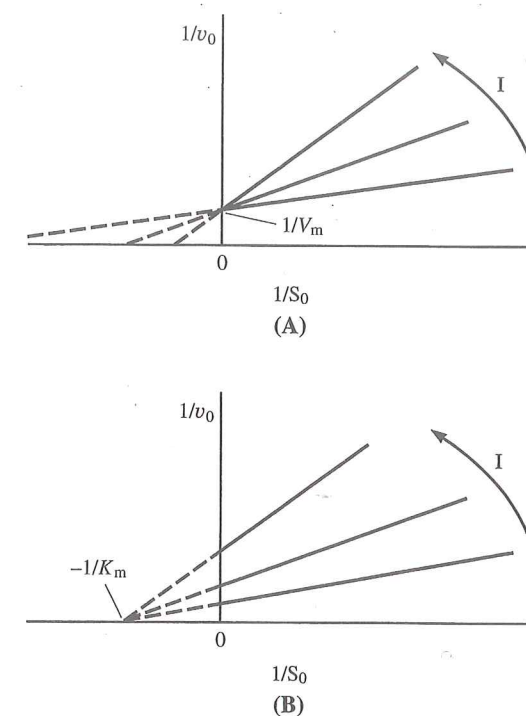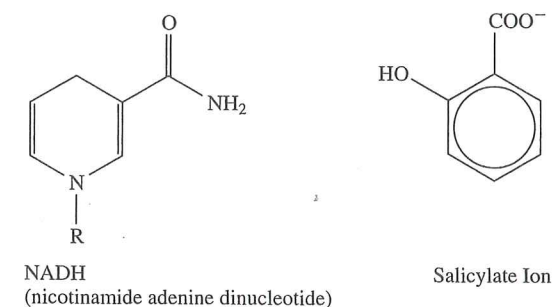
Figure 2.16

Effect of (A) competitive inhibition and (B) noncompetitive inhibition on the initial reaction rate.

and the Lineweaver-Burk equation is

$$\frac{1}{v_0} = \left[\frac{1}{V_m} + \frac{K_m}{V_m S_0}\right]\left[1 + \frac{[I]}{K_I}\right]. \tag{2.85}$$

Note that the presence of the inhibitor affects both the slope and intercept of the Lineweaver-Burk plot for noncompetitive inhibition, as shown in **Figure 2.16B.**

Methemoglobin reductase is an example of an enzyme that uses NADH to maintain hemoglobin in the active oxygen-carrying form. The salicylate ion is a noncompetitive inhibitor with respect to the substrate NADH.[n]


NADH
(nicotinamide adenine dinucleotide)

Salicylate Ion

[n]A. G. Splittgerber, K. Mitchell, G. Dahle, M. Puffer, and K. Blomquist, *J. Chem. Ed.* **52,** 680 (1975).

2.5.3   Autocatalysis

Not all reactions obey the simple behavior illustrated in **Figure 2.1,** in which the reactants decrease and products increase monotonically in time. Increasing attention has recently been paid to reactions in which species concentrations oscillate. Indeed, discontinuities in the rate of oscillation for such reactions as the concentrations change have helped to open a new area of science sometimes called chaos theory.[o] All oscillating reactions have some element of "autocatalysis," catalysis in which a product of one reaction appears as a catalyst in the same or another coupled reaction. It is interesting, and appropriate, to examine briefly such reactions here since they illustrate an interesting form of catalysis, provide another example for use of the steady-state approximation, and are fascinating in their own right.

Although the "Lotka" mechanism does not, so far as anyone knows, correspond to any observed chemical system, its simple mechanism illustrates the basic principles in more complex oscillatory systems. This mechanism has three steps:

$$A + X \xrightarrow{k_1} 2X,$$

$$X + Y \xrightarrow{k_2} 2Y, \tag{2.86}$$

$$Y \xrightarrow{k_3} Z.$$
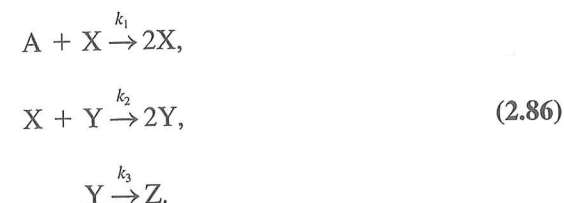
Suppose that reactant is continually supplied to the system so that the concentration of A does not change from its initial value [A(0)]. Then the concentrations of the intermediates X and Y will reach a steady state, while the concentration of product Z will increase with time. The steady-state equations for X and Y are

$$\frac{d[X]}{dt} = 0 = k_1[X][A(0)] - k_2[X][Y],$$

$$\frac{d[Y]}{dt} = 0 = k_2[X][Y] - k_3[Y]. \tag{2.87}$$

The steady-state values for [X] and [Y] are thus given by

$$k_2 Y_{ss} = k_1[A(0)],$$
$$k_2 X_{ss} = k_3. \tag{2.88}$$

We now consider perturbing the system in some way so that the concentrations of the intermediates change. Let the new concentrations X and Y be different from their steady-state values by time-dependent differences x and y:

$$[X] = x + X_{ss},$$
$$[Y] = y + Y_{ss}. \tag{2.89}$$

We wish to determine how x and y vary with time. Substitution of **equation 2.89** into **equation 2.87** leads to

[o]See, for example, the interesting book *Chaos: Making a New Science,* by James Gleick (Viking, New York, 1987).

$$\frac{dx}{dt} = k_1[A(0)][x + X_{ss}] - k_2[x + X_{ss}][y + Y_{ss}],$$

$$\frac{dy}{dt} = k_2[x + X_{ss}][y + Y_{ss}] - k_3[y + Y_{ss}], \tag{2.90}$$

or

$$\frac{dx}{dt} = x[k_1[A(0)] - k_2 Y_{ss}] + [k_1 X_{ss}[A(0)] - k_2 X_{ss} Y_{ss}]$$
$$- k_2 X_{ss} y - k_2 xy,$$

$$\frac{dy}{dt} = y[k_2 X_{ss} - k_3] + [k_2 X_{ss} Y_{ss} - k_3 Y_{ss}]$$
$$+ k_2 Y_{ss} x + k_2 xy. \tag{2.91}$$

Note that **equations 2.87** and **2.88** can be used to show that the terms of **equation 2.91** in square brackets are zero. If x and y are small displacements, then terms like xy can be neglected with respect to terms like xY_{ss} or yX_{ss}, so that

$$\frac{dx}{dt} = -k_2 X_{ss} y,$$

$$\frac{dy}{dt} = k_2 Y_{ss} x. \tag{2.92}$$

If we take the derivative of both sides of the first equation in **equation 2.92** and then use the second equation to substitute for the derivative of y, we obtain the second-order differential equation

$$\frac{d^2 x}{dt^2} + k_2^2 X_{ss} Y_{ss} x = 0. \tag{2.93}$$

A specific solution to this equation that allows $x = x_0$ and $y = 0$ at $t = 0$ is

$$x = x_0 \cos \omega t, \tag{2.94}$$

where

$$\omega^2 = k_2^2 X_{ss} Y_{ss} = k_1 k_3 [A(0)]. \tag{2.95}$$

A similar solution can be obtained for y. We thus see that, rather than decaying exponentially, the concentration displacements will oscillate indefinitely. The oscillation frequency will depend on the concentration to which A is maintained.

Many actual chemical reactions have been observed to oscillate. An often-cited but quite complex example is called the Belousov-Zhabotinsky reaction; a variant called the Briggs-Rauscher reaction exhibits an oscillating color change and is often used as a class demonstration.[p]

[p]B. P. Belousov, *Ref. Radiats. Med.* **145,** 1958 (1959); A. M. Zhabotinsky, *Dokl. Akad. Nauk SSSR* **157,** 392 (1964); T. S. Briggs and W. C. Rauscher, *J. Chem. Educ.* **50,** 496 (1973); see also "Oscillating Chemical Reactions," by E. S. Scott, R. Schreiner, L. R. Sharpe, B. Z. Shakhashiri, and G. E. Dirreen, in *Chemical Demonstrations, A Handbook for Teachers of Chemistry,* B. Z. Shakhashiri, Vol. 2, Chapter 7 (University of Wisconsin Press, Madison, 1985).

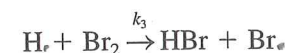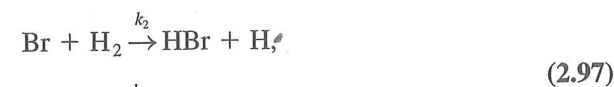## 2.6   FREE RADICAL REACTIONS: CHAINS AND BRANCHED CHAINS

Many gas-phase reactions take place by so-called "chain" mechanisms involving free radical carriers, molecules, or atoms with one or more unpaired electrons. These mechanisms always consist of at least three steps: an *initiation* step creates the radicals that carry the chain; one or more *chain* steps convert reactants to products using the radical(s) in the role of a catalyst; and a *termination* step stops the chain by consuming the chain carrying radicals. Since the radical species are usually in small concentration and are intermediates, the steady-state approximation can be used to determine the overall rate law, which sometimes takes a complex form. An example is the $H_2 + Br_2 \rightarrow 2$ HBr reaction, which we have already noted has the overall rate law $\frac{1}{2} d[HBr]/dt = k[H_2][Br_2]^{1/2}$. We now consider this reaction in detail.

2.6.1 $H_2 + Br_2$

A chain mechanism is consistent with the overall rate law for this reaction. The initiation step is the collisional production of Br atoms:

$$Br_2 + M \xrightarrow{k_1} 2 \, Br + M. \tag{2.96}$$

There are two chain steps:

$$Br + H_2 \xrightarrow{k_2} HBr + H, \tag{2.97}$$
$$H + Br_2 \xrightarrow{k_3} HBr + Br.$$

Note that the net result of the chain is to convert one molecule of Br_2 and one of H_2 into two of HBr while regenerating the radicals so that the chain can continue. The termination step in this case is simply the reverse of the initiation step:

$$2 \, Br + M \xrightarrow{k_{-1}} Br_2 + M. \tag{2.98}$$

The key point to realize is that the chain steps can occur many times for every initiation or termination and that these steps are principally responsible for conversion of reactants into products. We would thus expect that

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{1}{2}(k_2[Br][H_2] + k_3[H][Br_2]). \tag{2.99}$$

We use the steady-state approximation to solve for the concentration of Br and H radicals:

$$\frac{d[Br]}{dt} = 0$$

$$= 2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] - k_2[Br][H_2] + k_3[H][Br_2], \tag{2.100}$$

$$\frac{d[H]}{dt} = 0 = \hspace{3cm} + k_2[Br][H_2] - k_3[H][Br_2]$$

Addition of these two equations and then solution for [Br] gives

$$[Br] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Br_2]^{1/2}. \tag{2.101}$$

We also note that the second of these equations implies that the two bracketed terms on the right-hand side of **equation 2.99** are equal, so that

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{1}{2}(2k_2[Br][H_2])$$
$$= k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}. \tag{2.102}$$

Note that this expression is consistent with the overall rate law provided that $k = k_2(k_1/k_{-1})^{1/2}$. In actuality, this reaction is somewhat more complicated, as discussed in Problem 2.23.
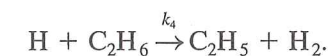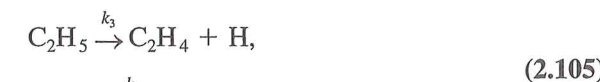
2.6.2   Rice-Herzfeld Mechanism

Many organic reactions also occur by free radical processes. For example, in 1934 F. O. Rice and K. F. Herzfeld showed that the decomposition of ethane to ethylene and hydrogen, while following first-order kinetics, actually has a rather more complicated mechanism. There are two initiation steps:

$$C_2H_6 \xrightarrow{k_1} 2 \, CH_3, \tag{2.103}$$

and

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5. \tag{2.104}$$

There are then two propagation steps:

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H, \tag{2.105}$$
$$H + C_2H_6 \xrightarrow{k_4} C_2H_5 + H_2.$$

Termination typically takes place by

$$H + C_2H_5 \xrightarrow{k_5} C_2H_6. \tag{2.106}$$

The steady-state approximation can be made on the radicals CH_3, C_2H_5, and H, and, after straightforward but rather tedious algebra (Problem 2.24), we obtain

$$-\frac{d[C_2H_6]}{dt} = \left[\frac{3}{2}k_1 + \left(\frac{k_1^2}{4} + \frac{k_1k_3k_4}{k_5}\right)^{1/2}\right][C_2H_6]. \tag{2.107}$$

Note that this agrees with the observation that the overall reaction is first order in C_2H_6.

A point of confusion often arises when considering radical reactions of this type. While the $H_2 + Br_2$ reaction mechanism gave no products other than the expected HBr, the ethane decomposition mechanism produces CH_4 in addition to the expected H_2 and C_2H_4. However, since the main chain is carried by the C_2H_5 radical in steps 3 and 4, the amount of CH_4 produced per molecule of H_2 or C_2H_4 is negligibly small. **Example 2.7** provides another illustration of a Rice-Herzfeld mechanism, in this case for the decomposition of acetaldehyde.
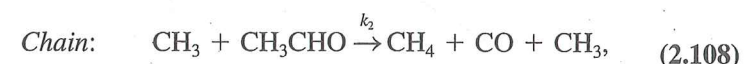
2.6.3   Branched Chain Reactions: Explosions

Explosions are simply reactions whose rates become more and more rapid as time proceeds. There are normally two causes for a rapid increase in rate, giving rise to two types of explosions. A *thermal explosion* takes place when the rate of heat conduction out of a vessel surrounding an exothermic series of reactions is too small to prevent a significant temperature rise in the vessel. According to the Arrhenius expression, most rates increase with increasing temperature, so that as the temperature rises, more reactants are consumed per unit time, creating more heat from the exothermic process, and causing the temperature to rise further. For a spherical vessel, the rate of heat loss due to thermal conductivity is proportional to the surface area of the vessel, while the rate of heat production is proportional to the amount of reactants, i.e., to the volume of the vessel, assuming the reactant concentrations are the same in both size vessels. Since the volume increases with the cube of radius while the surface area increases as the square, heat production will overcome heat loss in a large enough vessel. Explosions can thus occur unexpectedly if an exothermic reaction that ran smoothly in a small vessel is scaled up to obtain more product without proper attention to the thermal consequences.

example 2.7

The Rice-Herzfeld Mechanism for the Decomposition of Acetaldehyde

Objective   Show that the Rice-Herzfeld mechanism for the decomposition of acetaldehyde, listed below, is consistent with the observation that the overall rate of decomposition is (3/2)-order in acetaldehyde, and determine how the overall rate constant is related to those for the individual steps. The overall reaction is $CH_3CHO \rightarrow CH_4 + CO$, while the Rice-Herzfeld mechanism is

$$Initiation:\quad CH_3CHO \xrightarrow{k_1} CH_3 + CHO,$$

$$Chain:\quad CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CO + CH_3, \qquad (2.108)$$

$$Termination:\quad CH_3 + CH_3 \xrightarrow{k_3} C_2H_6.$$

Method   Determine the production rate of CH_4 and then use the steady-state approximation for the CH_3 intermediate.

Solution   The production rate of CH_4 is

$$\frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]. \qquad (2.109)$$

The concentration of $[CH_3]$ can be found from the steady state approximation:

$$\frac{d[CH_3]}{dt} = 0 = k_1[CH_3CHO] - 2k_3[CH_3]^2. \qquad (2.110)$$

Note that there is no net contribution to $[CH_3]$ from the second step, since for every mole consumed one mole is produced. Rearrangement of the steady-state equation yields

$$[CH_3] = \left(\frac{k_1}{2k_3}\right)^{1/2} [CH_3CHO]^{1/2}, \qquad (2.111)$$

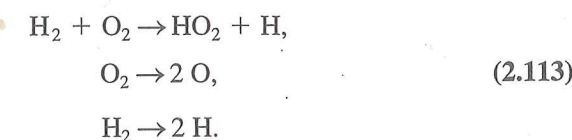and substitution of this into **equation 2.109** yields

$$\frac{d[CH_4]}{dt} = k_2 \left(\frac{k_1}{2k_3}\right)^{1/2} [CH_3CHO]^{3/2}. \qquad (2.112)$$
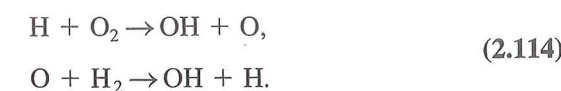
Consequently, the overall rate constant is $k_2(k_1/2k_3)^{1/2}$, and the mechanism is consistent with an overall order of 3/2.

The second type of explosion is caused by a *branched chain reaction*. The mechanism for the oxygen-hydrogen reaction provides a good example. The overall reaction is, of course, $2\,H_2 + O_2 \rightarrow 2\,H_2O$. The mechanism is complicated, but the following steps are the most important:

Initiation:

$$H_2 + O_2 \rightarrow HO_2 + H,$$
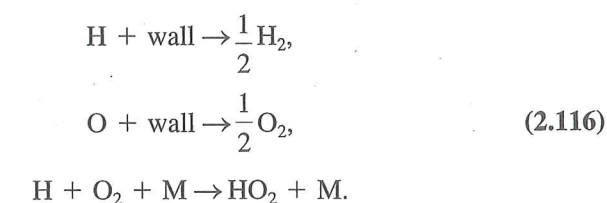$$O_2 \rightarrow 2\,O, \qquad (2.113)$$
$$H_2 \rightarrow 2\,H.$$

Chain Branching:

$$H + O_2 \rightarrow OH + O,$$
$$O + H_2 \rightarrow OH + H. \qquad (2.114)$$

Chain Propagation:

$$OH + H_2 \rightarrow H_2O + H. \qquad (2.115)$$

Termination:

$$H + wall \rightarrow \frac{1}{2}H_2,$$
$$O + wall \rightarrow \frac{1}{2}O_2, \qquad (2.116)$$
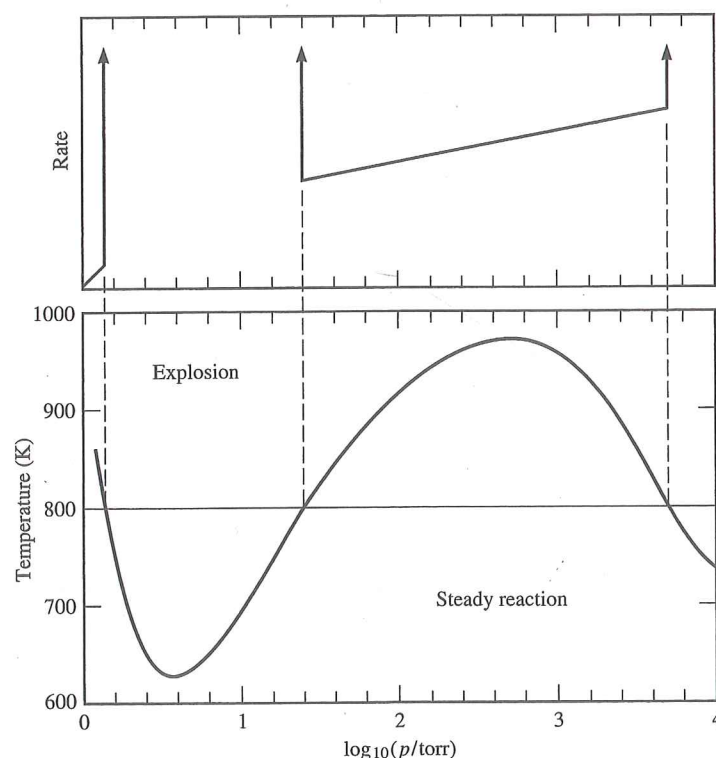$$H + O_2 + M \rightarrow HO_2 + M.$$

Like other chain reactions, this mechanism has initiation, propagation, and termination steps. Initiation of the reaction might be caused, for example, by the brief exposure of the reactant mixture to rapid heating from a spark or flame, in short, any reaction that creates free oxygen or hydrogen atoms. For example, the initiation of the hydrogen-oxygen explosion on the space shuttle *Challenger* was the heating of the external oxygen tank by flames from the propulsion rocket that escaped through the o-ring seals. Termination is caused either by collision of radicals with the wall, where they stick and recombine, or by recombination assisted by a third body, here called M. (While technically a radical, HO_2 is unreactive relative to O, H, and OH; it is treated here as a stable compound.) The propagation step is a normal

one, where one radical is consumed and another produced. But there are also chain branching steps, steps in which the net number of radicals increases. For example, in the first reaction of **equation 2.114** an H atom is consumed but an O atom and an OH radical are produced. If reactions such as those in **equation 2.114** are prevalent, the rate of the overall reaction can increase rapidly.

The overall reaction rate for a stoichiometric mixture of $2 H_2 + O_2$ is a complicated function of temperature, pressure, vessel size, and material. The rates for each step depend on temperature. The rate of termination due to diffusion of O and H to the walls depends on pressure and vessel size. The sticking probability for these radicals when they reach the wall depends on the vessel material. Finally, the rate of $H + O_2$ recombination depends on pressure. The bottom panel of **Figure 2.17** shows the dividing line in the T-p plane between the explosion and steady reaction regimes for a typical system, while the top panel schematically indicates the rate of the reaction as a function of total pressure for a temperature of 800 K. It is constructive to consider the dominant processes at 800 K as the pressure is increased.

For low pressures, the mean free path of the radicals O and H is large enough so that they reach the walls of the reaction vessel with high probability. Under these conditions, the termination steps dominate and the reaction proceeds in a controlled fashion. As the pressure increases, however, the chain branching steps start to dominate, and a branched chain explosion occurs. It is interesting to note, however, that a reaction mixture at higher total pressure would produce a steady reaction, a so-called hydrogen-oxygen flame. In this region, the pressure is sufficiently high that

the termination step, $H + O_2 + M \rightarrow HO_2 + M$, occurs with good probability. In this region, then, the high rate of chain termination prevents an explosion. At higher pressures still, the heat due to the exothermic reaction cannot be carried away as fast as it is produced, so that a thermal explosion occurs.

2.7   DETERMINING MECHANISMS FROM RATE LAWS

Most of the examples we have used so far indicate how to determine whether a mechanism consisting of several elementary steps is consistent with an overall rate law. A much more difficult problem is how to figure out a reasonable mechanism of elementary steps given the rate law. In general, since several mechanisms are usually consistent with an overall rate law, it is not possible to obtain a single answer to this question. Nor is it really possible to obtain *any* answer without what amounts to an educated guess. In this section, we examine ways to make our guesses educated.

There are two basic concepts that we can use as a guide. The first is the realization that, in many reactions, there is *one* step in the mechanism whose rate is much smaller than any other step. In such a case, the overall rate of the reaction is usually controlled by this *rate-limiting step*. The rate law then contains in its numerator the rate of this rate-limiting step.

The second concept is one that we have already encountered. When the rates of steps in the mechanism are comparable, it is still usually possible to assume that the concentration of reaction intermediates is low and varies slowly. This is just the *steady-state* hypothesis of Section 2.4.3.

Even with a few principles in hand, it is ultimately experience that provides the best guide to guessing mechanisms from overall rate laws. Fortunately, we already have some experience. Let us look back at the systems we have studied to see if we can determine how we might apply the two basic concepts to obtain clues for determining a plausible mechanism from the overall rate law.

We start our excursion with the rate-law result of the Lindemann mechanism for the overall reaction A $\rightarrow$ products:

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A][M]}{k_{-1}[M] + k_2}. \tag{2.117}$$

One obvious clue to this reaction is that the rate law depends on something other than the reactants or products, namely, the overall pressure of the gas mixture and not just the partial pressure of the reactant. Another clue comes in the complex form of the denominator. Recall that a mechanism that leads to this rate law is

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M,$$

$$A^* \overset{k_2}{\rightarrow} P. \tag{2.118}$$
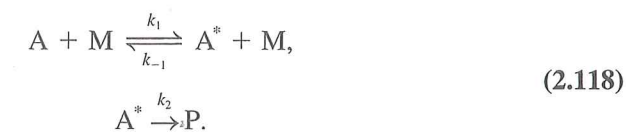
The complex form of the denominator comes from the fact that the intermediate in this reaction can disappear in two possible ways. Thus, we have already developed two clues: (1) complex denominators likely indicate that an intermediate in steady-state can disappear in more than one way and (2) the presence of something other than a reactant or product in the numerator (or, as it also turns out, in the denominator) likely indicates that an equilibrium step appears in the mechanism.

■ **Figure 2.17**

Explosion limits for a stoichiometric mixture of H_2 and O_2.