# Chemical Kinetics And Dynamics

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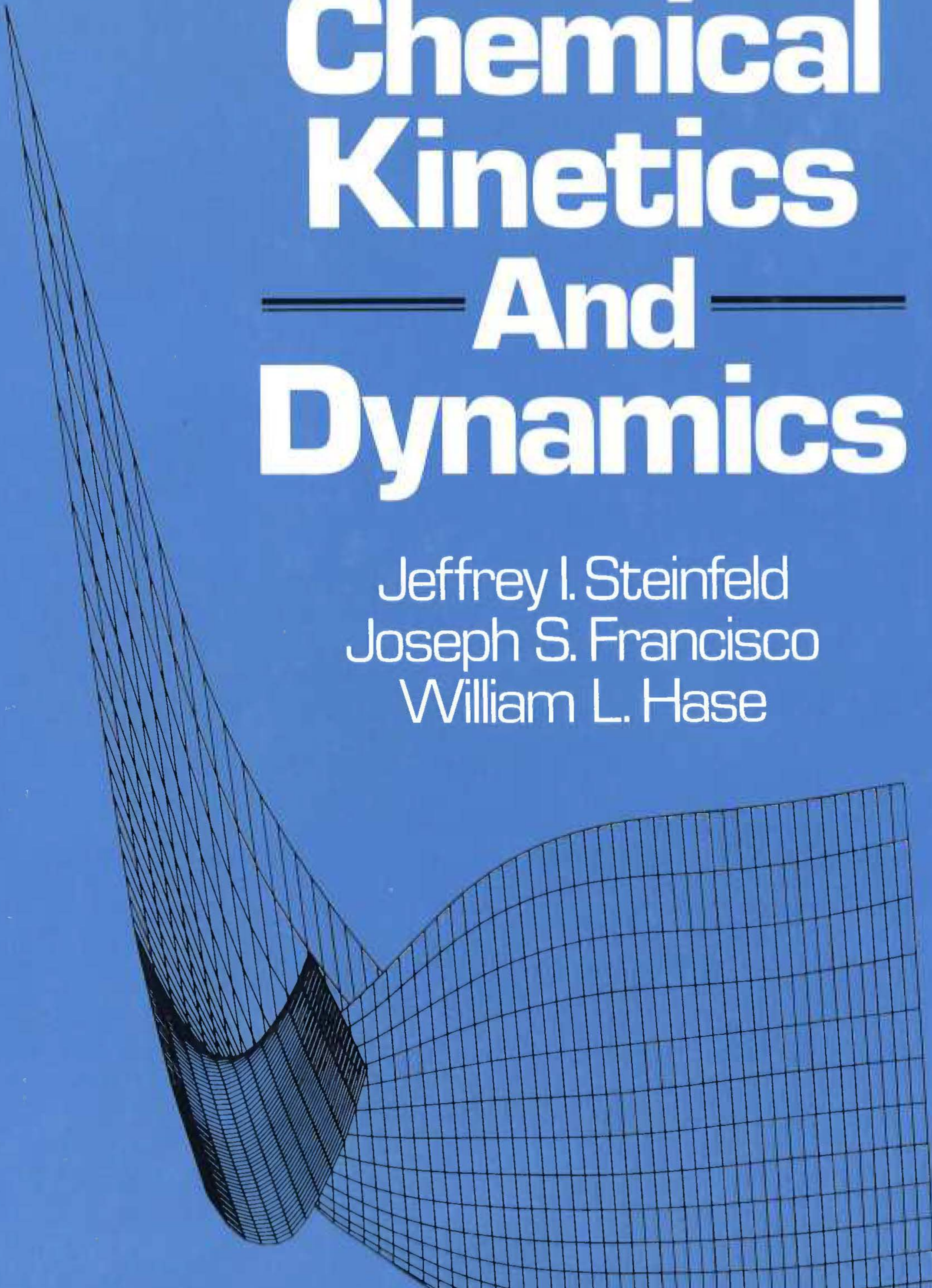

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# CHAPTER 1

# Basic Concepts of Kinetics

Among the most familiar characteristics of a material system is its capacity for *chemical change*. In a chemistry lecture, the demonstrator mixes two clear liquids and obtains a colored solid precipitate. Living organisms are born, grow, reproduce, and die. Even the formation of planetary rocks, oceans, and atmospheres consists of a set of chemical reactions. The time scale for these reactions may be anywhere from a few femtoseconds ($10^{-15}$ sec) to geologic times ($10^9$ years, or $10^{+16}$ sec).

The science of *thermodynamics* deals with chemical systems at equilibrium, which by definition means that their properties do not change with time. Most real systems are not at equilibrium and undergo chemical changes as they seek to approach the equilibrium state. *Chemical kinetics* deals with changes in chemical properties in time. As with thermodynamics, chemical kinetics can be understood in terms of a continuum model, without reference to the atomic nature of matter. The interpretation of chemical reactions in terms of the interactions of atoms and molecules is frequently called *reaction dynamics*. A knowledge of the dynamic basis for chemical reactions has, in fact, permitted us to design and engineer reactions for the production of an enormous number of compounds which we now regard as essential in our technological society.

We begin our study of chemical kinetics with definitions of the basic observable quantities, which are the chemical changes taking place in a system, and how these changes depend on time.

## 1.1 DEFINITION OF THE RATE OF A CHEMICAL REACTION

Broadly speaking, chemical kinetics may be described as the study of chemical systems whose composition changes with time. These changes may take place in the gas, liquid, or solid phase of a substance. A reaction occurring in a single phase is usually referred to as a *homogeneous* reaction, while a reaction which takes place at an interface between two phases is known as a *heterogeneous* reaction. An example of the latter is the reaction of a gas adsorbed on the surface of a solid.

The chemical change that takes place in any reaction may be represented by a *stoichiometric equation* such as

$$aA + bB \longrightarrow cC + dD \tag{1–1}$$

where $a$ and $b$ denote the number of moles of reactants A and B that react to yield $c$ and $d$ moles of products C and D. Various symbols are used in the expression which relates the reactants and products. For example, the formation of water from hydrogen and oxygen may be written as the balanced, irreversible chemical reaction

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{1–2}$$

In this simple example, the single arrow is used to indicate that the reaction proceeds from the left (reactant) side to the right (product) side as written: water does not spontaneously decompose to form hydrogen and oxygen. A double arrow in the stoichiometric equation is often used to denote a reversible reaction, that is, one which can proceed in either the forward or the reverse direction; an example is

$$H_2 + I_2 \rightleftarrows 2HI \tag{1–3}$$

While each of equations 1–2 and 1–3 describes an apparently simple chemical reaction, it so happens that neither of these reactions proceeds as written. Instead, the reactions involve the formation of one or more *intermediate* species, and include several steps. These steps are known as *elementary* reactions. An elementary reaction is one in which the indicated products are formed directly from the reactants, for example, in a direct collision between an A and a B molecule; intuitively, they correspond to processes occurring at the molecular level. In the hydrogen-oxygen reaction, a key elementary reaction is the attack of oxygen atoms on hydrogen molecules given by

$$O + H_2 \longrightarrow OH + H$$

while in the hydrogen-iodine reaction it is

$$2I + H_2 \longrightarrow H_2I + I$$

The details of these reactions are discussed in sections 15.2 and 2.3.2, respectively. In the meantime, note here that they involve atoms (O, I), free radicals (OH), and/or unstable intermediates ($H_2I$); this is often the case with elementary reactions.

The change in composition of the reaction mixture with time is the *rate of reaction, R*. For reaction 1–1, the rate of consumption of reactants is

$$R = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} \tag{1–4}$$

A standard convention in chemical kinetics is to use the chemical symbol enclosed in brackets for species concentration; thus, [X] denotes the concentration of X. The negative signs in equation 1–4 indicate that during the course of the reaction the concentration of reactants decreases as the reactants are consumed; conversely, a positive sign indicates that the concentration of products increases as those species are formed. Consequently, the rate of formation of products C and D can be written as

$$R = +\frac{1}{c}\frac{d[\mathrm{C}]}{dt} = +\frac{1}{d}\frac{d[\mathrm{D}]}{dt} \tag{1–5}$$

The factors $a$, $b$, $c$, and $d$ in equations 1–4 and 1–5 are referred to as the *stoichiometric coefficients* for the chemical entities taking part in the reaction. Since the concentrations of reactants and products are related by equation 1–1, measurement of the rate of change of any one of the reactants or products would suffice to determine the rate of reaction $R$. In the reaction 1–2, the rate of reaction would be

$$R = -\frac{1}{2}\frac{d[\mathrm{H_2}]}{dt} = -\frac{d[\mathrm{O_2}]}{dt} = +\frac{1}{2}\frac{d[\mathrm{H_2O}]}{dt} \tag{1–6}$$

A number of different units have been used for the reaction rate. The dimensionality of $R$ is

$$[\text{amount of material}][\text{volume}]^{-1}[\text{time}]^{-1}$$

or

$$[\text{concentration}][\text{time}]^{-1}$$

The standard SI unit of concentration is moles per cubic decimeter, abbreviated mol $dm^{-3}$. In the older literature on kinetics, one frequently finds the units mol $liter^{-1}$ for reactions in solution and mol $cm^{-3}$ for gas phase reactions. The SI unit is preferred, and should be used consistently. Multiplying moles $cm^{-3}$ by Avogadro's Number ($6.022 \times 10^{23}$) gives the units molecules $cm^{-3}$, which is still extensively used and, indeed, is convenient for gas phase reactions.

A subcommittee of the International Union of Pure and Applied Chemistry chaired by Laidler has attempted to standardize units, terminology, and notation in chemical kinetics.[1] We have attempted to follow the subcommittee's recommendations in this text.

## 1.2 ORDER AND MOLECULARITY OF A REACTION

In virtually all chemical reactions that have been studied experimentally, the reaction rate depends on the concentration of one or more of the reactants. In general, the rate may be expressed as a function $f$ of these concentrations,

$$R = f([\mathrm{A}],[\mathrm{B}]) \tag{1–7}$$

In some cases the reaction rate also depends on the concentration of one or more intermediate species, e.g., in enzymatic reactions (see chapter 5). In other cases the rate expression may involve the concentration of some species which do not appear in the stoichiometric equation 1–1; such species are known as *catalysts,* and will be discussed in chapter 5. In still other cases, the concentration of product molecules may appear in the rate expression.

The most frequently encountered functional dependence given by equation 1–7 is the rate's being proportional to a product of algebraic powers of the individual concentrations, i.e.,

$$R \propto [\mathrm{A}]^m[\mathrm{B}]^n \tag{1–8}$$

The exponents $m$ and $n$ may be integer, fractional, or negative. This proportionality can be converted to an equation by inserting a proportionality constant $k$, thus:

$$R = k\,[\mathrm{A}]^m[\mathrm{B}]^n \tag{1–9}$$

This equation is called a *rate equation* or *rate expression*. The exponent $m$ is the *order* of the reaction with respect to reactant A, and $n$ is the order with respect to reactant B. The proportionality constant $k$ is called the *rate constant*. The overall order of the reaction is simply $p = m + n$. A generalized expression for the rate of a reaction involving $K$ components is

$$R = k \prod_{i=1}^{K} c_i^{n_i} \tag{1–10}$$

The product is taken over the concentrations of each of the $K$ components of the reaction. The reaction order with respect to the $i$th component is $n_i$, $p = \Sigma_{i=1}^{K} n_i$ is the overall order of the reaction, and $k$ is the rate constant.

In equation 1–10, $k$ must have the units

$$[\text{concentration}]^{-(p-1)}[\text{time}]^{-1}$$

so for a second-order reaction, i.e., $m = n = 1$ in equation 1–8, the units would be $[\text{concentration}]^{-1}[\text{time}]^{-1}$, or $\mathrm{dm^3\ mol^{-1}\ sec^{-1}}$ in SI units. Note that the units of liter $\mathrm{mol^{-1}\ sec^{-1}}$ are frequently encountered in the older solution-kinetics literature, and $\mathrm{cm^3\ mol^{-1}\ sec^{-1}}$ or $\mathrm{cm^3\ molecule^{-1}\ sec^{-1}}$ are still encountered in the gas-kinetics literature.

Elementary reactions may be described by their *molecularity*, which specifies the number of reactants that are involved in the reaction step. If a reactant spontaneously decomposes to yield products in a single reaction step, given by the equation

$$\mathrm{A} \longrightarrow \text{products} \tag{1–11}$$

the reaction is termed *unimolecular*. An example of a unimolecular reaction is the dissociation of $N_2O_4$, represented by

$$N_2O_4 \longrightarrow 2NO_2$$

If two reactants A and B react with each other to give products, i.e.,

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products} \tag{1–12}$$

the reaction is termed *bimolecular*. An example of a bimolecular reaction would be a metathetical atom-transfer reaction such as

$$\mathrm{O} + \mathrm{H_2} \longrightarrow \mathrm{OH} + \mathrm{H}$$

or

$$\mathrm{F} + \mathrm{H_2} \longrightarrow \mathrm{HF} + \mathrm{H}$$

Both of these reactions are discussed in subsequent chapters.

Three reactants that come together to form products constitute a *termolecular* reaction. In principle, one could go on to specify the molecularity of four, five, etc., reactants involved in an elementary reaction, but such reactions have not been encountered in nature. The situation reflects the molecular basis of elementary reactions. A single, suitably energized molecule can decompose according to equation 1–11; such unimolecular processes are discussed in chapter 11. A collision between two molecules can lead to a bimolecular reaction according to equation 1–12; this is further discussed in chapters 8 and 10. At moderate to high gas pressures, termolecular processes can occur, such as three-body recombination, i.e.,

$$A + B + M \longrightarrow AB + M \tag{1–13}$$

However, physical processes involving simultaneous interaction of four or more independent particles are so rare in chemical kinetics as to be completely negligible.

An elementary reaction is one in which the molecularity and the overall order of the reaction are the same. Thus, a bimolecular elementary reaction is second order, a termolecular reaction third order, and so on. The reverse is not always true, however. For example, the hydrogen-iodine reaction 1–3 is second order in both directions, but bimolecular reactions between $H_2$ and $I_2$, and between two HI molecules, are thought not to occur. Instead, the reaction consists of several unimolecular, bimolecular, and possibly termolecular steps (see chapter 2).

A further distinction between molecularity and reaction order is that, while molecularity has only the integer values 0, 1, 2, and 3, order is an experimentally determined quantity which can take on noninteger values. In principle, these values could be any number between $-\infty$ and $+\infty$, but values between $-2$ and 3 are usually encountered in practice. Negative orders imply that the component associated with that order acts to slow down the reaction rate; such a component is termed an *inhibitor* for that reaction. Fractional values of the reaction order always imply a complex reaction mechanism (see section 1.6). An example of a fractional-order reaction is the thermal decomposition of acetaldehyde given by

$$CH_3CHO \xrightarrow{300\text{–}800^\circ C} CH_4 + CO \tag{1–14}$$

which has a $\frac{3}{2}$ reaction order, i.e.,

$$\frac{d[CH_4]}{dt} = (\text{constant})[CH_3CHO]^{3/2} \tag{1–15}$$

Similarly, under certain conditions the reaction of hydrogen with bromine

$$H_2 + Br_2 \longrightarrow 2HBr \tag{1–16}$$

has a $\frac{3}{2}$ reaction order, first order in $[H_2]$ and $\frac{1}{2}$ order in $[Br_2]$:

$$\frac{d[HBr]}{dt} = (\text{constant})[H_2][Br_2]^{1/2} \tag{1–17}$$

Under other conditions, reaction 1–16 can display an even more complicated behavior, viz.,

$$\frac{d[HBr]}{dt} = \frac{(\text{constant})[H_2][Br_2]^{1/2}}{1 + (\text{constant}')[HBr]} \tag{1–18}$$

The constants in equations 1–15, 1–17, and 1–18 are clearly not identifiable with an elementary reaction, but instead are phenomenological coefficients obtained by fitting the rate expression to experimental data. Such coefficients are more properly termed *rate coefficients,* rather than rate constants. The latter term should be reserved for the coefficients in rate expressions for elementary reactions, which follow a rate expression having the form of equation 1–10.

## 1.3 ELEMENTARY REACTION RATE LAWS

Thus far, we have defined the rate of reaction in terms of concentrations, orders, and reaction rate constants. Next, we consider the time behavior of the concentration of reactants in elementary reactions with simple orders. The time behavior is determined by integrating the rate law for a particular rate expression.

### 1.3.1 Zero-Order Reaction

The rate law for a reaction that is zero order is

$$R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k \tag{1–19}$$

Zero-order reactions are most often encountered in heterogeneous reactions on surfaces (see chapter 5). The rate of reaction for this case is independent of the concentration of the reacting substance. To find the time behavior of the reaction, equation 1–19 is put into the differential form

$$d[\mathrm{A}] = -kdt \tag{1–20}$$

and then integrated over the boundary limits $t_1$ and $t_2$. Assuming that the concentration of A at $t_1 = 0$ is $[\mathrm{A}]_0$, and at $t_2 = t$ is $[\mathrm{A}]_t$, equation 1–20 becomes

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = -k\int_{t_1=0}^{t_2=t} dt \tag{1–21}$$

Hence,

$$[\mathrm{A}]_t - [\mathrm{A}]_0 = -k(t - 0) \tag{1–22}$$

Consequently, the integrated form of the rate expression for the zero-order reaction is

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - kt \tag{1–23}$$

A plot of [A] versus time should yield a straight line with intercept $[\mathrm{A}]_0$ and slope $k$.

### 1.3.2 First-Order Reactions

A first-order reaction is one in which the rate of reaction depends only on one reactant. For example, the isomerization of methyl isocyanide, $CH_3NC$, is a first-order unimolecular reaction:

$$CH_3NC \longrightarrow CH_3CN \tag{1–24}$$

This type of equation can be represented symbolically as

$$A \longrightarrow B$$

and the rate of disappearance of A can be written as

$$R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^1 \qquad (1\text{–}25)$$

Note that the reaction is of order one in the reactant A. Thus, since only one A molecule disappears to produce one product B molecule, $a = 1$ and equation 1–25 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \qquad (1\text{–}26)$$

Integration of equation 1–26 leads to

$$-\int \frac{d[\mathrm{A}]}{[\mathrm{A}]} = k\int dt$$

$$-\ln[\mathrm{A}] = kt + \text{constant} \qquad (1\text{–}27)$$

If the boundary conditions are such that at $t = 0$ the initial value of A is $[\mathrm{A}]_0$, the constant of integration in equation 1–27 can be eliminated if we integrate over the boundary limits as follows:

$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = k\int_0^t dt \qquad (1\text{–}28)$$

This gives

$$-(\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0) = kt \qquad (1\text{–}29)$$

and hence

$$-\ln[\mathrm{A}]_t = kt - \ln[\mathrm{A}]_0 \qquad (1\text{–}30)$$

Thus, the constant in equation 1–27 is just

$$\text{constant} = -\ln[\mathrm{A}]_0 \qquad (1\text{–}31)$$

Equation 1–30 can be written in various forms. Some that are commonly used are

$$\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt \qquad (1\text{–}32a)$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt} \qquad (1\text{–}32b)$$

and

$$\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = e^{-kt} \qquad (1\text{–}32c)$$

These forms of the integrated rate expression for the first-order reaction are worth remembering. From the exponential form of equations 1–32b and 1–32c, one can determine a *time constant* $\tau$ which is called the *decay time* of the reaction. This quantity is defined as the time required for the concentration to decrease to $1/e$ of its initial value $[A]_0$, where $e \approx 2.7183$ is the base of the natural logarithm. The time $\tau$ is given by

$$\tau = \frac{1}{k} \tag{1–33}$$

In experimental determinations of the rate constant $k$, the integrated form of the rate law is often written in decimal logarithms as

$$\log_{10}[A]_t = \log_{10}[A]_0 - \frac{kt}{2.303} \tag{1–34}$$

and a semilog plot of $[A]_t$ versus $t$ will yield a straight line with $k/2.303$ as slope and $[A]_0$ as intercept.

### 1.3.3 Second-Order Reactions

There are two cases of second-order kinetics. The first is a reaction between two identical species, viz.,

$$A + A \longrightarrow \text{products} \tag{1–35}$$

The rate expression for this case is

$$R = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2 \tag{1–36}$$

The second case is an overall second-order reaction between two unlike species, given by

$$A + B \longrightarrow \text{products} \tag{1–37}$$

In this case, the reaction is first order in each of the reactants A and B and the rate expression is

$$R = -\frac{d[A]}{dt} = k[A][B] \tag{1–38}$$

Note the appearance of the stoichiometric coefficient $\frac{1}{2}$ in equation 1–36, but not in equation 1–38.

Let us consider the first case, given by equations 1–35 and 1–36. Although not an elementary reaction, the disproportionation of HI (equation 1–3) is a reaction which is exactly second order in a single reactant. Another example is the recombination of two identical radicals, such as two methyl radicals:

$$2CH_3 \longrightarrow C_2H_6 \tag{1–39}$$

We integrate the rate law, equation 1–36, to obtain

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = 2k \int_0^t dt \tag{1–40}$$

which gives

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} - 2kt \tag{1–41}$$

A plot of the inverse concentration of A ($[A]^{-1}$) versus time should yield a straight line with slope equal to $2k$ and intercept $1/[A]_0$.

To integrate the rate law for the second case, equations 1–37 and 1–38, it is convenient to define a progress variable $x$ which measures the progress of the reaction to products as

$$x = ([A]_0 - [A]_t) = ([B]_0 - [B]_t) \tag{1–42}$$

where $[A]_0$ and $[B]_0$ are the initial concentrations. The rate expression given by equation 1–38 can then be rewritten in terms of $x$ as

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x) \tag{1–43}$$

To find the time behavior, we integrate equation 1–43 thus:

$$\int_{x(0)}^{x(t)} \frac{dx}{([A]_0 - x)([B]_0 - x)} = k \int_0^t dt \tag{1–44}$$

To solve the integral on the left-hand side of equation 1–44, we separate the variables and use the method of partial fractions:

$$\int \frac{dx}{([A]_0 - x)([B]_0 - x)}$$

$$= \int \frac{dx}{([A]_0 - [B]_0)([B]_0 - x)} - \int \frac{dx}{([A]_0 - [B]_0)([A]_0 - x)} \tag{1–45}$$

Solving the right-hand side of equation 1–45 and equating it to the left-hand side of equation 1–44, we obtain, as the solution to the rate expression for the second case,

$$\frac{1}{([A]_0 - [B]_0)} \ln\left(\frac{[B]_0[A]_t}{[A]_0[B]_t}\right) = kt \tag{1–46}$$

In this case the experimental data may be plotted in the form of the left-hand side of the equation against $t$.

### 1.3.4 Third-Order Reactions

From the definition of overall reaction order in equation 1–10, we see that there are three possible types of third-order reactions: (1) 3A → products; (2) 2A + B → products; and (3) A + B + C → products. In the first case, in which the rate law depends on the third power of one reactant, the rate expression is

$$R \equiv -\frac{1}{3}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^3 \qquad (1\text{–}47)$$

This rate law can be integrated readily to obtain the solution

$$-\frac{1}{2}\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right) = 3kt \qquad (1\text{–}48)$$

Rearranging gives

$$\frac{1}{[\mathrm{A}]^2} = \frac{1}{[\mathrm{A}]_0^2} + 6kt \qquad (1\text{–}49)$$

A plot of the inverse squared concentration of A ($[\mathrm{A}]^{-2}$) with time should yield slope $6k$ and intercept $1/[\mathrm{A}]_0^2$.

The second case,

$$2\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \qquad (1\text{–}50)$$

which is second order in reactant A and first order in reactant B, has the overall order 3. The rate law for this reaction is

$$R \equiv -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2[\mathrm{B}] \qquad (1\text{–}51)$$

This rate expression can be integrated for two possible subcases. The first is when the concentration of B is so much greater than that of the reactant A ($[\mathrm{B}] \gg [\mathrm{A}]$), that the concentration of B does not change during the course of the reaction. Under this condition, the rate expression can be rewritten as

$$R \equiv -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k'[\mathrm{A}]^2 \qquad (1\text{–}52)$$

so that the third-order expression reduces to a "pseudo second-order" expression. The solution for this case is equation 1–41, i.e.,

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} - 2k't \qquad (1\text{–}53)$$

A plot of $[\mathrm{A}]^{-1}$ vs. time, for a fixed [B], should then yield slope $2k'$ and intercept $1/[\mathrm{A}]_0$; but note that the resulting rate coefficient is a function of the concentration of B, that is,

$$k' = k[\mathrm{B}] \qquad (1\text{–}54)$$

Forgetting that this rate coefficient contains an added concentration term can lead to errors in interpretation of data. A simple example of this type of reaction is the three-body recombination process, such as $\mathrm{I} + \mathrm{I} + \mathrm{M} \rightarrow \mathrm{I}_2 + \mathrm{M}$ and $\mathrm{O} + \mathrm{O}_2 + \mathrm{M} \rightarrow \mathrm{O}_3 + \mathrm{M}$. In these cases the third body acts to remove the excess energy from the recombining reactants, thereby stabilizing the molecular products.

The other instance in which equation 1–51 can be easily integrated is when the initial concentrations of the dissimilar reactants A and B are equal. In integrating the rate law for this case, subject to the stated initial conditions, it is once again convenient to introduce a progress variable as we did in solving the second-order reaction case. Accordingly, we define a progress variable $y$ by

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - 2y$$

and

$$[\mathrm{B}]_t = [\mathrm{B}]_0 - y$$

and with this condition we can rewrite equation 1–51 in terms of $y$ as

$$\frac{dy}{dt} = k([\mathrm{A}]_0 - 2y)^2([\mathrm{B}]_0 - y) \tag{1–55}$$

Upon rearranging, we obtain

$$\frac{dy}{([\mathrm{A}]_0 - 2y)^2([\mathrm{B}]_0 - y)} = k\,dt \tag{1–56}$$

This equation can be integrated by the method of partial fractions to yield

$$\frac{1}{([\mathrm{A}]_0 - 2[\mathrm{B}]_0)}\left(\frac{1}{[\mathrm{A}_0]} - \frac{1}{[\mathrm{A}]_t}\right) + \frac{1}{([\mathrm{A}]_0 - 2[\mathrm{B}]_0)^2}\ln\left(\frac{[\mathrm{A}]_t[\mathrm{B}]_0}{[\mathrm{A}]_0[\mathrm{B}]_t}\right) = kt \tag{1–57}$$

An example of such a reaction is the gas phase reaction between nitric oxide and oxygen

$$2\mathrm{NO} + \mathrm{O}_2 \longrightarrow 2\mathrm{NO}_2 \tag{1–58}$$

The third type of third-order reaction is first order in three different components, i.e.,

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \longrightarrow \text{product} \tag{1–59}$$

The rate law for this reaction is

$$R = \frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}][\mathrm{C}] \tag{1–60}$$

To solve for the integrated rate law expression in this case, we use the method of partial fractions as before. The solution is left as an exercise at the end of this chapter.

### 1.3.5 Reactions of General Order

There are no known examples of fourth-, fifth-, or higher order reactions in the chemical literature. The highest order which has been empirically encountered for chemical reactions is third order. Nevertheless, in this section we develop the general solution for a reaction which is $n$th order in one reactant, for $n$ equal to any integer or noninteger value. The rate expression for such a reaction is

$$R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n \tag{1–61}$$

A simple integration of this expression yields the result

$$\frac{1}{(n-1)}\left(\frac{1}{[A]_t^{n-1}}-\frac{1}{[A]_0^{n-1}}\right)=kt \tag{1–62}$$

which can be rewritten as

$$\frac{1}{[A]_t^{n-1}}-\frac{1}{[A]_0^{n-1}}=(n-1)kt \tag{1–63}$$

Equation 1–63 is valid for any value of $n$ except $n = 1$, in which case it is undefined and equation 1–32 must be used instead. Figure 1–1 shows several plots of concentration vs. time for various values of $n$.

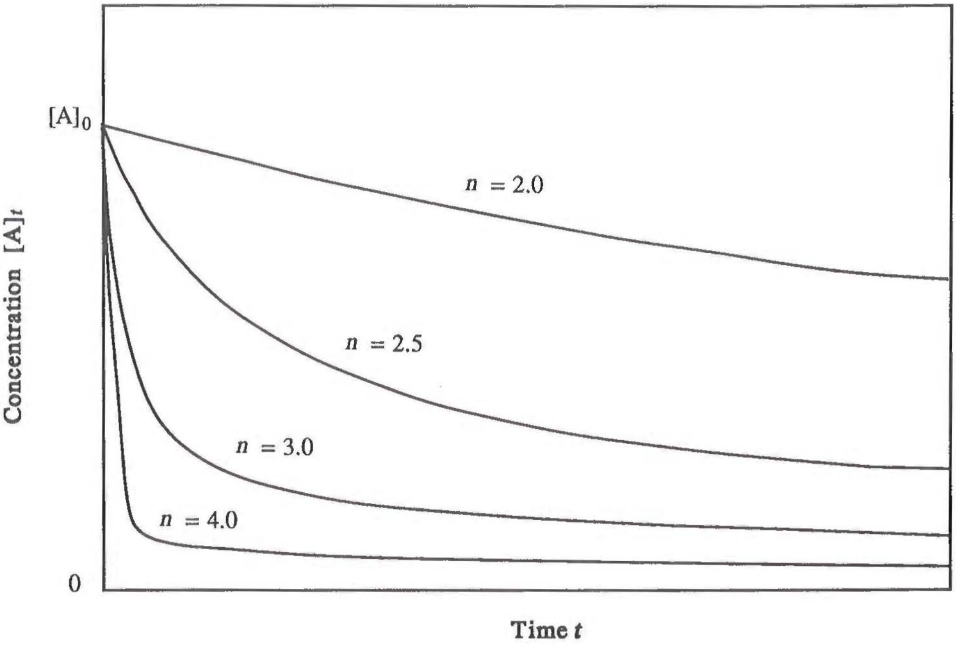

**Figure 1–1.** Plot of $[A]_t$ versus time for reaction of general order. The plot shows various functional behaviors for $n$ = 2, 2.5, 3, 3.5, and 4. Concentration and time are in arbitary units.

In the general case there is no simple plot that can be constructed to test the order of the reaction, as can be done for the first- and second-order cases. When the order $n$ is unknown, a van't Hoff plot can be constructed as an aid to deducing the order of the reaction. In a van't Hoff plot, the logarithm of the rate is plotted against the logarithm of the concentration of the reactant A. This is equivalent to making a plot of equation 1–63 on log-log graph paper. The slope of such a plot gives the order of the reaction $n$. Examples of van't Hoff plots for several reaction orders are shown in Figure 1–2.

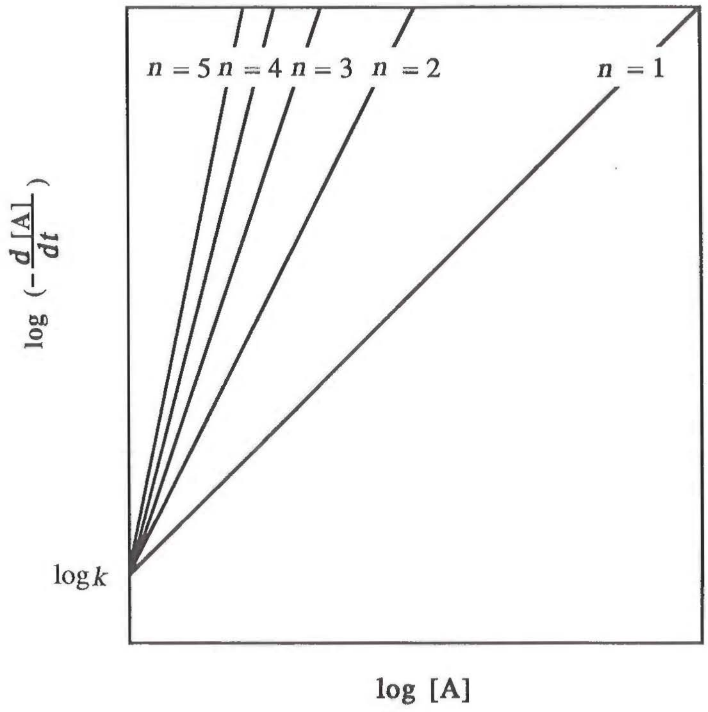

**Figure 1–2.** Van't Hoff plot of log $\left(-\frac{d[\mathrm{A}]}{dt}\right)$ versus log [A] for various reaction orders.

## 1.4 DETERMINATION OF REACTION ORDER: REACTION HALF-LIVES

Thus far, we have introduced the concept of a rate law and have shown that experimental rate laws can frequently be written as the product of concentrations of reacting species raised to some power; the exponents in such a rate law then define the order of the particular reaction. These reaction orders are empirically determined and may be nonintegral. We have also considered some simple rate laws and, by integrating them, have shown how experimental data can be plotted to enable the reaction order to be determined. The van't Hoff method has been introduced as a method for determining a general reaction order.

An alternative to the van't Hoff method, and one of the more popular methods for determining reaction order, is the *half-life method*. The reaction half-life $t_{1/2}$ is defined as the period of time necessary for the concentration of a specified reactant to reach one-half of its initial concentration. Measurement of $t_{1/2}$ as a function of initial reactant concentration can help establish the order with respect to that reactant. Consider the simple first-order reaction 1–11. The integrated rate equation is given by equation 1–32a,

$$\ln([\mathrm{A}]_t/[\mathrm{A}]_0) = -kt$$

By definition, at $t = t_{1/2}$, $[A]_t = [A]_0/2$; therefore, the rate equation can be rewritten as

$$-\ln\left(\frac{[A]_0/2}{[A]_0}\right) = kt_{1/2} \tag{1–64}$$

The half-life is then

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \tag{1–65}$$

Thus, for a first-order reaction, $t_{1/2}$ is independent of concentration. On the other hand, for a reaction of order $n > 1$ in a single reactant, the reaction half-life is

$$t_{1/2} = \frac{(2^{n-1} - 1)}{k(n-1)[A]_0^{n-1}} \tag{1–66}$$

where $k$ is the rate constant and $[A]_0$ is the initial concentration of the reactant. Thus, the half-life for orders $n > 1$ is a function of the initial concentration of the reactant; consequently, a plot of the logarithm of $t_{1/2}$ against the logarithm of $[A]_0$ should enable one to determine the reaction order. To illustrate this, let us take the logarithm of both sides of equation 1–66. We obtain

$$\log t_{1/2} = \log \frac{(2^{n-1} - 1)}{k(n-1)} - (n-1)\log[A]_0 \tag{1–67}$$

It is clear from this expression that the plot will be linear with a slope equal to $n - 1$, from which the order can be determined. With this information, and one or more absolute values of $t_{1/2}$, the rate constant can also be calculated. The reader is reminded that this procedure is valid only for reactions which are $n$th order in a single reactant.

Other methods of determining reaction orders are discussed in some earlier kinetics textbooks, including those by Hammes[3] and Benson[4].

## 1.5 TEMPERATURE DEPENDENCE OF RATE CONSTANTS: THE ARRHENIUS EQUATION

We have seen that rate expressions are often simple functions of reactant concentrations with a characteristic rate constant $k$. If the rate expression is correctly formulated, the rate constant should indeed be a constant—that is, it should not depend on the concentrations of species appearing in the rate law, or of any other species which may be present in the reaction mixture.* The rate constant should also be independent of time. It does, however, depend strongly on temperature. This behavior was described by Svante Arrhenius in 1889[5] on the basis of numerous experimental rate measurements. Arrhenius found that rate constants varied as the negative exponential of the reciprocal absolute temperature, that is,

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*The rate constant for reactions in liquid solutions may depend on pH, that is, $H^+$ concentration; this will be discussed in chapter 4.

$$k(T) = A \exp(-E_{\text{act}}/RT) \tag{1–68}$$

This relationship is now known as the *Arrhenius equation,* and a plot of ln $k$ (or $\log_{10} k$) vs. $1/T$ is called an *Arrhenius plot*. In the Arrhenius equation, the temperature dependence comes primarily from the exponential term, although the quantity $A$, referred to as the *pre-exponential* or the *frequency factor,* may have a weak temperature dependence, no more than some fractional power of $T$. The units of $A$ are the same as the units of the rate constant $k$, since the exponential term has no units. In the case of a first-order reaction, $A$ has units of $\text{sec}^{-1}$; for reactions of higher order, $A$ has units $(\text{concentration})^{1-p}\text{sec}^{-1}$. The temperature $T$ is, of course, in absolute or Kelvin units (degrees Celsius + 273.16).

The key quantity in the Arrhenius equation is the *activation energy* $E_{\text{act}}$. The activation energy can be thought of as the amount of energy which must be supplied to the reactants in order to get them to react with each other. Since this is a positive energy quantity, the majority of reactions have $k$ increasing with temperature. For some reactions, however, the rate decreases with temperature, implying a negative activation energy. Such reactions are generally complex, involving the formation of a weakly bound intermediate species. An example is the recombination of iodine atoms in the presence of a molecular third body M, which proceeds via the following steps:[6]

$$\mathrm{I} + \mathrm{M} \longrightarrow \mathrm{IM}$$

$$\mathrm{IM} + \mathrm{I} \longrightarrow \mathrm{I_2} + \mathrm{M}$$

The IM species is a van der Waals complex whose stability decreases with increasing temperature.

The standard method for obtaining $E_{\text{act}}$ is to graph experimental rate constant data on an Arrhenius plot, i.e., $\log_{10}k$ vs. $1/T$. The slope gives $E_{\text{act}}/2.303R$, where $R = 8.3145\ \text{J mol}^{-1}\text{K}^{-1}$. The units of $E_{\text{act}}$ are thus $\text{J mol}^{-1}$, but since the magnitudes of activation energies are typically in the range of a few to several hundred thousand $\text{J mol}^{-1}$, it is customary to report their values in $\text{kJ mol}^{-1}$. The older (non-SI) unit of calories or $\text{kcal mol}^{-1}$ is still often encountered, but should be discouraged. The conversion factor[7] is 1 calorie = 4.184 J.

The origin of the activation energy is a barrier on the potential energy surface between the reactants and products; this is discussed in detail in chapters 7 and 10. For the time being, the *enthalpy diagram* shown in Figure 1–3 may be instructive. This is simply a sketch of the thermodynamic energies associated with the reactants, the products, and a (for the moment) hypothetical *transition state* connecting the two. The energy difference between the reactants and products is the difference in their heats of formation and is given by

$$\Delta H^0_{\text{reaction}} = \Delta H^0_f(\text{products}) - \Delta H^0_f(\text{reactants}) \tag{1–69}$$

A reaction which is highly *endothermic,* that is, which has a large positive $\Delta H^0_{\text{reaction}}$, is not likely to proceed spontaneously except at very high temperatures. A highly *exothermic* reaction, however, may do so unless the activation energy required to reach the transition state is very high; in that case, the reaction will be slow at other than very high temperatures. The calculation of reaction exothermicities is often a

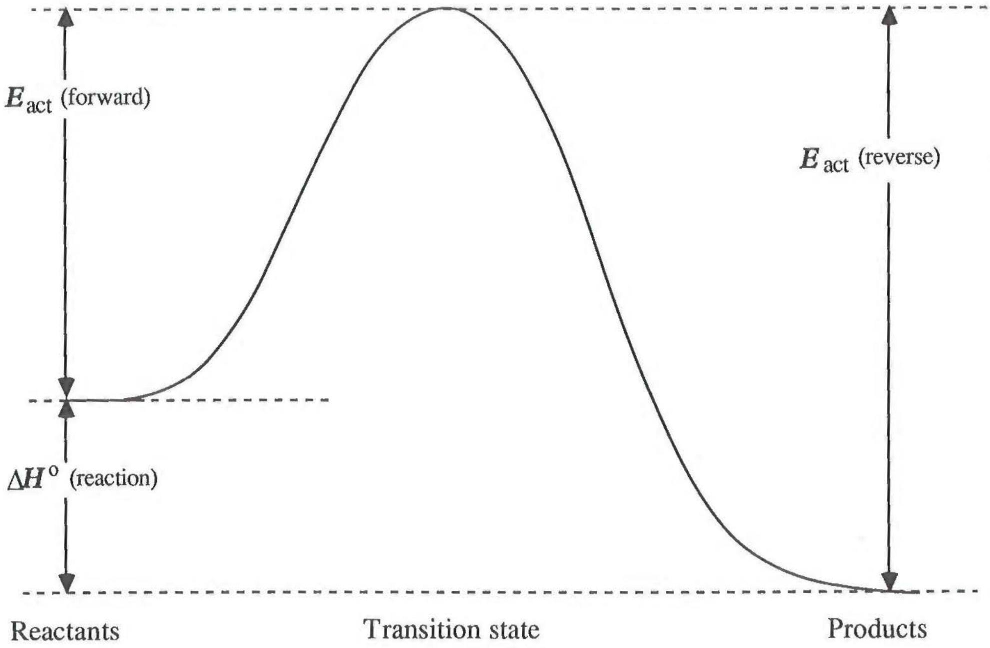

**Figure 1–3.** Enthalpy diagram for a chemical reaction.

helpful guide in assessing the relative importance of individual reactions in a complex mechanism.

An important relationship which may be established by inspection of Figure 1–3 is that between forward and reverse activation energies for a given reaction. Clearly,

$$E_{act}(\text{forward}) - E_{act}(\text{reverse}) = \Delta H^0_{\text{reaction}} \tag{1–70}$$

Thus, exothermic reactions have a larger activation energy for the reverse reaction, while the opposite is true for endothermic reactions.

## 1.6 REACTION MECHANISMS, MOLECULAR DYNAMICS, AND THE ROAD AHEAD

In this chapter we have concentrated mainly on elementary chemical reactions. We have examined ways in which the chemical kineticist can determine the reaction order from measurements of the time dependence of the reactant and product concentrations, and the reaction activation energy from the temperature dependence of the rate constant. Unfortunately, with just this amount of information it is not possible to achieve a complete understanding of most chemical reactions. This is because reactions that are studied experimentally rarely occur in a single step. More often, there is a complex series of elementary reactions which take place during the transformation of reactants into products. Reactions that consist of several elementary reaction steps are called *complex,* or *composite,* reactions. The *mechanism* of a complex reaction is the assembly of individual steps that make it up. One of the principal aims of experimental studies in chemical kinetics is to elucidate mechanisms and to describe the overall observed reaction process in terms of the elementary reaction steps which constitute the mechanism. In chapter 2, we consider various types of complex reactions together with methods for analyzing their kinetics. Chapter 3 deals with some of the experimental methods that can be used to carry out rate measurements on complex reaction systems, with emphasis on gas-phase reactions. Chapter 4 then goes on to treat reactions in liquid solutions, and in chapter 5 we consider catalyzed reactions, including those which occur at the gas-solid interface.

Chapters 2 through 5 deal primarily with chemical *kinetics,* that is, the phenomenological behavior of reactions. In chapters 6 through 13, we turn our attention to chemical *dynamics,* the description of chemical reactions at the molecular level. The approach there will be to attempt to isolate elementary reaction steps experimentally, to examine them in great detail, and to relate the findings to microscopic molecular properties. Finally, chapters 14 and 15 present some examples of kinetic systems, that is, large coupled reaction sets which describe complex real-world phenomena.

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## PROBLEMS

**1.1** **(a)** What fractions of the molecules in $H_2$ and $UF_6$ have kinetic energies greater than 100 kJ/mole at 300 K and at 3,000 K (neglect dissociation)?

**(b)** In what proportion of binary collisions does the kinetic energy along the line of centers exceed 50 kJ/mole at 100 K, at 300 K, and at 2,000 K?

**1.2** The units in the preceding problem were in kJ/mole, which is an example of SI units. Give values for the following quantities both in kJ/mole and in the indicated alternative units in parentheses:

**(a)** Heat capacity of liquid water at 15°C and 1 atm (calories/mole K).

**(b)** Vibrational fundamental frequency of $H^{35}Cl$ ($cm^{-1}$).

**(c)** Ionization potential of H atom (eV).

**(d)** R.M.S. average translational kinetic energy of $Br_2$ at 300 K (ergs/molecule).

**(e)** energy of $CO_2$ laser photons having a wavelength of 10.59 $\mu$m (Hz).

**1.3** **(a)** Derive the integrated rate equation for a reaction of $\frac{3}{2}$ order. Derive the expression for the half-life of such a reaction. Can you think of an example of such a reaction?

**(b)** Derive the integrated rate equation for a reaction of order *n*.

**1.4** The first-order gas reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ has $k_1 = 2.20 \times 10^{-5}\ s^{-1}$ at 593 K. What percent of a sample of $SO_2Cl_2$ would be decomposed by heating at 593 K for 1 hour? For 3 hours? How long will it take for half the $SO_2Cl_2$ to decompose?

**1.5** The kinetics of the formation of ethyl acetate from acetic acid and ethyl alcohol as homogeneously catalyzed by a constant amount of HCl has been studied by titrating 1-cc aliquots of the reaction mixture with 0.0612 N base at various times. The following data have been obtained at 25°C [O. Knoblauch, *Z. physik. Chem. 22*, 268 (1897)]:

Initial Concentrations

$[CH_3COOH] = 1.000$ M
$[C_2H_5OH] = 12.756$ M
$[H_2O] = 12.756$ M
$[CH_3COOC_2H_5] = 0$

| $t$, min | Base, cc | $t$, min | Base, cc |
|---|---|---|---|
| 0 | 24.37 | 148 | 18.29 |
| 44 | 22.20 | 313 | 14.14 |
| 62 | 21.35 | 384 | 13.40 |
| 108 | 19.50 | 442 | 13.09 |
| 117 | 19.26 | ∞ | 12.68 |

The overall reaction can be written as

$$CH_3COOH + C_2H_5OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

The reaction has been found to be first order with respect to each of the four reactants. Calculate the specific rate constants $k_1$ and $k_{-1}$. What is the equilibrium constant $K_1$ at 25°C?

**1.6** Nitrogen pentoxide decomposes according to the reaction $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ with rate constant $k$. The measured rates between 273 K and 338 K are as follows:

| $T$ (K) | 273 | 298 | 308 | 318 | 328 | 338 |
|---|---|---|---|---|---|---|
| $k$ ($\times 10^5$ sec$^{-1}$) | 0.0787 | 3.46 | 13.5 | 49.8 | 150 | 487 |

Make an Arrhenius plot of these data, and determine $E_{act}$ and $A$ for the first-order decomposition of nitrogen pentoxide [F. Daniels and F. H. Johnston, *J. Am. Chem. Soc. 43*, 53 (1921)].

**1.7** The reaction

$$NO_3 + NO \longrightarrow 2NO_2$$

is known to be an elementary process.

**(a)** Write the rate expression for the rate of disappearance of $NO_3$ and NO.
**(b)** Write the rate expression for the appearance of $NO_2$.
**(c)** Show how the rate constants in (a) and (b) are related.

**1.8** T-butyl bromide is converted into t-butyl alcohol in a solvent containing 90 percent acetone and 10 percent water. The reaction is given by

$$(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$$

The following table gives the data for the concentration of t-butyl bromide versus time [L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.* 960, 1940]:

| $t$ (min) | $(CH_3)_3CBr$(mol $\ell^{-1}$) |
|---|---|
| 0 | 0.1056 |
| 9 | 0.0961 |
| 18 | 0.0856 |
| 27 | 0.0767 |
| 40 | 0.0645 |
| 54 | 0.0536 |
| 72 | 0.0432 |
| 105 | 0.0270 |

What is the order of the reaction? What is the rate constant of the reaction? What is the half-life of the reaction?

**1.9** The reaction

$$A + B + C \longrightarrow \text{products}$$

has the rate expression

$$R = -\frac{d[A]}{dt} = k[A][B][C]$$

Derive the integral form of the rate expression.

**1.10** **(a)** What are the units of the rate constants of first-, second-, and third-order reactions if the concentrations are expressed in moles $cm^{-3}$ and the time is given in seconds? What are the conversion functions that must be used to convert to concentration units of molecules/$cm^3$ in each case?

**(b)** If a reaction obeyed the rate law

$$R = k[A]^{1/2}[B]^{2/3}$$

what would be the units of $k$?

**1.11** Write the rate expression for the reaction

$$2A + 3B \longrightarrow X$$

and derive the integrated rate expression for the reaction.

and equal to the steady-state concentration $[CH_3]_{ss}$. The second and third reactions in the mechanism given by equations 3–22 are the only significant reactions consuming $CH_3$. Since the $CH_3$ concentration is proportional to the $CH_3$ ion signal, $k_1$ can be determined by fitting the half-life of the $CH_3$ ion-count growth to its steady-state value, as shown in Figure 3–15.

## 3.3 TREATMENT OF KINETIC DATA

### 3.3.1 General Analysis of Kinetic Data

**3.3.1.1 Introduction.** Two questions usually arise when rate data are obtained experimentally. The first deals with the inherent errors in the data as contributed by instrumental factors and experimental procedures; the second pertains to how these errors determine the uncertainty in the fitted rate constants. Correct estimates of kinetic parameters and their uncertainties are fundamentally important for chemical kinetics, because such data are needed for assessing kinetic models and microscopic rate theories in chemical kinetics. These two questions are also important in assessing just how well correlated a postulated reaction mechanism is to the raw data. Since errors are inherent in any measurement correlations are never exact, and a method for judging whether a particular correlation is significant is needed to assess the model. This section is given over to considering briefly some of these points.

**3.3.1.2 Types of measurement errors.** No measurement can be made perfectly and with zero error; thus, it becomes important to know the uncertainty of a measurement and how different errors that arise from the experiment or the instrument enter into it. Furthermore, once sources of errors are identified, ways of reducing them may be undertaken. It is the duty of every experimental kineticist to take every precaution to minimize errors and to report the accuracy of the final result. The accuracy of kinetic results involves estimating the systematic errors in each observation in the experimental apparatus or procedure. Although this step is difficult to quantify, it is possible to correct for the errors incurred. The precision of the result depends on random or statistical errors, which are fluctuations in repeated measurements and are usually beyond the control of the experimentalist. To estimate such errors, we treat the experimental data statistically using standard methods to obtain the standard deviation in the results from the mean value. Knowing these uncertainties in the experimental data permits the uncertainty in the measured rate constants to be estimated and also enables us to further understand how these sources of errors contribute to the overall uncertainty in the measured rate. In this section our purpose is not to provide the reader with an extensive review of statistical methods of treating data (indeed, this has already been done by others[27–29]), but rather to acquaint the would-be kineticist with the procedures for analyzing and reporting kinetic data together with appropriate error limits.

*3.3.1.2.1 Systematic Errors.* Systematic errors in kinetic measurements have been discussed in some detail by Cvetanovic et al.[30–33] In kinetic measurements there are four kinds of systematic errors: (1) *instrumental* (shortcomings of the instruments or the effects of the environment on the instrument or its user); (2) *operational* (the personal judgment of the kineticist, which enters into readings of the instrument, and errors in instrument calibration); (3) *methodological* (inaccuracies in the modeling equations, which are imperfect approximations to the true solutions); and (4) *mechanistic* (errors introduced by inaccurate representations of the underlying chemical mechanism or some unrecognized chemical interference from secondary reactions or impurities in reagents). There are several ways of searching for systematic errors in measured kinetic parameters:

1. *Comparison of measured kinetic parameters under a variety of experimental conditions*. Inconsistencies between measured rate coefficients greater than the cumulative random error indicate the presence of systematic errors. Caution must be exercised since apparently consistent results can conceal systematic errors.
2. *Comparison of the absolute value of rate parameters obtained by different techniques*. Here, the importance of determining the same kinetic parameters by vastly different techniques cannot be overemphasized.
3. *Through insight and guidance from theoretical and semi-empirical methods such as those to be presented in later chapters.*

In chemical kinetics, an inadequate mechanism is frequently the largest source of systematic errors. If a mechanistic complication is the cause of systematic error, its magnitude and sign may be assessed by computer simulation. In this case, the reaction or reactions that may be significant are included. Once upper and lower bounds of the systematic error are estimated, it is possible to evaluate their contribution to the overall uncertainty in the results of the measurements. When upper ($e_s^u$) and lower ($e_s^L$) bounds of the systematic error are given, a correction for the error is given by the mean,

$$\bar{e}_s = \frac{(e_s^u + e_s^L)}{2} \tag{3–23}$$

In this case the remaining error becomes

$$\pm(e_s)_{\max} = \frac{\pm(e_s^u + e_s^L)}{2} \tag{3–24}$$

An excellent discussion of other ways of estimating systematic errors is given by Eisenhart.[34,35]

***3.3.1.2.2 Random Errors.*** Random errors are usually due to unknown causes and may occur even when all systematic errors have been accounted for. They also contribute to the uncertainty of the measured value. Because of their randomness, there is no known method of controlling or correcting these errors. The only way to offset them is to increase the number of repetitive measurements and use statistical means to obtain the estimate of the true value of the parameter under measurement. For a large number of observations, the random errors have a Gaussian distribution;[27,36] that is, the probability of their occurrence is given by

$$f(\epsilon) = \left(\frac{1}{\sigma\sqrt{2\pi}}\right)\exp\left(\frac{-(x-\mu)^2}{2\sigma^2}\right) \tag{3–25}$$

where $\epsilon$ is the magnitude of the random error given by $x - \mu$, and $\mu$ and $\sigma$ are moments of the distribution. The quantity $\mu$ is the *mean* of the population, and $\sigma$ is the *standard deviation* of the population—it measures true spread of the individual observations about the mean. The term $x - \mu$ represents the magnitude of the random error in an individual measurement.

***3.3.1.2.3 Propagation of Errors.*** Rate constants of chemical reactions are calculated from experimental measurements of quantities such as gas pressure, intensity alteration, intensity of chemiluminescence or fluorescence, etc. Consequently, the uncertainty in the rate constant is dependent on the individual uncertainties in these measured parameters. For example, consider a resonance fluorescence experiment done in a flow system. The critical parameters affecting the results of measurement are (1) gas flow, (2) pressure, (3) temperature, (4) distance, and (5) light intensity. Table 3–1 provides a list of typical uncertainty ranges for these parameters.[37] Uncertainties in these values together with scatter in the kinetic data ultimately determine the precision of reported results. Using the propagation-of-errors method,[27,28,36] the overall uncertainty in the measured parameter is given by

$$\sigma_k = \left[\sum_i \left(\frac{\partial f}{\partial \phi_i}\sigma_i\right)^2\right]^{1/2} \tag{3–26}$$

where the $\sigma_i$ are the uncertainties in the measurement parameters and the partial derivatives $(\partial f/\partial \phi_i)$ are measured at the sample mean of the measurement parameters.

**TABLE 3–1** RANDOM ERROR SOURCES AND MAGNITUDES IN EXPERIMENTAL FLOW-TUBE MEASUREMENTS (FROM REF. 37)

| Measurement (units) | Device/method used | Range used | Uncertainty range[a] |
|---|---|---|---|
| Gas flow, $u$ | Volume displacement | 0.05–250 | 0.01–15 |
| (mliter (STP)$\sec^{-1}$) | Critical flow orifices | 5–500 | 1.0–5.0 |
| Pressure, $P$ (torr) | Closed-end manometers | 1–1000 | 0.1–5.0 |
| | Bourdon gauges | 1–50 | 0.1–2.5 |
| | U-tube manometer | 0.5–20 | 0.05–1.0 |
| Temperature, $T$ (°C) | Chromel-alumel thermocouple | −80–200 | 0.1 |
| | Pt vs. Pt-Rh thermocouple | 300–2000 | 10–60 |
| Distance, $z$ (cm) | Centimeter scale | 0–100 | 0.05 |
| Light intensity | | | |
| $I$ (mV) | Absorption-monochromator/PMT | 10–100 | 0.5–2.0 |
| $F$ (mV) | Fluorescence-light filter/PMT | 1–20 | 0.1–1.0 |
| $I_{CL}$(pA) | Chemiluminescence-calibrated monochromator/PMT | 0.1–500 | 0.02–50[b] |

[a] Values correspond to uncertainties at extremes of range; units are the same as measurement units.

[b] Includes contribution of scatter in detection system calibration (≈±5%) used to obtain absolute intensities.

Let us determine the precision of a simple first-order rate constant from a flow reaction system (see section 3.2.1.2.2). The specific rate constant $k$ is given by

$$k = \frac{-v(\ln[A]_1 - \ln[A]_2}{(z_1 - z_2)} \tag{3–27}$$

where $[A]_1$ and $[A]_2$ are the concentrations of A present at the distances $z_1$ and $z_2$, respectively, and $v = u/A$ is the linear gas flow velocity. If we assume that errors in the measured quantities are independent of each other, then we can use equation 3–26 to estimate the uncertainty $\Delta k$ in $k$ as follows:

$$(\Delta k)^2 = \left(\frac{\partial k}{\partial z_1}\right)^2 (\Delta z_1)^2 + \left(\frac{\partial k}{\partial z_2}\right)^2 (\Delta z_2)^2 + \left(\frac{\partial k}{\partial \ln[A]_1}\right)^2 (\Delta \ln[A]_1)^2 + \left(\frac{\partial k}{\partial \ln[A]_2}\right)^2 (\Delta \ln[A]_2)^2 + \left(\frac{\partial k}{\partial v}\right)^2 (\Delta v)^2 \tag{3–28}$$

The relative error can be found by dividing through by $k^2$ and then multiplying and dividing each term by the square of the independent variable:

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{z_1}{k}\frac{\partial k}{\partial z_1}\right)^2 \left(\frac{\Delta z_1}{z_1}\right)^2 + \left(\frac{z_2}{k}\frac{\partial k}{\partial z_2}\right)^2 \left(\frac{\Delta z_z}{z_z}\right)^2 + \left(\frac{\ln[A]_1}{k}\frac{\partial k}{\partial \ln[A]_1}\right)^2 \left(\frac{\Delta \ln[A]_1}{\ln[A]_1}\right)^2 + \left(\frac{\ln[A]_2}{k}\frac{\partial k}{\partial \ln[A]_2}\right)^2 \left(\frac{\Delta \ln[A]_2}{\ln[A]_2}\right)^2 + \left(\frac{v}{k}\frac{\partial k}{\partial v}\right)^2 \left(\frac{\Delta v}{v}\right)^2 \tag{3–29}$$

We use equation 3–27 to calculate the partial derivatives, and if we substitute the values in equation 3–29, we obtain

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{z_1}{z_1 z_2}\right)^2 \left(\frac{\Delta z_1}{z_1}\right)^2 + \left(\frac{z_2}{z_1 z_2}\right)^2 \left(\frac{\Delta z_2}{z_2}\right)^2 + \left(\frac{\ln[A]_1}{\ln[A]_1 - \ln[A]_2}\right)^2 \left(\frac{\Delta \ln[A]_1}{\ln[A]_1}\right)^2 + \left(\frac{\ln[A]_2}{\ln[A]_1 - \ln[A]_2}\right)^2 \left(\frac{\Delta \ln[A]_2}{\ln[A]_2}\right)^2 \tag{3–30}$$

To show how we use equation 3–30, suppose that for a particular reaction $z_1 - z_2 = 100$ cm, $[A]_2 = 0.80[A]_1$, the relative error in determining $[A]_1$ and $[A]_2$ is about ±1%, the flow velocity is 400 cm/sec, its uncertainty is ±5 cm/sec, and the uncertainty in the distance is ±0.1 cm. Substituting these values into equation 3–30, we obtain, for the precision in $k$,

$$\begin{aligned}\frac{\Delta k}{k} &= \pm\{(0.005)^2 + (0.001)^2 + (0.0448)^2 + (0.0448)^2 + (0.0125)^2\}^{0.5} \\ &= \pm 0.0645\end{aligned} \tag{3–31}$$

so the expected error is ±6.5%.

### 3.3.1.3 Evaluation of rate constants

***3.3.1.3.1 Least-Squares Analysis.*** Once the uncertainties in each measurement are known, how does one determine the uncertainties in the rate constant? Here, we turn to the question of relating the mechanistic model expressed in some mathematical form to the actual experimental rate data. Since there are errors in the measurements and perhaps some inaccuracies in the model, it is often difficult to obtain an exact fit. Consequently, it becomes difficult to judge the appropriateness of the model to the experimental data by inspection. Assuming that the errors, excluding systematic errors, are random, a suitable technique typically used in kinetic data treatment is the least-squares method.[27,36,38] To estimate values of parameters in the model, we must minimize some measure of the errors. In the least-squares method the measure of error is defined as the sum of squares of the errors of the individual measurements. If we have some model to be fitted to the form

$$\mathbf{y} = f(\mathbf{p},t) \tag{3–32}$$

where **y** is the set of experimental data points and **p** are parameters we wish to find, the least-squares criterion gives

$$Q = \sum_{j=1}^{M} \omega_j[y_j - f(\mathbf{p},t_j)]^2 = \sum_{j=1}^{M} \omega_j \epsilon_j \tag{3–33}$$

In this equation, $\epsilon_j = y_j - f(\mathbf{p},t_j)$ represents the residual error given by the difference between the observed value $y_j$ and the calculated value $f(\mathbf{p},t_j)$, which is then weighted by $\omega_j$ for each observation. It is the quantity $Q$ that is minimized with respect to estimated parameters.

There are two cases associated with the least-squares procedure. In the linear least-squares case, the functional form of the values of **y** are presumed to follow some general linear equation of the form

$$y = p_1 + p_2 t \tag{3–34}$$

In the second case, the function $y$ has a nonlinear form. For many cases in kinetics, the general linear functional form is more commonly used. If the $y$ values have unequal weights, equation 3–33 can be rewritten as

$$Q = \sum_{j=1}^{M} \omega_j[y_j - (p_1 + p_2 t_j)]^2 \tag{3–35}$$

The derivatives of Q with respect to both $p_1$ and $p_2$ must be taken and equated to zero in order to find the optimal values. Taking the derivative of equation 3–33 with respect to $p_1$ yields

$$\frac{dQ}{dp_1} = -2 \sum_{j=1}^{M} \omega_j(y_j - p_1 - p_2 t_j) = 0 \tag{3–36}$$

so that

$$p_1 = \frac{\sum_{j=1}^{M} \omega_j y_j - p_2 \sum_{j=1}^{M} \omega_j t_j}{\sum_{j=1}^{M} \omega_j} \tag{3–37}$$

Thus, we now have an equation which relates the optimal value of $p_1$ to the optimal value of $p_2$ and the means of the $y$ and $t$ values. Taking the derivative of $Q$ with respect to $p_2$ yields

$$\frac{dQ}{dp_2} = -2 \sum_{j=1}^{M} t_j \omega_j (y_j - p_1 - p_2 t_j) = 0 \tag{3–38}$$

Rewriting this expression, we obtain

$$\sum_{j=1}^{M} \omega_j t_j y_j - p_1 \sum_{j=1}^{M} \omega_j t_j - p_2 \sum_{j=1}^{M} t_j^2 = 0 \tag{3–39}$$

Substituting equation 3–36 into equation 3–38 yields

$$p_2 = \frac{(\Sigma\omega_j)(\Sigma\omega_j t_j y_j - (\Sigma\omega_j t_j)(\Sigma\omega_j y_j)}{(\Sigma\omega_j)(\Sigma\omega_j t_j^2)(\Sigma\omega_j t_j)^2} \tag{3–40a}$$

and substituting this into equation 3–37 yields

$$p_1 = \frac{\Sigma\omega_j t_j^2 \Sigma\omega_j y_j - \Sigma\omega_j t_j \Sigma\omega_j t_j y_j}{(\Sigma\omega_j)(\Sigma\omega_j t_j^2) - (\Sigma\omega_j t_j)^2} \tag{3–40b}$$

The standard deviations of $p_1$ and $p_2$ are useful indicators of the goodness of fit. They are given by

$$\sigma(p_1) = \sigma\left(\frac{\Sigma\omega_j t_j^2}{(\Sigma\omega_j)(\Sigma\omega_j t_j^2) - (\Sigma\omega_j t_j)^2}\right)^{1/2} \tag{3–41}$$

and

$$\sigma(p_2) = \sigma\left(\frac{\Sigma\omega_j t_j}{(\Sigma\omega_j)(\Sigma\omega_j t_j^2) - \Sigma\omega_j t_j)^2}\right)^{1/2} \tag{3–42}$$

where

$$\sigma = \left(\frac{\sum_{j=1}^{M} \omega_j (y_j - y_j^*)^2}{(M - 1)}\right)^{1/2} \tag{3–43}$$

In this expression, $y_j^*$ are the computed values for $y_j$ from $y = p_1 + p_2 t$ using the computed values of $p_1$ and $p_2$. A more general derivation of the linear least-squares expression from matrix methods is given in Appendix 3–1.

There are other measures of the quality of fit of the data. The simplest is the root mean square (rms) deviation, which is

$$\text{rms error} = \left(\frac{\sum_{j=1}^{M} (\omega_j \epsilon_j)^2}{n}\right)^{1/2} \tag{3–44}$$

where $n$ is the number of data points. Another commonly used quantity is the correlation coefficient, which allows the significance of correlation to be tested. This quantity is given by

$$r = \frac{\Sigma\omega_j t_j \Sigma\omega_j y_j - n\Sigma\omega_j t_j y_j}{[(\Sigma\omega_j y_j)^2 - n(\Sigma\omega_j y_j^2)][(\Sigma\omega_j t_j)^2 - n(\Sigma\omega_j t_j^2)]} \tag{3–45}$$

When $r = 1$, there is a perfect correlation between the calculated line and experimental points; when $r = 0$, the data cannot be correlated linearly. If kinetic data are reasonably fitted, the correlation is generally $R > 0.95$, while poor correlations have $R < 0.9$.

Although the linear least-squares method is widely used in the treatment of kinetic data, it does have its limitations. One such limitation is that the method applies only to cases that can be expressed in linear form. Thus, for most complex kinetic models, the linear least-squares method is not applicable. Sometimes the equation can be linearized with respect to the constants by simple rearrangement. For example, the expression for the concentration-vs.-time dependence of the second-order reaction, $A + A \xrightarrow{\kappa}$ products, is

$$[A] = \frac{[A]_0}{1 + \kappa[A]_0 t} \tag{3–46}$$

This form is nonlinear, but it can be rewritten linearly as

$$\frac{1}{[A]} = \frac{1}{[A]_0} + \kappa t \tag{3–47}$$

This form is identical to equation 3–34 with $1/[A] = y$, $1/[A]_0 = p_1$, and $\kappa = p_2$. When an equation is linearized by either rearrangement or transformation, the original errors are often not preserved. It may then be the case that statistical weights have to be adjusted appropriately in order to obtain the correct estimates of $p_1$ and $p_2$ by the least-squares method.[30–33] Furthermore, for models that involve several dependent variables, linearization is not feasible. In such cases we turn to the nonlinear least-squares method,[39] which does not require that the model equations be linear in the unknown parameters. Nonlinear least-square methods are beyond the scope of this treatment.

***3.3.1.3.2 Evaluation of Rate Constants at a Given Temperature from Direct Measurements.*** A simple illustration of the use of the least-squares method to evaluate rate constants from experimental determinations is illuminating. Let us consider how the rate constant for the recombination of methyl radicals is measured using the laser photolysis time-resolved diode laser absorption technique (see section 3.2.2.2). The rate equation for the recombination reaction

$$CH_3 + CH_3 \xrightarrow{\kappa_1} C_2H_6$$

is given by

$$\frac{d[CH_3]}{dt} = -2\kappa_1 [CH_3]^2 \tag{3–48}$$

which yields, upon integration,

$$\frac{[CH_3]_0}{[CH_3]} = 1 + 2\kappa_1 [CH_3]_0(t - t_0) \tag{3–49}$$

In the experiment the measured quantity is the voltage ($V$) on the voltage meter corresponding to the signal from the HgCdTe infrared detector. According to Beer's law

$$I = I_0 \exp(-\epsilon c \ell) \tag{3–50}$$

where $\epsilon$ is the molar extinction, $c$ the molar concentration, and $\ell$ the absorption path length. If $\epsilon c \ell$ is very small (weak absorption), we can expand equation 3–50 via a Taylor series and truncate the expansion beyond the linear term to obtain

$$I = I_0(1 - \epsilon c \ell) \tag{3–51}$$

Consequently, the concentration $c$ is given as

$$c = \frac{(\epsilon \ell)^{-1}(I_0 - I)}{I} \tag{3–52}$$

From equation 3–52, we see that the concentration of the absorbing molecule is proportional to the relative change in the transmittance $I$. Since the transmittance is proportional to the voltage, we have

$$c \propto \frac{(V_0 - V)}{V} = \frac{S}{V_0} \tag{3–53}$$

where $S$ is the strength of the signal which is the difference between the voltage for $c = 0$ and $c \neq 0$. Now, we can rewrite equation 3–49 as

$$\frac{S(t_0)}{S(t)} = 1 + 2\kappa_1[\mathrm{CH_3}]_0(t - t_0) \tag{3–54}$$

and if we let

$$y = \frac{S(t_0)}{S(t)} - 1 \tag{3–55}$$

$\kappa' = 2\kappa_1[\mathrm{CH_3}]_0$, and $x = t - t_0$, we get a simple expression of the form

$$y = \kappa' x \tag{3–56}$$

Using the formula of linear least-squares fitting described in section 3.3.1.3.1, we get

$$\sigma_{\kappa'} = \frac{\sigma}{\left[\sum_i \omega_i x_i^2\right]^{1/2}} \tag{3–57}$$

where

$$\sigma = \frac{(\Sigma \omega_j (y_j - \kappa_1 x_i)^2)^{1/2}}{n - 1} \tag{3–58}$$

$$\omega_i = \frac{c^2}{\sigma_i^2} \tag{3–59}$$

and where $n$ is the number of $y_i$ measurements and $c$ is an arbitrary proportionality constant. To evaluate $\sigma_i$, we apply the propagation-of-errors formula, equation 3–26, as follows:

$$\sigma_i = \left[\left(\frac{\partial y}{\partial S(t_0)}\sigma_S(t_0)\right)^2 + \left(\frac{\partial y}{\partial S(t_i)}\sigma_S(t_i)\right)^2\right]^{1/2} \qquad (3\text{–}60)$$

This is no more than

$$\sigma_i = \left[\left(\frac{\sigma_S(t_0)}{S(t_0)}\right)^2 + \left(\frac{\sigma_S(t_i)}{S(t_i)}\right)^2\right]^{1/2}\frac{S(t_0)}{S(t_i)} \qquad (3\text{–}61)$$

where $\sigma_S(t_0)$ and $\sigma_S(t_i)$ are the standard deviations of measured signal at $t = t_0$ and $t = t_i$, respectively. To evaluate the standard deviation of $\kappa'$, we substitute equations 3–60 and 3–61 into equations 3–58 and 3–59. To evaluate the standard deviation of $\kappa_1$, we again apply equation 3–26 to the expression

$$\kappa_1 = \frac{\kappa'}{2[\mathrm{CH_3}]_0} \qquad (3\text{–}62)$$

to obtain

$$\sigma_{\kappa_1} = \left[\left(\frac{\partial \kappa_1}{\partial \kappa'}\sigma_{\kappa'}\right)^2 + \left(\left(\frac{\partial \kappa_1}{\partial [\mathrm{CH_3}]_0}\right)\sigma_{[\mathrm{CH_3}]_0}\right)^2\right]^{1/2} \qquad (3\text{–}63)$$

giving

$$\sigma_{\kappa_1} = \kappa_1\left[\left(\frac{\sigma_{\kappa'}}{\kappa_1}\right)^2 + \left(\frac{\sigma_{[\mathrm{CH_3}]_0}}{[\mathrm{CH_3}]_0}\right)^2\right]^{1/2} \qquad (3\text{–}64)$$

Now, $[\mathrm{CH_3}]_0$ is proportional to the pressure $P_0$ of the initial reactant ($\mathrm{CH_3I}$) and the photolysis laser fluence $\Phi$, i.e.,

$$[\mathrm{CH_3}]_0 \propto P_0(\mathrm{CH_3})\Phi \qquad (3\text{–}65)$$

So again, using the equation 3–26 with equation 3–65, we obtain

$$\sigma[\mathrm{CH_3}]_0 = [\mathrm{CH_3}]_0\left\{\left(\frac{\sigma_{P_0}}{P_0}\right)^2 + \left(\frac{\sigma_\Phi}{\Phi}\right)^2\right\}^{1/2} \qquad (3\text{–}66)$$

Finally,

$$\sigma_{\kappa_1} = \kappa_1\left[\left(\frac{\sigma_{\kappa'}}{\kappa'}\right)^2 + \left(\frac{\sigma_{P_0}}{P_0}\right)^2 + \left(\frac{\sigma_\Phi}{\Phi}\right)^2\right\}^{1/2} \qquad (3\text{–}67)$$

The quantity $\sigma'_\kappa$ is the standard deviation of the sample mean value $\kappa' = 2\kappa_1[\mathrm{CH_3}]_0$ obtained by evaluating equations 3–57 through 3–61, $\sigma_{p_0}$ is the standard deviation of the sample mean value of the reactant $(\mathrm{CH_3I})_0$ pressure, and $\sigma_\Phi$ is the standard deviation of the sample mean value of photolysis laser fluence.

***3.3.1.3.3 Evaluation of Temperature-Dependent Rate Constants.*** Perhaps the simplest illustration of the use of the least-squares method to analyze kinetic data is in evaluating Arrhenius parameters from temperature-dependent rate data. In the form

$$\kappa(T) = A \exp\left(\frac{-E_{\text{act}}}{RT}\right) \tag{3-68}$$

the temperature rate expression is nonlinear. Accordingly, if the linear least-square method is to be used to evaluate the coefficients, this expression must be linearized. The common practice is to transform equation 3–68 to the logarithmic form

$$\ln \kappa(T) = \ln A - \frac{B}{T} \tag{3-69}$$

where $B = E_{\text{act}}/R$. Then, to obtain $E_{\text{act}}$ and $A$ (the preexponential factor), a linear least-squares fit can be performed on equation 3–69 rather than using a nonlinear fit to equation 3–68. However, when equation 3–68 is thus linearized and a least-square fit performed, the weights of the $\kappa(T)$ values must be adjusted to the weight of $\ln \kappa(T)$ to ensure that the least-squares procedure does indeed minimize the residuals of the measured rate constant $\kappa(T)$.

***3.3.1.3.4 Reporting Kinetic Data.*** Results of kinetic measurements have great value for anyone who uses them, particularly for those performing atmospheric and combustion modeling. However, the results are useful only when they are accompanied by realistic estimates of their overall uncertainty. In reporting kinetic data, it is recommended[34] that information regarding both random and systematic errors be given. In particular, one should report known and even suspected systematic errors and, when available, estimates of their bounds and how the estimates were obtained. The value of the random error of the sample mean should be reported at a confidence level of at least $\pm 2\sigma$. In reporting kinetic data, the form $a \pm b$ is used, but only when the exact meaning of the uncertainty $\pm b$ is explicitly and clearly stated.

**3.3.2 Sensitivity Analysis** In chemical kinetics it is often the case that the concentrations of chemical species are known more precisely than the rate constants of the kinetic mechanism. Consequently, in analyzing results from kinetic experiments, it is important to assess the effects of such parameter uncertainties on the predicted concentrations of the various intermediate and product species. Such information can be useful in identifying those rate constants which need to be determined more precisely, and may also help the experimentalist decide which concentration to monitor in order to improve the estimate of a specific rate constant. An analysis of this type is known as a *sensitivity analysis*.[40–48] Its purpose is to assess the sensitivity of the system's solutions to changes in input parameters, which in turn can be of enormous help in specifying the reaction mechanism and in designing experimental measurements.

How does one carry out a sensitivity analysis? Suppose we have a kinetic mechanism described by a set of coupled first-order differential equations having the following general form:

$$\frac{dy_i}{dt} = f_i(y_1, y_2, \ldots, y_N, t, \kappa_1, \kappa_2, \ldots, \kappa_M) \tag{3-70}$$

where there are N chemical components with concentrations $y_i$ and $M$ reactions in