For an autocatalytic reaction some product B must be present if the reaction is to proceed. Starting with a small concentration of B, the rate rises as B is formed, and when A is used up, the rate must drop to zero. A plot of concentration versus time gives a straight line through the origin as shown in Figure 3-12.

**IRREVERSIBLE REACTIONS IN SERIES**

Consider a first order reaction in series as \( A \xrightarrow{k_1} B \xrightarrow{k_2} C \). The rate equations for a constant volume batch system (i.e., constant density) are:

\[
(-r_A) = -\frac{dC_A}{dt} = k_1 C_A \quad (3-127)
\]

\[
(-r_B)_{\text{net}} = -\frac{dC_B}{dt} = k_2 C_B - k_1 C_A \quad (3-128)
\]

\[
(+r_C) = \frac{dC_C}{dt} = k_2 C_B \quad (3-129)
\]

\[
\text{ln} \left( \frac{C_A}{C_A_0} \right) \cdot \frac{C_B}{C_{B_0}}
\]

Slope = \( C_k \)

**Figure 3-12.** Autocatalytic reaction.
The initial conditions are at time $t = 0$, $C_A = C_{A0}$ and $C_B = 0$, $C_C = 0$. From stoichiometry:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount at time $t = 0$</td>
<td>$C_{A0}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Amount at time $t = t$</td>
<td>$C_A$</td>
<td>$C_B$</td>
<td>$C_C$</td>
</tr>
<tr>
<td>Amounts that have reacted</td>
<td>$C_{A0} - C_A$</td>
<td>$C_B$</td>
<td>$C_C$</td>
</tr>
</tbody>
</table>

and from stoichiometry $C_{A0} - C_A = C_B = C_C$.

From Equation 3-127, the concentration of $A$ is obtained by integration

$$\frac{dC_A}{dt} = -k_1C_A$$  \hspace{1cm} (3-130)

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{dt} = -k_1 \int_0^t dt$$  \hspace{1cm} (3-131)

$$\ln \frac{C_A}{C_{A0}} = -k_1t$$

Therefore,

$$C_A = C_{A0}e^{-k_1t}$$  \hspace{1cm} (3-132)

The variation in concentration of $B$ is obtained by substituting the concentration of $A$ from Equation 3-132 into Equation 3-128:

$$\frac{dC_B}{dt} + k_2C_B = k_1C_{A0}e^{-k_1t}$$  \hspace{1cm} (3-133)

Equation 3-133 is a first order linear differential equation of the form $dy/dx + Py = Q$. The integrating factor is $IF = e^{\int Pdx}$, and the solution is $ye^{\int Pdx} = \int Qe^{\int Pdx}dx + \text{Constant}$. Applying this general procedure to Equation 3-133, the integrating factor is $IF = e^{\int k_2dt}$. Multiplying Equation 3-133 by the integrating factor gives

$$e^{\int k_2dt} \frac{dC_B}{dt} + k_2C_Be^{\int k_2dt} = k_1C_A e^{\int k_2dt}$$  \hspace{1cm} (3-134)
\[
\frac{d}{dt}(C_B e^{k_2 t}) = k_1 C_A e^{k_2 t}
\]  \hspace{1cm} (3-135)

\[C_B e^{k_2 t} = \int k_1 C_A e^{k_2 t} dt + \text{Const.} \]  \hspace{1cm} (3-136)

where \(\text{Const.} = \text{constant}\).

\[= k_1 C_A \int e^{-k_1 t} \cdot e^{k_2 t} dt + \text{Const.} \]  \hspace{1cm} (3-137)

\[= k_1 C_A \int e^{(k_2 - k_1)t} dt + \text{Const.} \]  \hspace{1cm} (3-138)

\[C_B e^{k_2 t} = \frac{k_1 C_A e^{(k_2 - k_1)t}}{(k_2 - k_1)} + \text{Const.} \]  \hspace{1cm} (3-139)

At time \(t = 0\), the concentration of component B is \(C_B = 0\). Therefore, the constant \(\text{Const.}\) becomes

\[\text{Const.} = - \frac{k_1 C_A}{k_2 - k_1} \]  \hspace{1cm} (3-140)

Therefore, Equation 3-139 becomes

\[C_B e^{k_2 t} = \frac{k_1 C_A e^{(k_2 - k_1)t}}{k_2 - k_1} - \frac{k_1 C_A}{k_2 - k_1} \]  \hspace{1cm} (3-141)

and

\[C_B = \frac{k_1 C_A e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 C_A e^{-k_2 t}}{k_2 - k_1} \]  \hspace{1cm} (3-142)

The final concentration of B is:

\[C_B = \frac{k_1 C_A}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \]  \hspace{1cm} (3-143)
To obtain the maximum concentration of B, differentiate Equation 3-143 with respect to time $t$, which gives

$$\frac{dC_B}{dt} = \frac{k_1 C_{AO}}{k_2 - k_1}\left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right]$$

(3-144)

The values of $k_1$ and $k_2$ govern the location and maximum concentration of B, and this occurs at $dC_B/dt = 0$, $t = t_{\text{max}}$. Equation 3-144 becomes:

$$0 = -\frac{k_1^2 C_{AO} e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 k_2 C_{AO} e^{-k_2 t}}{k_2 - k_1}$$

$$\frac{k_1^2 C_{AO} e^{-k_1 t}}{k_2 - k_1} = \frac{k_1 k_2 C_{AO} e^{-k_2 t}}{k_2 - k_1}$$

(3-145)

$$e^{(k_2 - k_1)t_{\text{max}}} = \frac{k_2}{k_1}$$

(3-146)

$$t_{\text{max}} (k_2 - k_1) = \ln \left(\frac{k_2}{k_1}\right)$$

The maximum concentration of B occurs at

$$t_{\text{max}} = \frac{\ln \left(\frac{k_2}{k_1}\right)}{k_2 - k_1}$$

(3-147)

At $t_{\text{max}}$

$$k_2 e^{-t_{\text{max}} k_2} = k_1 e^{-t_{\text{max}} k_1}$$

(3-148)

Substituting for $e^{-k_1 t}$ in Equation 3-147 gives

$$\frac{C_{B_{\text{max}}}}{C_{AO}} = \frac{1}{(k_2 - k_1)} \left\{k_2 e^{-k_2 t_{\text{max}}} - k_1 e^{-k_2 t_{\text{max}}}\right\} = e^{-k_2 t_{\text{max}}}$$

(3-149)
Substituting Equation 3-147 into Equation 3-149 gives

$$\frac{C_{\text{B}_{\text{max}}}}{C_{\text{AO}}} = e^{-k_2 \left[ \ln \left( \frac{k_2}{k_1} \right) \right]} \quad (3-150)$$

Taking the natural logarithm gives

$$\ln \frac{C_{\text{B}_{\text{max}}}}{C_{\text{AO}}} = \left( -\frac{k_2}{k_2 - k_1} \right) \ln \left( \frac{k_2}{k_1} \right) \quad (3-151)$$

Treating $k_2/(k_2 - k_1)$ as an exponent and removing the natural logarithm gives

$$\frac{C_{\text{B}_{\text{max}}}}{C_{\text{AO}}} = \left( \frac{k_1}{k_2} \right)^{k_2/(k_2 - k_1)} \quad (3-152)$$

This shows that $C_{\text{B}_{\text{max}}}/C_{\text{AO}}$ depends only on $k_1$ and $k_2$, and $k_2$ can be evaluated from $C_{\text{B}_{\text{max}}}/C_{\text{AO}}$ at $t_{\text{max}}$.

From stoichiometry:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount at time $t = 0$</td>
<td>$C_{\text{AO}}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Amount at time $t = t$</td>
<td>$C_A$</td>
<td>$C_B$</td>
<td>$C_C$</td>
</tr>
</tbody>
</table>

and from stoichiometry, $(C_{\text{AO}} - C_A) = (C_B + C_C)$. That is, $C_C = (C_{\text{AO}} - C_A) - C_B$. The concentration of $C$ in terms of $C_{\text{AO}}$, $k_1$, and $k_2$ are:

$$\frac{C_C}{C_{\text{AO}}} = \left\{ 1 - e^{-k_1 t} - \left( \frac{k_1}{k_2 - k_1} \right) \left( e^{-k_1 t} - e^{-k_2 t} \right) \right\}$$

$$= \left\{ 1 + \frac{k_1}{k_2 - k_1} e^{-k_2 t} - \frac{k_2}{k_2 - k_1} e^{-k_1 t} \right\} \quad (3-153)$$
The concentrations of components A, B, and C vary with time. The concentration profiles of A, B, and C in a batch system using the differential Equations 3-127, 3-128, and 3-129 and velocity constants $k_1$ and $k_2$, and employing the Runge-Kutta fourth order numerical method are reviewed in Chapter 5. Important features of consecutive reactions occur in substitution processes. For example $\text{CH}_4 + \text{Cl}_2 = \text{CH}_3\text{Cl} + \text{HCl}$ and $\text{CH}_3\text{Cl} + \text{Cl}_2 = \text{CH}_2\text{Cl}_2 + \text{HCl}$, and so forth. They also occur frequently in oxidation processes, where the desired product may further oxidize to give an undesired product. An example is the oxidation of methanol, where the desired formaldehyde is readily degraded to carbon dioxide: $\text{CH}_3\text{OH} \rightarrow \text{HCHO} \rightarrow \text{CO}_2$.

The formation of resins, tarry matter by consecutive reaction, is prevalent in organic reactions. Figure 3-13a shows the time variations in the concentrations of A, B, and C as given by these equations. The concentration of A falls exponentially, while B goes through a maximum. Since the formation rate of C is proportional to the concentration of B, this rate is initially zero and is a maximum when B reaches its maximum value.

Kinetic Equations 3-143 and 3-153 are obeyed by nucleides undergoing radioactive decay, where the rate constant $k_1$ is large and $k_2$ is small. The reactant A is converted rapidly into the intermediate B, which slowly forms C. Figure 3-13b shows plots of the exponentials $e^{-k_1t}$ and $e^{-k_2t}$ and of their difference. Since $k_2$ is small, the exponential $e^{-k_2t}$ shows a slow decay while $e^{-k_1t}$ shows a rapid decline. The difference of $e^{-k_2t} - e^{-k_1t}$ is shown by the dashed line in Figure 3-13b. The concentration of B is (Equation 3-143) equal to this difference multiplied by $C_{AO}$ (since $k_1 \gg k_2$). Therefore, the concentration of B rapidly rises to the value of $C_{AO}$ and then slowly declines. The rise in concentration C then approximately follows the simple first-order law. Conversely, when $k_1$ is small and $k_2$ is large ($k_2 \gg k_1$), the concentration of B is given by Equation 3-143:

$$C_B = \frac{k_1 C_{AO}}{k_2} \left( e^{-k_1t} - e^{-k_2t} \right)$$  \hspace{1cm} (3-154)

At $t = 0$, $C_B = 0$, but after a short time, relative to the duration of the reaction, the difference $e^{-k_1t} - e^{-k_2t}$ reaches the value of unity. The concentration of B is then $C_{AO}k_1/k_2$, which is much less than $C_{AO}$. After this short induction period, the concentration of B remains almost
Figure 3-13. (a) Variations in the concentrations of A, B, and C for a reaction occurring by the mechanism $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$. (b) Variations with time of the exponentials when $k_1 \gg k_2$. (c) Variations of the exponentials when $k_2 \gg k_1$.

constant, so that generally $dC_B/dt = 0$, the basis of the steady-state treatment.

**FIRST ORDER REVERSIBLE REACTIONS**

Consider the reaction $\text{A} \rightleftharpoons_{k_1}^{k_2} \text{B}$. The rate equation for a constant volume batch system is:
(−r_A) = \frac{dC_A}{dt} = k_1C_A - k_2C_B \quad (3-155)

From stoichiometry:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount at time t = 0</td>
<td>C_{AO}</td>
</tr>
<tr>
<td>Amount at time t = t</td>
<td>C_A</td>
</tr>
<tr>
<td>Amounts that have reacted</td>
<td>C_{AO} - C_A</td>
</tr>
</tbody>
</table>

and the concentration of B is

C_B = (C_{AO} - C_A) + C_{BO} \quad (3-156)

Substituting Equation 3-156 into Equation 3-155, rearranging and integrating between the limits gives:

\[ \int_{C_{AO}}^{C_A} \frac{dC_A}{k_1C_A - k_2\left(C_{AO} - C_A\right) + C_{BO}} = \int_{0}^{t} dt \quad (3-157) \]

\[ -\int_{C_{AO}}^{C_A} \frac{dC_A}{(k_1 + k_2)C_A - k_2\left(C_{AO} - C_B\right)} = \int_{0}^{t} dt \quad (3-158) \]

\[ -\frac{1}{(k_1 + k_2)} \int_{C_{AO}}^{C_A} \frac{dC_A}{C_A - \left(\frac{k_2}{k_1 + k_2}\right)\left(C_{AO} - C_{BO}\right)} = \int_{0}^{t} dt \quad (3-159) \]

where

\[ \alpha = \left(\frac{k_2}{k_1 + k_2}\right)\left(C_{AO} - C_{BO}\right) \quad (3-160) \]

Substituting Equation 3-160 into Equation 3-159 becomes

\[ -\frac{1}{k_1 + k_2} \int_{C_{AO}}^{C_A} \frac{dC_A}{C_A - \alpha} = \int_{0}^{t} dt \quad (3-161) \]
Integrating Equation 3-161 between the boundary conditions \( t = 0 \), \( C_A = C_{AO} \) and \( t = t, C_A = C_A \) gives

\[
-\frac{1}{k_1 + k_2} \ln \left[ C_A - \alpha \frac{C_A}{C_{AO}} \right] = t
\]  
(3-162)

That is:

\[
-\frac{1}{k_1 + k_2} \left[ \ln (C_A - \alpha) - \ln \left( C_{AO} - \alpha \right) \right] = t
\]  
(3-163)

Substituting Equation 3-160 into Equation 3-163 gives

\[
-\ln \left( C_A - \frac{k_2 \left( C_{AO} - C_{BO} \right)}{k_1 + k_2} \right)
\]  
(3-164)

\[
-\ln \left( C_{AO} - \frac{k_2 \left( C_{AO} - C_{BO} \right)}{k_1 + k_2} \right) = (k_1 + k_2)t
\]

or

\[
-\ln \left[ \left( k_1 + k_2 \right) C_A - k_2 C_{AO} + k_2 C_{BO} \right] = (k_1 + k_2)t
\]  
(3-165)

\[
-\ln \left[ \frac{k_1 C_{AO} + k_2 C_{AO} - k_2 C_{AO} + k_2 C_{BO}}{k_1 + k_2} \right] = (k_1 + k_2)t
\]

or

\[
-\ln \left[ \left( \frac{k_1 + 1}{k_2} \right) C_A - \left( C_{AO} - C_{BO} \right) \right] = (k_1 + k_2)t
\]  
(3-166)

\[
-\ln \left[ \left( \frac{k_1}{k_2} \right) C_{AO} + C_{BO} \right] = (k_1 + k_2)t
\]  
(3-167)
At equilibrium with concentrations of A and B as $C_{Ae}$, $C_{Be}$, respectively, then $k_1 C_{Ae} = k_2 C_{Be}$. Since $dC_A/dt = 0$ at equilibrium,

$$\frac{k_1}{k_2} = \frac{C_{Be}}{C_{Ae}}$$  (3-168)

Substituting Equation 3-168 into Equation 3-167 gives

$$-\ln \left( \frac{C_{Be}/C_{Ae} + 1}{C_{Be} \cdot C_{AO} + C_{BO}} \right) = (k_1 + k_2) t$$  (3-169)

A plot of

$$-\ln \left( \frac{(C_{Be}/C_{Ae} + 1) \cdot C_A - (C_{AO} - C_{BO})}{(C_{Be}/C_{Ae}) \cdot C_{AO} + C_{BO}} \right)$$

versus time $t$ gives a straight line with the slope $(k_1 + k_2)$. From the slope and the equilibrium constant $K$, $k_1$ and $k_2$ can be determined. Figure 3-14 shows a plot of the reversible first order reaction.
Examples of first-order reversible reactions are gas phase cis-trans isomerization, isomerizations in various types of hydrocarbon systems, and the racemization of $\alpha$ and $\beta$ glucoses. An example of a catalytic reaction is the ortho-para hydrogen conversion on a nickel catalyst.

**SECOND ORDER REVERSIBLE REACTIONS**

Bimolecular-type second order reactions are:

\[
A + B \xrightleftharpoons[k_2]{k_1} C + D
\]  
(3-170)

\[
2A \xrightleftharpoons[k_2]{k_1} C + D
\]  
(3-171)

\[
2A \xrightleftharpoons[k_2]{k_1} 2C
\]  
(3-172)

\[
A + B \xrightleftharpoons[k_2]{k_1} 2C
\]  
(3-173)

With the restrictions that \( C_{AO} = C_{BO} \) and \( C_{CO} = C_{DO} = 0 \) in Equation 3-170, the rate equation for a constant volume batch system becomes

\[
(-r_A) = -\frac{dC_A}{dt} = C_{AO} \frac{dX_A}{dt} = k_1 C_A^2 - k_2 C_C^2
\]  
(3-174)

\[
= k_1 C_{AO}^2 (1 - X_A)^2 - \frac{k_2}{k_1} X_A^2
\]  
(3-175)

where the fractional conversion \( X_A = 0 \) at \( t = 0 \). At equilibrium, \( dX_A/dt = 0 \) and the final solution is:

\[
\ln \left[ \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} \right] = 2k_1 C_{AO} \left( \frac{1}{X_{Ae}} - 1 \right) t
\]  
(3-176)
All other reversible second-order rate equations have the same solution with the boundary conditions assumed in Equation 3-176. Table 3-4 gives solutions for some reversible reactions.

**GENERAL REVERSIBLE REACTIONS**

Integrating the rate equation is often difficult for orders greater than 1 or 2. Therefore, the differential method of analysis is used to search the form of the rate equation. If a complex equation of the type below fits the data, the rate equation is:

$$\begin{align*}
\frac{dx}{dt} &= ka x - k_x x \\
\frac{dx}{dt} &= ka x - k_x x - k_I x \\
\frac{dx}{dt} &= ka x - k_x x - k_I x \\
\frac{dx}{dt} &= ka x - k_x x - k_I x - k_{II} x \\
\frac{dx}{dt} &= ka x - k_x x - k_I x - k_{II} x
\end{align*}$$

Table 3-4

**Rate equations for opposing reactions**

<table>
<thead>
<tr>
<th>Stoichiometric equation</th>
<th>Rate equation**</th>
<th>Differential form</th>
<th>Integrated form</th>
</tr>
</thead>
<tbody>
<tr>
<td>A→Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{x_x - x} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>A→Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}(x + x_0) )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>2A→Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}\left( \frac{x}{2} \right) )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>A→2Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>A→Y + Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x)^2 - k_{-1}x^2 )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>A + B→Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x)^2 - k_{-1}x )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
<tr>
<td>A + B→Y + Z</td>
<td>( \frac{dx}{dt} = k_1(a_0 - x)^2 - k_{-1}x^2 )</td>
<td>= ( \frac{x_x}{a_0} \ln \left( \frac{x_x}{a_0(x_0 - x)} \right) = k_1t )</td>
<td></td>
</tr>
</tbody>
</table>

**In all cases x is the amount of A consumed per unit volume. The concentration of B is taken to be the same as that of A.**

Modeling of Chemical Kinetics and Reactor Design

\[-r_A = -\frac{dC_A}{dt} = k_1 \frac{C_A}{1 + k_2 C_A}\]  \hspace{1cm} (3-177)

Taking the reciprocals of Equation 3-177 gives

\[\frac{1}{(-r_A)} = \frac{1 + k_2 C_A}{k_1 C_A} = \frac{1}{k_1 C_A} + \frac{k_2}{k_1}\]  \hspace{1cm} (3-178)

Plotting \(1/(-r_A)\) versus \(1/C_A\) would give a straight line with the slope equal to \(1/k_1\) and an intercept of \(k_2/k_1\). Another analysis method involves multiplying each side of Equation 3-178 by \(k_1/k_2\) and solving for \((-r_A)\) to give

\[-r_A = k_1 \frac{(-r_A)}{k_2 C_A} \hspace{1cm} (3-179)\]

Plotting \((-r_A)\) versus \((-r_A)/C_A\) gives a straight line with the slope equal to \(-1/k_2\) and the intercept equal to \(k_1/k_2\).

**SIMULTANEOUS IRREVERSIBLE SIDE REACTION**

Consider the chemical reactions

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
& \xleftarrow{k_2} C
\end{align*}
\]

in which the reactions are first order, the initial concentration of A is \(C_{AO}\), and both the concentrations of B and C are zero. The rate equations representing the reactions for a constant volume batch system are:

For component A \((-r_A) = -\frac{dC_A}{dt} = (k_1 + k_2)C_A\)  \hspace{1cm} (3-180)

For component B \((+r_B) = \frac{dC_B}{dt} = k_1 C_A\)  \hspace{1cm} (3-181)
For component C \((+r_C) = \frac{dC}{dt} = k_2 C_A\) (3-182)

Rearranging and integrating Equation 3-180 between the limits gives

\[
-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = \int_0^t (k_1 + k_2) dt
\]

(3-183)

\[-\ln \frac{C_A}{C_{AO}} = (k_1 + k_2)t\] (3-184)

The solution for the concentration of A is

\[C_A = C_{AO} e^{-(k_1 + k_2)t}\] (3-185)

Substituting Equation 3-185 into Equation 3-181, rearranging and integrating gives

\[
\int_0^{C_B} \frac{dC_B}{C_{AO} e^{- (k_1 + k_2) t}} = k_1 \int_0^t dt
\]

(3-186)

Further rearrangement of Equation 3-186 gives

\[
\frac{1}{C_{AO}} \int_0^{C_B} dC_B = k_1 \int_0^t e^{- (k_1 + k_2) t} + \text{Constant}
\]

(3-187)

\[
\frac{C_B}{C_{AO}} = \frac{k_1}{(k_1 + k_2)} e^{-(k_1 + k_2)t} + \text{Constant}
\]

(3-188)

At \(t = 0, C_B = 0\)

\[
\text{Constant} = \frac{k_1}{(k_1 + k_2)}
\]

The solution for concentration of B is
Correspondingly, the solution for the concentration of C is

\[ C_C = \frac{C_A 0 k_2}{(k_1 + k_2)} \left\{ 1 - e^{-(k_1 + k_2) t} \right\} \] (3-190)

Concentration profiles can be developed with time using the differential Equations 3-180, 3-181, and 3-182, respectively, with the Runge-Kutta fourth order method at known values of \( k_1 \) and \( k_2 \) for a batch system.

**PSEUDO-ORDER REACTION**

The results of the types of reaction being considered show that the treatment of kinetic data becomes rapidly more complex as the reaction order increases. In cases where the reaction conditions are such that the concentrations of one or more of the species occurring in the rate equation remain constant, these terms may be included in the rate constant \( k \). The reactions can be attributed to lower order reactions. These types of reactions can be defined as pseudo-\( n \)th order, where \( n \) is the sum of the exponents of those concentrations that change during the reaction. An example of this type of reaction is in catalytic reaction, where the catalyst concentration remains constant during the reactions.

A kinetic study of a reaction can be simplified by running the reaction with one or more of the components in large excess, so that the concentration remains effectively constant. Mc Tigue and Sime [2] consider the oxidation of aliphatic aldehydes such that ethanal with bromine in aqueous solution follows second-order kinetics:

\[ \text{Br}_2 + \text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{H}^+ + 2\text{Br}^- \] (3-191)

The rate equation of the reaction for a constant volume batch system is

\[ \frac{-dC_{\text{Br}_2}}{dt} = k_2 C_{\text{CH}_3\text{CHO}} C_{\text{Br}_2} \] (3-192)
If there is excessively large aldehyde, its concentration remains constant and the reaction can be referred to as pseudo-first order kinetics. Equation 3-192 can be rewritten as

\[-\frac{dC_{Br2}}{dt} = k_1 C_{Br2}\]  

(3-193)

where

\[k_1 = k_2 C_{CH_3CHO}\]  

(3-194)

The second order rate constant \(k_2\) is \(k_2 = k_1 / C_{CH_3CHO}\), and can be determined by measuring \(k_1\) at known aldehyde concentrations. The use of excess reagent concentrations has important practical consequences where physical methods, such as light absorption or conductance, are used to monitor reactions.

**PRACTICAL MEASUREMENTS OF REACTION RATES**

Many techniques have been employed in kinetic studies to determine reaction rate constants and reaction orders from either reactant or product concentrations at known times. The most desirable analytical methods allow continuous and rapid measurement of the concentration of a particular component. Any of the methods used to monitor the course of reaction must satisfy the following criteria:

- The method should not interfere with the system by affecting the kinetic processes occurring during the investigation.
- It must give an exact measure of the extent of the reaction.
- The measurement should be representative of the system at the time it is made or at the time the sample analyzed was taken.

Analyses of kinetic data are based on identifying the constants of a rate equation involving the law of mass action and some transfer phenomena. The law of mass action is expressed in terms of concentrations of the species. Therefore, the chemical composition is required as a function of time. Laboratory techniques are used to determine the chemical composition using an instrument that is suitably calibrated to give the required data. The techniques used are classified into two categories, namely chemical and physical methods.
Chemical methods involve removing a portion of the reacting system, quenching of the reaction, inhibition of the reaction that occurs within the sample, and direct determination of concentration using standard analytical techniques—a spectroscopic method. These methods provide absolute values of the concentration of the various species that are present in the reaction mixture. However, it is difficult to automate chemical methods, as the sampling procedure does not provide a continuous record of the reaction progress. They are also not applicable to very fast reaction techniques.

Physical methods involve measuring a physical property of the system as the reaction progresses. It is often possible to obtain a continuous record of the values of the property being measured, which can be transformed into a continuous record of reactant and product concentrations. Examples of physical methods that vary linearly with concentrations include conductance (ionic reagents), absorption of visible or ultraviolet light, optical density, the total pressure of gaseous systems under nearly ideal conditions, and the rotations of polarized light. An essential feature of physical methods involves continuous, rapid response measurement without the need for sampling.

Physical techniques can be used to investigate first order reactions because the absolute concentrations of the reactants or products are not required. Dixon et. al [3] studied the base hydrolysis of cobalt complex, \([\text{Co(NH}_3\text{)}_5\text{L}]^{3+}\), where \(\text{L} = (\text{CH}_3\text{)}_2\text{SO}, (\text{NH}_2\text{)}_2\text{C} = \text{O}, (\text{CH}_3\text{)}\text{O}_3\text{P} = \text{O}\) in glycine buffers.

\[
[\text{Co(NH}_3\text{)}_5\text{L}]^{3+} \xrightarrow{\text{OH}^-} [\text{Co(NH}_3\text{)}_5\text{OH}]^{2+} + \text{L}
\]  

(3-195)

The rate equation is:

\[
-\frac{d[\text{Co(NH}_3\text{)}_5\text{L}]^{3+}}{dt} = k[\text{Co(NH}_3\text{)}_5\text{L}]^{3+}
\]  

(3-196)

The release of dimethyl sulfoxide is accompanied by an increase in absorbance (D) at 325 nm. The absorbance D is defined as \(\log(I_o/I)\), where \(I_o\) and \(I\) are the intensities of the incident and transmitted light, respectively. Figure 3-15 illustrates the relationship between concentration and absorbance changes for the hydrolysis of the cobalt...
Reaction Rate Expression

The values of the absorbance during the reaction are related to the concentration of the cobalt complex and is represented by \( C \) as follows:

\[
C_0 \propto (D_\infty - D_0); \quad C_0 = \text{Const. } (D_\infty - D_0)
\]

\[
C \propto (D_\infty - D); \quad C = \text{Const. } (D_\infty - D)
\]

\( (3-197) \)

**Figure 3-15.** Relationship between concentration and absorbance changes for the hydrolysis of \([\text{Co(NH}_3]_5\text{L}]^{3+}\).
where Const. is a proportionality constant related to the absorption coefficients of the reactants and products at 325 nm.

Substituting Equation 3-197 into the integrated first order reaction Equation 3-33 gives the corresponding equations expressed in terms of the solution absorbance:

$$\ln (D_\infty - D) = -kt + \ln (D_\infty - D_0)$$

(3-198)

or

$$D_\infty - D = (D_\infty - D_0)e^{-kt}$$

(3-199)

Equation 3-199 infers that the absorbance approaches the value at the end of the reaction (infinity value) with the same rate constant $k$ as that for the reaction expressed in terms of the reactant concentration. The required rate constant can be determined from the slope of a plot of $\ln (D_\infty - D_0)$ versus time. The same equations can be written for reactions monitored in terms of optical rotation or conductance.

In the case of a second order reaction, an example is the alkaline hydrolysis of an ester as represented by the following equation:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \xrightarrow{k_2} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$

(3-200)

The rate equation for a constant volume batch system is

$$-\frac{dC_{\text{CH}_3\text{COOC}_2\text{H}_5}}{dt} = k_2C_{\text{CH}_3\text{COOC}_2\text{H}_5}C_{\text{OH}^-}$$

(3-201)

Substituting Equation 3-197 into Equation 3-53 gives the following equation for the change in absorbance at the selected wavelength.

$$\frac{1}{(D_\infty - D) - \frac{1}{(D_\infty - D_0)} = \text{Const.}k_2t$$

(3-202)

A plot of $1/(D_\infty - D)$ versus time $t$ is linear with the slope $= \text{Const.}k_2$. The rate constant $k_2$ is determined if the proportionality constant Const. is known, between the absorbance change and the extent of the reaction. The proportionality constant can either be determined by calibrating the system or, more accurately, by studying the reaction under pseudo-first order conditions.
Another useful technique in kinetic studies is the measurement of the total pressure in an isothermal constant volume system. This method is employed to follow the course of homogeneous gas phase reactions that involve a change in the total number of gaseous molecules present in the reaction system. An example is the hydrogenation of an alkene over a catalyst (e.g., platinum, palladium, or nickel catalyst) to yield an alkane:

\[ C_nH_{2n} + H_2 \xrightarrow{\text{Pt, Pd, or Ni catalyst}} C_nH_{2n+2} \]  

(3-203)

Nickel is the least active of these catalysts and requires an elevated temperature and pressure, whereas platinum and palladium function adequately at ordinary temperatures and pressures. An example is butylene to butane:

\[ C_4H_8 + H_2 \rightarrow C_4H_{10} \]  

(3-204)

In gaseous reactions, the composition term in the rate equation is often expressed as the partial pressure of the reacting species. These pressures are then transformed to concentration.

Consider the reaction \( A \rightarrow \) products. The rate equation is:

\[ (-r_A) = k_p p_A^n = k C_A^n \]  

(3-205)

where

\[ (-r_A) = \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \quad \left( \frac{\text{mol}}{1 \cdot \text{s}} \right) \]

\[ k_p = \frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}^n \cdot \text{s}} \quad \left( \frac{\text{mol}}{1 \cdot \text{atm}^n \cdot \text{s}} \right) \]

\[ p_A^n = \text{Pa}^n \quad \left( \text{atm}^n \right) \]

\[ k = \left( \frac{\text{mol}}{\text{m}^3} \right)^{1-n} \text{s}^{-1} \quad \left( \frac{\text{mol}}{1 \cdot \text{s}} \right)^{1-n} \text{s}^{-1} \]

For ideal gases, the partial pressure is expressed as:
\[ p_A = C_A RT \]  \hspace{1cm} (3-206)

where

\[ p_A = \text{Pascal, Pa} \quad \text{or} \quad \text{atm} \]

\[ C_A = \frac{\text{mol}}{\text{m}^3} \quad \left( \frac{\text{mol}}{\text{l}} \right) \]

\[ R = 8.314 \frac{\text{m}^3\text{Pa}}{\text{mol} \cdot \text{K}} \quad \text{or} \quad 0.082 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \]

Caution must be exercised when the rate equations with gas phase reactions are expressed in terms of the partial pressure as compared to concentration. This is because each rate gives different activation energy for the same data and for the same reaction. Levenspiel [4] suggests that the difference can be ignored for reactions with reasonably high activation energies as the amount is only a few kJ.

Pressure measurement devices such as a manometer are used without disturbing the system being monitored. Another type of reacting system that can be monitored involves one of the products being quantitatively removed by a solid or liquid reagent that does not affect the reaction. An example is the removal of an acid formed by reactions in the gas phase using hydroxide solutions. From the reaction stoichiometry and measurements of the total pressure as a function of time, it is possible to determine the extent of the reaction and the partial pressure or concentrations of the reactant and product species at the time of measurement.

Consider the following gaseous reaction \( aA + bB \rightarrow cC + dD \). Pressure and concentration are related, and for a constant volume reactor with changing number of moles during reaction, the total pressure (\( \pi \)) changes with time, \( t \). For an ideal gas, with any reactant A or B, the partial pressure is expressed as:

\[ p_A = C_A RT = p_{AO} + \frac{a}{\Delta n} (\pi_O - \pi) \]  \hspace{1cm} (3-207)

where

\[ \Delta n = (c + d) - (a + b) \]  \hspace{1cm} (3-208)
For any product C or D, the partial pressure is expressed as:

$$p_C = C_RT = p_{CO} - \frac{c}{\Delta n} (\pi_O - \pi) \quad (3-209)$$

For an ideal gas at both constant temperature and pressure, but with changing number of moles during reaction, Levenspiel relates that

$$V = V_O (1 + \varepsilon_A X_A) \quad (3-210)$$

where

$$\varepsilon_A = \frac{V_{all_A reacted} - V_{no reaction}}{V_{no reaction}}$$

Levenspiel considers the cases where the relationship between concentration and conversion of reacting specie is not obvious, but depends on a number of factors.

**CASE 1: CONSTANT DENSITY SYSTEMS**

This case includes most liquid reactions and also those gas reactions that operate at both constant temperature and pressure with no change in the number of moles during reaction. The relationship between concentration $C_A$ and fractional conversion $X_A$ is as follows:

$$X_A = 1 - \frac{C_A}{C_{AO}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{AO}}$$

$$\frac{C_A}{C_{AO}} = 1 - X_A \quad \text{and} \quad dC_A = -C_{AO}dX_A \quad (3-212)$$

where $\varepsilon_A = 0$. The changes in B and C to A are

$$\frac{C_{AO} - C_A}{a} = \frac{C_B - C_B}{b} = \frac{C_C - C_{CO}}{c} \quad (3-213)$$

or


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\[ \frac{C_{AO} X_A}{a} = \frac{C_{BO} X_B}{b} \]  

\[ (3-214) \]

**CASE 2: CHANGING DENSITY GASES**

This case involves constant temperature \( T \) and total pressure \( \pi \). In this case, the density changes since the number of moles change during the reaction, and the volume of a fluid element changes linearly with conversion or \( V = V_O (1 + \epsilon_A X_A) \). The relationship between \( C_A \) and \( X_A \) is as follows:

\[ X_A = \frac{C_{AO} - C_A}{C_{AO} + \epsilon_A C_A} \quad \text{and} \quad dX_A = \frac{C_{AO} (1 + \epsilon_A) dC_A}{(1 + \epsilon_A C_A)^2} \]

\[ (3-215) \]

\[ \frac{y_A}{y_{AO}} = \frac{C_A}{C_{AO}} \frac{1 - X_A}{1 + \epsilon_A X_A} \quad \text{and} \quad \frac{dC_A}{C_{AO}} = \frac{-1 + \epsilon_A}{(1 + \epsilon_A X_A)^2} dX_A \]

for \( \epsilon_A \neq 0 \), where \( y_A \) = mole fraction of component A. The changes between the reactants are:

\[ \epsilon_A X_A = \epsilon_B X_B \]  

\[ (3-216) \]

\[ \frac{a \epsilon_A}{C_{AO}} = \frac{b \epsilon_B}{C_{BO}} \]  

\[ (3-217) \]

and for the products and inerts:

\[ \frac{y_C}{y_{AO}} = \frac{C_C}{C_{AO}} \frac{(c/a) X_A + C_{CO}/C_{AO}}{1 + \epsilon_A X_A} \]  

\[ (3-218) \]

\[ \frac{y_I}{y_{IO}} = \frac{C_I}{C_{IO}} \frac{1}{1 + \epsilon_A X_A} \]  

\[ (3-219) \]

**CASE 3: GASES WITH VARYING DENSITY, TEMPERATURE, AND TOTAL PRESSURE**

Consider the following reaction: \( aA + bB \rightarrow cC; a + b \neq c \). For an ideal gas behavior with reactant A as the key component, the relationship between concentration \( C_A \), \( C_{AB} \), \( C_C \), and \( X_A \) are as follows:
Reaction Rate Expression

\[ X_A = \frac{1 - \frac{C_A}{C_{AO}} \left( \frac{T \pi_O}{T_O \pi} \right)}{1 + \varepsilon_A \frac{C_A}{C_{AO}} \left( \frac{T \pi_O}{T_O \pi} \right)} \quad \text{or} \quad \frac{C_A}{C_{AO}} = \frac{1 - X_A}{1 + \varepsilon_A X_A \left( \frac{T_O \pi}{T \pi} \right)} \] (3-220)

\[ X_A = \frac{C_{BO}}{C_{AO}} - \frac{C_B}{C_{AO}} \left( \frac{T \pi_O}{T \pi} \right) \quad \text{or} \quad \frac{C_B}{C_{AO}} = \frac{C_{BO}}{C_{AO}} - \frac{b}{a} X_A \left( \frac{T \pi_O}{T \pi} \right) \] (3-221)

\[ X_A = \frac{C_C}{C_{AO}} \left( \frac{T \pi_O}{T_O \pi} \right) - \frac{C_{CO}}{C_{AO}} \quad \text{or} \quad \frac{C_{CO}}{C_{AO}} = \frac{C_C}{C_{AO}} + \frac{c}{a} X_A \left( \frac{T \pi_O}{T \pi_O} \right) \] (3-222)

where \( \varepsilon_A \) is evaluated from stoichiometry at constant temperature \( T \) and total pressure \( \pi \).

For a high-pressure non-ideal gas behavior, the term \( (T \pi/O/\pi) \) is replaced by \( (Z_0T/O/\pi/ZT\pi_O) \), where \( Z \) is the compressibility factor. To change to another key reactant \( B \), then

\[ \frac{a \varepsilon_A}{C_{AO}} = \frac{C_B}{C_{BO}} \quad \text{and} \quad \frac{C_{AO}X_A}{a} = \frac{C_{BO}X_B}{b} \] (3-223)

For liquids or isothermal gases with no change in pressure and density, \( \varepsilon_A \rightarrow 0 \) and \( (T \pi/O/\pi) \rightarrow 1 \). Other forms of physical methods include optical measurements that can be used to monitor the course of various reactions such as colorimetry, fluorescence, optical rotation, and refractive indices. Various spectroscopic techniques have been employed in kinetic studies. The absorption of a reacting system of electromagnetic radiation (light, microwaves) is a designated property of the system composition and dimensions. Among the various forms of spectroscopic methods that can be used in kinetic studies are nuclear magnetic resonance, electron spin resonance spectroscopy, visible ultraviolet, and infrared. Figure 3-16 shows a flowchart that will help to
Figure 3-16. Interpretation of rate data. (Source: Curl, R. L., 1968. Unpublished notes, University of Michigan.)

determine the rate equation for isothermal batch reaction systems in which only one chemical reaction occurs.

Level 1 in the chart indicates that when the reaction rate law is known, the integral method of analysis may be used after performing an experiment to evaluate the specific reaction rate. This procedure
is useful when the reaction order and specific rate at one temperature are already known from previous experiments, and the specific reaction rate at some other temperature is sought. If the reaction rate constant \( k \) at two or more different temperatures is known, it is possible to determine the activation energy and the frequency factor.

Level 2 involves the trial-and-error method. After trying zero, first, second, and finally third order, if none of these orders fit the data, another analysis method should be tried. When the reaction order is unknown, cannot be guessed, and the reaction is irreversible, proceed to level 4. If the reaction rate depends on only one species (e.g., isomerization or decomposition reactions), use the differential method that requires only one experiment, or the method of half-lives that requires many experiments, to determine the specific reaction rate and order. However, where certain constraints imposed by a given reaction prevent collating experimental data other than in the initial rate period, neither the differential nor the half-life method may be suitable. Examples include a solid-liquid reactions, where flaking or crumbling of the solid occurs, and certain autocatalytic and simultaneous reactions. In such instances, it is usually best to use the initial rate plot method given in level 5. In this technique, the initial rate is measured at various initial concentrations of the reacting species. The reaction order can be determined from a plot of the logarithm of the initial reaction rate, \( \ln(–r_{AO}) \), against the logarithm of the initial concentration, \( \ln C_{AO} \). The two methods of analysis that require only one experiment to determine the reaction order and the specific rate constant are the integral method (level 2) and the differential method.

If the reaction rate depends on more than one species, use the method of excess coupled either with the half-life method or the differential method. If the method of excess is not suitable, an initial rate plot may be constructed by varying the concentration of one reactant while the concentrations of the others are held constant. This process is repeated until the orders of reaction of each species and the specific reaction rate are evaluated. At level 5, the least-squares analysis can be employed.

Figure 3-16 is helpful in the logical planning of a series of kinetic experiments to determine reaction orders and specific rate constants. However, it is important to remember the main goals and design of the entire experimental analysis. Table 3-5 gives methods used to determine direct or indirect measurements of a species concentration.

(text continued on page 168)
### Table 3-5

<table>
<thead>
<tr>
<th>Methods of analysis</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Physical methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Temperature change</td>
<td>Endothermic or exothermic reactions that are performed adiabatically.</td>
<td>Chem. Engr. Sci., 21 (1966), 397.</td>
</tr>
<tr>
<td>2. Optical methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Absorption spectrometry</td>
<td>Transitions within molecules, which can be studies by the selective absorption of electromagnetic radiation. Transitions between electronic levels are found in the UV and visible regions; those between vibrational levels, within the same electronic level are in the IR region. (1) Visible</td>
<td>J. Chem. Ed. 49, No. 8 (1972), 539. I.E.C. Process Design &amp; Development, 8, No. 1, (1969), 120.</td>
</tr>
<tr>
<td></td>
<td>Reactions involving one (or at most two) colored compound(s).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) Ultraviolet</td>
<td>The determination of organic compounds, especially aromatic and heterocyclic substances or compounds with conjugated bonds.</td>
</tr>
</tbody>
</table>
(3) Infrared
Organic compounds only.

(4) Atomic absorption
Metallic ions.

b. Polarimetry
Liquid phase reactions involving optically active species.

c. Refractometry
Reaction in which there is a measurable difference between the refractive index of the reactants and that of the products.

3. Electrochemical methods

a. Potentiometry
Used in the measurement of the potentials of nonpolarized electrodes under conditions of zero current. Seldom used in organic reactions.

b. Voltammetry and polarography
Used for dilute electrolytic solutions. Not applicable to reactions that are catalyzed by mercury.

c. Conductimetry
Reactions involving a change in the number of kind of ions present, thereby changing the electrical conductivity. Suitable for both organic and inorganic reactions.

4. Nuclear methods

a. Magnetic resonance spectrometry
(1) Nuclear magnetic resonance
Used primarily for compounds containing hydrogen.
### Table 3-5 (continued)

<table>
<thead>
<tr>
<th>Methods of analysis</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(radioisotopes)</td>
<td></td>
<td>I.E.C. Product Research and Development, 8, No. 4, (1969), 319,</td>
</tr>
</tbody>
</table>

5. Methods of interphase separations


(text continued from page 165)

Most of the references listed refer to a specific chemical kinetics experiment in which the corresponding method analysis was used to obtain the rate data.

**DETERMINING REACTION RATE DATA**

The principal techniques used to determine reaction rate functions from the experimental data are differential and integral methods.

**Differential Method**

This method is based on differentiating the concentration versus time data in order to obtain the actual rate of reaction to be tested. All the terms in the equation including the derivative \( \frac{dC_i}{dt} \) are determined, and the goodness of fit are tested with the experimental
data. The following procedures are used to determine the rate constant $k$ and the concentration dependence of the rate equation $f(C_i)$.

1. Set a hypothesis as to the form of the concentration dependent of the rate function $f(C_i)$. This can be of the form

$$(-r_A) = -\frac{dC_A}{dt} = kf(C_i) \quad (3-224)$$

2. From the experimental data of concentration versus time, determine the reaction rate at various times.
3. Draw a smooth curve through these data.
4. Determine the slope of this curve at selected values of the concentration. The slopes are the rates of reaction at these compositions.
5. Calculate $f(C_i)$ for each composition.
6. Prepare a plot of reaction rate ($-dC_A/dt$) versus $f(C_i)$. If the plot is linear and passes through the origin, the rate equation is consistent with the data, otherwise another equation should be tested. Figure 3-17 shows a schematic of the differential method.

**Integral Method**

This method estimates the reaction order based on the reaction stoichiometry and assumptions concerning its mechanism. The assumed rate equation is then integrated to obtain a relation between the composition and time. The following procedures are used for determining the rate equations:

1. Set a hypothesis as to the mathematical form of the reaction rate function. In a constant volume system, the rate equation for the disappearance of reactant $A$ is

$$(-r_A) = -\frac{dC_A}{dt} = kf(C_A) \quad (3-225)$$

2. Separate the variables and integrate Equation 3-225 to give

$$-\int_{C_A0}^{C_A} \frac{dC_A}{f(C_A)} = k\int_0^1 dt \quad (3-226)$$
Figure 3-17. Schematics of the differential method for data analysis.
3. Plot the calculated values as shown in Figure 3-18 to give a straight line of slope $k$.

4. From experimentally determined values of the integral of Equation 3-226, plot these at corresponding times as shown in Figure 3-18.

5. If the data yield a satisfactory straight line passing through the origin, then the reaction rate equation (assumed in step 1) is said to be consistent with the experimental data. The slope of the line is equal to the reaction rate constant $k$. However, if the data do not fall on a satisfactory straight line, return to step 1 and try another rate equation.

REGRESSION ANALYSES

LINEAR REGRESSION

If the rate law depends on the concentration of more than one component, and it is not possible to use the method of one component being in excess, a linearized least squares method can be used. The purpose of regression analysis is to determine a functional relationship between the dependent variable (e.g., the reaction rate) and the various independent variables (e.g., the concentrations).

\[
- \int_{C_{AO}}^{C_A} \frac{dC_A}{f(C_A)}
\]

Slope = $k$

Figure 3-18. Test of reaction rate data using the integral method.
Consider a mole balance on a constant volume batch reactor represented by

\[-\frac{dC_A}{dt} = kC_A^aC_B^b\]

(3-227)

Using the method of initial rates gives

\[\left(\frac{-dC_A}{dt}\right)_o = (-r_A)_o = kC_{AO}^aC_{BO}^b\]

(3-228)

Taking the logarithms of both sides of Equation 3-228 gives

\[\ln\left(\frac{-dC_A}{dt}\right) = \ln k + a\ln C_{AO} + b\ln C_{BO}\]

(3-229)

This can be represented in the form

\[Y = C_0 + C_1X_1 + C_2X_2\]

(3-230)

where \(Y = \ln (-dC_A/dt), C_0 = \ln k, X_1 = \ln C_{AO}, X_2 = \ln C_{BO}, C_1 = a,\)
and \(C_2 = b.\) If \(N\) experimental runs are performed, then for the \(i\)th
run, Equation 3-230 becomes

\[Y_i = C_0 + C_1X_{1,i} + C_2X_{2,i}\]

(3-231)

where \(X_{1,i} = \ln C_{AO,i},\) with \(C_{AO,i}\) being the initial concentration of \(A\)
for the \(i\)th run. Solving for the unknowns \(C_0, C_1,\) and \(C_2\) for \(N\) experimental
runs, \(i = 1, 2, 3 \ldots N,\) gives

\[\sum_{i=1}^{N} Y_i = NC_0 + C_1\sum_{i=1}^{N} X_{1i} + C_2\sum_{i=1}^{N} X_{2i}\]

(3-232)

\[\sum_{i=1}^{N} X_{1i}Y_i = C_0\sum_{i=1}^{N} X_{1i} + C_1\sum_{i=1}^{N} X_{1i}^2 + C_2\sum_{i=1}^{N} X_{1i}X_{2i}\]

(3-233)

\[\sum_{i=1}^{N} X_{2i}Y_i = C_0\sum_{i=1}^{N} X_{2i} + C_1\sum_{i=1}^{N} X_{1i}X_{2i} + C_2\sum_{i=1}^{N} X_{2i}^2\]

(3-234)
Equations 3-232, 3-233, and 3-234 can be solved simultaneously to determine the unknowns $C_0$, $C_1$, and $C_2$, which are the rate constant $k$, and the orders (a and b) of the reaction respectively. This type of problem is best expedited using a computer program. Appendix A reviews the multiple regression that is being employed to determine the rate constant $k$ and the orders (a and b) of the reaction. The computer program (PROG3) on the CD-ROM determines the rate constant $k$ and the orders (a and b) of the reaction. Other parameters such as the reaction order, frequency factor $k_0$, and activation energy $E_a$ can be determined using regression analysis.

**NONLINEAR ANALYSIS**

Another method for determining rate law parameters is to employ a search for those parameter values that minimize the sum of the squared difference of measured reaction rate and the calculated reaction rate. In performing $N$ experiments, the parameter values can be determined (e.g., $E_a$, $C_0$, $C_1$, and $C_2$) that minimize the quantity:

$$\sigma^2 = \frac{s^2}{N-K} = \sum_{i=1}^{N} \frac{(r_{im} - r_{ic})^2}{N-K-1}$$

(3-235)

where $\sigma^2 = \text{variance}$

$s^2 = \Sigma (r_{im} - r_{ic})^2$

$N = \text{number of runs}$

$K = \text{number of parameters to be determined}$

$r_{im} = \text{measured reaction rate for run } i$

$r_{ic} = \text{calculated reaction rate for run } i$

Nonlinear least squares curve fitting using the Microsoft Solver is reviewed in Appendix B.

**WEIGHTED LEAST SQUARES ANALYSIS**

A weighted least-squares analysis is used for a better estimate of rate law parameters where the variance is not constant throughout the range of measured variables. If the error in measurement is corrected, then the relative error in the dependent variable will increase as the independent variable increases or decreases.

Consider a first order reaction with the final concentration expressed by $C_A = C_{AO}e^{-kt}$. If the error in concentration measurement is 0.01$C_{AO}$,
the relative error in the concentration measurement \(0.01C_{AO}/C_A(t)\) increases with time. It is possible to minimize the sum of N measurements by:

\[
\sigma^2 = \sum_{i=1}^{N} W_i [y_i(\text{exp tl}) - y_i(\text{calc})]^2
\]  

(3-236)

where \(W_i\) is the weighing factor.

The weighted least-squares analysis is important for estimating parameters involving exponents. Examples are the concentration time data for an irreversible first order reaction expressed by \(C_A = C_{AO}e^{-kt}\), and the reaction rate-temperature data expressed by \((-r_A) = k_0C_Ae^{-E_A/RT}\). These equations are of the form

\[Y = Ae^{-BX}\]

(3-237)

where \(Y = C_A\) or \((-r_A)\) and \(X = t\) or \(1/T\), respectively.

Linearizing Equation 3-237 gives

\[\ln Y = \ln A - BX\]

(3-238)

It is also possible to determine \(A\) and \(B\) that minimize the weighted sum of squares. The weighting function is the square of the independent variable, and the function to be minimized is

\[
\sigma^2 = \sum_{i=1}^{N} y_i^2 [\ln y_i(\text{exp tl}) - \ln y_i(\text{calc})]^2
\]  

(3-239)

VALIDITY OF LEAST SQUARES FITTING

The validity of least squares model fitting is dependent on four principal assumptions concerning the random error term \(\epsilon\), which is inherent in the use of least squares. The assumptions as illustrated by Bacon and Downie [6] are as follows:

Assumption 1: The values of the operating variables are known exactly. In practice, this is interpreted to mean that any uncertainty associated with a value of an operating variable has much less effect on the response value than the uncertainty associated with a measured value of the response itself.

Assumption 2: The form of the model is appropriate. Statistically, this is expressed as \(E(\epsilon) = 0\) for all data, where \(\epsilon\) is the random error.
**Assumption 3:** The variance of the random error term is constant over the ranges of the operating variables used to collect the data. When the variance of the random error term varies over the operating range, then either weighted least squares must be used or a transformation of the data must be made. However, this may be violated by certain transformations of the model.

**Assumption 4:** There is no systematic association of the random error for any one data point with the random error for any other data point. Statistically this is expressed as: 
\[ \text{Correlation} (\varepsilon_u, \varepsilon_v) = 0 \]

where \( \varepsilon_u = \text{random error for experimental run number } u \)
\( \varepsilon_v = \text{random error for experimental run number } v \)

**PROBLEMS AND ERRORS IN FITTING RATE MODELS**

Several methods are used to fit rate models, the two most common of which often give erroneous results. The first is the transformation of a proposed rate model to achieve a model form that is linear in the parameters. An example is the nonlinear model:

\[ r = kC_A^a C_B^b \]  

which can be transformed into linear form by taking logarithm of both sides

\[ \ln r = \ln k + a \ln C_A + b \ln C_B \]  

Equation 3-241 is a linear model of the form

\[ Y = C_0 + C_1X_1 + C_2X_2 \]

where \( X_1 = \ln C_A \) and \( X_2 = \ln C_B \).

Another example of model transformation to achieve linearity is the change from the nonlinear rate equation

\[ r = \frac{k_0 k_1 C_A}{1 + k_1 C_A + k_2 C_B} \]

to the equation
which is of the linear form

\[ Y = C_O + C_1X_1 + C_2X_2 \]  

(3-245)

where \( X_1 = 1/C_A \) and \( X_2 = C_B/C_A \).

The practice of transforming a nonlinear model into linear form can result in invalid estimates of the coefficients and consequent misinterpretation of the fitted model. The problem is associated with the assumption of a constant error variance (Assumption 3). If the measured rates \( r \) have a constant error variance, then the errors associated with \( \ln r \) (Equation 3-241) or \( 1/r \) (Equation 3-244) will not have a constant error variance. The degree of violation will depend on the range of the measured reaction rate values. If the data contain both very small rates and very large rates, then the error variance will change appreciably over the data set and ordinary least squares estimates of the coefficients will give poor estimates. However, if the rate values are not spread over a large range, then model transformations of Equations 3-241 and 3-244 will not significantly distort the estimated coefficients. An illustration of the effects of linearizing model transformation of Equation 3-240 is given in Example 3-1.

Generally, a model form is first proposed (i.e., a hypothesis that must be tested) using plots of the data. A simple plot can show obvious inadequacies in the model form and can suggest a better form. Alternatively, it can show excessive scatter in the data and warn against overconfidence in an adequate fit. The least squares estimates of the parameters are determined using a weighted or an optimization (i.e., trial-and-error) search procedure if required. This gives the best estimates if the assumptions are valid. Further testing the adequacy of the fitted model requires using both plots of the residuals and the sum of squares of the residuals. Finally, an estimate should be made of the precision of each parameter estimate by statistical analysis (e.g., 95% confidence intervals for the parameters).

Often, one or more model forms in chemical reaction kinetics may fit the data. Although it is tempting to want to justify a specific model as the mechanism of the reaction, it is preferable to only infer that the model could be the mechanism. It is also desirable that the reaction mechanism taking place be understood in order to solve a problem in
reactor design. This is because knowledge of the mechanism will make it possible to fit the experimental data to a theoretical rate expression, which will be more reliable than an empirical fit. Also, the mechanism may require some modifications and optimization for the final design.

Example 3-1

The oxidation of $\text{Fe(CN)}_6^{4-}$ to $\text{Fe(CN)}_6^{3-}$ by peroxidisulfate, $\text{S}_2\text{O}_8^{2-}$, can be monitored spectrophotometrically by observing the increase in absorbance at 420 nm, $D_{420}$, in a well-mixed batch system. Assume that the kinetic scheme is:

$$\text{Fe(CN)}_6^{4-} + \frac{1}{2} \text{S}_2\text{O}_8^{2-} \rightarrow k_2 \text{Fe(CN)}_6^{3-} + \text{SO}_4^{2-}$$

$$\frac{d}{dt}[\text{Fe(CN)}_6^{4-}] = k_2[\text{Fe(CN)}_6^{4-}][\text{S}_2\text{O}_8^{2-}]$$

Using pseudo-first order conditions with $[\text{S}_2\text{O}_8^{2-}] = 1.8 \times 10^{-2}\text{M}$ and $[\text{Fe(CN)}_6^{4-}] = 6.5 \times 10^{-4}\text{M}$, the following absorbances were recorded at 25°C:

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>900</th>
<th>1,800</th>
<th>2,700</th>
<th>3,600</th>
<th>4,500</th>
<th>$\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{420}$</td>
<td>0.120</td>
<td>0.290</td>
<td>0.420</td>
<td>0.510</td>
<td>0.581</td>
<td>0.632</td>
<td>0.781</td>
</tr>
</tbody>
</table>

Calculate the pseudo-first order rate constant $k_1 = k_2[S_2O_8^{2-}]$ and, hence, $k_2$.

Solution

Table 3-6 gives $D_{\infty} - D$ with time $t$. For a first order rate law, the rate equation is expressed by

$$\ln \left( \frac{D_{\infty} - D}{D_{\infty} - D_0} \right) = -k_1 t$$

Equation 3-246 is further expressed by

$$\ln (D_{\infty} - D) = \ln (D_{\infty} - D_0) - k_1 t$$

(3-247)
that is,

\[ D_{\infty} - D = (D_{\infty} - D_0)e^{-k_1t} \]  \hspace{1cm} (3-248)

Equation 3-248 is of the form

\[ Y = Ae^{BX} \]  \hspace{1cm} (3-249)

Linearizing Equation 3-249 gives

\[ \ln Y = \ln A + BX \]  \hspace{1cm} (3-250)

The computer program PROG1 determines the constants \( A \) and \( B \) from the regression analysis. Table 3-7 gives the results of the program with the slope \(-B\) equal to the reaction rate constant \( k_1 \). Figure 3-19 shows a plot of \( \ln (D_{\infty} - D) \) against time \( t \).

<p>| Table 3-6 |
|-----------------|-------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>( t(\text{sec}) )</th>
<th>( D_{420} )</th>
<th>( D_{\infty} - D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.120</td>
<td>0.661</td>
</tr>
<tr>
<td>900</td>
<td>0.290</td>
<td>0.491</td>
</tr>
<tr>
<td>1,800</td>
<td>0.420</td>
<td>0.361</td>
</tr>
<tr>
<td>2,700</td>
<td>0.510</td>
<td>0.271</td>
</tr>
<tr>
<td>3,600</td>
<td>0.581</td>
<td>0.200</td>
</tr>
<tr>
<td>4,500</td>
<td>0.632</td>
<td>0.149</td>
</tr>
<tr>
<td>( \infty )</td>
<td>0.781</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<p>| Table 3-7 |
|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>( t(\text{sec}) )</th>
<th>( \ln (D_{\infty} - D) )</th>
<th>( \ln (D_{\infty} - D) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.414</td>
<td>-0.416</td>
</tr>
<tr>
<td>900</td>
<td>-1.711</td>
<td>-0.713</td>
</tr>
<tr>
<td>1,800</td>
<td>-1.019</td>
<td>-1.011</td>
</tr>
<tr>
<td>2,700</td>
<td>-1.306</td>
<td>-1.309</td>
</tr>
<tr>
<td>3,600</td>
<td>-1.609</td>
<td>-1.609</td>
</tr>
<tr>
<td>4,500</td>
<td>-1.904</td>
<td>-1.904</td>
</tr>
</tbody>
</table>
The constants for the equation \( Y = A \cdot \exp(B \cdot X) \) are:

- \( A = 0.660 \)
- \( B = -33112 \times 10^{-3} \)
- Correlation Coefficient = 0.99997

The results give the pseudo-first order rate constant, and \( k_1 = 3.312 \times 10^{-4} \text{ sec}^{-1} \) and \( k_2 \) can be calculated as follows:

\[
k_2 = \frac{k_1}{[S_2O_8^{2-}]} = \frac{3.312 \times 10^{-4}}{1.8 \times 10^{-2}} \left( \frac{1}{\text{sec}} \cdot \frac{1}{\text{M}} \right)
\]

\[
k_2 = 1.84 \times 10^{-2} \text{ M}^{-1} \cdot \text{sec}^{-1}
\]

**Example 3-2**

First order rate constant \( k \), for the rotation about the C-N bond in N, N-dimethylnicotinamide (3) measured at different temperatures by nuclear magnetic resonance (NMR) are:

<table>
<thead>
<tr>
<th>( T^\circ \text{C} )</th>
<th>10.0</th>
<th>15.7</th>
<th>21.5</th>
<th>27.5</th>
<th>33.2</th>
<th>38.5</th>
<th>45.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k \text{ sec}^{-1} )</td>
<td>2.08</td>
<td>4.57</td>
<td>8.24</td>
<td>15.8</td>
<td>28.4</td>
<td>46.1</td>
<td>93.5</td>
</tr>
</tbody>
</table>
Determine the activation energy, $E$, and the pre-exponential factor, $k_0$, for the rotation.

**Solution**

The activation energy $E$ is a measure of the temperature sensitivity of the rate constant. A high $E$ corresponds to a rate constant that increases rapidly with temperature. From the Arrhenius equation

$$k_T = k_0 \exp\left(-\frac{E}{RT}\right)$$

where $k_T$ = rate constant at known temperature

$k_0$ = pre-exponential factor

$E$ = activation energy

$R$ = gas constant (8.314 J/mol • K)

$T$ = absolute temperature ($K = 273.15 + ^\circ C$)

It is possible to determine the activation energy $E$ and the pre-exponential factor $k_0$.

Linearizing Equation 3-251 gives

$$\ln k_T = \ln k_0 - \frac{E}{RT}$$

By plotting $\ln k_T$ against $1/T$, the slope equal to $-E/R$ is obtained and the intercept equal to $\ln k_0$. From these known constants, activation energy $E$ and the pre-exponential factor $k_0$ are determined. Equation 3-251 is of the form

<table>
<thead>
<tr>
<th>$T(^\circ C)$</th>
<th>$k$(sec$^{-1}$)</th>
<th>$T$(K)</th>
<th>$1/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.08</td>
<td>283.15</td>
<td>0.00353</td>
</tr>
<tr>
<td>15.7</td>
<td>4.57</td>
<td>288.15</td>
<td>0.00346</td>
</tr>
<tr>
<td>21.5</td>
<td>8.24</td>
<td>294.65</td>
<td>0.00339</td>
</tr>
<tr>
<td>27.5</td>
<td>15.8</td>
<td>300.65</td>
<td>0.00333</td>
</tr>
<tr>
<td>33.2</td>
<td>28.4</td>
<td>306.35</td>
<td>0.00326</td>
</tr>
<tr>
<td>38.5</td>
<td>46.1</td>
<td>311.65</td>
<td>0.00321</td>
</tr>
<tr>
<td>45.7</td>
<td>93.5</td>
<td>318.85</td>
<td>0.00314</td>
</tr>
</tbody>
</table>
Reaction Rate Expression

\[ Y = Ae^{BX} \]  (3-253)

Linearizing Equation 3-253 gives

\[ \ln Y = \ln A + BX \]  (3-254)

where \( \ln Y = \ln k_T \)
\( \ln A = \ln k_O \)
\( B = -\frac{E}{R} \)
\( X = \frac{1}{T} \)

The computer program PROG1 determines the values of constants A and B. Table 3-9 gives the results of the program and the constants A and B.

The constants for the equation are:

- \( A = 78728 \times 10^{15} \)
- \( B = -0.94869 \times 10^4 \)
- Correlation Coefficient = 0.99966

The slope \( B = -\frac{E}{R} = -0.9487 \times 10^4 \) and \( A = k_O = 7.873 \times 10^{14} \).

The activation energy \( E = R \times B = 8.314 \times 10^4 \) (J/mol) and \( E = 78.9 \times 10^3 \) J/mol. The pre-exponential factor is \( k_O = 7.87 \times 10^{14} \) sec\(^{-1}\).

Figure 3-20 gives a plot of \( \ln k_T \) against \( 1/T \).

**Example 3-3**

R. T. Dillon (1932) studied the reaction between ethylene bromide and potassium iodide in 99\% methanol with the following data:

<table>
<thead>
<tr>
<th>1/T</th>
<th>Actual In k(sec(^{-1}))</th>
<th>Estimated In k(sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00353</td>
<td>0.732</td>
<td>0.795</td>
</tr>
<tr>
<td>0.00346</td>
<td>1.520</td>
<td>1.456</td>
</tr>
<tr>
<td>0.00339</td>
<td>2.109</td>
<td>2.103</td>
</tr>
<tr>
<td>0.00333</td>
<td>2.760</td>
<td>2.745</td>
</tr>
<tr>
<td>0.00326</td>
<td>3.346</td>
<td>3.332</td>
</tr>
<tr>
<td>0.00321</td>
<td>3.831</td>
<td>3.859</td>
</tr>
<tr>
<td>0.00314</td>
<td>4.538</td>
<td>4.546</td>
</tr>
</tbody>
</table>
C₂H₄Br₂ + 3KI → C₂H₄ + 2KBr + KI₃

Temperature: 59.72°C
Initial KI concentration: 0.1531 kmol/m³
Initial C₂H₄Br₂ concentration: 0.02864 kmol/m³

<table>
<thead>
<tr>
<th>Time, ksec</th>
<th>Fraction dibromide reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.7</td>
<td>0.2863</td>
</tr>
<tr>
<td>40.5</td>
<td>0.3630</td>
</tr>
<tr>
<td>47.7</td>
<td>0.4099</td>
</tr>
<tr>
<td>55.8</td>
<td>0.4572</td>
</tr>
<tr>
<td>62.1</td>
<td>0.4890</td>
</tr>
<tr>
<td>72.9</td>
<td>0.5396</td>
</tr>
<tr>
<td>83.7</td>
<td>0.5795</td>
</tr>
</tbody>
</table>

Determine the second order reaction rate constant.