Chapter 3

Interpretation of Batch Reactor Data

A rate equation characterizes the rate of reaction, and its form may either be suggested by theoretical considerations or simply be the result of an empirical curve-fitting procedure. In any case, the value of the constants of the equation can only be found by experiment; predictive methods are inadequate at present.

The determination of the rate equation is usually a two-step procedure; first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constants is found, yielding the complete rate equation.

Equipment by which empirical information is obtained can be divided into two types, the *batch* and *flow* reactors. The batch reactor is simply a container to hold the contents while they react. All that has to be determined is the extent of reaction at various times, and this can be followed in a number of ways, for example:

1. By following the concentration of a given component.
2. By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.
3. By following the change in total pressure of a constant-volume system.
4. By following the change in volume of a constant-pressure system.

The experimental batch reactor is usually operated isothermally and at constant volume because it is easy to interpret the results of such runs. This reactor is a relatively simple device adaptable to small-scale laboratory set-ups, and it needs but little auxiliary equipment or instrumentation. Thus, it is used whenever possible for obtaining homogeneous kinetic data. This chapter deals with the batch reactor.

The flow reactor is used primarily in the study of the kinetics of heterogeneous reactions. Planning of experiments and interpretation of data obtained in flow reactors are considered in later chapters.

There are two procedures for analyzing kinetic data, the *integral* and the *differential* methods. In the integral method of analysis we guess a particular form of rate equation and, after appropriate integration and mathematical manipulation, predict that the plot of a certain concentration function versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained, then the rate equation is said to satisfactorily fit the data.

In the differential method of analysis we test the fit of the rate expression to the data directly and without any integration. However, since the rate expression is a differential equation, we must first find $(1/V)(dN/dt)$ from the data before attempting the fitting procedure.

There are advantages and disadvantages to each method. The integral method is easy to use and is recommended when testing specific mechanisms, or relatively simple rate expressions, or when the data are so scattered that we cannot reliably find the derivatives needed in the differential method. The differential method is useful in more complicated situations but requires more accurate or larger amounts of data. The integral method can only test this or that particular mechanism or rate form; the differential method can be used to develop or build up a rate equation to fit the data.

In general, it is suggested that integral analysis be attempted first, and, if not successful, that the differential method be tried.

3.1 CONSTANT-VOLUME BATCH REACTOR

When we mention the constant-volume batch reactor we are really referring to the volume of reaction mixture, and not the volume of reactor. Thus, this term actually means a *constant-density reaction system*. Most liquid-phase reactions as well as all gas-phase reactions occurring in a constant-volume bomb fall in this class.

In a constant-volume system the measure of reaction rate of component i becomes

$$\boxed{r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt}} \tag{1}$$

or for ideal gases, where $C = p/\mathbf{R}T$,

$$\boxed{r_i = \frac{1}{\mathbf{R}T}\frac{dp_i}{dt}} \tag{2}$$

Thus, the rate of reaction of any component is given by the rate of change of its concentration or partial pressure; so no matter how we choose to follow the progress of the reaction, we must eventually relate this measure to the concentration or partial pressure if we are to follow the rate of reaction.

For gas reactions with changing numbers of moles, a simple way of finding the reaction rate is to follow the change in total pressure π of the system. Let us see how this is done.

Analysis of Total Pressure Data Obtained in a Constant-Volume System. For isothermal gas reactions where the number of moles of material changes during reaction, let us develop the general expression which relates the changing total pressure of the system π to the changing concentration or partial pressure of any of the reaction components.

Write the general stoichiometric equation, and under each term indicate the number of moles of that component:

$$
\begin{array}{llllllllll}
 & a\mathrm{A} & + & b\mathrm{B} & + \cdots = & r\mathrm{R} & + & s\mathrm{S} & + \cdots & \\
\text{At time 0:} & N_{\mathrm{A0}} & & N_{\mathrm{B0}} & & N_{\mathrm{R0}} & & N_{\mathrm{S0}} & & N_{\text{inert}} \\
\text{At time } t\text{:} & N_{\mathrm{A}} = N_{\mathrm{A0}} - ax & & N_{\mathrm{B}} = N_{\mathrm{B0}} - bx & & N_{\mathrm{R}} = N_{\mathrm{R0}} + rx & & N_{\mathrm{S}} = N_{\mathrm{S0}} + sx & & N_{\text{inert}}
\end{array}
$$

Initially the total number of moles present in the system is

$$N_0 = N_{\mathrm{A0}} + N_{\mathrm{B0}} + \cdots + N_{\mathrm{R0}} + N_{\mathrm{S0}} + \cdots + N_{\text{inert}}$$

but at time t it is

$$N = N_0 + x(r + s + \cdots - a - b - \cdots) = N_0 + x\,\Delta n \tag{3}$$

where

$$\Delta n = r + s + \cdots - a - b - \cdots$$

Assuming that the ideal gas law holds, we may write for any reactant, say Ain the system of volume V

$$C_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{\mathbf{R}T} = \frac{N_{\mathrm{A}}}{V} = \frac{N_{\mathrm{A0}} - ax}{V} \tag{4}$$

Combining Eqs. 3 and 4 we obtain

$$C_{\mathrm{A}} = \frac{N_{\mathrm{A0}}}{V} - \frac{a}{\Delta n}\frac{N - N_0}{V}$$

or

$$\boxed{p_{\mathrm{A}} = C_{\mathrm{A}}\mathbf{R}T = p_{\mathrm{A0}} - \frac{a}{\Delta n}(\pi - \pi_0)} \tag{5}$$

Equation 5 gives the concentration or partial pressure of reactant A as a function of the total pressure π at time t, initial partial pressure of A, p_{A0}, and initial total pressure of the system, π_0.

Similarly, for any product R we can find

$$\boxed{p_{\mathrm{R}} = C_{\mathrm{R}}\mathbf{R}T = p_{\mathrm{R0}} + \frac{r}{\Delta n}(\pi - \pi_0)} \tag{6}$$

Equations 5 and 6 are the desired relationships between total pressure of the system and the partial pressure of reacting materials.

It should be emphasized that if the precise stoichiometry is not known, or if more than one stoichiometric equation is needed to represent the reaction, then the "total pressure" procedure cannot be used.

The Conversion. Let us introduce one other useful term, the fractional conversion, or the fraction of any reactant, say A, converted to something else, or the fraction of A reacted away. We call this, simply, the conversion of A, with symbol X_A.

Suppose that N_{A0} is the initial amount of A in the reactor at time $t = 0$, and that N_A is the amount present at time t. Then the conversion of A in the constant volume system is given by

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A/V}{N_{A0}/V} = 1 - \frac{C_A}{C_{A0}} \tag{7}$$

and

$$dX_A = -\frac{dC_A}{C_{A0}} \tag{8}$$

We will develop the equations in this chapter in terms of concentration of reaction components and also in terms of conversions.

Later we will relate X_A and C_A for the more general case where the volume of the system does not stay constant.

Integral Method of Analysis of Data

General Procedure. The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown and used in the cases next treated. It should be noted that the integral method is especially useful for fitting simple reaction types corresponding to elementary reactions. Let us take up these kinetic forms.

Irreversible Unimolecular-Type First-Order Reactions. Consider the reaction

$$A \rightarrow \text{products} \tag{9}$$

Suppose we wish to test the first-order rate equation of the following type,

$$-r_A = -\frac{dC_A}{dt} = kC_A \tag{10}$$

for this reaction. Separating and integrating we obtain

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$$

or

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{11}$$

In terms of conversion (see Eqs. 7 and 8), the rate equation, Eq. 10, becomes

$$\frac{dX_A}{dt} = k(1 - X_A)$$

which on rearranging and integrating gives

$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

or

$$\boxed{-\ln(1 - X_A) = kt} \qquad \textbf{(12)}$$

A plot of $\ln(1 - X_A)$ or $\ln(C_A/C_{A0})$ vs. t, as shown in Fig. 3.1, gives a straight line through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

Caution. We should point out that equations such as

$$-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$$

are first order but are not amenable to this kind of analysis; hence, not all first-order reactions can be treated as shown above.

Irreversible Bimolecular-Type Second-Order Reactions. Consider the reaction

$$A + B \rightarrow \text{products} \qquad \textbf{(13}\textbf{\textit{a}}\textbf{)}$$

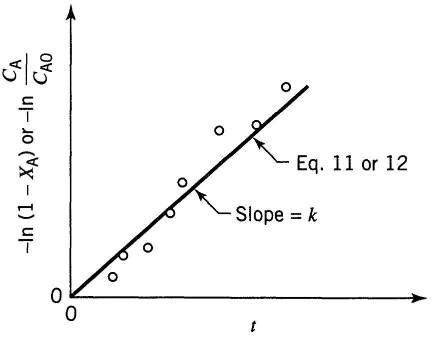


Figure 3.1 Test for the first-order rate equation, Eq. 10.

with corresponding rate equation

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \qquad \textbf{(13}b\textbf{)}$$

Noting that the amounts of A and B that have reacted at any time t are equal and given by $C_{A0}X_A$, we may write Eqs. 13a and b in terms of X_A as

$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

Letting $M = C_{B0}/C_{A0}$ be the initial molar ratio of reactants, we obtain

$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A)$$

which on separation and formal integration becomes

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}k\int_0^t dt$$

After breakdown into partial fractions, integration, and rearrangement, the final result in a number of different forms is

$$\boxed{\begin{aligned} \ln\frac{1 - X_B}{1 - X_A} &= \ln\frac{M - X_A}{M(1 - X_A)} = \ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{C_B}{MC_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \qquad M \neq 1 \end{aligned}} \qquad \textbf{(14)}$$

Figure 3.2 shows two equivalent ways of obtaining a linear plot between the concentration function and time for this second-order rate law.

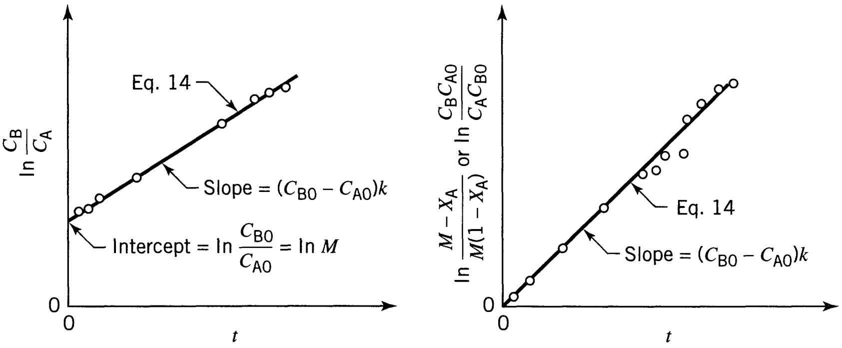


Figure 3.2 Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$, or for the second-order reaction, Eq. 13.

If C_{B0} is much larger than C_{A0}, C_B remains approximately constant at all times, and Eq. 14 approaches Eq. 11 or 12 for the first-order reaction. Thus, the second-order reaction becomes a pseudo first-order reaction.

Caution 1. In the special case where reactants are introduced in their stoichiometric ratio, the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evaluation. This difficulty is avoided if we go back to the original differential rate expression and solve it for this particular reactant ratio. Thus, for the second-order reaction with equal initial concentrations of A and B, or for the reaction

$$2A \rightarrow \text{products} \tag{15a}$$

the defining second-order differential equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2 \tag{15b}$$

which on integration yields

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = kt} \tag{16}$$

Plotting the variables as shown in Fig. 3.3 provides a test for this rate expression.

In practice we should choose reactant ratios either equal to or widely different from the stoichiometric ratio.

Caution 2. The integrated expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction

$$A + 2B \rightarrow \text{products} \tag{17a}$$

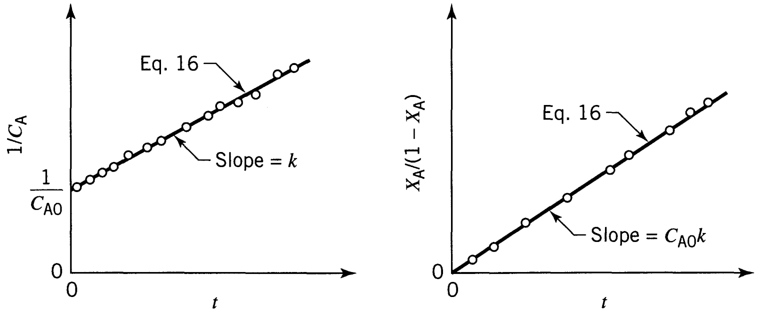


Figure 3.3 Test for the bimolecular mechanisms, $A + B \rightarrow R$ with $C_{A0} = C_{B0}$, or for the second-order reaction of Eq. 15.

is first order with respect to both A and B, hence second order overall, or

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B = kC_{A0}^2(1 - X_A)(M - 2X_A) \tag{17b}$$

The integrated form is

$$\boxed{\ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \qquad M \neq 2} \tag{18}$$

When a stoichiometric reactant ratio is used the integrated form is

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1 - X_A} = 2kt, \qquad M = 2} \tag{19}$$

These two cautions apply to all reaction types. Thus, special forms for the integrated expressions appear whenever reactants are used in stoichiometric ratios, or when the reaction is not elementary.

Irreversible Trimolecular-Type Third-Order Reactions. For the reaction

$$A + B + D \rightarrow \text{products} \tag{20a}$$

let the rate equation be

$$-r_A = -\frac{dC_A}{dt} = kC_AC_BC_D \tag{20b}$$

or in terms of X_A

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}^3(1 - X_A)\left(\frac{C_{B0}}{C_{A0}} - X_A\right)\left(\frac{C_{D0}}{C_{A0}} - X_A\right)$$

On separation of variables, breakdown into partial fractions, and integration, we obtain after manipulation

$$\begin{aligned}\frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})}\ln\frac{C_{A0}}{C_A} + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})}\ln\frac{C_{B0}}{C_B}\\ + \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})}\ln\frac{C_{D0}}{C_D} = kt\end{aligned} \tag{21}$$

Now if C_{D0} is much larger than both C_{A0} and C_{B0}, the reaction becomes second order and Eq. 21 reduces to Eq. 14.

All trimolecular reactions found so far are of the form of Eq. 22 or 25. Thus

$$\mathrm{A} + 2\mathrm{B} \rightarrow \mathrm{R} \quad \text{with} \quad -r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt} = kC_{\mathrm{A}}C_{\mathrm{B}}^2 \tag{22}$$

In terms of conversions the rate of reaction becomes

$$\frac{dX_{\mathrm{A}}}{dt} = kC_{\mathrm{A0}}^2 (1 - X_{\mathrm{A}})(M - 2X_{\mathrm{A}})^2$$

where $M = C_{\mathrm{B0}}/C_{\mathrm{A0}}$. On integration this gives

$$\boxed{\frac{(2C_{\mathrm{A0}} - C_{\mathrm{B0}})(C_{\mathrm{B0}} - C_{\mathrm{B}})}{C_{\mathrm{B0}}C_{\mathrm{B}}} + \ln \frac{C_{\mathrm{A0}}C_{\mathrm{B}}}{C_{\mathrm{A}}C_{\mathrm{B0}}} = (2C_{\mathrm{A0}} - C_{\mathrm{B0}})^2 kt, \qquad M \neq 2} \tag{23}$$

or

$$\boxed{\frac{1}{C_{\mathrm{A}}^2} - \frac{1}{C_{\mathrm{A0}}^2} = 8kt, \qquad M = 2} \tag{24}$$

Similarly, for the reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{R} \quad \text{with} \quad -r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt} = kC_{\mathrm{A}}C_{\mathrm{B}}^2 \tag{25}$$

integration gives

$$\boxed{\frac{(C_{\mathrm{A0}} - C_{\mathrm{B0}})(C_{\mathrm{B0}} - C_{\mathrm{B}})}{C_{\mathrm{B0}}C_{\mathrm{B}}} + \ln \frac{C_{\mathrm{A0}}C_{\mathrm{B}}}{C_{\mathrm{B0}}C_{\mathrm{A}}} = (C_{\mathrm{A0}} - C_{\mathrm{B0}})^2 kt, \qquad M \neq 1} \tag{26}$$

or

$$\boxed{\frac{1}{C_{\mathrm{A}}^2} - \frac{1}{C_{\mathrm{A0}}^2} = 2kt, \qquad M = 1} \tag{27}$$

Empirical Rate Equations of *n*th Order. When the mechanism of reaction is not known, we often attempt to fit the data with an *n*th-order rate equation of the form

$$-r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt} = kC_{\mathrm{A}}^n \tag{28}$$

which on separation and integration yields

$$\boxed{C_{\mathrm{A}}^{1-n} - C_{\mathrm{A0}}^{1-n} = (n - 1)kt, \qquad n \neq 1} \tag{29}$$

The order n cannot be found explicitly from Eq. 29, so a trial-and-error solution must be made. This is not too difficult, however. Just select a value for n and calculate k. The value of n which minimizes the variation in k is the desired value of n.

One curious feature of this rate form is that reactions with order $n > 1$ can never go to completion in finite time. On the other hand, for orders $n < 1$ this rate form predicts that the reactant concentration will fall to zero and then become negative at some finite time, found from Eq. 29, so

$$C_A = 0 \quad \text{at} \quad t \geq \frac{C_{A0}^{1-n}}{(1-n)k}$$

Since the real concentration cannot fall below zero we should not carry out the integration beyond this time for $n < 1$. Also, as a consequence of this feature, in real systems the observed fractional order will shift upward to unity as reactant is depleted.

Zero-Order Reactions. A reaction is of zero order when the rate of reaction is independent of the concentration of materials; thus

$$-r_A = -\frac{dC_A}{dt} = k \tag{30}$$

Integrating and noting that C_A can never become negative, we obtain directly

$$\boxed{\begin{aligned} C_{A0} - C_A = C_{A0}X_A = kt \quad &\text{for} \quad t < \frac{C_{A0}}{k} \\ C_A = 0 \quad &\text{for} \quad t \geq \frac{C_{A0}}{k} \end{aligned}} \tag{31}$$

which means that the conversion is proportional to time, as shown in Fig. 3.4.

As a rule, reactions are of zero order only in certain concentration ranges—the higher concentrations. If the concentration is lowered far enough, we usually

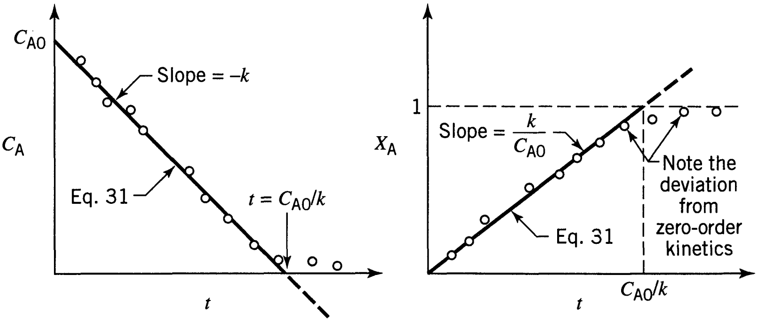


Figure 3.4 Test for a zero-order reaction, or rate equation, Eq. 30.

find that the reaction becomes concentration-dependent, in which case the order rises from zero.

In general, zero-order reactions are those whose rates are determined by some factor other than the concentration of the reacting materials, e.g., the intensity of radiation within the vat for photochemical reactions, or the surface available in certain solid catalyzed gas reactions. It is important, then, to define the rate of zero-order reactions so that this other factor is included and properly accounted for.

Overall Order of Irreversible Reactions from the Half-Life $t_{1/2}$. Sometimes, for the irreversible reaction

$$\alpha A + \beta B + \cdots \rightarrow \text{products}$$

we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \cdots$$

If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction. Thus, for reactants A and B at any time $C_B/C_A = \beta/\alpha$, and we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a\left(\frac{\beta}{\alpha}C_A\right)^b \cdots = \underbrace{k\left(\frac{\beta}{\alpha}\right)^b \cdots}_{\tilde{k}} \underbrace{C_A^{a+b+\cdots}}_{C_A^n}$$

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n \qquad \textbf{(32)}$$

Integrating for $n \neq 1$ gives

$$C_A^{1-n} - C_{A0}^{1-n} = \tilde{k}(n-1)t$$

Defining the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

$$\boxed{t_{1/2} = \frac{(0.5)^{1-n} - 1}{\tilde{k}(n-1)} C_{A0}^{1-n}} \qquad \textbf{(33}\boldsymbol{a}\textbf{)}$$

This expression shows that a plot of log $t_{1/2}$ vs. log C_{A0} gives a straight line of slope $1 - n$, as shown in Fig. 3.5.

The half-life method requires making a series of runs, each at a different initial concentration, and shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased

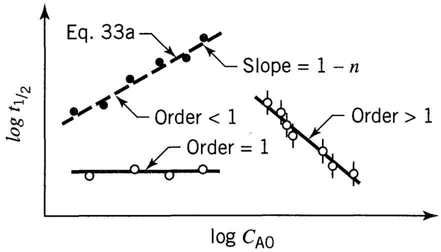


Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

concentration for orders less than one, and is independent of initial concentration for reactions of first order.

Numerous variations of this procedure are possible. For instance, by having all but one component, say Ain large excess, we can find the order with respect to that one component. For this situation the general expression reduces to

$$-\frac{dC_A}{dt} = \hat{k}C_A^a$$

where

$$\hat{k} = k(C_{B0}^b \cdots) \quad \text{and} \quad C_B \cong C_{B0}$$

And here is another variation of the half-life method.

Fractional Life Method t_F. The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F. The derivation is a direct extension of the half-life method giving

$$\boxed{t_F = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}} \qquad \textbf{(33}\textbf{\textit{b}}\textbf{)}$$

Thus, a plot of log t_F versus log C_{A0}, as shown in Fig. 3.5, will give the reaction order.

Example E3.1 illustrates this approach.

Irreversible Reactions in Parallel. Consider the simplest case, A decomposing by two competing paths, both elementary reactions:

$$\left.\begin{array}{l} A \xrightarrow{k_1} R \\ A \xrightarrow{k_2} S \end{array}\right\}$$

The rates of change of the three components are given by

$$-r_A = -\frac{dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A \tag{34}$$

$$r_R = \frac{dC_R}{dt} = k_1C_A \tag{35}$$

$$r_S = \frac{dC_S}{dt} = k_2C_A \tag{36}$$

This is the first time we have encountered multiple reactions. For these in general, if it is necessary to write N stoichiometric equations to describe what is happening, then it is necessary to follow the decomposition of N reaction components to describe the kinetics. Thus, in this system following C_A, or C_R, or C_S alone will not give both k_1 and k_2. At least two components must be followed. Then, from the stoichiometry, noting that $C_A + C_R + C_S$ is constant, we can find the concentration of the third component.

The k values are found using all three differential rate equations. First of all, Eq. 34, which is of simple first order, is integrated to give

$$\boxed{-\ln\frac{C_A}{C_{A0}} = (k_1 + k_2)t} \tag{37}$$

When plotted as in Fig. 3.6, the slope is $k_1 + k_2$. Then dividing Eq. 35 by Eq. 36 we obtain the following (Fig. 3.6).

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

which when integrated gives simply

$$\boxed{\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}} \tag{38}$$

This result is shown in Fig. 3.6. Thus, the slope of a plot of C_R versus C_S gives the ratio k_1/k_2. Knowing k_1/k_2 as well as $k_1 + k_2$ gives k_1 and k_2. Typical concentration-time curves of the three components in a batch reactor for the case where $C_{R0} = C_{S0} = 0$ and $k_1 > k_2$ are shown in Fig. 3.7.

Reactions in parallel are considered in detail in Chapter 7.

Homogeneous Catalyzed Reactions. Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the uncatalyzed and catalyzed reactions,

$$\left.\begin{aligned} A &\xrightarrow{k_1} R \\ A + C &\xrightarrow{k_2} R + C \end{aligned}\right\}$$

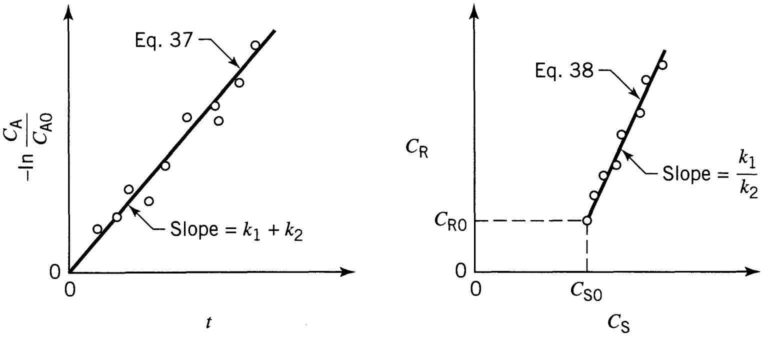


Figure 3.6 Evaluation of the rate constants for two competing elementary first-order reactions of the type $A \begin{matrix} \nearrow R \\ \searrow S \end{matrix}$.

with corresponding reaction rates

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A$$

$$-\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

This means that the reaction would proceed even without a catalyst present and that the rate of the catalyzed reaction is directly proportional to the catalyst concentration. The overall rate of disappearance of reactant A is then

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_C = (k_1 + k_2 C_C) C_A \tag{39}$$

On integration, noting that the catalyst concentration remains unchanged, we have

$$-\ln \frac{C_A}{C_{A0}} = -\ln (1 - X_A) = (k_1 + k_2 C_C) t = k_{\text{observed}}\, t \tag{40}$$

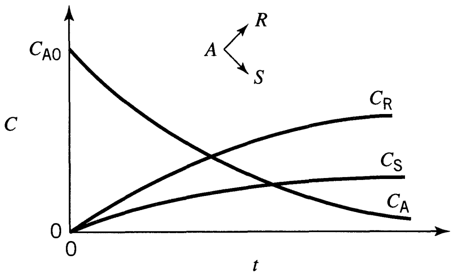


Figure 3.7 Typical concentration-time curves for competing reactions.

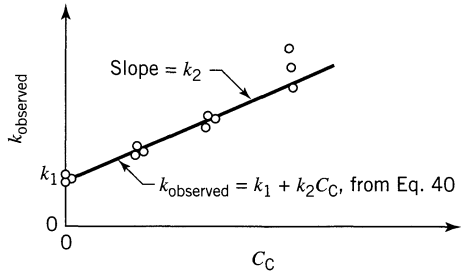


Figure 3.8 Rate constants for a homogeneous catalyzed reaction from a series of runs with different catalyst concentrations.

Making a series of runs with different catalyst concentrations allows us to find k_1 and k_2. This is done by plotting the observed k value against the catalyst concentrations as shown in Fig. 3.8. The slope of such a plot is k_2 and the intercept k_1.

Autocatalytic Reactions. A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction is

$$A + R \rightarrow R + R \tag{41a}$$

for which the rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_AC_R \tag{41b}$$

Because the total number of moles of A and R remain unchanged as A is consumed, we may write that at any time

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

Thus, the rate equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Rearranging and breaking into partial fractions, we obtain

$$-\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0}\left(\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right) = k\,dt$$

which on integration gives

$$\boxed{\ln\frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln\frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0kt = (C_{A0} + C_{R0})\,kt} \tag{42}$$

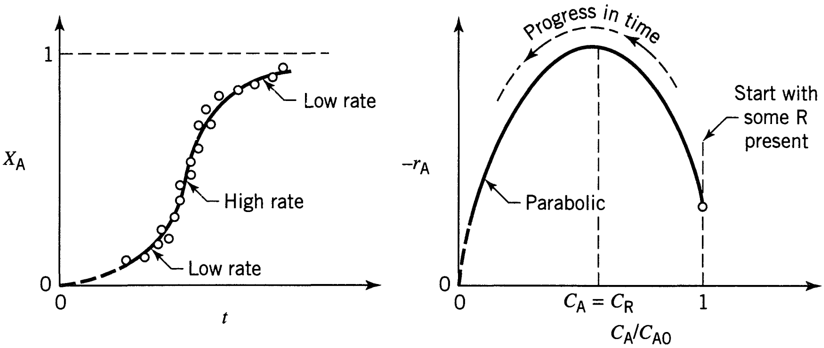


Figure 3.9 Conversion-time and rate-concentration curves for autocatalytic reaction of Eq. 41. This shape is typical for this type of reaction.

In terms of the initial reactant ratio $M = C_{R0}/C_{A0}$ and fractional conversion of A, this can be written as

$$\boxed{\ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)kt = (C_{A0} + C_{R0})kt} \tag{43}$$

For an autocatalytic reaction in a batch reactor some product R must be present if the reaction is to proceed at all. Starting with a very small concentration of R, we see qualitatively that the rate will rise as R is formed. At the other extreme, when A is just about used up the rate must drop to zero. This result is given in Fig. 3.9, which shows that the rate follows a parabola, with a maximum where the concentrations of A and R are equal.

To test for an autocatalytic reaction, plot the time and concentration coordinates of Eq. 42 or 43, as shown in Fig. 3.10 and see whether a straight line passing through zero is obtained.

Autocatalytic reactions are considered in more detail in Chapter 6.

Irreversible Reactions in Series. We first consider consecutive unimolecular-type first-order reactions such as

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

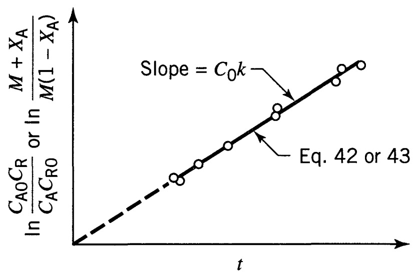


Figure 3.10 Test for the autocatalytic reaction of Eq. 41.

whose rate equations for the three components are

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \tag{44}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \tag{45}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \tag{46}$$

Let us start with a concentration C_{A0} of A, no R or S present, and see how the concentrations of the components change with time. By integration of Eq. 44 we find the concentration of A to be

$$\boxed{-\ln \frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t}} \tag{47}$$

To find the changing concentration of R, substitute the concentration of A from Eq. 47 into the differential equation governing the rate of change of R, Eq. 45; thus

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t} \tag{48}$$

which is a first-order linear differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

By multiplying through with the integrating factor $e^{\int P\,dx}$ the solution is

$$y e^{\int P\,dx} = \int Q e^{\int P\,dx}\, dx + \text{constant}$$

Applying this general procedure to the integration of Eq. 48, we find that the integrating factor is $e^{k_2 t}$. The constant of integration is found to be $-k_1 C_{A0}/(k_2 - k_1)$ from the initial conditions $C_{R0} = 0$ at $t = 0$, and the final expression for the changing concentration of R is

$$\boxed{C_R = C_{A0} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right)} \tag{49}$$

Noting that there is no change in total number of moles, the stoichiometry relates the concentrations of reacting components by

$$C_{A0} = C_A + C_R + C_S$$

which with Eqs. 47 and 49 gives

$$\boxed{C_S = C_{A0}\left(1 + \frac{k_2}{k_1 - k_2}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right)} \tag{50}$$

Thus, we have found how the concentrations of components A, R, and S vary with time.

Now if k_2 is much larger than k_1, Eq. 50 reduces to

$$C_S = C_{A0}(1 - e^{-k_1 t}), \qquad k_2 \gg k_1$$

In other words, the rate is determined by k_1 or the first step of the two-step reaction.

If k_1 is much larger than k_2, then

$$C_S = C_{A0}(1 - e^{-k_2 t}), \qquad k_1 \gg k_2$$

which is a first-order reaction governed by k_2, the slower step in the two-step reaction. Thus, in general, for any number of reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.

As may be expected, the values of k_1 and k_2 also govern the location and maximum concentration of R. This may be found by differentiating Eq. 49 and setting $dC_R/dt = 0$. The time at which the maximum concentration of R occurs is thus

$$\boxed{t_{\max} = \frac{1}{k_{\text{log mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}} \tag{51}$$

The maximum concentration of R is found by combining Eqs. 49 and 51 to give

$$\boxed{\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}} \tag{52}$$

Figure 3.11 shows the general characteristics of the concentration-time curves for the three components; A decreases exponentially, R rises to a maximum and then falls, and S rises continuously, the greatest rate of increase of S occurring where R is a maximum. In particular, this figure shows that one can evaluate k_1 and k_2 by noting the maximum concentration of intermediate and the time when this maximum is reached. Chapter 8 covers series reactions in more detail.

For a longer chain of reactions, say

$$A \rightarrow R \rightarrow S \rightarrow T \rightarrow U$$

the treatment is similar, though more cumbersome than the two-step reaction just considered. Figure 3.12 illustrates typical concentration-time curves for this situation.

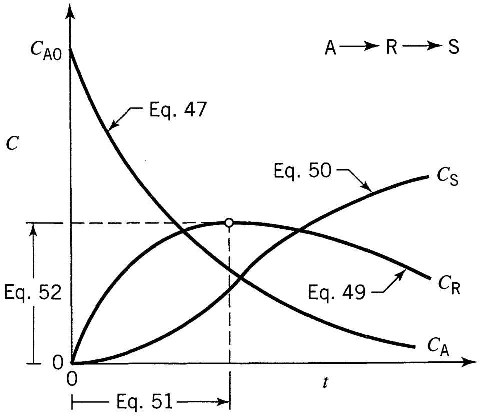


Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

First-Order Reversible Reactions. Though no reaction ever goes to completion, we can consider many reactions to be essentially irreversible because of the large value of the equilibrium constant. These are the situations we have examined up to this point. Let us now consider reactions for which complete conversion cannot be assumed. The simplest case is the opposed unimolecular-type reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R, \qquad K_C = K = \text{equilibrium constant} \tag{53a}$$

Starting with a concentration ratio $M = C_{R0}/C_{A0}$ the rate equation is

$$\begin{aligned}\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} &= k_1C_A - k_2C_R \\ &= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A)\end{aligned} \tag{53b}$$

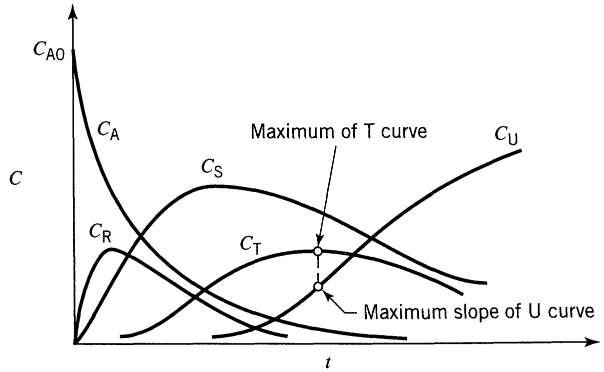


Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.

Now at equilibrium $dC_A/dt = 0$. Hence from Eq. 53 we find the fractional conversion of A at equilibrium conditions to be

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

and the equilibrium constant to be

$$K_C = \frac{k_1}{k_2}$$

Combining the above three equations we obtain, in terms of the equilibrium conversion,

$$\frac{dX_A}{dt} = \frac{k_1 (M + 1)}{M + X_{Ae}} (X_{Ae} - X_A)$$

With conversions measured in terms of X_{Ae}, this may be looked on as a pseudo first-order irreversible reaction which on integration gives

$$\boxed{-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M + 1}{M + X_{Ae}} k_1 t} \qquad \textbf{(54)}$$

A plot of $-\ln (1 - X_A/X_{Ae})$ vs. t, as shown in Fig. 3.13, gives a straight line.

The similarity between equations for the first-order irreversible and reversible reactions can be seen by comparing Eq. 12 with Eq. 54 or by comparing Fig. 3.1 with Fig. 3.13. Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{Ae} = 0$, or $X_{Ae} = 1$, or $K_C = \infty$.

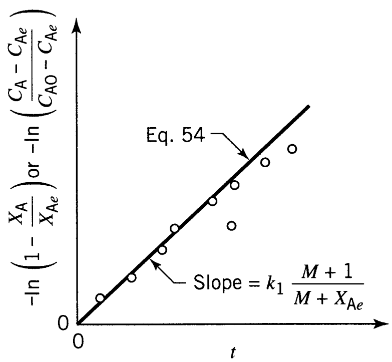


Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

Second-Order Reversible Reactions. For the bimolecular-type second-order reactions

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} R + S \tag{55a}$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R + S \tag{55b}$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2R \tag{55c}$$

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2R \tag{55d}$$

with the restrictions that $C_{A0} = C_{B0}$ and $C_{R0} = C_{S0} = 0$, the integrated rate equations for A and B are all identical, as follows

$$\boxed{\ln \frac{X_{A_e} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2k_1 \left(\frac{1}{X_{Ae}} - 1\right) C_{A0}t} \tag{56}$$

A plot as shown in Fig. 3.14 can then be used to test the adequacy of these kinetics.

Reversible Reactions in General. For orders other than one or two, integration of the rate equation becomes cumbersome. So if Eq. 54 or 56 is not able to fit the data, then the search for an adequate rate equation is best done by the differential method.

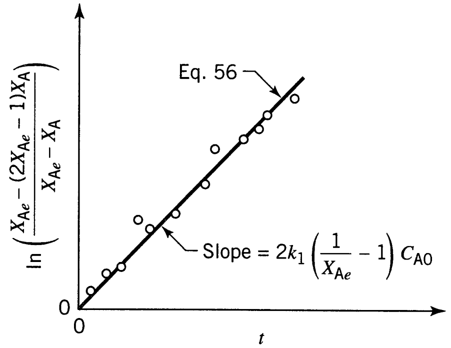


Figure 3.14 Test for the reversible bimolecular reactions of Eq. 55.

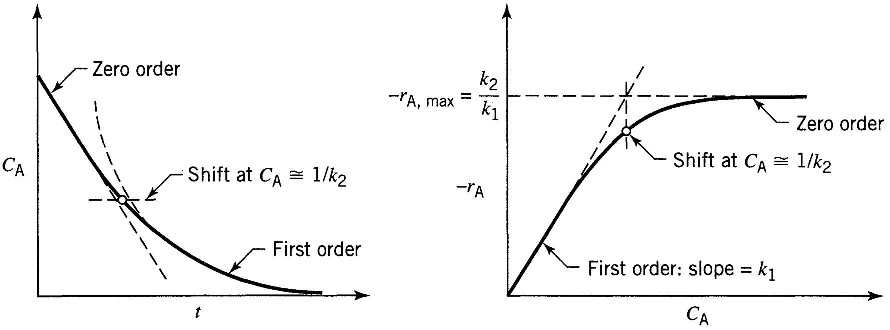


Figure 3.15 Behavior of a reaction that follows Eq. 57.

Reactions of Shifting Order. In searching for a kinetic equation it may be found that the data are well fitted by one reaction order at high concentrations but by another order at low concentrations. Consider the reaction

$$A \rightarrow R \quad \text{with} \quad -r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \tag{57}$$

From this rate equation we see

At high C_A (or $k_2C_A \gg 1$)—the reaction is of zero order with rate constant k_1/k_2

At low C_A (or $k_2C_A \ll 1$)—the reaction is of first order with rate constant k_1

This behavior is shown in Fig. 3.15.

To apply the integral method, separate variables and integrate Eq. 57. This gives

$$\boxed{\ln \frac{C_{A0}}{C_A} + k_2 (C_{A0} - C_A) = k_1 t} \tag{58a}$$

To linearize, rearrange Eq. 58*a* to give

$$\boxed{\frac{C_{A0} - C_A}{\ln (C_{A0}/C_A)} = -\frac{1}{k_2} + \frac{k_1}{k_2}\left(\frac{t}{\ln (C_{A0}/C_A)}\right)} \tag{58b}$$

or

$$\boxed{\frac{\ln (C_{A0}/C_A)}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A}} \tag{58c}$$

Two ways to test this rate form are then shown in Fig. 3.16.

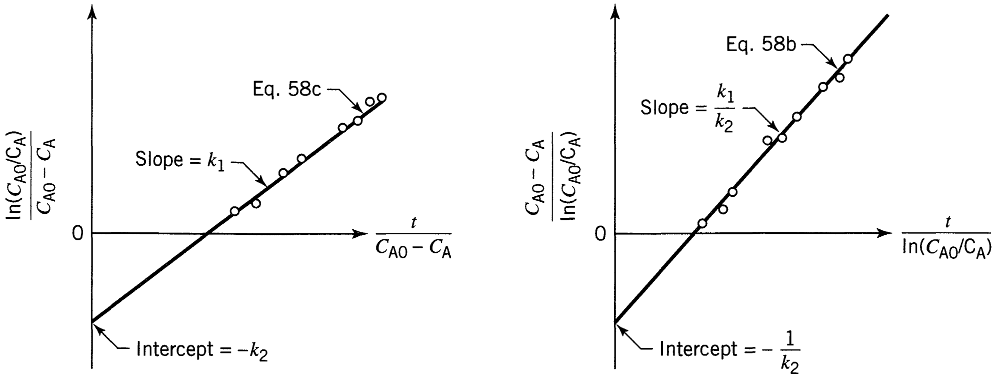


Figure 3.16 Test of the rate equation, Eq. 57, by integral analysis.

By similar reasoning to the above we can show that the general rate form

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{1 + k_2 C_A^n} \tag{59}$$

shifts from order $m - n$ at high concentration to order m at low concentration, the transition taking place where $k_2 C_A^n \cong 1$. This type of equation can then be used to fit data of any two orders.

Another form which can account for this shift is

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{(1 + k_2 C_A)^n} \tag{60}$$

Mechanism studies may suggest which form to use. In any case, if one of these equation forms will fit the data, so will the other.

The rate form of Eq. 57 and some of its generalizations are used to represent a number of widely different kinds of reactions. For example, in homogeneous systems this form is used for enzyme-catalyzed reactions where it is suggested by mechanistic studies (see the Michaelis-Menten mechanism in Chap. 2 and in Chap. 27). It is also used to represent the kinetics of surface-catalyzed reactions.

In mechanistic studies, this form of equation appears whenever the rate-controlling step of a reaction is viewed to involve the association of reactant with some quantity that is present in limited but fixed amounts; for example, the association of reactant with enzyme to form a complex, or the association of gaseous reactant with an active site on the catalyst surface.

EXAMPLE 3.1 FIND A RATE EQUATION USING THE INTEGRAL METHOD

Reactant A decomposes in a batch reactor

$$A \rightarrow \text{products}$$

The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data.

Column 1	Column 2	Column 3	Column 4
Time t, s	Concentration C_A, mol/liter	$\ln\frac{C_{A0}}{C_A}$	$\frac{1}{C_A}$
0	$C_{A0} = 10$	ln 10/10 = 0	0.1
20	8	ln 10/8 = 0.2231	0.125
40	6	0.511	0.167
60	5	0.6931	0.200
120	3	1.204	0.333
180	2	1.609	0.500
300	1	2.303	1.000
Reported data		Calculated	

SOLUTION

Guess First-Order Kinetics. Start by guessing the simplest rate form, or first-order kinetics. This means that ln C_{A0}/C_A vs. t should give a straight line, see Eq. 11 or 12, or Fig. 3.1. So column 3 is calculated and the plot of Fig. E3.1*a* is made. Unfortunately, this does not give a straight line, so first-order kinetics cannot reasonably represent the data, and we must guess another rate form.

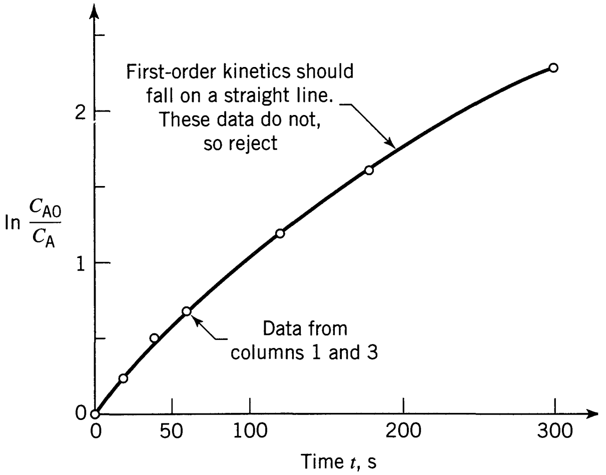


Figure E3.1*a*

Guess Second-Order Kinetics. Equation 16 tells that $1/C_A$ vs. t should give a straight line. So calculate column 4, plot column 1 vs. column 4, as shown in Fig. E3.1*b*. Again, this does not give a straight line, so a second-order kinetic form is rejected.

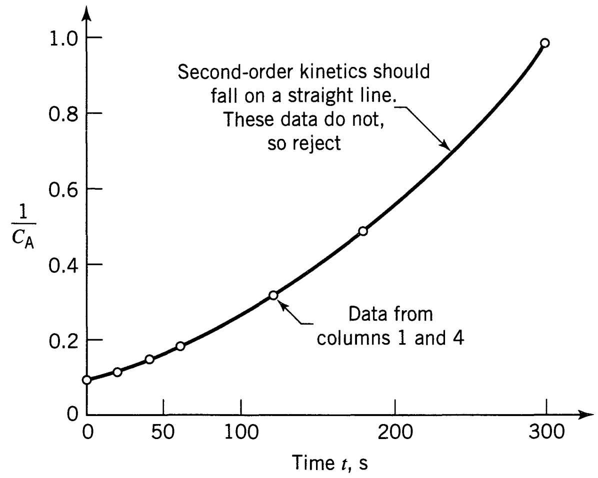


Figure E3.1*b*

Guess nth-Order Kinetics. Let's plan to use the fractional life method with F = 80%. Then Eq. 33*b* becomes

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} C_{A0}^{1-n} \tag{i}$$

Next take logarithms

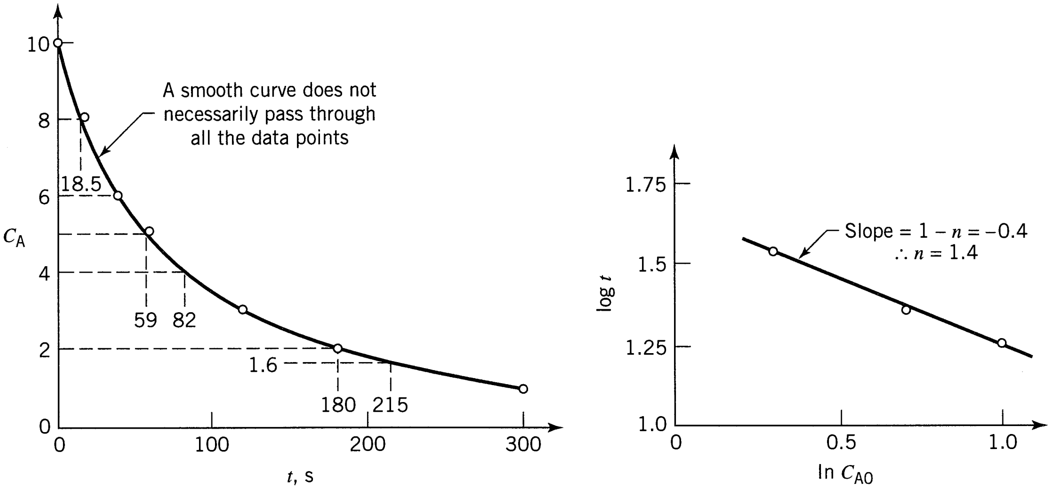
$$\underbrace{\log t_F}_{y} = \underbrace{\overbrace{\log\left(\frac{0.8^{1-n}-1}{k(n-1)}\right)}^{\text{a constant}}}_{a} + \underbrace{(1-n)\log C_{A0}}_{bx} \tag{ii}$$

The procedure is as follows. First accurately plot the C_A vs. t data, draw a smooth curve to represent the data (most important) as shown in Fig. E3.1*c*, then pick C_{A0} = 10, 5, and 2 and fill in the following table from this figure.

C_{A0}	$C_{A\,end}$ (= $0.8C_{A0}$)	Time needed t_F, s	$\log t_F$	$\log C_{A0}$
10	8	0 → 18.5 = 18.5	log 18.5 = 1.27	1.00
5	4	59 → 82 = 23	1.36	0.70
2	1.6	180 → 215 = 35	1.54	0.30

From the curve, not the data

Next, plot $\log t_F$ vs. $\log C_{A0}$, as shown in Fig. E3.1*d* and find the slope.



Figures E3.1*c* and *E3.1d*

We now have the reaction order. To evaluate the rate constant, take any point on the C_A vs. t curve. Pick $C_{A0} = 10$, for which $t_F = 18.5$ s. Replacing all values into Eq. (i) gives

$$18.5 = \frac{(0.8)^{1-1.4} - 1}{k(1.4 - 1)} 10^{1-1.4}$$

from which

$$k = 0.005$$

Therefore, the rate equation that represents this reaction is

$$\underline{\underline{-r_A = \left(0.005 \frac{\text{liter}^{0.4}}{\text{mol}^{0.4}\cdot\text{s}}\right) C_A^{1.4}, \qquad \frac{\text{mol}}{\text{liter}\cdot\text{s}}}}$$

■

Differential Method of Analysis of Data

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC_i/dt, and testing the goodness of fit of the equation with experiment.

The procedure is as follows.

1. Plot the C_A vs. t data, and then by eye carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.
2. Determine the slope of this curve at suitably selected concentration values. These slopes $dC_A/dt = r_A$ are the rates of reaction at these compositions.

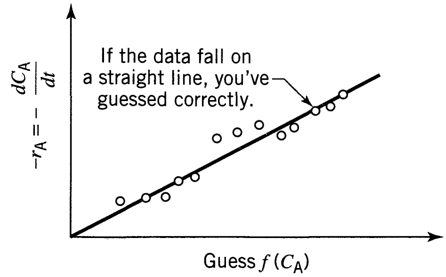


Figure 3.17 Test for the particular rate form $-r_A = kf(C_A)$ by the differential method.

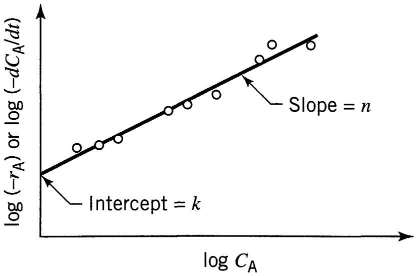


Figure 3.18 Test for an nth-order rate form by the differential method.

3. Now search for a rate expression to represent this r_A vs. C_A data, either by
   - **(a)** picking and testing a particular rate form, $-r_A = kf(C_A)$, see Fig. 17, or
   - **(b)** testing an nth-order form $-r_A = kC_A^n$ by taking logarithms of the rate equation (see Fig. 3.18).

With certain simpler rate equations, however, mathematical manipulation may be able to yield an expression suitable for graphical testing. As an example, consider a set of C_A vs. t data to which we want to fit the M–M equation

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \tag{57}$$

which has already been treated by the integral method of analysis. By the differential method we can obtain $-r_A$ vs. C_A. However, how do we make a straight-line plot to evaluate k_1 and k_2? As suggested, let us manipulate Eq. 57 to obtain a more useful expression. Thus, taking reciprocals we obtain

$$\frac{1}{(-r_A)} = \frac{1}{k_1 C_A} + \frac{k_2}{k_1} \tag{61}$$

and a plot of $1/(-r_A)$ vs. $1/C_A$ is linear, as shown in Fig. 3.19.

Alternatively, a different manipulation (multiply Eq. 61 by $k_1(-r_A)/k_2$) yields another form, also suitable for testing, thus

$$(-r_A) = \frac{k_1}{k_2} - \frac{1}{k_2}\left[\frac{(-r_A)}{C_A}\right] \tag{62}$$

A plot of $-r_A$ vs. $(-r_A)/C_A$ is linear, as shown in Fig. 3.19.

Whenever a rate equation can be manipulated to give a linear plot, this becomes a simple way of testing the equation. So, with any given problem we must use good judgment in planning our experimental program.

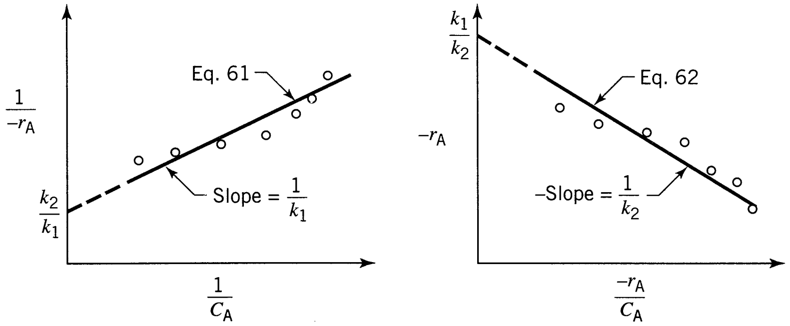


Figure 3.19 Two ways of testing the rate equation $-r_A = k_1C_A/(1 + k_2C_A)$ by differential analysis.

EXAMPLE 3.2 FIND A RATE EQUATION TO FIT A SET OF DATA USING THE DIFFERENTIAL METHOD

Try to fit an nth-order rate equation to the concentration vs. time data of Example 3.1.

SOLUTION

The data are tabulated in the following columns 1 and 2 and are plotted in Fig. E3.2*a*.

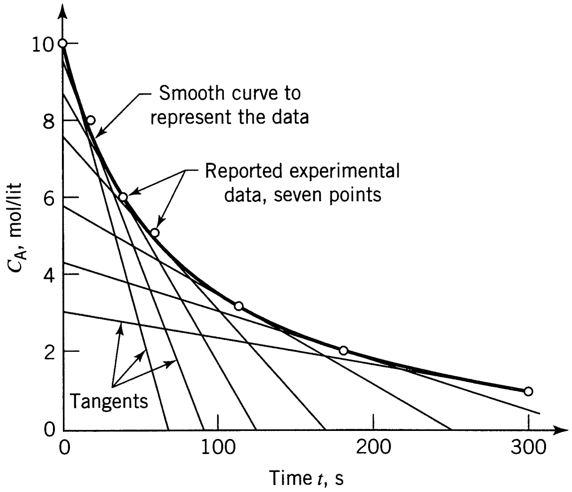


Figure E3.2*a*

Column 1	Column 2	Column 3	Column 4	Column 5
Time t, s	Concentration C_A, mol/liter	Slope, from Fig. E3.2*a* (dC_A/dt)	$\log_{10}(-dC_A/dt)$	$\log_{10} C_A$
0	10	$(10 - 0)/(0 - 75) = -0.1333$	−0.875	1.000
20	8	$(10 - 0)/(-3 - 94) = -0.1031$	−0.987	0.903
40	6	$(10 - 0)/(-21 - 131) = -0.0658$	−1.182	0.778
60	5	$(8 - 0)/(-15 - 180) = -0.0410$	−1.387	0.699
120	3	$(6 - 0)/(-10 - 252) = -0.0238$	−1.623	0.477
180	2	$(4 - 1)/(24 - 255) = -0.0108$	−1.967	0.301
300	1	$(3 - 1)/(-10 - 300) = -0.0065$	−2.187	0.000

Now carefully draw a smooth curve to represent the data and at $C_A = 10$, 8, 6, 5, 3, 2, 1, draw tangents to the curve, and evaluate them (see column 3).

Next, to fit an *n*th-order rate equation to this data, or

$$-r_A = -\frac{dC_A}{dt} = kC_A^n$$

take logarithms of both sides (see columns 3 and 4), or

$$\underbrace{\log_{10}\left(-\frac{dC_A}{dt}\right)}_{y} = \underbrace{\log_{10}k}_{\text{intercept}} + \underset{\text{slope}}{n}\underbrace{\log_{10}C_A}_{x}$$

and plot as in Fig. E3.2*b*. The slope and intercept of the best line gives *n* and *k* (see Fig.E3.2*b*). So the rate equation is

$$-r_A = -\frac{dC_A}{dt} = \left(0.005\,\frac{\text{liter}^{0.43}}{\text{mol}^{0.43}\cdot\text{s}}\right) C_A^{1.43}, \quad \frac{\text{mol}}{\text{liter}\cdot\text{s}}$$

Warning. In step 1, if you use a computer to fit a polynomial to the data it could lead to disaster. For example, consider fitting a sixth-degree polynomial to the seven data points, or an $(n - 1)$ degree polynomial to n points.

Fitting by eye you'd get a smooth curve, as shown in Fig. E3.2*c*. But if a computer is used to obtain a polynomial that would pass through all the points the result would very well be as shown in Fig. E3.2*d*.

Now, which of these curves makes more sense and which would you use? This is why we say "draw a smooth curve by eye to represent the data." But beware, to draw such a curve is not that simple. Take care.

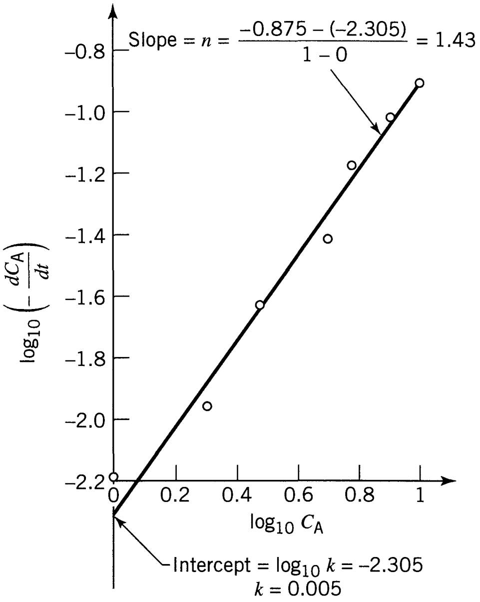


Figure E3.2*b*

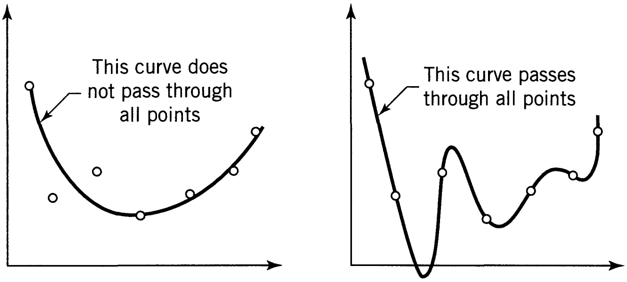


Figure E3.2*c*, *d* The same seven points fitted by curves two different ways.

3.2 VARYING-VOLUME BATCH REACTOR

These reactors are much more complex than the simple constant-volume batch reactor. Their main use would be in the microprocessing field where a capillary tube with a movable bead would represent the reactor (see Fig. 3.20).

The progress of the reaction is followed by noting the movement of the bead with time, a much simpler procedure than trying to measure the composition of the mixture, especially for microreactors. Thus,

V_0 = initial volume of the reactor

V = the volume at time t.

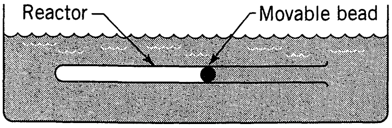


Figure 3.20 A varying-volume batch reactor.

This kind of reactor can be used for isothermal constant pressure operations, of reactions having a single stoichiometry. For such systems the volume is linearly related to the conversion, or

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A} \tag{63a}$$

or

$$dX_A = \frac{dV}{V_0 \varepsilon_A} \tag{63b}$$

where ε_A is the fractional change in volume of the system between no conversion and complete conversion of reactant A. Thus

$$\boxed{\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}} \tag{64}$$

As an example of the use of ε_A, consider the isothermal gas-phase reaction

$$A \rightarrow 4R$$

By starting with pure reactant A,

$$\varepsilon_A = \frac{4 - 1}{1} = 3$$

but with 50% inerts present at the start, two volumes of reactant mixture yield, on complete conversion, five volumes of product mixture. In this case

$$\varepsilon_A = \frac{5 - 2}{2} = 1.5$$

We see, then, that ε_A accounts for both the reaction stoichiometry and the presence of inerts. Noting that

$$N_A = N_{A0}(1 - X_A) \tag{65}$$

we have, on combining with Eq. 63,

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0}\frac{1 - X_A}{1 + \varepsilon_A X_A}$$

Thus

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} \tag{66}$$

which is the relationship between conversion and concentration for isothermal varying-volume (or varying-density) systems satisfying the linearity assumption of Eq. 63.

The rate of reaction (disappearance of component A), is, in general

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$$

Replacing V from Eq. 63a and N_A from Eq. 65 we end up with the rate in terms of the conversion

$$-r_A = \frac{C_{A0}}{(1 + \varepsilon_A X_A)}\frac{dX_A}{dt}$$

or in terms of volume, from Eqs. 63

$$-r_A = \frac{C_{A0}}{V\varepsilon_A}\cdot\frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A}\cdot\frac{d(\ln V)}{dt} \tag{67}$$

Differential Method of Analysis

The procedure for differential analysis of isothermal varying volume data is the same as for the constant-volume situation except that we replace

$$\frac{dC_A}{dt} \quad \text{with} \quad \frac{C_{A0}}{V\varepsilon_A}\frac{dV}{dt} \quad \text{or} \quad \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} \tag{68}$$

This means plot ln V vs. t and take slopes.

Integral Method of Analysis

Unfortunately, only a few of the simpler rate forms integrate to give manageable V vs. t expressions. Let us look at these.

Zero-Order Reactions For a homogeneous zero-order reaction the rate of change of any reactant A is independent of the concentration of materials, or

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = k \tag{69}$$

Integrating gives

$$\boxed{\frac{C_{A0}}{\varepsilon_A}\ln\frac{V}{V_0} = kt} \tag{70}$$

As shown in Fig. 3.21, the logarithm of the fractional change in volume versus time yields a straight line of slope $k\varepsilon_A/C_{A0}$.

First-Order Reactions. For a unimolecular-type first-order reaction the rate of change of reactant A is

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A = kC_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right) \tag{71}$$

Replacing X_A by V from Eqs. 63 and integrating gives

$$\boxed{-\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right) = kt,\ \Delta V = V - V_0} \tag{72}$$

A semilogarithmic plot of Eq. 72, as shown in Fig. 3.22, yields a straight line of slope k.

Second-Order Reactions. For a bimolecular-type second-order reaction

$$2A \rightarrow \text{products}$$

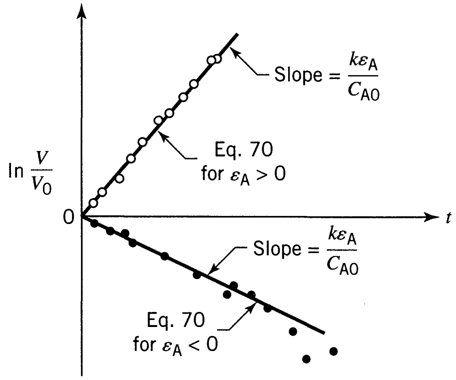


Figure 3.21 Test for a homogeneous zero-order reaction, Eq. 69, in a constant-pressure, varying volume reactor.

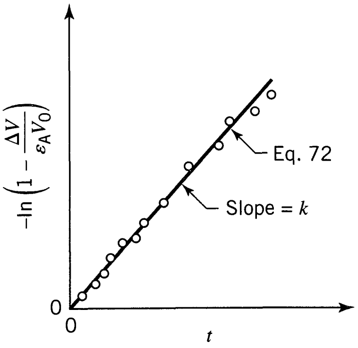


Figure 3.22 Test for a first-order reaction, Eq. 71, in a constant-pressure, varying-volume reactor.

or

$$A + B \rightarrow \text{products}, \quad \text{with} \quad C_{A0} = C_{B0}$$

the rate is given by

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d\ln V}{dt} = kC_A^2 = kC_{A0}^2\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right)^2$$

Replacing X_A by V from Eqs. 63 and then integrating gives, after much algebraic manipulation,

$$\boxed{\frac{(1 + \varepsilon_A)\Delta V}{V_0\varepsilon_A - \Delta V} + \varepsilon_A \ln\left(1 - \frac{\Delta V}{V_0\varepsilon_A}\right) = kC_{A0}t} \tag{73}$$

Figure 3.23 shows how to test for those kinetics.

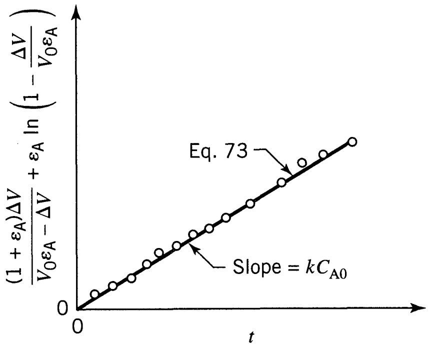


Figure 3.23 Test for the second-order reaction, Eq. 73, in a constant-pressure, varying-volume reactor.

***n*th-Order and Other Reactions.** For all rate forms other than zero-, first-, and second-order the integral method of analysis is not useful.

3.3 TEMPERATURE AND REACTION RATE

So far we have examined the effect of concentration of reactants and products on the rate of reaction, all at a given temperature level. To obtain the complete rate equation, we also need to know the role of temperature on reaction rate. Now in a typical rate equation we have

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kf(C)$$

and it is the reaction rate constant, the concentration-independent term, which is affected by the temperature, whereas the concentration-dependent terms $f(C)$ usually remain unchanged at different temperatures.

Chemical theory predicts that the rate constant should be temperature-dependent in the following manner:

$$k \propto T^m e^{-\mathbf{E}/\mathbf{R}T}$$

However, since the exponential term is much more temperature-sensitive than the power term, we can reasonably consider the rate constants to vary approximately as $e^{-\mathbf{E}/\mathbf{R}T}$.

Thus, after finding the concentration dependency of the reaction rate, we can then examine for the variation of the rate constant with temperature by an Arrhenius-type relationship

$$k = k_0 e^{-\mathbf{E}/\mathbf{R}T}, \qquad \mathbf{E} = \left[\frac{\text{J}}{\text{mol}}\right] \qquad \textbf{(2.34)} \text{ or } \textbf{(74)}$$

This is conveniently determined by plotting ln k versus $1/T$, as shown in Fig. 3.24.

If the rate constant is found at two different temperatures we have from Chap. 2,

$$\ln\frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{or} \quad \mathbf{E} = \frac{\mathbf{R}T_1T_2}{T_2 - T_1}\ln\frac{k_2}{k_1} \qquad \textbf{(2.35)} \text{ or } \textbf{(75)}$$

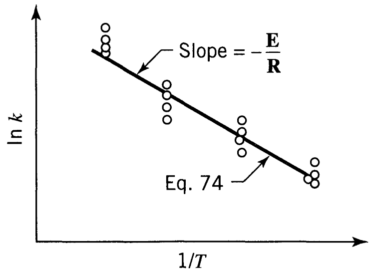


Figure 3.24 Temperature dependency of a reaction according to Arrhenius' law.

Finally, as mentioned in Chap. 2, a shift in **E** with temperature reflects a change in controlling mechanism of reaction. Since this is likely to be accompanied by a change in concentration dependency, this possibility should also be examined.

Warning on Using Pressure Measures. When dealing with gases, engineers and chemists often measure compositions in terms of partial and total pressures, and then develop their rate equations in terms of pressures, without realizing that this can lead to problems. The reason is that the activation energy calculated when using these units is incorrect. Let us illustrate.

EXAMPLE 3.4 *CORRECT AND INCORRECT* **E** *VALUES*

Experimental studies of a specific decomposition of A in a batch reactor using pressure units show exactly the same rate at two different temperatures:

$$\begin{aligned} &\text{at } 400\text{ K} \quad -r_A = 2.3\,p_A^2 \\ &\text{at } 500\text{ K} \quad -r_A = 2.3\,p_A^2 \end{aligned} \qquad \text{where} \quad \begin{cases} -r_A = \left[\dfrac{\text{mol}}{\text{m}^3\cdot\text{s}}\right] \\ p_A = [\text{atm}] \end{cases}$$

(a) Evaluate the activation using these units

(b) Transform the rate expressions into concentration units and then evaluate the activation energy.

The pressure is not excessive, so the ideal gas law can be used.

SOLUTION

(a) ***Using Pressure Units.*** We see right away that a change in temperature does not affect the rate of reaction. This means that

$$\underline{\underline{\mathbf{E} = 0}}$$

Alternatively, we can find **E** by going through the calculations. Thus

$$\ln\frac{k_2}{k_1} = \ln\frac{2.3}{2.3} = 0$$

hence replacing in Eq. 75 shows that

$$\underline{\underline{\mathbf{E} = 0}}$$

(b) ***Transform p_A into C_A, then find* E.** First write the rate equations with all units shown:

$$-r_A, \frac{\text{mol}}{\text{m}^3\cdot\text{s}} = \left(2.3, \frac{\text{mol}}{\text{m}^3\cdot\text{s}\cdot\text{atm}^2}\right)(p_A^2, \text{atm}^2)$$

Next change p_A to C_A. From ideal gas law

$$p_A = \frac{n_A}{V}\mathbf{R}T = C_A\mathbf{R}T$$

Combining the two preceding equations

$$-r_A = 2.3C_A^2\mathbf{R}^2T^2$$

At 400 K

$$-r_{A1} = 2.3\frac{\text{mol}}{\text{m}^3\cdot\text{s}\cdot\text{atm}^2}\cdot C_A^2\left(82.06\times10^{-6}\frac{\text{m}^3\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)^2(400\text{ K})^2$$

$$= 0.0025C_A^2 \quad \text{where} \quad k_1 = 0.0025\frac{\text{m}^3}{\text{mol}\cdot\text{s}}$$

At 500 K, similarly

$$-r_{A2} = 0.0039C_A^2 \quad \text{where} \quad k_2 = 0.0039\frac{\text{m}^3}{\text{mol}\cdot\text{s}}$$

Here we see that in concentration units the rate constants are not independent of temperature. Evaluating the activation energy from Eq. 75, and replacing numbers gives

$$\mathbf{E} = \frac{(8.314)(400)(500)}{500-400}\ln\frac{0.0039}{0.0025}$$

or

$$\underline{\underline{\mathbf{E} = 7394\frac{\text{J}}{\text{mol}}}}$$

This example shows that **E** values differ when either *p* or *C* used to measure concentrations of materials. ■

Final Notes

1. Chemistry (collision theory or transition state theory) has developed the equations for reaction rates and activation energies in terms of concentration.
2. Literature tabulations for **E** and $-r_A$ for homogeneous reactions are normally based on concentrations. The clue to this is that the units for the rate constant are often s^{-1}, liter/mol·s, etc., without pressure appearing in the units.

3. It is a good idea when making runs at different temperatures first to change all p values to C values by using the relationships

$p_A = C_A\mathbf{R}T$ for ideal gases

$p_A = zC_A\mathbf{R}T$ for nonideal gases, where z = compressibility factor

and then proceed to solve the problem. This will avoid confusion on units later on, especially if the reaction is reversible or involves liquids and/or solids as well as gases.

3.4 THE SEARCH FOR A RATE EQUATION

In searching for a rate equation and mechanism to fit a set of experimental data, we would like answers to two questions:

1. Have we the correct mechanism and corresponding type of rate equation?
2. Once we have the right form of rate equation, do we have the best values for the rate constants in the equation?

The difficult question to answer is the first of the preceding two questions. Let us see why this is so.

Suppose we have a set of data and we wish to find out whether any one of the families of curves—parabolas, cubics, hyperbolas, exponentials, etc., each representing a different rate family—really fits these data better than any other. This question cannot be answered simply; neither can high-powered mathematical or statistical methods help in deciding for us. The one exception to this conclusion occurs when one of the families being compared is a straight line. For this situation we can simply, consistently, and fairly reliably tell whether the straight line does not reasonably fit the data. Thus, we have what is essentially a negative test, one that allows us to reject a straight line family when there is sufficient evidence against it.

All the rate equations in this chapter were manipulated mathematically into a linearized form because of this particular property of the family of straight lines that allows it to be tested and rejected.

Three methods are commonly used to test for the linearity of a set of points. These are as follows:

Calculation of k from Individual Data Points. With a rate equation at hand, the rate constant can be found for each experimental point by either the integral or differential method. If no trend in k values is discernible, the rate equation is considered to be satisfactory and the k values are averaged.

Now the k values calculated this way are the slopes of lines joining the individual points to the origin. So for the same magnitude of scatter on the graph the k values calculated for points near the origin (low conversion) will vary widely, whereas those calculated for points far from the origin will show little variation (Fig. 3.25). This fact can make it difficult to decide whether k is constant and, if so, what is its best mean value.

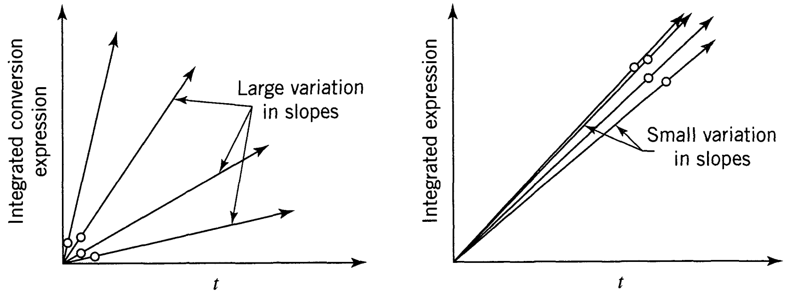


Figure 3.25 How the location of the experimental points influences the scatter in calculated k values.

Calculation of k from Pairs of Data Points. k values can be calculated from successive pairs of experimental points. For large data scatter, however, or for points close together, this procedure will give widely different k values from which k_{mean} will be difficult to determine. In fact, finding k_{mean} by this procedure for points located at equal intervals on the x-axis is equivalent to considering only the two extreme data points while ignoring all the data points in between. This fact can easily be verified. Figure 3.26 illustrates this procedure.

This is a poor method in all respects and is not recommended for testing the linearity of data or for finding mean values of rate constants.

Graphical Method of Fitting Data. Actually, the preceding methods do not require making a plot of the data to obtain k values. With the graphical method the data are plotted and then examined for deviations from linearity. The decision whether a straight line gives a satisfactory fit is usually made intuitively by using good judgment when looking at the data. When in doubt we should take more data.

The graphical procedure is probably the safest, soundest, and most reliable method for evaluating the fit of rate equations to the data, and should be used whenever possible. For this reason we stress this method here.

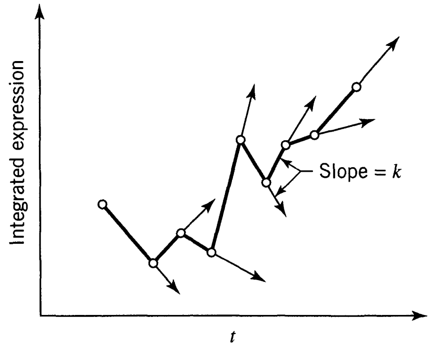


Figure 3.26 Calculated k values from successive experimental points are likely to fluctuate widely.

RELATED READINGS

Frost, A. A., and Pearson, R. G., *Kinetics and Mechanism*, 2nd ed., John Wiley & Sons, New York, 1961.

Laidler, K. J., *Chemical Kinetics*, 2nd ed., McGraw-Hill, New York, 1965.

PROBLEMS

3.1. If $-r_A = -(dC_A/dt) = 0.2$ mol/liter·sec when $C_A = 1$ mol/liter, what is the rate of reaction when $C_A = 10$ mol/liter?
Note: the order of reaction is not known.

3.2. Liquid A decomposes by first-order kinetics, and in a batch reactor 50% of A is converted in a 5-minute run. How much longer would it take to reach 75% conversion?

3.3. Repeat the previous problem for second-order kinetics.

3.4. A 10-minute experimental run shows that 75% of liquid reactant is converted to product by a ½-order rate. What would be the fraction converted in a half-hour run?

3.5. In a homogeneous isothermal liquid polymerization, 20% of the monomer disappears in 34 minutes for initial monomer concentration of 0.04 and also for 0.8 mol/liter. What rate equation represents the disappearance of the monomer?

3.6. After 8 minutes in a batch reactor, reactant ($C_{A0} = 1$ mol/liter) is 80% converted; after 18 minutes, conversion is 90%. Find a rate equation to represent this reaction.

3.7. Snake-Eyes Magoo is a man of habit. For instance, his Friday evenings are all alike—into the joint with his week's salary of $180, steady gambling at "2-up" for two hours, then home to his family leaving $45 behind. Snake Eyes's betting pattern is predictable. He always bets in amounts proportional to his cash at hand, and his losses are also predictable—at a rate proportional to his cash at hand. This week Snake-Eyes received a raise in salary, so he played for three hours, but as usual went home with $135. How much was his raise?

3.8. Find the overall order of the irreversible reaction

$$2H_2 + 2NO \rightarrow N_2 + 2H_2O$$

from the following constant-volume data using equimolar amounts of hydrogen and nitric oxide:

Total pressure, mm Hg	200	240	280	320	360
Half-life, sec	265	186	115	104	67

3.9. The first-order reversible liquid reaction

$$A \rightleftarrows R, \quad C_{A0} = 0.5\ \text{mol/liter}, \quad C_{R0} = 0$$

takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction.

3.10. Aqueous A reacts to form R ($A \rightarrow R$) and in the first minute in a batch reactor its concentration drops from $C_{A0} = 2.03$ mol/liter to $C_{Af} = 1.97$ mol/liter. Find the rate equation for the reaction if the kinetics are second-order with respect to A.

3.11. Aqueous A at a concentration $C_{A0} = 1$ mol/liter is introduced into a batch reactor where it reacts away to form product R according to stoichiometry $A \rightarrow R$. The concentration of A in the reactor is monitored at various times, as shown below:

t, min	0	100	200	300	400
C_A, mol/m^3	1000	500	333	250	200

For $C_{A0} = 500$ mol/m^3 find the conversion of reactant after 5 hours in the batch reactor.

3.12. Find the rate for the reaction of Problem 11.

3.13. Betahundert Bashby likes to play the gaming tables for relaxation. He does not expect to win, and he doesn't, so he picks games in which losses are a given small fraction of the money bet. He plays steadily without a break, and the sizes of his bets are proportional to the money he has. If at "galloping dominoes" it takes him 4 hours to lose half of his money and it takes him 2 hours to lose half of his money at "chuk-a-luck," how long can he play both games simultaneously if he starts with $1000 and quits when he has $10 left, which is just enough for a quick nip and carfare home?

3.14. For the elementary reactions in series

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad k_1 = k_2, \quad \text{at } t = 0 \quad \begin{cases} C_A = C_{A0}, \\ C_{R0} = C_{S0} = 0 \end{cases}$$

find the maximum concentration of R and when it is reached.

3.15. At room temperature sucrose is hydrolyzed by the catalytic action of the enzyme sucrase as follows:

$$\text{sucrose} \xrightarrow{\text{sucrase}} \text{products}$$

Starting with a sucrose concentration $C_{A0} = 1.0$ millimol/liter and an enzyme concentration $C_{E0} = 0.01$ millimol/liter, the following kinetic data are obtained in a batch reactor (concentrations calculated from optical rotation measurements):

C_A, millimol/liter	0.84	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006	0.0025
t, hr	1	2	3	4	5	6	7	8	9	10	11

Determine whether these data can be reasonably fitted by a kinetic equation of the Michaelis–Menten type, or

$$-r_A = \frac{k_3 C_A C_{E0}}{C_A + C_M} \quad \text{where} \quad C_M = \text{Michaelis constant}$$

If the fit is reasonable, evaluate the constants k_3 and C_M. Solve by the integral method.

3.16. Repeat the above problem, except this time solve by the differential method.

3.17. An ampoule of radioactive Kr-89 (half life = 76 minutes) is set aside for a day. What does this do to the activity of the ampoule? Note that radioactive decay is a first-order process.

3.18. Enzyme E catalyzes the transformation of reactant A to product R as follows:

$$A \xrightarrow{\text{enzyme}} R, \qquad -r_A = \frac{200 C_A C_{E0}}{2 + C_A} \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

If we introduce enzyme ($C_{E0} = 0.001$ mol/liter) and reactant ($C_{A0} = 10$ mol/liter) into a batch reactor and let the reaction proceed, find the time needed for the concentration of reactant to drop to 0.025 mol/liter. Note that the concentration of enzyme remains unchanged during the reaction.

3.19. Find the conversion after 1 hour in a batch reactor for

$$A \rightarrow R, \quad -r_A = 3C_A^{0.5} \frac{\text{mol}}{\text{liter} \cdot \text{hr}}, \quad C_{A0} = 1 \text{ mol/liter}$$

Table P3.20

t, min	$C_2H_5SO_4H$, mol/liter	t, min	$C_2H_5SO_4H$, mol/liter
0	0	180	4.11
41	1.18	194	4.31
48	1.38	212	4.45
55	1.63	267	4.86
75	2.24	318	5.15
96	2.75	368	5.32
127	3.31	379	5.35
146	3.76	410	5.42
162	3.81	∞	(5.80)

3.20. M. Hellin and J. C. Jungers, *Bull. soc. chim. France,* **386** (1957), present the data in Table P3.20 on the reaction of sulfuric acid with diethylsulfate in aqueous solution at 22.9°C:

$$H_2SO_4 + (C_2H_5)_2SO_4 \rightarrow 2C_2H_5SO_4H$$

Initial concentrations of H_2SO_4 and $(C_2H_5)_2SO_4$ are each 5.5 mol/liter. Find a rate equation for this reaction.

3.21. A small reaction bomb fitted with a sensitive pressure-measuring device is flushed out and then filled with pure reactant A at 1-atm pressure. The operation is carried out at 25°C, a temperature low enough that the reaction does not proceed to any appreciable extent. The temperature is then raised as rapidly as possible to 100°C by plunging the bomb into boiling water, and the readings in Table P3.21 are obtained. The stoichiometry of the reaction is $2A \rightarrow B$, and after leaving the bomb in the bath over the weekend the contents are analyzed for A; none can be found. Find a rate equation in units of moles, liters, and minutes which will satisfactorily fit the data.

Table P3.21

T, min	π, atm	T, min	π, atm
1	1.14	7	0.850
2	1.04	8	0.832
3	0.982	9	0.815
4	0.940	10	0.800
5	0.905	15	0.754
6	0.870	20	0.728

3.22. For the reaction A → R, second-order kinetics and $C_{A0} = 1$ mol/liter, we get 50% conversion after 1 hour in a batch reactor. What will be the conversion and concentration of A after 1 hour if $C_{A0} = 10$ mol/liter?

3.23. For the decomposition A → R, $C_{A0} = 1$ mol/liter, in a batch reactor conversion is 75% after 1 hour, and is just complete after 2 hours. Find a rate equation to represent these kinetics.

3.24. In the presence of a homogeneous catalyst of given concentration, aqueous reactant A is converted to product at the following rates, and C_A alone determines this rate:

C_A, mol/liter	1	2	4	6	7	9	12
$-r_A$, mol/liter·hr	0.06	0.1	0.25	1.0	2.0	1.0	0.5

We plan to run this reaction in a batch reactor at the same catalyst concentration as used in getting the above data. Find the time needed to lower the concentration of A from $C_{A0} = 10$ mol/liter to $C_{Af} = 2$ mol/liter.

3.25. The following data are obtained at 0°C in a constant-volume batch reactor using pure gaseous A:

Time, min	0	2	4	6	8	10	12	14	∞
Partial pressure of A, mm	760	600	475	390	320	275	240	215	150

The stoichiometry of the decomposition is A → 2.5R. Find a rate equation which satisfactorily represents this decomposition.

3.26. Example 3.1*c* showed how to find a rate equation by using the fractional life method where F = 80%. Take the data from that example and find the rate equation by using the half-life method. As a suggestion, why not take $C_{A0} = 10$, 6, and 2?

3.27. When a concentrated urea solution is stored it slowly condenses to biuret by the following elementary reaction:

$$2\,NH_2\text{–}CO\text{–}NH_2 \rightarrow NH_2\text{–}CO\text{–}NH\text{–}CO\text{–}NH_2 + NH_3$$

To study the rate of condensation a sample of urea ($C = 20$ mol/liter) is stored at 100°C and after 7 hr 40 min we find that 1 mol% has turned into biuret. Find the rate equation for this condensation reaction. [Data from W. M. Butt, *Pak. I. Ch. E.,* **1,** 99 (1973).]

3.28. The presence of substance *C* seems to increase the rate of reaction of A and B, A + B → AB. We suspect that *C* acts catalytically by combining with one of the reactants to form an intermediate, which then reacts further. From the rate data in Table P3.28 suggest a mechanism and rate equation for this reaction.

Table P3.28

[A]	[B]	[C]	r_{AB}
1	3	0.02	9
3	1	0.02	5
4	4	0.04	32
2	2	0.01	6
2	4	0.03	20
1	2	0.05	12

3.29. Find the first-order rate constant for the disappearance of A in the gas reaction $2A \rightarrow R$ if, on holding the pressure constant, the volume of the reaction mixture, starting with 80% A, decreases by 20% in 3 min.

3.30. Find the first-order rate constant for the disappearance of A in the gas reaction $A \rightarrow 1.6R$ if the volume of the reaction mixture, starting with pure Aincreases by 50% in 4 min. The total pressure within the system stays constant at 1.2 atm, and the temperature is 25°C.

3.31. The thermal decomposition of hydrogen iodide

$$2HI \rightarrow H_2 + I_2$$

is reported by M. Bodenstein [*Z. phys. chem.,* **29,** 295 (1899)] as follows:

T, °C	508	427	393	356	283
k, cm³/mol · s	0.1059	0.003 10	0.000 588	80.9×10^{-6}	0.942×10^{-6}

Find the complete rate equation for this reaction. Use units of joules, moles, cm³, and seconds.