Chapter 3
REACTION KINETICS

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INTRODUCTION

The goal of a mass balance analysis is to describe the mass or concentration of a substance as a function of time and location in a given physical system. Ultimately, for the mass balance equation to be solvable, each term in it must be reduced to a form in which time and location are the only independent variables, and mass or concentration is the only dependent variable. In Chapter 1, the advective and diffusive/dispersive terms of mass balances were explored and expressed in a way that met this criterion. Each of those terms was deconstructed into one component that reflects the dependence of concentration on location ($\nabla c$), plus other components that characterize the physical system and the chemical properties of the substance of interest ($Q, V, D, \varepsilon$, etc.). Similarly, it was shown that the storage term ($\partial (cV)/\partial t$) can often be separated into components representing the system volume and the change in concentration over time or the system flow rate and the change in concentration over space (between the influent effluent streams), depending on the particular mass balance formulation. In Chapter 2, the parameters describing system hydraulics were explored further, and ways to evaluate those parameters were presented.

In this chapter, we focus on the reaction term in the mass balance equation, exploring ways in which that term can be evaluated from experimental data and models for its dependence on concentration and temperature. In subsequent chapters, the values of the physical and chemical parameters that characterize each term in the mass balance for specific types of processes are explored, so that complex aquatic systems such as water and wastewater treatment facilities, in which flow, mixing, and chemical reaction occur simultaneously, can be analyzed.

FUNDAMENTALS AND TERMINOLOGY

The Reaction Rate Term in Well-Mixed Batch Reactors

The kinetics of a chemical reaction cannot be determined solely by its overall stoichiometry or by theoretical considerations, but rather must be determined experimentally. (Theoretical kinetics have been developed from quantum mechanical considerations for some very simple reactions under idealized conditions, but it is not currently possible to apply such approaches to more complex systems.) To evaluate the kinetics of a particular reaction, experiments might be carried out using any of a variety of reactor types and under a wide range of conditions. The simplest and most common approach for studying reaction kinetics is to characterize the rate at which the substances

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1Many textbooks have been written devoted to reaction kinetics and reactor engineering. An excellent introductory text, on which much of the material in this chapter is based, is Chemical Reaction Engineering, by Levenspiel (3rd ed., Wiley, 1999).
of interest are generated or destroyed in a well mixed, batch (no flow) reactor. The analysis of such a reactor involves writing one or more mass balances in which the control volume includes all the fluid in the system.

\[
\frac{\partial (c_i V)}{\partial t} = Q (c_{i,\text{in}} - c_{i,\text{out}}) + \left( D_i + \varepsilon \right) \frac{\partial^2 c_i}{\partial x^2} V + (r_{i,V} + r_{i,\sigma} \sigma) V \quad \text{(1)}
\]

Because the solution is well mixed, the concentration is identical throughout the control volume, so \( V \) can be taken out of the differential in the storage term. In addition, since there is no flow into or out of the reactor, the advective term is zero, and since the aqueous phase ends at the boundaries of the control volume, the diffusive term is zero as well. Thus, the mass balance can be simplified as follows:

\[
\frac{dc_i}{dt} = r_i \quad \text{(2)}
\]

where \( r_i = r_{i,V} + r_{i,\sigma} \sigma \).\(^2\)

The overall reaction rate, \( r_i \), has dimensions of mass per volume per time and may be either positive (if the reaction forms the substance under consideration) or negative (if the reaction destroys it). Unfortunately, the simplicity of Equation 2 leads to a common error whereby the term \( dc_i/dt \) is substituted for the reaction rate \( r_i \) in other mass balances. While the equality is valid for a batch system, it is not necessarily valid for other systems.

**Reaction Rate Terms for Different Species Participating in the Same Reaction**

Consider the following generic chemical reaction:

\[
aA + bB \rightarrow pP \quad \text{(3)}
\]

Defining \( c_i \) as the concentration of \( i \) in moles per liter, the volume-normalized mass balances on \( A, B, \) and \( P \) in a batch system can be expressed as follows:

---

\(^2\) For simplicity, unless otherwise noted, the discussion in this chapter assumes that the substances of interest do not participate in surface reactions \( (r_{i,\sigma} = 0) \), so \( r_{i,V} = r_i \). The extension to include interfacial reactions is straightforward. Examples including such reactions are provided in subsequent chapters.
where all the terms have units such as moles per liter per second. If those units are used, the reaction stoichiometry requires that the three rates be related by:

\[
\begin{align*}
-\frac{1}{a} \frac{dc_A}{dt} &= -\frac{1}{b} \frac{dc_B}{dt} = \frac{1}{p} \frac{dc_P}{dt} \\
\frac{dc_A}{dt} &= \frac{a}{b} \frac{dc_B}{dt} = \frac{a}{p} \frac{dc_P}{dt}
\end{align*}
\] (4a)

EXAMPLE 1. Hexavalent chromium (i.e., Cr in the +VI oxidation state) is found in many industrial wastes, forming a variety of chemical species. The treatment of these wastes often involves reduction of the hexavalent Cr to trivalent (+3) Cr, in which state the metal is very likely to precipitate as chromium hydroxide (\(\text{Cr(OH)}_3(s)\)). This treatment approach is attractive both because trivalent Cr is much less of a health hazard than hexavalent Cr (which is a carcinogen) and because the precipitated \(\text{Cr(OH)}_3(s)\) can be removed from the system by settling and/or filtration.

The dominant form of hexavalent Cr in mildly acidic, dilute wastes is as the bichromate ion, \(\text{HCrO}_4^-\). Reaction of this ion with \(\text{Fe}^{2+}\) (ferrous) ions can generate \(\text{Cr(OH)}_3(s)\) and \(\text{Fe(OH)}_3(s)\), as shown below:

\[
\text{HCrO}_4^- + 3 \text{Fe}^{2+} + 8 \text{H}_2 \text{O} \rightarrow 3 \text{Fe(OH)}_3(s) + \text{Cr(OH)}_3(s) + 5 \text{H}^+
\]

Assuming that the reaction rate is proportional to the first powers of the concentrations of \(\text{HCrO}_4^-\) and \(\text{Fe}^{2+}\), and defining \(k_2\) as the reaction rate constant in the rate expression for \(\text{HCrO}_4^-\), write the rate expressions for \(\text{HCrO}_4^-\), \(\text{Fe}^{2+}\), and alkalinity in terms of \(k_2\) and the species’ concentrations. (Note: each mole of \(\text{H}^+\) produced destroys one equivalent of alkalinity.)

Answer. The rates of reaction of the three constituents of interest are linked by the reaction stoichiometry. Given that \(k_2\) is defined as the rate constant for the reaction of \(\text{HCrO}_4^-\), the rate expressions are:
Elementary and Overall Reactions

The step-by-step sequence of molecular collisions that converts reactants to products is called the reaction mechanism, and each step in that sequence is called an elementary reaction. Thus, if a reaction \( A + B \rightarrow P \) occurs by a collision between one molecule of \( A \) and one molecule of \( B \) to form one molecule of \( P \), that reaction is elementary. For elementary reactions only, the reaction rate expression is related directly to the stoichiometry. Specifically, if the reaction \( A + B \rightarrow P \) is elementary, the reaction rate must be proportional to the chemical activities and/or concentrations of the reactants, as given by the following, equivalent expressions:

\[
\frac{r_A}{r_B} = -r_p = -k_A \gamma_A \gamma_B c_A c_B
\]  \hspace{1cm} (5a)

\[
= -k_A \gamma_A \gamma_B c_A c_B
\]  \hspace{1cm} (5b)

\[
= -k_A c_A c_B
\]  \hspace{1cm} (5c)

The term \( a_i \) represents the chemical activity of species \( i \), \( \gamma_i \) represents the activity coefficient of \( i \), and the \( k \) terms (\( k_A \) and \( k_A' \)) are referred to as rate constants, with \( k_A = k_A' \gamma_A \gamma_B \). The choice of whether to represent the rate expression in terms of chemical activities (Equation 5a) or concentrations (Equations 5b and 5c) (or, for that matter, as a mixture of concentrations and activities) is somewhat arbitrary. Use of concentration-based values is more common, but the activity-based values are more convenient in a few applications. In particular, if water is a reactant in an elementary reaction, it is common to write the rate expression using the activity of water (which is close to 1.0 under virtually all conditions of interest) rather than its concentration (55.5 mol/L). For reactions among dissolved species in ideal solutions (\( \gamma = 1.0 \) for all constituents), the numerical values of concentration and activity are identical, so the distinction between \( k \) and \( k' \) becomes unimportant; in non-ideal solutions, the values of both \( k \) and \( k' \) depend on the ionic strength of the solution.\(^3\) Unless otherwise specified, the ideal solution assumption is made throughout this text.

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\(^3\) The dependence of the rate constants can be explained and modeled, in large part, using the activated complex theory of reaction kinetics. This theory is outlined later in the chapter and is discussed in detail in most physical chemistry textbooks.
The idea that the rate of an elementary reaction is proportional to the concentrations of the reacting species should make some intuitive sense. Reactions occur by molecules colliding. Therefore, the rate at which reactions occur is expected to be proportional to the rate of collisions between the reacting constituents, which, in turn, is proportional to their respective concentrations.

The rate of collisions between dissolved molecules, and thus the maximum possible rate at which they can react with one another, can be estimated based on their diffusion coefficients. The mathematics of that analysis were first described by Smoluchowski in 1917, starting with the following equation for the rate of encounters (encounters per unit volume per unit time) of uncharged molecules:

\[
\text{Rate of Encounters} = 4\pi \left(\lambda_A + \lambda_B\right) \left(D_A + D_B\right) N_{\text{Av}} c_A c_B
\]  

(6)

(*check exponent on \(N_{\text{Av}.}\)) In this equation, \(N_{\text{Av}}\) is Avogadro’s number, and \(\lambda_i\) and \(D_i\) are the radius and diffusion coefficient, respectively, of molecule \(i\), and \(c_i\) is the concentration of \(i\) in moles per unit volume. If the molecules are assumed to behave as hard spheres moving through a continuum, the diffusion coefficients \(D_A\) and \(D_B\) can be related to the radii of the molecules through a relationship known as the Stokes-Einstein equation, in which case the rate of encounters becomes:

\[
\text{Rate of Encounters} = \frac{2RT}{3\mu} \left(2 + \frac{\lambda_A^2 + \lambda_B^2}{\lambda_A \lambda_B}\right) c_A c_B
\]  

(7)

where \(\mu\) is the solution viscosity.

The maximum possible rate of reaction between species \(A\) and \(B\) equals the rate at which they encounter one another. Thus, Equation 7 expresses the maximum rate of a bimolecular, elementary reaction between uncharged species. According to Equation 5c, the rate of any such reaction can be expressed as the product of a rate constant and the concentrations of the reacting species. Thus, the expression prior to the product \(c_A c_B\) in Equation 7, i.e.,

\[
\frac{2RT}{3\mu} \left(2 + \frac{\lambda_A^2 + \lambda_B^2}{\lambda_A \lambda_B}\right)
\]

can be interpreted as the maximum possible value of the rate constant \((k_{\text{max}})\) for a reaction between two uncharged species. In aqueous solutions at room temperature, this expression has a value on the order of \(10^{10}\) (mol/L)\(^{-1}\)s\(^{-1}\). The corresponding value for encounters and \(k_{\text{max}}\) can be up to about an

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4 An encounter is defined as an instance in which the two molecules are adjacent to one another. It is estimated that, each time dissolved molecules encounter one another in water at room temperature, they collide from 20 to 200 times before diffusing away.

5 The Stokes-Einstein equation is **. This equation is derived in many textbooks dealing with molecular motion in fluids. See, for example, *Diffusion*, by Cussler (**) or *Water Chemistry*, by Benjamin (McGraw-Hill, 2001).
order of magnitude larger if the reacting species are oppositely charged ions, and up to about two orders of magnitude lower if they are ions with like charges. Reactions that proceed at rates close to these maximum predicted values are said to be diffusion controlled.

Although the measured reaction rates of some proton-transfer (acid-base) reactions approach those estimated based on diffusion control, the vast majority of reactions of interest in water and wastewater treatment are slower by several orders of magnitude than would be predicted based on Equation 35. In such cases, the factor controlling the rate of the reaction is thought to be the energy of the collisions, rather than simply their frequency. That is, many collisions might occur, but relatively few of them are thought to be sufficiently energetic to lead to the rearrangement of chemical bonds needed to form the product. The rates of such reactions are referred to as being chemically controlled.

The reaction $2A \rightarrow P$ can be written equivalently as $A + A \rightarrow P$. Therefore, according to the above reasoning, if this reaction were elementary, the reaction rate of $A$ would be:

$$r_A = -k_A c_A = -k_A c_A^2$$  \hspace{1cm} (8)

Extending the reasoning to the case of a general elementary reaction $aA + bB \rightarrow pP$:

$$r_A = -k_A c_A^{a/b} c_B^b$$  \hspace{1cm} (9)

The rates of many elementary reactions in solution can be represented by expressions of the form: $r_A = -k_A c_A$. At first glance, such an expression would appear to suggest that the reaction proceeds in the absence of molecular collisions (because it depends on the concentration of a single species raised to the first power). A few reactions do indeed proceed at a rate that is governed by the speed of processes occurring within individual molecules, independent of their collisions with other molecules in the system. An important example of such a reaction is radioactive decay, a process that proceeds at the same rate regardless of intermolecular collision frequencies. However, in environmental engineering systems, and particularly in aquatic systems, elementary reactions that have a rate expression of the form $r_A = -k_A c_A$ occur via collisions with bulk solvent (i.e., water) molecules, and the rate expression shown actually represents a simplification of the true rate expression, which includes the activity of water. Thus, for instance, the true forward reaction rate of an acid dissociation process (HA + H₂O → H₃O⁺ + A⁻) might be $r_{HA} = -k_{HA} c_{HA} a_{H₂O}$, but when this expression is combined with the assumption that $a_{H₂O} = 1.0$, the result is $r_{HA} = -k_{HA} c_{HA}$.

**EXAMPLE 2**

The hydration of CO₂ to form H₂CO₃, as shown in the following reaction, is elementary and relatively slow.
\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]

The reaction rate expression can be represented as
\[r_{\text{H}_2\text{CO}_3} = k_{\text{hyd}}c_{\text{CO}_2(aq)},\]
with \(k_{\text{hyd}}\) equal to approximately 0.03 s\(^{-1}\). (This rate expression is a simplification of the more complete expression \(r_{\text{H}_2\text{CO}_3} = k_{\text{hyd}}c_{\text{CO}_2(aq)}a_{\text{H}_2\text{O}}\), based on the assumption that \(a_{\text{H}_2\text{O}} \approx 1.0\).) Determine the instantaneous rate of hydration in an ideal solution containing \(10^{-5}\) mol/L \(\text{CO}_2(aq)\). Give the result as the fraction of the \(\text{CO}_2(aq)\) that is being hydrated per second.

**Solution.** Substituting the initial values into the rate expression, the rate of hydration is:

\[
r_{\text{H}_2\text{CO}_3} = k_{\text{hyd}}c_{\text{CO}_2(aq)} = (0.03 \text{ s}^{-1}) \left(10^{-5} \text{ mol L}^{-1}\right) = 3.00 \times 10^{-7} \text{ mol L}^{-1}\text{s}
\]

Since the initial concentration of \(\text{CO}_2(aq)\) is \(10^{-5}\) mol/L, the fractional rate of hydration is

\[
\frac{3 \times 10^{-7} \text{ mol L}^{-1}\text{s}}{10^{-5} \text{ mol L}^{-1}} = 0.03 \text{ s}^{-1}, \text{ or } 3\% \text{ per second.}
\]

Although the discussion above provides a simple approach for assessing the dependence of reaction rates on reactant concentrations for elementary reactions, few net reactions of interest are in fact elementary; i.e., the products that can be detected and measured at the macroscopic scale are rarely formed directly from the reactants in the manner expressed by the overall stoichiometry. Rather, the reaction mechanism by which the final products are formed usually consists of two or more elementary reactions, so the overall, observable reactions are non-elementary. In fact, a completely rigorous analysis would indicate that a net reaction always represents a combination of at least two reactions, since any reaction that is proceeding forward (\(A \rightarrow B\)) is, in theory, simultaneously proceeding in the reverse direction (\(A \leftarrow B\)). In many situations, the reaction in one direction can be ignored, and the overall reaction is treated as though it were irreversible; the criteria for such an approximation are discussed in some detail later in the chapter.

In addition to participating in a given reaction in both the forward and reverse directions, a chemical species might participate in more than one independent reaction simultaneously, i.e., in multiple reactions with different stoichiometries. If the dominant reactions affecting a particular species cause it to be produced by one reaction and consumed by another, the reactions are said to be sequential, consecutive, or series reactions. For instance, a pair of sequential reactions would be expected to proceed if
either A or P were added to a solution in which the reactions $ A \leftrightarrow B \leftrightarrow P $ could occur. If the intermediate species in such a sequence were detectable, then the individual steps could be easily established, and the two individual reactions ($ A \leftrightarrow B $ and $ B \leftrightarrow P $) could be characterized independently. However, in many cases, the intermediate is a highly unstable species that is never present at a detectable level. In such cases, the overall reaction $ A \leftrightarrow P $ appears to be the only reaction occurring, and rate expressions can be developed that appear to fully describe the forward and reverse steps in that overall reaction. (The expressions are not, in fact, rigorously correct, but the errors might be undetectably small, being related to small changes in the concentration of B as the reaction proceeds.) In effect, the overall reaction $ A \leftrightarrow P $ can be treated as a single reaction in each direction. However, the rate expression for the overall reaction is not necessarily related to the stoichiometry in the simple way expressed by Equations 5, 8, and 9.

If the dominant reactions affecting a species cause it to be consumed in more than one reaction simultaneously, the reactions are said to operate in parallel and to be competitive for that reactant. For instance, if the reaction combination described above ($ A \leftrightarrow B \leftrightarrow P $) could occur, and if B were added to the solution instead of A or P, the two independent reactions (formation of A and formation of P) would be competitive for B, and the reactions might be re-written in a way that emphasized this competition:

$$ B \leftrightarrow A $$

$$ B \leftrightarrow P $$

In many cases, a group of reactions is sequential for some species and competitive for others. The above discussion points out that, although sequential and competitive reactions might appear to be quite different, in some cases they are simply two different views of the same reaction. As a result, they can and should be analyzed by the same mathematical formalism, without undue focus on identifying the category to which a given reaction belongs. To emphasize this basic similarity, combinations of reactions that simultaneously affect a group of chemical species are referred to simply as reaction networks in this text.

**Power Law Rate Expressions**

As is always the case for elementary reactions, the reaction rate expressions for many non-elementary reactions take the form of the product of a rate constant and the activities or concentrations of several components, each raised to some power, as follows:

$$ r_A = -k_A a_A^\alpha a_B^\beta $$

$$ r_A = -k_A c_A^\alpha c_B^\beta $$

where $ k_A = k_A^{\gamma_A \gamma_B} $. 

When the rate expression takes this simple form, the sum of the exponents ($\alpha + \beta$) is called the overall order of the reaction, and the reaction is said to be $\alpha$-order with respect to $A$ and $\beta$-order with respect to $B$. $\alpha$ and $\beta$ are not necessarily integers and are not necessarily the stoichiometric coefficients of $A$ and $B$ in the reaction. Many reactions have rate expressions that do not take this form; in such cases, one cannot speak of the reaction order.

It is important to understand the distinction between the exponents $\alpha$ and $\beta$ in this equation, and $a$ and $b$ in Equation 9. Specifically, $\alpha$ and $\beta$ are nothing more than empirical constants that fit a simple model equation to experimental data. If the equation fits the data adequately, then it provides a concise and convenient way to summarize those data, and we might use it to predict the system behavior under conditions that have not been studied experimentally; if it does not fit the data, then we have to search for another mathematical formulation that does. However, regardless of the outcome, the overall equation and the individual exponents have no inherent, fundamental interpretation. In particular, the equation is not limited to any specific type of reaction, and if $\alpha$ and $\beta$ happen to correspond to the stoichiometric coefficients of the reactants $A$ and $B$, respectively, that result might mean that the reaction is elementary, or it might be purely coincidental. On the other hand, if the reaction of interest is elementary, the exponents in Equation 10a and 10b must be the stoichiometric coefficients of the reactants in that reaction. As noted earlier, this situation is the exception rather than the rule for most reactions of interest in environmental engineering.

**EVALUATING REACTION RATE EXPRESSIONS**

The characterization of the kinetics of a reaction can be divided roughly into three components. The central component in most engineering studies is the empirical determination of the rate expression as a function of the reactants’ concentrations. The term reactants is used broadly here to refer to all species that participate in the elementary reactions leading to the overall reaction, even if those species do not appear in the net reaction stoichiometry. In this component of the analysis, empirical data describing the reaction rate under a few conditions are collected, and an overall rate expression is proposed and used to predict the reaction kinetics under different conditions. Those predictions are then tested experimentally, and the proposed rate expression is accepted or modified, as necessary, based on how well the predictions match the experimental results. Ideally, the cycling between experimental and modeling efforts continues until the rate expression successfully describes the kinetics over a wide range of conditions.

Characterization of the overall rate expression, without regard to the molecular level reaction mechanism, is usually sufficient for design purposes and is often all that can be accomplished in an engineering study. Nevertheless, a deeper understanding of the mechanism can be useful for interpreting or predicting the effects of various design choices. Therefore, a second component of the analysis is sometimes carried out, in which an attempt is made to describe the reaction mechanism, i.e., the elementary reactions that combine to yield the overall reaction. This component is closely linked to the first one, and the two are often used to inform one another. That is, the proposed overall rate expression is developed by postulating a reaction mechanism and applying
the concepts developed in the preceding section to describe the kinetics of those reactions. In carrying out this analysis, it is important to keep in mind that kinetics data provide only indirect support for a proposed mechanism; they can never prove unambiguously that a mechanism is correct.

The third component of the analysis of reaction kinetics includes characterizing the effects of factors other than reactant concentrations on reactions rates. The most important of these factors is usually temperature. The remainder of this chapter describes approaches for carrying out each of the three components described above.

**Determination of the Rate Expression and Prediction of Reaction Progress for Irreversible Reactions**

Generally, the information available for analysis of a rate expression includes the stoichiometry of the reaction and some experimental data describing the concentration versus time profiles for one or more species that participate in it. Such experiments may be conducted in any type of reactor. In the current analysis, it is assumed that the data are generated by studying the reaction in a well-mixed batch reactor. It is also assumed for simplicity that the conditions under which the data are collected assure that the reactions are approximately irreversible. In such a case, the mass balance reduces to Equation 2 \( \frac{dc_i}{dt} = r_i \). The data are usually analyzed by one of two techniques, referred to as the integral and differential methods, which are described next.

**Integral Methods: Rates Dependent on a Single Constituent**

The integral method consists of postulating a rate expression, substituting it into Equation 2, integrating, and comparing the predicted \( c_i \) versus \( t \) response to the experimental one. For instance, if we postulated that a reaction \( A \rightarrow B \) was first-order with respect to \( A \) and independent of the concentration of \( B \) (i.e., \( r_A = -k_A c_A \)), the differential and integrated forms of Equation 2 would be as follows:

\[
\frac{dc_A}{dt} = -k_A c_A \tag{11}
\]

\[
\int_{c_A(0)}^{c_A(t)} \frac{dc_A}{c_A} = -k_A \int_0^t dt \tag{12}
\]

\[
\ln c_A(t) - \ln c_A(0) = \ln \frac{c_A(t)}{c_A(0)} = -k_A t \tag{13a}
\]

\[
c_A(t) = c_A(0) \exp \left( -k_A t \right) \tag{13b}
\]

where \( c_A(t) \) is the concentration of \( A \) remaining at time \( t \), and \( c_A(0) \) is the initial concentration. The result is that the concentration of \( A \) decays exponentially over time, as
shown in Figure 3.1a for a reactant that is present at a concentration of 100 µmol/L at time zero. Thus, if we suspected that a reaction was first order with respect to A, we could plot the experimental data as \( \ln c_A(t) \) versus \( t \); if the plot was linear (as in Figure 3.1b), the slope would be identified as \( -k_1 \), and the reaction could be treated as first order. (Keep in mind that such a result would not prove that the reaction as written is an elementary reaction.) If the plot was not linear, the conclusion would be that the reaction rate expression was not the postulated one, and other rate expressions might be tried.

If the rate expression being tested is of the form \( r_A = k_A c_A^n \), the prediction of the concentration versus time profile follows the above derivation and is relatively straightforward; the differential and integrated equations for reactions that are of such a form are presented in Table 3.1. Some straightforward algebra allows the preceding results to be put in a form that can be used to solve directly for the final concentration as a function of initial concentration and reaction time. These expressions are also shown in Table 3.1.
Figure 3. 1. Two plots of the concentration vs. time profile for a first order, irreversible reaction with $c(0) = 100 \, \mu\text{mol/L}$ and $k_1 = 0.1 \, \text{min}^{-1}$: (a) Unmodified data ($c_A$ versus $t$); (b) Linearized data ($\ln c_A(t)$ versus $t$).
Table 3.1. Differential and integral forms of the reaction rate expression for an $n^{th}$ order reaction occurring in a batch reactor

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Differential form</th>
<th>Integral form</th>
<th>Solution after integration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>$r_A = \frac{dc_A}{dt} = -k_0$</td>
<td>$\int dc_A = -k_0 \int dt$</td>
<td>$c_A(t) - c_A(0) = k_0t$ (14a)</td>
</tr>
<tr>
<td>One</td>
<td>$r_A = \frac{dc_A}{dt} = -k_1c_A$</td>
<td>$\int \frac{dc_A}{c_A} = -k_1 \int dt$</td>
<td>$\ln \frac{c_A(t)}{c_A(0)} = -k_1t$ (13a)</td>
</tr>
<tr>
<td>Two</td>
<td>$r_A = \frac{dc_A}{dt} = -k_2c_A^2$</td>
<td>$\int \frac{dc_A}{c_A^2} = -k_2 \int dt$</td>
<td>$\frac{1}{c_A(t)} - \frac{1}{c_A(0)} = k_2t$ (15a)</td>
</tr>
<tr>
<td>Any $n \neq 1$</td>
<td>$r_A = \frac{dc_A}{dt} = -k_nc_A^n$</td>
<td>$\int \frac{dc_A}{c_A^n} = -k_n \int dt$</td>
<td>$\frac{1}{n-1}(c_A(t)^{1-n} - c_A(0)^{1-n}) = k_nt$ (16a)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Solution of rate equation for $c_A(t)$</th>
<th>Typical units for $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>$c_A(t) = c_A(0) - k_0t$</td>
<td>mol/L-s</td>
</tr>
<tr>
<td>One</td>
<td>$c_A(t) = c_A(0) \exp(-k_1t)$</td>
<td>$\frac{1}{s}$</td>
</tr>
<tr>
<td>Two</td>
<td>$c_A(t) = \left( \frac{1}{c_A(0)} + k_2t \right)^{-1}$</td>
<td>L/mol-s</td>
</tr>
<tr>
<td>Any $n \neq 1$</td>
<td>$c_A(t) = \left[ \left{ c_A(0) \right}^{1-n} + (n-1)k_nt \right]^{-1}$</td>
<td>$\left( \frac{mol}{L} \right)^{1-n} \frac{1}{s}$</td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

The oxidation of nitrite ion by monochloramine can proceed via the reaction shown below.

$$\text{NO}_2^- + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NH}_4^+ + \text{Cl}^-$$

In a wastewater solution containing 10 mg/L monochloramine at pH 7.5, the rate expression for this reaction can be approximated as

$$r_{\text{NO}_2^-} = -k_{\text{NO}_2^-}^{1.7}, \text{ with } k = 2.3 \left( \frac{\text{L}}{\text{mol}} \right)^{0.7} \text{ min}^{-1}. \text{ (a) If the wastewater initially}$$
contains 3x10^{-4} \text{ mol/L NO}_2^-, how much NO}_2^- would remain after 30 minutes of reaction in a well-mixed batch reactor? **stoichiometry

(b) How much time would be required for 90% of the NO}_2^- to be oxidized, if all other conditions were held constant?

**Solution.**

(a) Substituting values into the appropriate form of Equation 16b, the expression for the concentration of NO}_2^- remaining after 30 minutes is:

\[
c_{\text{NO}_2^-}(t) = \left[ \left( \frac{c_{\text{NO}_2^-}(0)}{k_n} \right)^{\frac{1}{1-n}} + (n-1)k_n t \right]^{\frac{1}{1-n}}
\]

\[
c_{\text{NO}_2^-}(30\text{min}) = \left[ \left( 3\times10^{-4} \text{ mol/L} \right)^{1.7} + (1.7-1) \left( 2.3 \text{ L}^{0.7} \text{ mol}^{-0.7} \text{-min} \right)(30\text{min}) \right]^{\frac{1}{1.7}}
\]

\[
= 2.41\times10^{-4} \text{ mol/L}
\]

(b) When 90% of the NO}_2^- has been oxidized, only 10% (or 3x10^{-5} \text{ mol/L}) remains. Using Equation 16a, the time required to achieve this amount of conversion is:

\[
t = \frac{1}{k_n (n-1)} \left( \{c_{\text{NO}_2^-}(t)\}^{\frac{1}{1-n}} - \{c_{\text{NO}_2^-}(0)\}^{\frac{1}{1-n}} \right)
\]

\[
= \frac{1}{2.3 \text{ L}^{0.7} \text{ mol}^{-0.7} \text{-min} \left( 1.7-1 \right)} \left[ \left( 3\times10^{-5} \text{ mol/L} \right)^{1.7} - \left( 3\times10^{-4} \text{ mol/L} \right)^{1.7} \right]
\]

\[
= 729 \text{ min}
\]

Based on the equations in Table 3.1, we could test whether a reaction was zero-order or second-order with respect to A by plotting c_A(t) or 1/c_A(t) versus t, respectively. If either plot was a straight line, the order of the reaction would be known, and the slope would indicate the rate constant. Similarly, as shown earlier, we could test the linearity of a plot of ln c_A(t) versus t to determine if a reaction were first order. However, in many cases n is not an integer. Using Equation 16 in conjunction with an undirected search for the value of n in such a case is tedious, at best, and is also unlikely to succeed. In such cases, n can often be determined based on the amount of time required for the concentration of A to be reduced to one-half of its initial value, i.e., the value of t when c_A(t) = 0.5c_A(0). Defining that time as the half-time, t_{1/2}, and substituting the expression
\( c_A(t_{1/2}) = 0.5c_A(t) \) into Equations 13 through 16 we obtain the relationships shown in Table 3.2.
Table 3.2. Expressions for the time required for the concentration of a substance to decrease to half of its initial value for $n$th order reactions occurring in a batch reactor.

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Integrated Rate Expression</th>
<th>Condition at $t_{1/2}$</th>
<th>Value of $t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$c_A(t) - c_A(0) = k_0t$</td>
<td>$0.5c_A(0) = k_0t_{1/2}$</td>
<td>$t_{1/2} = \frac{0.5}{k_0}c_A(0)$ (17)</td>
</tr>
<tr>
<td>1</td>
<td>$\ln \frac{c_A(t)}{c_A(0)} = -k_1t$</td>
<td>$\ln 0.5 = -k_1t_{1/2}$</td>
<td>$t_{1/2} = \frac{\ln 2}{k_1}$ (18)</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{c_A(t)} - \frac{1}{c_A(0)} = k_2t$</td>
<td>$\frac{1}{c_A(0)} = k_2t_{1/2}$</td>
<td>$t_{1/2} = \frac{1}{k_2c_A(0)}$ (19)</td>
</tr>
<tr>
<td>Any $n \neq 1$</td>
<td>$\frac{1}{n-1}\left{c_A(t)\right}^{1-n} - \left{c_A(0)\right}^{1-n} = k_nt$</td>
<td>$\frac{1}{n-1}\left{0.5c_A(0)\right}^{1-n} - \left{c_A(0)\right}^{1-n} = k_nt_{1/2}$</td>
<td>$t_{1/2} = \frac{2^{n-1} - 1}{k_n(n-1)}\left{c_A(0)\right}^{1-n}$ (20)</td>
</tr>
</tbody>
</table>
The equation for $t_{1/2}$ when $n \neq 1$ indicates that, for any reaction that has a rate expression of the form $r_A = k_n c_A^n$, with $n \neq 1$, the half-time is directly proportional to $\{c_A(0)^{1-n}\}$. Taking the logarithm of both sides of that equation, we obtain:

$$\log t_{1/2} = \log \left\{ \frac{2^{n-1} - 1}{k_n (n-1)} \{c_A(0)^{1-n}\} \right\}$$

$$= \log k^* + (1-n) \log c_A(0)$$

where $k^* = \frac{2^{n-1} - 1}{k_n (n-1)}$.

In addition, Equation 18 indicates that the value of $t_{1/2}$ for reactions with $n = 1$ is $\ln 2/k_1$; i.e., it is independent of $c_A(0)$. Formally, then, $\log t_{1/2}$ for reactions with $n = 1$, like $t_{1/2}$ for reactions with $n \neq 1$, can be written in the form shown on the right of Equation 22, except in this case $k^*$ would equal $\ln 2/k_1$.

Thus, although the half-time for a first order reaction cannot be computed using the same equation as is used for reactions with other values of $n$, Equation 22 applies for any $n^{th}$ order reaction. As a consequence, the hypothesis that the reaction rate is $n^{th}$ order with respect to a single species can be tested, and the value of $n$ can be determined, by plotting $\log t_{1/2}$ vs. $\log c_A(0)$. If the plot is linear, then the hypothesis is valid, and the slope equals $1-n$ (Figure 3.2). Furthermore, since the initial concentration defined as $c_A(0)$ need not truly be the concentration at the beginning of the experiment, several data points for a plot of $\log t_{1/2}$ versus $\log c_A(0)$ can be obtained from a single experiment. That is, one could choose several times during a test, define each time as $t = 0$ and the corresponding concentration as $c_A(0)$, and then determine how long it takes from that time for the concentration of $A$ in the system to decrease by one-half. Similarly, the choice of $c_A(t)/c_A(0) = 0.5$ is arbitrary; in theory, one could derive equally valid results for any choice of $c_A(t)/c_A(0)$. 


Figure 3.2. Logarithm of half-time as a function of initial concentration for irreversible reactions with rate expressions of the type \( r_A = -kc_A^n \), in batch reactors.

**EXAMPLE 4**

The following data were collected in a batch system in which the reaction \( A \rightarrow P \) was proceeding.

<table>
<thead>
<tr>
<th>( t, \text{ min} )</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_A, 10^{-4} M )</td>
<td>25</td>
<td>12.9</td>
<td>7.9</td>
<td>5.2</td>
<td>3.6</td>
<td>2.8</td>
<td>1.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

(a) Assuming that the rate expression is \( n^{\text{th}} \) order with respect to \( A \), find the value of \( n \).

(b) What is the rate constant?

(c) How much \( A \) will be present in solution after 60 minutes?

*Solution.* (a) A plot of \( c_A \) versus \( t \) is shown below (Figure Ex4-1).
According to the approach described above, we can determine the value of \( n \) by plotting \( \log t_{1/2} \) vs. \( \log c(0) \). To do so, we can pick several times during the experiment, define each as \( t = 0 \), and determine how long it takes for the concentration of \( A \) to decrease by 50%. This approach works fine for \( t < 10 \) minutes, but for later times, it is difficult to determine the half-time because of the flatness of the curve. If the data at \( t > 10 \) minutes are trustworthy, then we should make an effort to include them in the analysis. That can be done by plotting the data as \( \log c_A \) versus \( t \), and noting that a 50% decrease in \( c_A \) corresponds to a decrease of 0.3 units in the value of \( \log c_A \) (because \( \log 0.5 = -0.3 \)). The data for such a plot are shown below, and the plot is shown in Figure Ex4-2, from which it is clear that the logarithmic transformation makes the identification of \( t_{1/2} \) at \( t > 10 \) min much easier.

<table>
<thead>
<tr>
<th>( t ), min</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log c_A )</td>
<td>−2.60</td>
<td>−2.89</td>
<td>−3.10</td>
<td>−3.28</td>
<td>−3.44</td>
<td>−3.55</td>
<td>−3.80</td>
<td>−4.00</td>
</tr>
</tbody>
</table>
**Figure Ex4-2. Data from Figure Ex4-1 replotted as log \( c \) versus \( t \).**

Drawing a smooth curve through the data in Figure Ex4-2 and choosing several points throughout the experiment as starting points, the following table can be developed.

<table>
<thead>
<tr>
<th>( t_1 )</th>
<th>( c_A(t_1) )</th>
<th>( \log c_A(t_1) )</th>
<th>( \log c_A(t_2) )</th>
<th>( t_2 )</th>
<th>( t_{1/2} = (t_2 - t_1) )</th>
<th>( \log(t_{1/2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.50x10(^{-3})</td>
<td>-2.60</td>
<td>-2.90</td>
<td>2.2</td>
<td>2.2</td>
<td>0.34</td>
</tr>
<tr>
<td>1.5</td>
<td>1.58 x10(^{-3})</td>
<td>-2.80</td>
<td>-3.10</td>
<td>4.0</td>
<td>2.5</td>
<td>0.40</td>
</tr>
<tr>
<td>3.0</td>
<td>1.04 x10(^{-3})</td>
<td>-2.98</td>
<td>-3.28</td>
<td>6.4</td>
<td>3.4</td>
<td>0.53</td>
</tr>
<tr>
<td>5.0</td>
<td>6.49 x10(^{-4})</td>
<td>-3.19</td>
<td>-3.49</td>
<td>9.2</td>
<td>4.2</td>
<td>0.62</td>
</tr>
<tr>
<td>8.0</td>
<td>3.90 x10(^{-4})</td>
<td>-3.41</td>
<td>-3.71</td>
<td>13.4</td>
<td>5.4</td>
<td>0.73</td>
</tr>
<tr>
<td>11.0</td>
<td>2.59 x10(^{-4})</td>
<td>-3.59</td>
<td>-3.89</td>
<td>17.8</td>
<td>6.8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The values in the first three columns above identify the various initial conditions that we will consider. The first column shows the times that we will define as \( t = 0 \); we refer to each of these times as \( t_1 \). The second and third columns show the concentrations \( (c) \) and \( \log c \) values corresponding to each value of \( t_1 \).

We designate the half-time for each initial condition (i.e., for each \( c_A(t_1) \) value) as \( t_2 \). At \( t = t_2 \), \( c_A \) must equal 0.5\( c_A(t_1) \), so \( \log c_A(t_2) = \)
\[
\log 0.5 + \log c_A(t_A) = -0.3 + \log c_A(t_A). \]
These \( \log c_A(t_2) \) values are shown in the fourth column. We then use Figure Ex4-2 to estimate the value of \( t_2 \) from the known \( \log c_A(t_2) \); these values are shown in the fifth column. Finally, the various \( t_{1/2} \) values are computed as \( t_2 - t_1 \).

A plot of \( \log t_{1/2} \) versus \( \log c_A(t_1) \) is shown in Figure Ex4-3. The data can be reasonably approximated by a straight line with a slope of \(-0.5\), indicating that the reaction can be modeled as an \( n^{th} \) order reaction with \( n = 1.5 \).

\[
y = -0.51x - 1.00
\]

Figure Ex4-3. Log of half-time vs. log of initial concentration for various starting points.

(b) The \( \log t_{1/2} \) vs. \( \log c_A(0) \) plot developed above is, in essence, a plot of Equation 22 for the example system. Therefore, \( y \)-intercept of the plot can be equated with \( \log k^* \). (Note that the intercept is at the point where \( \log c_A(0) = 0 \), which is far to the right of the data shown in Figure Ex4-3.) In the current case, that value is \( \log k^* = -1.00 \), so \( k^* = +0.10 \). The value of \( k_n \) can then be found from:

\[
k_n = \frac{2^{n-1} - 1}{k^* (n-1)}
\]
The computed value of $k_n$ is 8.28, with dimensions of $(\text{L/mol})^{0.5}\cdot\text{min}^{-1}$.

(c) According to Equation 16b, we can find the concentration remaining at any time by:

$$c_A(t) = \left[\left\{c_A(0)\right\}^{1-n} + (n-1)k_n t\right]^{1-n}$$

For the given conditions, $c_A(0)$ is $2.5\times10^{-3} \text{ mol/L}$, $n$ is 1.5, and $k_n$ is $8.28 \text{ (L/mol)}^{0.5}\cdot\text{min}^{-1}$, yielding a value of $c_A(60 \text{ min}) = 1.39\times10^{-5} \text{ mol/L}$.

**Integral Methods: Rates Dependent on a Multiple Constituents**

The methods presented above can be used to determine the reaction order and the rate constant for rate expressions of the form $r_A = k_n c_A^n$. However, as noted previously, many rate expressions include the concentrations of more than one reactant. What can be done to characterize those rate expressions?

A reasonable first hypothesis might be that the rate expression for a reaction $aA + bB \rightarrow pP$ has the form:

$$r_A = -k_n c_A^\alpha c_B^\beta c_P^\gamma$$

(23)

In such a case, if the reaction were taking place in a batch reactor, the mass balance on $A$ could be written and simplified to show the expected change in the concentration of $A$ over time:

$$\frac{dc_A}{dt} = -k_n c_A^\alpha c_B^\beta c_P^\gamma$$

(24)

One could then use the stoichiometric relationships to express $c_B$ and $c_P$ in terms of $c_A$. For instance, if the stoichiometry were $A + 2B \rightarrow 2P$, then two moles of $B$ would disappear and two moles of $P$ would appear for each mole of $A$ disappearing. As a result, assuming all concentrations were expressed in moles per liter, we could write:

$$c_B(t) - c_B(0) = 2 (c_A(t) - c_A(0)) = 2\Delta c_A$$

(25a)

$$c_P(t) - c_P(0) = -2 (c_A(t) - c_A(0)) = -2\Delta c_A$$

(25b)

Assuming the initial concentrations of all three species were known, we could solve Equations 25a and 25b for $c_B(t)$ and $c_P(t)$, respectively, and substitute those expressions into Equation 24 to eliminate $c_B$ and $c_P$ from the rate expression:
\[ \frac{dc_A}{dt} = -k_A c_A^\alpha (c_B(0) - 2\Delta c_A)^\beta (c_P(0) + 2\Delta c_A)^\gamma \] (26)

However, the resulting expression still contains three unknown constants (\(\alpha\), \(\beta\), and \(\gamma\)) and would be difficult to integrate analytically, even if those constants were known. One way to avoid this complication is to start with such high concentrations of species \(B\) and \(P\) that the change in their concentrations is negligible compared to their initial concentrations. In that case, the following approximations would apply:

\[ \frac{dc_A}{dt} \approx -k_A c_A^\alpha (c_B(0))^\beta (c_P(0))^\gamma \] (27)

\[ \frac{dc_A}{dt} \approx -k_A' c_A^\alpha \] (28)

where \(k_A' = k_A (c_B(0))^\beta (c_P(0))^\gamma\). Although the values of \(\beta\) and \(\gamma\) in Equation 27 are not necessarily known, they are constant, and, since \(c_B(0)\) and \(c_P(0)\) are also constant, the product \((c_B(0))^\beta (c_P(0))^\gamma\) can be incorporated into \(k_A'\), as shown. In this way, the reaction becomes pseudo-\(\alpha\)-order overall and can be integrated and analyzed using the equations in Table 3.1. Once the reaction order with respect to \(A\) was known, similar experiments could be conducted using great excesses of \(A\) and \(B\), or \(A\) and \(P\), to determine the reaction orders with respect to the other two species. Note that even if the dependence on \(c_B\) and \(c_P\) is not of the power-law form, this technique can still be used to isolate and evaluate the dependence of the reaction rate on \(c_A\), if that dependence is consistent with a power-law function.

**EXAMPLE 5**

Oxidation of sulfide in natural waters is an extremely complex process, due in part to the large number of intermediate products and side reactions. For instance, in addition to sulfate, the products of the reaction might include \(S^0\), \(SO_3^{2-}\), \(S_2O_3^{2-}\), and several other sulfur species. Nevertheless, Chen and Morris (EST 6, 529 (1972)) reported good agreement of oxidation rates with the empirical equation:

\[ r_{S(II)} = k c_S^{1.34} c_{O_2}^{0.56} \]

where \(S\) is the total sulfur in the \(-II\) oxidation state, i.e.,

\[ c_S = c_{H_2S} + c_{HS^-} + c_{S^{2-}}. \]

For a solution at pH 7.5, \(k\) was reported to be 11.97 (mol/L)\(^{-0.9}\)h\(^{-1}\). A batch system contains 2.0 x 10\(^{-4}\) mol/L total dissolved sulfide and is buffered at pH 7.5. Assuming the overall reaction is
HS\(^-\) + 2 O\(_2\) ⇌ SO\(_4^{2-}\) + H\(^+\), determine the percentage of the initial total sulfide that reacts over a 400-h reaction period for the following initial concentrations of dissolved oxygen:

a) 4.0x10\(^{-3}\) mol/L (much more O\(_2\) than is required to oxidize all the sulfide)

b) 4.0x10\(^{-4}\) mol/L (exactly the concentration of O\(_2\) that is required to oxidize all the sulfide)

c) 3.0x10\(^{-4}\) mol/L (less O\(_2\) than is required to oxidize all the sulfide)

Solution. a) For \(c_S(0) = 2.0x10^{-4}\) mol/L, the maximum amount of O\(_2\) that could react is 4.0x10\(^{-4}\) mol/L, or 10% of \(c_O(0)\). Under these circumstances, it seems reasonable to assume that \(c_O\) is approximately constant throughout the experiment at the value \(c_O(0)\). Then, noting that, for a batch system, the rate of oxidation equals the rate of change of concentration of \(c_S\):

\[
\frac{dc_S}{dt} = \frac{1.34}{0.56} \cdot (-0.34) \cdot c_S - \frac{1.34}{0.56} \cdot c_O\]

where \(k' = k \cdot \left(c_O(0)^{0.56} = \left(11.97 \text{ (mol/L)}^{-0.9} \text{ h}^{-1}\right) \left(4 \times 10^{-3} \text{ (mol/L)}\right)^{0.56} = 0.543 \text{ (mol/L)}^{-0.34} \text{ h}^{-1}\right)\). The above expression is the rate expression for a pseudo-\(n\)th order reaction occurring in a batch system. The solution to the equation, after integration, is given by Equation 16b in Table 3.1, with \(n = 1.34\). Plugging in the appropriate values for the current problem, we obtain:

\[
c_A(t) = \left[\left(c_A(0)\right)^{1-n} + (n-1)k_n t \right]^{1-n} \quad \text{(16b)}
\]

\[
c_s(400) = \left[\left(c_s(0)\right)^{-0.34} + 0.34 \cdot \frac{0.543}{\text{h}} \left(400 \text{ h}\right) \right]^{-0.34}
\]

\[
= 1.67 \times 10^{-6} \text{ mol/L}
\]
\[
\text{% reacted} = \frac{2.0 \times 10^{-4} \text{ mol L}^{-1} - 1.67 \times 10^{-6} \text{ mol L}^{-1}}{2.0 \times 10^{-4} \text{ mol L}^{-1}} \times 100\%
\]

\[
= 99.2\%
\]

Two moles of O\(_2\) are consumed for each mole of S oxidized, so the amount of O\(_2\) reacted is \((0.992)(2.0 \times 10^{-4} \text{ mol/L})(2)\), or \(3.97 \times 10^{-4} \text{ mol/L}\). This is about 10% of the initial O\(_2\) concentration, so the assumption of approximately constant O\(_2\) is reasonable. If we wanted to be more accurate, we could re-solve the problem using an average, but still constant O\(_2\) concentration of \(0.95c_{O_2}(0)\), or to be as accurate as possible, we could consider the O\(_2\) concentration to vary over time, as described in part c below.

b) The key to solving the problem for the case where \(c_{O_2}(0) = 2c_S(0)\) is to note that, by stoichiometry, the amount of O\(_2\) consumed \((-\Delta c_{O_2})\), is twice the amount of S consumed \((-\Delta c_S)\). Thus,

\[
\Delta c_{O_2} = 2\Delta c_S
\]

\[
c_{O_2}(t) - c_{O_2}(0) = 2(c_S(t) - c_S(0))
\]

Substituting the initial values, we obtain:

\[
c_{O_2}(t) - 4 \times 10^{-4} \text{ mol L}^{-1} = 2\left( c_S(t) - 2 \times 10^{-4} \text{ mol L}^{-1} \right)
\]

\[
c_{O_2}(t) = 2c_S(t)
\]

That is, since the initial O\(_2\) and S concentrations are in the stoichiometric ratio, there is a very simple relationship between \(c_{O_2}\) and \(c_S\) throughout the course of the reaction. Substituting this relationship into the general rate equation:

\[
-\frac{dc_S}{dt} = k c_S^{1.34} c_{O_2}^{0.56}
\]

\[
= k c_S^{1.34} (2c_S)^{0.56}
\]

\[
= 2^{0.56} k c_S^{1.90} = k' c_S^{1.90}
\]
where \( k'' = 2^{0.56} \times 11.97 \left( \text{mol/L} \right)^{-0.9} \frac{1}{\text{h}} = 17.6 \left( \text{mol/L} \right)^{-0.9} \frac{1}{\text{h}} \)

Once again, we have a pseudo-\( n \)th order reaction, in this case with \( n = 1.90 \), so we can again invoke Equation 16b in Table 3.1. The result is:

\[
c_s(400) = \left[ (c_s(0))^{-0.90} + 0.90 \left( 17.6 \left( \text{mol/L} \right)^{-0.90} \frac{1}{\text{h}} \right)(400 \text{ h}) \right]^{\frac{1}{-0.90}}
\]

\[
= 4.31 \times 10^{-5} \text{ mol/L}
\]

amount reacted = \((2.0 \times 10^{-4} - 4.31 \times 10^{-5})\text{mol/L} = 1.57 \times 10^{-4} \text{ mol/L}
\]

fraction reacted = \(1.57 / 2.0 = 0.78 = 78\%\)

Note that the extent of oxidation is considerably less than in part \( a \) because the concentration of \( \text{O}_2 \) throughout the reaction period is less in this case.

c) In this case, the reactants are not present in their stoichiometric ratio, and neither reactant can be approximated to be constant during the course of the reaction. The differential equation cannot be solved analytically, but a numerical solution is possible. Taking small time steps, the amounts of \( \text{S} \) and \( \text{O}_2 \) consumed during each step can be approximated from the rate expression:

\[
- \frac{dc_s}{dt} = k c_s^{1.34} c_{O_2}^{0.56}
\]

\[
\Delta c_s \approx -k c_s^{1.34} c_{O_2}^{0.56} \Delta t
\]

\[
\Delta c_{O_2} = 2 \Delta c_s
\]

Based on a spreadsheet analysis using 1-h time steps and the recursive equation \( c_s(t + \Delta t) = c_s(t) + \Delta c_s \), the course of the reaction is followed. The concentrations of \( \text{S} \) and \( \text{O}_2 \) as a function of time are shown in Figure Ex5-1 below. After 400 h, 69\% of the sulfide has reacted.
The preceding discussion and example suggest various ways in which the dependence of the rate expression on individual reactant concentrations might be assessed. Most of these methods succeed only in cases where the dependence of the reaction rate on the reactant of interest is of the power-law form; the effect of other, non-power-law constituents can be eliminated by causing them to be present in great excess, but the rate dependence on those reactants cannot be assessed directly by the methods presented. The dependence of the reaction rate on the concentrations of such constituents can only be determined by trial and error. Often, even if the dependence does not follow a power-law expression over the entire concentration range of interest, the methods outlined above can be used to approximate the effect of a given species by a power-law expression over certain ranges. For instance, the rate expression \( r_A = \frac{k_1 c_A c_B}{k_2 + c_A} \) can be approximated as first order with respect to species \( A \) if \( c_A \ll k_2 \), and zero order with respect to \( A \) if \( c_A \gg k_2 \).\(^6\) In other cases, it might be necessary to use different rate equations to characterize different ranges of \( c \).

\(^6\)This rate expression, commonly referred to as the Michaelis-Menten expression, has special significance in biological waste treatment processes and is derived later in this chapter.
Differential Methods

Differential methods for analyzing reaction rate expressions are very similar to integral methods, except that they rely on analysis of $dc_A/dt$, rather than $c_A$, as a function of time or reactant concentration. These methods are generally somewhat less reliable than integral methods, because the rate of change of a constituent is usually more difficult to measure than its absolute concentration, although modern instrumentation comes close to eliminating this drawback for many constituents. In any case, differential analysis is sometimes the only acceptable choice. For instance, if the products from a reaction alter its rate, and if one is interested in the reaction rate in the absence of product, the initial reaction rate could be evaluated in experiments at several different initial reactant concentrations. To minimize the effect of product on the reaction rate, each experiment might have to be terminated shortly after it began, so the only data available would be the initial rate of reaction as a function of initial reactant concentration. Hypothesized rate expressions could be tested by comparing the data with the appropriate differential form of the rate expression.

For example, if the hypothesis is that the rate expression is of the form $r_A = -k_n c_A^n$, and the experiment is conducted in a batch system (so $r_A = dc_A/dt$), the logarithm of the absolute value of the experimental reaction rate could be plotted against the logarithm of the initial concentration. If the hypothesized rate expression were correct, the result would be a straight line of slope $n$ and intercept $\ln k_n$:

$$\frac{dc_A}{dt} = -k_n c_A^n$$  \hspace{1cm} (29)

$$\ln \left( -\frac{dc_A}{dt} \right) = \ln k_n + n \ln c_A$$  \hspace{1cm} (30)

EXAMPLE 6

Luthy and Bruce (EST 13, 1481-1487, 1979) studied the interactions of cyanide, sulfide, and thiocyanate as part of an investigation of the treatability of wastewater from coke manufacturing and iron making. In their study of the reaction between polysulfide ($S_xS^{2-}$) and cyanide ($CN^-$) to form a smaller polysulfide molecule ($S_{x-1}S^{2-}$) and thiocyanide ($SCN^-$), they used the initial rate method to minimize the effects of the reaction products on reaction kinetics. An idealized, hypothetical reaction of this sort is shown below.

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^-$$

The data from an experiment at pH 10 are shown in Figure Ex6-1, with rates computed from the thiocyanide production during a 5-minute period. In each experiment, one of the reactant concentrations was fixed and the
other was varied (as indicated in the figure legend), and the rate of SCN$^-$ formation was monitored. Assuming that the reaction rate is a power law function of the concentrations of the reactants, estimate the rate constant and the reaction order with respect to each reactant.

**Figure Ex6-1. Initial rate of SCN$^-$ formation at pH 10, as a function of polysulfide or cyanide concentration.** After Luthy and Bruce (1979).

**Solution.** The two lines shown indicate the reaction rate as a function of the poly-S concentration for a fixed total cyanide concentration (through the triangles) and as a function of the total cyanide concentration for a fixed poly-S concentration (through the squares). The fact that both data sets can be fit with straight lines on a log-log plot confirms that the rate expression is of the form:

\[ r_{SCN^-} = k c_{CN}^a c_{S,S_int}^b \]

The slopes of the two lines in the graph indicate that the reaction is approximately 0.51 order with respect to total cyanide and 0.87 order with respect to polysulfide. Each data point shown provides an independent set of $c_{CN_{int}}$, $c_{S,S_int}$, and $r_{SCN^-}$ values that can be used in conjunction with the above rate expression to evaluate $k$. By plotting $r_{SCN^-}$ vs. $c_{CN_{int}}^a c_{S,S_int}^b$, with $a = 0.51$ and $b = 0.87$ (Figure Ex6-2), can determine $k$ as the best-fit value of the slope, equal in this case to 0.27 (mol/L)$^{-0.38}$/min.
As shown above, the half-time of a reaction is often a useful quantity for analyzing the rate expression. This value gives a rough indication of the time frame over which the reaction proceeds. For instance, if a reaction has a half-time of one day, and the time available for the reaction to proceed is only a few minutes, then one can safely assume that the extent of reaction will be very small. At the other extreme, over the course of a few weeks, the reaction would probably proceed nearly to its endpoint (either complete disappearance of reactant or equilibrium between reactants and products).

The time required for a reaction to proceed a significant extent toward its final endpoint is called the characteristic reaction time, $t_{\text{char}}$. Because “significant” is an imprecise term, the quantitative definition of the characteristic time is somewhat arbitrary; however, since the concept is used only to give a rough idea of how much the reaction proceeds in a given situation, this arbitrariness poses no major problem. Although the half-time of a reaction would be an acceptable definition of the characteristic time, the most commonly used definitions correspond to slightly more than 50% reaction, at least for first order reactions. Defining $c(\infty)$ as the concentration of the reactive substance that would be present after an infinite amount of time passed, the most common definitions of the characteristic time are:
• **Definition 1**: the time required for the difference between the instantaneous concentration \( c(0) \) and the ultimate concentration \( c(\infty) \) to be reduced to \( 1/e \) of its initial value in a batch reactor, i.e., the time at which \( \left| c(t) - c(\infty) \right| \) equals \( \frac{1}{e} [c(0) - c(\infty)] \).

• **Definition 2**: the time that would be required for the concentration of the reactive substance to reach its ultimate value \( c(\infty) \) in a batch reactor if the reaction rate stayed at its initial value continuously.

Characteristic times based on the first definition can be computed for irreversible decay reactions (for which \( c(\infty) \) is approximately zero) using the equations in Table 3.1. Since the initial rate of a reaction can be determined from the rate expression and the initial reactant concentrations, the calculation of the characteristic time according to the second definition is also straightforward. The resulting equations for computing the characteristic time of irreversible reactions with power-law rate expressions are shown in Table 3.3.

Table 3.3. Characteristic Times of Irreversible \( n^{th} \) Order Reactions

<table>
<thead>
<tr>
<th>Value of ( n ) in ( r = k_n c^n )</th>
<th>( t_{\text{char}} ) (Definition 1)</th>
<th>( t_{\text{char}} ) (Definition 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 0 )</td>
<td>( \frac{c_A(0)}{k_0} (1-e) )</td>
<td>( \frac{c_A(0)}{k_0} )</td>
</tr>
<tr>
<td>( n = 1 )</td>
<td>( k_1^{-1} )</td>
<td>( k_1^{-1} )</td>
</tr>
<tr>
<td>( n = 2 )</td>
<td>( \frac{e-1}{k_2 c_A(0)} )</td>
<td>( \frac{1}{k_2 c_A(0)} )</td>
</tr>
<tr>
<td>( n \neq 1 )</td>
<td>( \frac{e^{n-1} - 1}{n-1} )</td>
<td>( \frac{1}{k_n [c_A(0)]^{n-1}} )</td>
</tr>
</tbody>
</table>

**EXAMPLE 7**

(a) Plot concentration versus time profiles for irreversible reactions with the following rate expressions: \( r_1 = -k_1 c \) and \( r_2 = -k_2 c^2 \), with \( k_1 = 0.015/\text{min} \) and \( k_2 = 10^{4.0} \text{ L/mol-min} \), respectively. For each reaction, consider \( c(0) \) values of \( 10^{-3} \) and \( 10^{-6} \text{ mol/L} \).

(b) Compute characteristic reaction times for the reactions described in part a, using each of the definitions given above and each initial condition specified. Also, determine the fraction of the constituent that remains after 1, 2, and 5 characteristic times have elapsed.
Solution.

(a) The concentration vs. time profiles for the various systems can be computed with Equations 13b and 15b for the first and second order reaction, respectively. The results are shown in Figure Ex7-1.

\[ k_1 = 0.015 \text{ min}^{-1}; \quad k_2 = 10^{4.0} \text{ L/mol-min.} \]

Figure Ex7-1. Fraction of initial reactant remaining as a function of time for first and second order, irreversible reactions taking place in a batch reactor.

(b) The characteristic time for each case of interest can be computed using the equations in Table 3.3; the results are shown in Table Ex7-1. Several points are worth noting about these results. First, the characteristic time for the first order reaction is independent of \( c(0) \) and is the same when computed according to either definition. By contrast, the characteristic time for the second order reaction (and, in fact, for all reaction orders other than 1) depends strongly on \( c(0) \) and also differs when calculated according to the two definitions of \( t_{\text{char}} \). In the current example, \( t_{\text{char}} \) becomes dramatically shorter when \( c(0) \) is larger. On the other hand, although the absolute value of \( t_{\text{char}} \) for the second order reaction changes dramatically when \( c(0) \) changes, the fractional conversion of the reactant after 1, 2, or 5 characteristic times have elapsed is independent of \( c(0) \).

Finally, although the fractional conversion of the reactant after a given number of characteristic reaction times does depend on the details of the rate expression, it is
clear that a significant fraction of the original concentration remains after 1 or 2 characteristic times have elapsed, whereas the reactant is substantially depleted after 5 characteristic times have elapsed.

Table Ex7-1. Characteristic Times of Irreversible First and Second Order Reactions

<table>
<thead>
<tr>
<th>Reaction Order $n$</th>
<th>$c(0)$, mol/L</th>
<th>$-r(0)$, mol/L-min</th>
<th>Characteristic Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Def # 1</td>
</tr>
<tr>
<td>1</td>
<td>$10^{-3}$</td>
<td>$5 \times 10^{-6}$</td>
<td>66.7</td>
</tr>
<tr>
<td>1</td>
<td>$10^{-6}$</td>
<td>$5 \times 10^{-9}$</td>
<td>66.7</td>
</tr>
<tr>
<td>2</td>
<td>$10^{-3}$</td>
<td>$10^{-2}$</td>
<td>0.172</td>
</tr>
<tr>
<td>2</td>
<td>$10^{-6}$</td>
<td>$10^{-8}$</td>
<td>172</td>
</tr>
</tbody>
</table>

In a well-mixed batch reactor

The utility of the $t_{char}$ concept is that it provides a simple, unifying framework for comparing and predicting the progress of vastly different reactions (reaction orders, rate constants, rate expressions, and initial conditions) and for understanding the time frames in which a reaction can be considered to have proceeded either a negligible amount or nearly to completion. A reaction time equal to $3t_{char}$ is a commonly used criterion for making the latter assumption, but, as shown in Table 3.3 and Example 7, substantially longer times than $3t_{char}$ might be required for the assumption to be valid in batch systems if the reaction order is greater than 1.

Characteristic times can also be defined for physical systems such as reactors, and for transport processes such as diffusion and dispersion. Comparison of the characteristic times of various processes affecting a constituent is a powerful tool for understanding its behavior, and such comparisons are made for increasingly complex systems in subsequent chapters.

**EXAMPLE 8**

Assume the reactions described in Example 7 are occurring in a continuous flow system with a hydraulic residence time of 1.0 minute. Evaluate qualitatively whether the first and second order irreversible reactions...
with \( c(0) = 10^{-6} \text{ mol/L} \) or \( 10^{-3} \text{ mol/L} \) would proceed to a significant extent, based on their characteristic reaction times.

**Solution.** The characteristic times of the various reactions are given in Table Ex7-1. The characteristic reaction times for the first order reaction with either value of \( c(0) \) and for the second order reaction with \( c(0) = 10^{-6} \text{ mol/L} \) are >100 min. Since the average amount of time that aliquots of influent spend in the reactor is less than one one-hundredth of the characteristic reaction time, the reactions would probably proceed to a negligible extent in the reactor. By contrast, for the second order reaction with \( c(0) = 10^{-3} \text{ mol/L} \) \( (t_{\text{char}} < 0.2 \text{ min}) \), the reactant would be very substantially depleted. Techniques for computing the exact extent of conversion in various types of reactors are presented in Chapter 4.

### Analysis of Multiple Simultaneous Reactions

The preceding section describes approaches that might allow one to determine the rate expression for an overall, irreversible reaction. Such a reaction might be elementary, or it might represent a network of linked elementary reactions that together can be described by a single overall rate expression. In this section, two types of linked reactions – reversible reactions and sequential reactions – are analyzed. In addition to introducing a key concept related to sequential reactions (the rate-limiting step), the analysis illustrates the conceptual basis for complex rate expressions and the wide range of overall expressions that can result from combinations of relatively simple reactions.

#### Reversible Reactions

**Reversibility of Reactions and its Relation to Chemical Equilibrium**

All chemical reactions are reversible, at least to some extent; a reaction that can proceed along a given pathway can, in all cases, follow the identical path in the opposite direction. If a reaction were truly irreversible, it would proceed until at least one of the reactants was completely depleted, and the equilibrium constant for the reaction would be infinite. No such reaction is known, although some reactions do approach this limit. Rather, reactions proceed until they reach an equilibrium condition, wherein all reactants and products are present, but there is no net driving force for the reaction to proceed in either direction. Thus, when a chemical reaction is at equilibrium, there is no net generation of the corresponding reactants or products by that reaction.

The quantitative representation of chemical equilibrium is the equilibrium constant expression, i.e., the ratio, in a system that has attained equilibrium, of the chemical activities of the products divided by those of the reactants, with each term raised to a power corresponding to its stoichiometric coefficient. The calculation of equilibrium constants from thermodynamic data and the determination of the equilibrium condition of a system are central components of water chemistry courses and are described in many textbooks. Note that the term equilibrium and the corresponding constant can be applied only to a reaction and not to an individual species.
The concept of chemical equilibrium is connected to that of reaction reversibility, because equilibrium is attained when the forward and reverse reactions proceed at equal rates, thereby preventing any net change in the concentrations of reactants or products. Therefore, it is not surprising that the equilibrium constant for a reaction can be derived from kinetics considerations. For instance, if the following forward and reverse reactions are elementary, and if, for the system under study, they are the only reactions affecting the concentration of \( A \), then the net reaction rate of \( A \) is given by Equation 31:

\[
aA + bB \xrightleftharpoons{k_{AP}}^{k_{PA}} pP + rR
\]

\[
r_A = -k_{AP}'(a_A)^a(a_R)^b + k_{PA}'(a_P)^p(a_R)^r
\]  

(31)

At equilibrium, the magnitudes of the forward and reverse reaction rates are equal, so:

\[
k_{AP}'(a_{A,eq})^a(a_{R,eq})^b = k_{PA}'(a_{P,eq})^p(a_{R,eq})^r
\]  

(32)

\[
\frac{k_{AP}'}{k_{PA}'} = \frac{(a_{P,eq})^p(a_{R,eq})^r}{(a_{A,eq})^a(a_{B,eq})^b}
\]  

(33)

where the subscript \( eq \) is included in the activity terms to indicate that Equations 32 and 33 are valid only at equilibrium. Since the right-hand side of Equation 33 is defined as the equilibrium constant for the reaction, the equation can be written as:

\[
\frac{k_{AP}'}{k_{PA}'} = K_{eq}
\]  

(34)

Equation 34 indicates that the equilibrium constant for any elementary reaction equals the ratio of the activity-based forward and reverse rate constants. Since equilibrium constants are defined in terms of chemical activities, this is one situation in which the distinction between concentration-based and activity-based rate constants is important. As noted earlier, if all the reactants are ideal solutes, the activity-based and concentration-based rate constants are identical; in such a case, the equilibrium constant would also equal the ratio of forward and reverse concentration-based rate constants \( k_{AP}/k_{PA} \).

In the above analysis, it is assumed that \( A \) does not participate in any reactions other than the one shown, so equilibrium is the condition where \( r_A = 0 \). In general, however, \( r_A \) describes an entire reactive system and includes the rates of formation of \( A \) by all

\[\text{In this text, rate constants are, in general, subscripted to indicate direction and reversibility of the reaction. For instance, if the reaction is considered irreversible (}A\rightleftharpoons P\), the rate constant is written as \( k_A \). If it is reversible (}A\rightleftharpoons P\), the rate constants for the forward and back reactions are written as \( k_{AP} \) and \( k_{PA} \), respectively.\]
reactions in that system. Therefore, the condition \( r_A = 0 \) in a system does not necessarily imply that any particular reaction in that system is at equilibrium.

**EXAMPLE 9**

The hydration of \( \text{CO}_2(aq) \) to form \( \text{H}_2\text{CO}_3 \) was characterized in Example 2 as being elementary and therefore first order with respect to both \( \text{CO}_2(aq) \) and water. In that example, a mixed rate constant including the concentration of \( \text{CO}_2(aq) \) and the activity of water was given as 0.03 s\(^{-1}\). Assuming that the \( \text{CO}_2(aq) \) behaves ideally, the same numerical value of the rate constant applies when the rate expression for hydration is written using the activity of \( \text{CO}_2(aq) \) instead of the concentration, although the units of the rate constant are different. Specifically, the reaction rate expression and rate constant would be:

\[
r_{\text{CO}_2(aq)} = -k_{\text{hyd}}' a_{\text{CO}_2(aq)} a_{\text{H}_2\text{O}}
\]

\[
k_{\text{hyd}}' = 0.03 \text{ mol L}^{-1} \text{s}^{-1}
\]

(a) Given that the equilibrium constant for the hydration reaction is \( 1.6 \times 10^{-3} \) and assuming that both hydration and dehydration are elementary reactions, what are the activity-based rate expression and reaction rate constant for dehydration of \( \text{H}_2\text{CO}_3 \)?

(b) In an ideal solution initially containing \( 10^{-4} \) mol/L each of \( \text{H}_2\text{CO}_3 \) and \( \text{CO}_2(aq) \), in which direction would the reaction proceed and what would the net rate of reaction be?

**Solution.** (a) The reaction for dehydration of \( \text{H}_2\text{CO}_3 \) is

\[
\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2(aq) + \text{H}_2\text{O}.
\]

The equilibrium constant for the hydration reaction is given as:

\[
1.6 \times 10^{-3} = \frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{CO}_2(aq)} a_{\text{H}_2\text{O}}}
\]

Since the equilibrium constant for a reaction is the ratio of the forward and reverse activity-based elementary rate constants, we can find \( k_{\text{dehyd}}' \) for the activity-based rate expression as follows:

\[
K_{\text{eq,hyd}} = \frac{k_{\text{hyd}}'}{k_{\text{dehyd}}'}
\]
(b) In an ideal solution containing $10^{-4}$ mol/L each of the hydrated and unhydrated species, the activity of each carbon species would be $10^{-4}$ and that of water would be 1.0. The rate of the hydration reaction would therefore be $k_{\text{hyd}} \cdot a_{H_2CO_3(aq)} = (0.03 \text{ mol/L-s})(1.0)(10^{-4})$, or $3 \times 10^{-6}$ mol/L-s. The dehydration rate would be $k_{\text{dehyd}} \cdot a_{H_2O} = (18.75 \text{ mol/L-s})(10^{-1})$, or $1.875 \times 10^{-3}$ mol/L-s. Thus, for the given conditions, the dehydration reaction would be proceeding more than 600 times as fast as the hydration reaction, so the net change in speciation would be dehydration of $H_2CO_3$.

The simple relationship shown in Equation 34 between the rate constants and the equilibrium constant applies only for elementary reactions. For a non-elementary reaction, the equilibrium constant can still be derived by equating the forward and reverse reaction rates for the overall reaction at equilibrium. However, in that case, the forward and reverse rate expressions contain more than one rate constant, and the resulting equilibrium expression is more complex than Equation 34.

Kinetics of Reversible Reactions

The approach of a reversible reaction to equilibrium in a batch reactor can be analyzed following the same procedures as are used above to analyze irreversible reactions. That is, the rate expression for the overall reaction (in this case, including both the forward and reverse reactions) can be written and integrated. For instance, for a reaction $A \leftrightarrow B$ in which the forward and reverse reactions are both elementary, the net rate of reaction of $A$ is:

$$r_A = -k_{AB}c_A + k_{BA}c_B$$

(35)

The equilibrium constant $K_{eq}$ is the ratio of the forward and reverse rate constants, so Equation 35 can be re-written as follows:

$$r_A = -k_{AB}c_A + \frac{k_{AB}}{K_{eq}}c_B$$

(36)

$$r_A = -k_{AB}c_A + k_{AB}^*c_A = k_{AB}^*(c_A^*-c_A)$$

(37)
where \( c_A^* = \frac{c_B}{K_{eq}} \). Note that, by its definition, \( c_A^* \) is the concentration of \( A \) that would be in equilibrium with \( c_B \). Thus, \( c_A^* \) is a hypothetical concentration, and it is a variable, i.e., it changes as the concentration of \( B \) changes. The expression in parentheses in Equation 37 is the instantaneous difference between the actual concentration of \( A \) and the concentration that would be in equilibrium with \( B \) at that instant, i.e., it is the instantaneous extent of disequilibrium of the reaction \( A \leftrightarrow B \). Thus, the equation indicates that the net rate of the reaction is directly proportional to the gap between the current conditions and a corresponding, hypothetical equilibrium condition.

Equation 37 bears a strong resemblance to Equation 11, the mass balance for an irreversible first order reaction in a batch reactor. The only difference between the equations is that the driving force in the case of the reversible reaction is the extent of disequilibrium, rather than the concentration of \( A \). In fact, since \( c_A^* \) is essentially zero for an irreversible reaction, the rate expression for the irreversible reaction (Equation 11) is seen to be a limiting case of the more general expression for the reversible system (Equation 37).

Defining the extent of disequilibrium as \( \hat{c}_A \) \((\hat{c}_A \equiv c_A^* - c_A^0)\), and noting that, by stoichiometry, \( dc_A = -dc_B \), \( dc_A \) can be written in terms of \( dc_A \) as follows:

\[
dc_A = dc_A^* - dc_A = \frac{dc_B}{K_{eq}} - dc_A = \frac{dc_A}{K_{eq}} - dc_A = -\left(\frac{1}{K_{eq}} + 1\right)dc_A = - \left(\frac{k_{BA}}{k_{AB}} + 1\right)dc_A
\]

(38)

\[
dc_A = - \left(\frac{k_{BA}}{k_{AB}} + 1\right)^{-1} dc_A = - \frac{k_{AB}}{k_{AB} + k_{BA}} d\hat{c}_A
\]

(39)

For a reaction occurring in a batch reactor, \( r_A \) can be equated with \( dc_A / dt \).
Substituting that equality and Equation 39 into the left side of Equation 37, and the definition of \( \hat{c}_A \) into the right side, we obtain:

\[
- \frac{k_{AB}}{k_{AB} + k_{BA}} \frac{d\hat{c}_A}{dt} = k_{AB} \hat{c}_A
\]

(40)

\[
\int_{\hat{c}_A(0)}^{\hat{c}_A(t)} \frac{d\hat{c}_A}{\hat{c}_A} = -(k_{AB} + k_{BA}) \int_0^t dt
\]

(41)

\[
\hat{c}_A(t) = \hat{c}_A(0) \exp \left\{ - \left( k_{AB} + k_{BA} \right) t \right\}
\]

(42)

Equation 42, which applies to first order reversible reactions, is analogous to Equation 13b for first order irreversible reactions. The differences are that the key
variable in Equation 42 is the extent of disequilibrium \( \hat{c}_A \), or \( c_A^* - c_A \) rather than the absolute concentration; the final condition \( \hat{c}_A = 0 \) is equilibrium between \( A \) and \( B \) rather than complete disappearance of \( A \); and the rate constant for approach to equilibrium is the sum of the rate constants of the forward and reverse reactions.

To compute the actual concentrations of \( A \) and \( B \) at any time, we can substitute back into Equation 42 to replace the \( \hat{c}_A \) terms with \( \frac{c_B}{K_{eq}} - c_A \) and \( k_r \) with \( K_{eq}/k_f \). Then, using a mass balance on \( A \) to replace \( c_B(t) \) with \( c_A(0) + c_B(0) - c_A(t) \), and carrying out some algebra, we obtain the following result:

\[
   c_A(t) = \frac{c_A(0) + c_B(0)}{K_{eq} + 1} + \frac{K_{eq}c_A(0) - c_B(0)}{K_{eq} + 1} \exp \left\{ -\frac{K_{eq} + 1}{K_{eq}} k_{Ar} t \right\}
\]

(43)

The first term on the right of Equation 43 can also be expressed as \( c_{eq} \), the ultimate, equilibrium concentration of \( A \) in the system. The concentration of \( B \) at any time can be found by substituting the above expression into the mass balance on \( A \) noted above.

Although the exact form of the equations for other stoichiometries and other rate expressions is more complex, the principal conclusion, that the rate of approach to equilibrium is a direct function of the extent of disequilibrium, holds in all cases. Note that this conclusion applies when comparing the rate of a given reaction under different conditions. It does not imply that, when comparing two different reactions, the one farther from equilibrium will proceed more quickly.

**EXAMPLE 10**

Plot the extent of disequilibrium of \( H_2CO_3 \) in the dehydration reaction (i.e., \( \hat{c}_{H_2CO_3} \)) and the concentrations of \( CO_2(aq) \) and \( H_2CO_3 \) versus time in the batch system described in part b of Example 9. What are the concentrations of \( CO_2(aq) \) and \( H_2CO_3 \) after 0.2 s? Assume that the pH does not change during the equilibration process.

**Solution.** If the forward and reverse reactions of interest were both first order, we could determine \( \hat{c}_{H_2CO_3} \) as a function of time using Equation 42. In the current case, the dehydration (forward) reaction is first order and can be written based on the activity or the concentration of \( H_2CO_3 \) as follows:

\[
   r_{dehyd} = k_{dehyd} a_{H_2CO_3} = k_{dehyd} c_{H_2CO_3}
\]

where \( k_{dehyd} = 18.75 \text{ mol/L-s} \) and; for an ideal solution, \( k_{dehyd} = 18.75 \text{ s}^{-1} \).
On the other hand, the reverse reaction of interest (CO$_2$(aq) hydration) is second order overall (first order with respect to each CO$_2$(aq) and H$_2$O). However, as indicated in Example 2, the activity of water is constant and equal to 1.0 throughout the reaction period, so the hydration reaction is pseudo-first order, with a concentration-based rate constant of 0.03 s$^{-1}$.

Thus, Equation 42 can be applied to evaluate the rate at which H$_2$CO$_3$ disequilibrium dissipates for the dehydration reaction. In this case, the values corresponding to $k_{AB}$ and $k_{BA}$ in Equation 42 are 18.75 s$^{-1}$ and 0.03 s$^{-1}$, respectively.

The initial extent of H$_2$CO$_3$ disequilibrium ($\hat{c}_{H_2CO_3}(0)$) can be found from the initial concentrations of CO$_2$(aq) and H$_2$CO$_3$, in conjunction with the equilibrium constant for the hydration reaction, which was given in Example 9 as 1.6x10$^{-3}$. The calculation is as follows:

$$\hat{c}_{H_2CO_3}(0) = c_{H_2CO_3}(0) - c_{H_2CO_3}(0)$$

$$= K_{eq,hyd}c_{CO_2(aq)} - c_{H_2CO_3}(0)$$

$$= (1.6x10^{-3})(10^{-4.0} \text{ mol/L}) - 10^{-4} \text{ mol/L} = -9.984x10^{-5} \text{ mol/L}$$

The negative value indicates that the equilibrium concentration of H$_2$CO$_3$ is smaller than the initial concentration, so H$_2$CO$_3$ must disappear from solution for the reaction to reach equilibrium.

Applying Equation 42, the extent of disequilibrium decreases over time at a rate given by:

$$\hat{c}_{H_2CO_3}(t) = \hat{c}_{H_2CO_3}(0) \exp\{-(k_{hyd} + k_{dehyd})t\}$$

$$= \left(-9.984x10^{-5} \frac{\text{mol}}{L}\right) \exp\{-(0.03 + 18.75)t\}$$

$$\hat{c}_{H_2CO_3}(t) = \left(-9.984x10^{-5} \frac{\text{mol}}{L}\right) \exp(-18.78t)$$

The above equation for the decay of $\hat{c}_{H_2CO_3}$ over time is plotted in Figure Ex10-1.
Figure Ex10-1. The extent of disequilibrium of $\text{H}_2\text{CO}_3$ with respect to dehydration as a function of time, for the conditions specified in the problem statement.

The time profile of the $\text{H}_2\text{CO}_3$ concentration for this system can be computed using Equation 43, which is rewritten below with terms applicable to this problem substituted for the generic terms shown in the original equation:

$$c_{\text{H}_2\text{CO}_3}(t) = \frac{c_{\text{H}_2\text{CO}_3}(0) + c_{\text{CO}_2(aq)}(0)}{K_{\text{dehyd}} + 1} + \frac{K_{\text{dehyd}} c_{\text{H}_2\text{CO}_3}(0) - c_{\text{CO}_2(aq)}(0)}{K_{\text{dehyd}} + 1} \exp \left\{ -\frac{K_{\text{dehyd}} + 1}{K_{\text{dehyd}}} k_{\text{dehyd}} t \right\}$$

The initial concentrations of $\text{H}_2\text{CO}_3$ and $\text{CO}_2(aq)$ are known, as is $k_{\text{dehyd}}$. The equilibrium constant for the dehydration reaction ($K_{\text{dehyd}}$) has not been given explicitly, but it can be computed as the inverse of $K_{\text{hyd}}$, or 625. Thus, all the information needed to compute $c_{\text{H}_2\text{CO}_3}$ as a function of time is known. Once that concentration profile is determined, the corresponding profile of $c_{\text{CO}_2(aq)}$ can be computed by a mass balance on total dissolved carbon, i.e., $c_{\text{CO}_2(aq)}(t) = c_{\text{H}_2\text{CO}_3}(0) + c_{\text{CO}_2(aq)}(0) - c_{\text{H}_2\text{CO}_3}(t)$.

The results are shown in Figure Ex10-2. The system is very nearly equilibrated within a few tenths of a second. At $t = 0.2$ s, the computed
concentrations are \( c_{\text{H}_2\text{CO}_3} = 2.6 \times 10^{-6} \text{ mol/L} \), and \( c_{\text{CO}_2(aq)} = 1.974 \times 10^{-4} \text{ mol/L} \), i.e., almost 99% of the total dissolved carbon is present as the dehydrated species.

(Note that, in this example, the extent of disequilibrium is defined in terms of a concentration difference. A similar definition based on an activity difference could also be defined and used in the same way. In this case, since we are making the ideal solution assumption, the same values would apply in either case.)

---

**Figure Ex10-2.** The approach to equilibrium of a system initially containing \(10^{-4}\) mol/L each of \(\text{H}_2\text{CO}_3\) and \(\text{CO}_2(aq)\). Note that the ordinate scale is logarithmic.

**Characteristic Times and Limiting Cases for Reversible Reactions**

The characteristic time of a reaction was defined above in two different ways, and its meaning was explored with respect to the extent to which irreversible reactions would proceed in various scenarios. The same approach can be used to explore either the forward or reverse direction of a reversible reaction. In the case of a reversible reaction, however, we are more often interested in the characteristic time for the composite of the forward and reverse reactions. Put another way, we are interested in \( \hat{t}_{\text{char}} \) for the approach of \( \hat{c}_A(t) \) to zero, i.e., the approach of the system to equilibrium.
For reactions that are first order in both the forward and reverse directions, the characteristic time for the overall reaction can be established by analogy with that for unidirectional reactions, as shown in Table 3.

Table 3.4. Characteristic times for unidirectional and bi-directional (reversible) reactions.

<table>
<thead>
<tr>
<th>Integrated rate expression$^{a)}$</th>
<th>Eq.#</th>
<th>$t_{\text{char}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irreversible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_A(t) = c_A(0)\exp(-k,t)$</td>
<td>(13b)</td>
<td>$\frac{1}{k_i}$</td>
</tr>
<tr>
<td>Reversible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\dot{c}<em>A(t) = \dot{c}<em>A(0)\exp{-(k</em>{AB} + k</em>{BA})t}$</td>
<td>(42)</td>
<td>$\frac{1}{k_{AB} + k_{BA}}$</td>
</tr>
</tbody>
</table>

$^{a)}$For a batch system

The result makes it apparent that the characteristic time for the overall reaction is shorter than that for either the forward or reverse reaction in isolation ($\frac{1}{k_{AB}}$ or $\frac{1}{k_{BA}}$, respectively). In many cases, one of the rate constants is so much larger than the other one that the overall characteristic time for the reversible reaction can be approximated as the inverse of the larger of the rate constants for the individual (forward and reverse) reactions. Put another way, the characteristic time for the overall reaction is approximately equal to the shorter of the characteristic times of the two individual reactions. Note that this observation is consistent with the results of Example 10. In that case, $t_{\text{char}}$ values for the dehydration and hydration reactions (equal to $1/k_{\text{dehyd}}$ and $1/k_{\text{hyd}}$, respectively) are 0.053 s and 33.3 s, yielding a value of 0.053 s for $t_{\text{char}}$ for the overall reaction. Consistent with this value of $t_{\text{char}}$, the reaction was nearly at equilibrium after 0.2 s (approximately $4t_{\text{char}}$) had elapsed.

**EXAMPLE 11**

Consider the progress of a reversible reaction $A \leftrightarrow B$ taking place in a batch reactor with two different initial conditions: one in which $c_A(0) = 100 \mu\text{mol/L}$ and $c_B(0) = 0 \mu\text{mol/L}$, and another in which these two concentrations are reversed. Assume that both the forward and reverse reactions are first order, with $k_{AB} = 1 \text{ min}^{-1}$ and $k_{BA} = 0.1 \text{ min}^{-1}$, so that the equilibrium constant, equal to the ratio of the rate constants, is $K_{eq} = 10$. How rapidly would these two systems approach equilibrium, and how does the rate of approach to equilibrium in each system compare to the rates of the individual reactions?

**Solution.** The changes in the concentrations of the two reactants over time in each system can be computed using Equation 43. For the first condition to be considered ($c_A(0)= 100 \mu\text{mol/L}$), the conversion is rapid initially. However, within a few minutes the equilibrium condition ($c_A = 9.1 \mu\text{mol/L}$, $c_B = 90.9 \mu\text{mol/L}$) is approached, and the reaction slows to a negligible net rate (Figure Ex11-Error! Bookmark not defined..a). In this
system, conversion of $A$ to $B$ is the dominant reaction occurring as equilibrium is approached. The characteristic time for that reaction is 1 minute ($= 1/k_{AB}$), so the fact that the overall reaction is substantially complete in a few minutes is not surprising.

When the initial conditions are changed to $c_A(0) = 0 \, \mu$mol/L, $c_B(0) = 100 \, \mu$mol/L, the dominant reaction that proceeds as the system approaches equilibrium is $B \rightarrow A$, which has a characteristic time of 10 minutes. Nevertheless, consistent with the calculation above of the characteristic time for the overall reaction (which is independent of the initial conditions for first order reactions), the approach to equilibrium is just as rapid in this case as in the previous one (Figure Ex11-1b). The same results are shown in a slightly different way in Figure Ex11-2, in which the extent of disequilibrium ($\hat{c}_A$) and the logarithm of that value are plotted against time. Consistent with Equation 42, the semi-logarithmic plot demonstrates that the extent of disequilibrium decreases by one natural log unit with each increment of time equal to $t_{\text{char}}$. 
Figure Ex11-1. Concentration vs. time profiles for A and B in a batch reactor, for the reversible reaction $A \leftrightarrow B$, with $k_A = 1.0/\text{min}$, $k_B = 0.1/\text{min}$.
(a) $c_A(0) = 100 \ \mu\text{mol/L}$, and $c_B(0) = 0 \ \mu\text{mol/L}$; (b) $c_A(0) = 0 \ \mu\text{mol/L}$, and $c_B(0) = 100 \ \mu\text{mol/L}$.
<table>
<thead>
<tr>
<th>Extent of disequilibrium</th>
<th>(μmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_A(0) = 0$, $c_B(0) = 100 , \mu$mol/L</td>
<td>0</td>
</tr>
<tr>
<td>$c_A(0) = 100 , \mu$mol/L, $c_B(0) = 0$</td>
<td>1.0E+02</td>
</tr>
<tr>
<td>Both slopes $= 1/t_{\text{char}} = 1.1 , \text{min}^{-1}$</td>
<td>1.0E-01</td>
</tr>
</tbody>
</table>

Both slopes $= 1/t_{\text{char}} = 1.1 \, \text{min}^{-1}$
Figure Ex 11-2. The decline in the extent of disequilibrium in the hypothetical system described in the text. Note that the natural logarithm of the extent of disequilibrium declines by one unit for each time increment equal to $t_{\text{char}}$, regardless of the net direction in which the reaction is proceeding. (The absolute value of the extent of disequilibrium is used in the second diagram, since the logarithm of a negative number is undefined.)

Simplification of Reaction Rate Expressions by Analysis of Limiting Cases

Very Rapid and Very Slow Approach to Equilibrium as Limiting Cases

Based on Equation 42, if either the forward or reverse rate of an equilibrium reaction is very fast, then it is reasonable to assume that the reaction reaches equilibrium quickly, perhaps even so quickly that the approach to equilibrium can be ignored. The most important reaction in environmental engineering for which this assumption applies is the dissociation and formation of water. The elementary forward and reverse reactions for this overall reaction are both second order: $2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$, with forward and reverse concentration-based rate constants of approximately $4.5 \times 10^{-7}$ (mol/L)$^{-1}$s$^{-1}$ and $1.4 \times 10^{11}$ (mol/L)$^{-1}$s$^{-1}$, respectively.\(^8\) Using Definition 1 to compute the characteristic time of a second order reaction, the characteristic times of the forward and reverse reactions at pH 7.0 are about 19 hours and $10^{-4}$ second, respectively. Although the characteristic time of the reaction forming H$_2$O depends on the exact conditions in the system, it is always orders of magnitude shorter than the characteristic time of the dissociation reaction, and therefore equilibrium is always approached at a rate corresponding to the characteristic time of the water-forming reaction. Furthermore, as long as the characteristic time of the water-forming reaction is significantly less than 1 s, the reaction will be essentially complete almost immediately after any transient change in the acid content of a solution, at least for the time frames normally associated with environmental engineering processes.

Thus, for instance, when a strong acid is added to an aqueous solution, the pH of the solution decreases, and the relationship $a_{\text{OH}^-} = 10^{-14} / a_{\text{H}^+}$ applies almost instantly; one need not consider that, after the acid increases the H$^+$ concentration, it might take some time before the OH$^-$ concentration adjusts to the new situation. This assumption allows one to calculate the OH$^-$ concentration in any solution where the pH is known, without conducting a kinetics analysis. The same assumption applies to most acid/base reactions, as well as many other reactions of importance in water and wastewater treatment systems.

\(^8\)The ratio $k_f/k_r$ yields the equilibrium constant based on the concentration of all species. Defining the activity of water to be 1.0 when its concentration is 55.5 mol/L converts this equilibrium constant to the conventional value of $10^{-14.0}$.  

49
At the other extreme, if the characteristic times for both the forward and reverse directions of a reaction are much longer than the time frame of interest, then the reaction proceeds negligibly towards equilibrium during that time. One need not conduct a kinetics analysis in this situation either, because the reacting species can be treated as non-reactive, i.e., inert.

**Reaction Quotients, Equilibrium and the Assumption of Irreversibility**

The assumption that a reaction is irreversible can simplify kinetics analysis significantly, and such an assumption is made implicitly for many important reactions in environmental engineering. For instance, when hypochlorous acid (HOCl) is added to water as a disinfectant, it can react with contaminants in the water and be converted to chloride ion (Cl\(^-\)). Although, in theory, some chloride ions could revert to HOCl molecules, the rate of such reversion is negligibly small, and it is never considered in an analysis of the system. Similarly, it is never considered necessary to account for the reversion of corroded pipe materials back to their metallic form, or the spontaneous conversion of carbon dioxide and water to organic matter (in the absence of photosynthesis). The dissociation of many strong acids, bases, and salts, e.g., H\(_2\)SO\(_4\), NaOH, and Al\(_2\)(SO\(_4\))\(_3\)\(\cdot\)xH\(_2\)O (alum), is also commonly treated as being irreversible. In this section, features of reaction rate expressions and equilibrium constants that can support an assumption of irreversibility are explored.

Consider the following generic elementary reaction and corresponding activity-based rate expression:

\[
aA + bB \xrightarrow{k_{PA}} pP + rR
\]

\[
\begin{align*}
r_A &= -k_{AP}a_a^a a_b^b + k_{PA}a_p^p a_r^r \\
&= -k_{AP}a_a^a a_b^b + k_{PA}a_p^p a_r^r
\end{align*}
\]

If the reaction is not at equilibrium, the net rate of formation of A is non-zero.

Multiplying and dividing the right-hand side of Equation 44 by \(k_{AP}a_a^a a_b^b\), and then rearranging, we obtain:

\[
r_A = \frac{-k_{AP}a_a^a a_b^b + k_{PA}a_p^p a_r^r}{k_{AP}a_a^a a_b^b} k_{AP}a_a^a a_b^b
\]

\[
r_A = -1 + \frac{a_p^p a_r^r / a_a^a a_b^b}{k_{PA} / k_{AP}} k_{AP}a_a^a a_b^b
\]

\[
r_A = -1 + \frac{Q}{K_{eq}} k_{AP}a_a^a a_b^b
\]
where $Q$ is the called the *reaction quotient* and is a ratio of activities analogous to the equilibrium constant, but not restricted to equilibrium conditions. If $Q$ is either much larger or much smaller than $K_{eq}$ the system is far from equilibrium; if $Q$ is close to $K_{eq}$ the system is near equilibrium; and if $Q$ equals $K_{eq}$ the system is at equilibrium.\(^9\)

According to Equation 47, if $Q$ is either much larger or much smaller than $K_{eq}$ the following approximations apply:

<table>
<thead>
<tr>
<th>$Q \gg K_{eq}$</th>
<th>$Q \ll K_{eq}$</th>
</tr>
</thead>
</table>
| \begin{align*}
  r_A &= \frac{Q}{K_{eq}} - k_{AP}' a_a^a a_b^b \quad (48a) \\
  &\approx \frac{a_a^a a_b^b}{k_{AP}' / k_{PA}'} + k_{AP}' a_a^a a_b^b \quad (48b) \\
  &\approx k_{PA}' a_a^a a_b^b \\
\end{align*} | \begin{align*}
  r_A &= -k_{AP}' a_a^a a_b^b \quad (49) \\
\end{align*} |

Equations 48c and 49 are the rates of the reverse reaction alone and the forward reaction alone, respectively (the negative sign in Equation 49 indicates that the net change is disappearance of $A$). Thus, when the system is far from equilibrium, the overall rate of reaction can be approximated by the reaction in only one direction. Put another way, a reaction that is approximately irreversible is one that is far from equilibrium. The same result can be seen for the specific case of first order forward and reverse reactions by letting $c_A^*$ be either much larger or much smaller than $c_A$ in Equation 37.

Note that neither the equilibrium constant ($K_{eq}$) nor the instantaneous ratio of reactant activities to product activities ($Q$) can, by itself, indicate whether a reaction may be considered irreversible. Rather, the issue of reversibility hinges on the ratio of these quantities. Furthermore, because of certain universal aspects of the relationship between rate constants and the equilibrium constant, the term in parentheses in Equation 47 appears in the net rate expression not just for elementary reactions, but for all non-elementary reactions as well. As a result, the conclusion that reactions are approximately irreversible if $Q$ is much larger or much smaller than $K_{eq}$ is also universal, i.e., it applies even to non-elementary reactions.

The discussion above indicates that *any* reaction might be reversible in some circumstances and approximately irreversible in others. Although the determination of whether a reaction can be treated as irreversible depends on the particular goals of the analysis, in most cases it would seem reasonable to assume that a reaction is irreversible.

\(^9\)The conventional thermodynamic measure of chemical disequilibrium is the molar Gibbs energy change associated with the reaction (\(\Delta G_r\)), which is directly related to the ratio of $Q$ to $K_{eq}$: 
\[
\Delta G_r = RT \ln \left( \frac{Q}{K_{eq}} \right).
\]
if, throughout the time frame of interest, the rate in one direction is at least one to two orders of magnitude faster than the rate in the other direction.

**EXAMPLE 12**

Do you think the H$_2$CO$_3$ dehydration reaction could be treated as irreversible under the conditions evaluated in part b of Example 9?

*Solution.* Since the analysis in Example 9b indicates that dehydration would initial proceed >600 times as fast as hydration, it seems reasonable to ignore the hydration reaction and treat the reaction at that instant as an irreversible dehydration process. Note, however, that as the reaction proceeds, the extent of disequilibrium diminishes, so the assumption becomes less justifiable over time. In fact, the results shown in Example 10 suggest that the assumption of irreversibility would be poor after just 0.1-0.2 s.

**Nearly Complete Reaction as a Limiting Case**

The equilibrium condition for some reactions lies so far to one extreme that they can be considered irreversible under virtually all conditions of interest in environmental engineering. A few examples of such reactions were cited above. In such cases, and given enough time, the reaction would proceed until one of the reactants was virtually completely depleted. Therefore, if the equilibrium condition for a reaction lies far toward the product side, and if the time frame of interest is much longer than the characteristic reaction time, the approximation of *complete* or *stoichiometric reaction* applies. This approximation implies that 100% of the added reactant is converted to product (unless, of course, one of the other reactants runs out first). The assumption of complete, stoichiometric reaction is often made when estimating the amounts of solids that form when precipitation reactions are induced in water treatment systems. For instance, in many situations, it is assumed that all the aluminum or iron that is added to a water treatment system precipitates as the corresponding hydroxide solid (Al(OH)$_3$(s) or Fe(OH)$_3$(s)). Similarly, many analytical tests are based on the assumption that the constituent being analyzed reacts completely with the added reagents.

**Summary of Limiting Cases**

The various limiting cases used to simplify reaction rate expressions are summarized and compared in the Table 3.5.
Table 3.5. Summary of limiting cases under which the reaction rate expression can be simplified.

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Corresponding Criteria and Effect</th>
</tr>
</thead>
</table>
| Irreversible Reaction                  | Forward rate >> Reverse rate (or vice versa);  
  $t_{\text{char}}$ >> time available for reaction;  
  Reaction far from equilibrium;  
  *Simplifies the rate expression in the mass balance* |
| Reaction at Equilibrium                | Forward rate = Reverse rate;  
  $t_{\text{char}}$ << time available for reaction;  
  *Eliminates the forward and reverse rate terms for a given reaction from the mass balance, and substitutes the equilibrium relationship between reactants and products* |
| Stoichiometric or Complete Reaction    | Equilibrium lies far to product side and $t_{\text{char}}$ << time available for reaction;  
  *Eliminates the forward and reverse rate terms for a given reaction from mass balance, and substitutes a relationship based on stoichiometry* |

**EXAMPLE 13**

Alum is frequently added to waters and wastewaters in order to increase the size of suspended particulate matter and thereby facilitate its removal by settling or filtration. Often, much of the Al added with the alum precipitates as Al(OH)$_3$(s) by the reaction shown below.

$$\text{Al}^{3+} + 3 \text{OH}^- \leftrightarrow \text{Al(OH)}_3(s)$$

The equilibrium constant for the above reaction written with the reactants and products reversed (i.e., for the dissolution of Al(OH)$_3(s)$) is referred to as the solubility product of the solid and is designated $K_{s0}$. For Al(OH)$_3(s)$, $K_{s0} = 10^{-31.62}$.

If the solution pH is known, and if the Al(OH)$_3(s)$ that precipitates is a pure solid (and therefore can be assigned an activity of 1.0), the solubility product can be used to compute the activity of free aquo Al$^{3+}$ ions, i.e., $a_{\text{Al}^{3+}}$. The equilibrium constants for formation of soluble Al$_x$(OH)$_{3y-x}$ species can then be used to calculate the activity of these species. At pH 6.0, the activity of all soluble Al species is about 200 times that of Al$^{3+}$.

Consider a system in which enough alum is added to a wastewater to provide a total of 30 mg/L Al to the solution. The alum dissolves
completely, but Al(OH)$_3$(s) then precipitates. The pH of the wastewater throughout the process is 6.0.

(a) Considering only formation of the hydroxo complexes (i.e., ignoring other inorganic and all organic complexes), compute $Q/K$ for the precipitation reaction shortly after the alum is first added. Assume that, at that time, all of the alum has dissolved, the Al-OH complexes have formed, and a very small amount of solid has precipitated. Do you think that precipitation of Al(OH)$_3$(s) can be treated as irreversible at this time? Assume ideal behavior of the solutes.

(b) Precipitation of Al(OH)$_3$(s) is rapid compared to the hydraulic residence time in the reactor under consideration. Do you think that the precipitation reaction could be treated as going to completion for the purposes of computing sludge production? Could the precipitation process be treated as going to completion for the purposes of estimating the amount of Al remaining in solution?

Solution. (a) The total amount of Al added to the solution is:

$$c_{\text{Al}_{\text{tot}}} = \left(30 \frac{\text{mg}}{\text{L}} \right) \left( \frac{1 \text{ mol Al}}{27000 \text{mg}} \right) = 1.1 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

According to the problem statement, shortly after the alum addition, all of Al added is present as soluble species, and one two-hundredth of that Al is present as free Al$^{3+}$. Thus, at that time, the concentration of free aquo Al$^{3+}$ is $c_{\text{Al}_{\text{tot}}}/200$, or $5.5 \times 10^{-6}$ mol/L. The precipitation reaction is the reverse of the reaction shown in the problem statement, so the value of $Q$ is computed as the product $(a_{\text{Al}^{3+}} a_{\text{OH}^-})^{-1}$. The value of $K_{\text{eq}}$ for the precipitation reaction is $K_{\text{s0}}^{-1}$, and, at pH 6.0, $a_{\text{OH}^-}$ is $10^{-8.0}$. Thus, $Q/K$ for the reaction is:

$$Q = \frac{(a_{\text{Al}^{3+}} a_{\text{OH}^-})^{-1}}{K_{\text{s0}}^{-1}} = \left[ \left(5.5 \times 10^{-6} \right) \left(10^{-8.0} \right)^{3} \right]^{-1} = 0.0044$$

Since $Q$ is less than $K$, the reaction is not at equilibrium and will proceed to the right (precipitation of Al(OH)$_3$(s)). The ratio of $Q$ to $K$ is more than two orders of magnitude different from 1.0, meaning that the extent of disequilibrium is substantial, so it would be reasonable to treat the initial reaction as irreversible.
(b) The final equilibrium activity of Al\(^{3+}\) is given by the solubility product. Because the solution pH is assumed to remain at 6.0 throughout the process, \(a_{\text{Al}^{3+}}\) at equilibrium can be computed as follows:

\[
a_{\text{Al}^{3+}} = \frac{K_{s0}}{a_{\text{OH}^-}^3} = \frac{10^{-31.62}}{(10^{-8.0})^3} = 10^{-7.62}
\]

Again equating the numerical values of \(a_{\text{Al}^{3+}}\) and \(c_{\text{Al}^{3+}}\), we conclude that \(c_{\text{Al}^{3+}}\) at equilibrium is \(10^{-7.62}\) mol/L. The final concentration of total dissolved aluminum is \(200c_{\text{Al}^{3+}}\), or \(4.8 \times 10^{-6}\) mol/L (0.13 mg/L). This concentration is only approximately 0.43% of the total Al added, so >99% of the Al that was added precipitates, and the assumption of stoichiometric precipitation would be a good one. Keep in mind though, that in a real system, some of the Al might form soluble complexes with ligands other than \(\text{OH}^-\), and some colloidal \(\text{Al(OH)}_3\) might remain suspended in the effluent. As a result, the concentration of total Al in the effluent could be substantially greater than computed based on the assumption that it comprises only species of the type \(\text{Al}_y(\text{OH})_x\).

If the precipitation process were treated as going to completion to estimate the soluble Al in the effluent, the estimate of that concentration would be zero. Whether or not ignoring Al in the effluent is an acceptable assumption depends on the ultimate use of the conclusion. If we were interested in potential effects of dissolved Al on the receiving water, for instance, the assumption might not be justified, since relatively small additions of Al to that receiving water might have a significant effect. On the other hand, when computing the total dissolved solids (TDS) of the effluent, the contribution of the Al species would almost certainly be negligible. Thus, in this example, as always, the validity of an assumption depends on the context in which the assumption is made and in which the data are being interpreted.

**Reaction Networks**

Reaction networks are systems in which reactants are affected by two or more independent reactions. Reaction networks can include consecutive or competitive reactions, or a combination of both. The form of the reaction rate expression for the overall network depends, of course, on the details of the reaction pathways and the magnitudes of the rate constants. As is the case for reversible reactions, the analysis can be simplified significantly if certain limiting assumptions apply.

The analysis of some simple reaction networks is presented in this section. The initial analysis focuses on groups of irreversible, consecutive reactions, after which the effect of reaction reversibility is considered. The analysis begins with a few numerical
simulations, the results of which allow some generalizations to be made about the behavior of the various reactants and the characteristic times of the overall reactions. The results are also used to identify limiting conditions that might be applicable in certain situations and that can simplify the mathematical analysis of the system. Finally, an historically important overall reaction rate expression is developed based on the presumed reaction mechanism.

The Progress of Consecutive Reactions, and the Rate Controlling Step

As material progresses through a reaction sequence, one can imagine that, at each step, it encounters a resistance that prevents it from being converted instantly into the next species. When chemicals encounter such a sequence of resistances, they tend to build up immediately upstream of high-resistance transition points. In this aspect, the process is identical to water flowing through a series of tanks connected by pipes with partially-open valves (Figure 3.3), or traffic on a road with toll booths located every few miles. In each of these systems, material (chemical species, water, or cars) builds up behind the points where the resistance to progress is greatest. If the resistance at one point in the sequence is much greater than that at any other point, that point represents a bottleneck that limits the rate at which the overall sequence can proceed. In the case of sequential chemical reactions, the reaction imposing the greatest resistance to the progression of the overall reaction is called the rate determining, rate limiting, or rate controlling step. In these cases, greater resistance is synonymous with increased characteristic time, so the rate controlling step can also be defined as the step with the longest characteristic time.
Figure 3.3. A sequence of tanks, with the rate at which water leaves each tank controlled by a valve. The rate at which water exits the overall system is controlled by the tightest valve (on the pipe leaving the third tank in the sequence), behind which water accumulates.
Consider, for example, the progress of the reaction network \( A \rightarrow B \rightarrow P \) in a batch reactor, in which each reaction is first order. The rate of change of the concentrations of \( A \), \( B \), and \( P \) in the system can be derived from the corresponding mass balances, yielding:

\[
\frac{dc_A}{dt} = -k_A c_A \tag{50}
\]

\[
\frac{dc_B}{dt} = k_A c_A - k_B c_B \tag{51}
\]

\[
\frac{dc_P}{dt} = k_B c_B \tag{52}
\]

What can we surmise about the general patterns of the concentrations of \( A \), \( B \), and \( P \) as the reaction proceeds? First, we note that species \( A \) will disappear at exactly the same rate that it would if the reaction \( A \rightarrow B \) were taking place in isolation, i.e.,

\[ c_A(t) = c_A(0) \exp(-k_A t) \]

the “downstream” reaction of \( B \) to form \( P \) has no effect on the reaction rate of \( A \).

As species \( A \) is depleted, species \( B \) forms, and its concentration initially increases. However, its rate of formation is \( k_A c_A \), and since \( c_A \) is steadily decreasing, the rate at which \( B \) forms decreases steadily as \( c_A \) declines. At the same time, \( B \) is being converted to \( P \) at a rate proportional to \( c_B \), i.e., the rate of disappearance of \( B \) increases as \( c_B \) increases. Thus, the overall pattern we would expect is for \( B \) to accumulate initially, until its rate of formation \( (k_A c_A) \) equals its rate of disappearance \( (k_B c_B) \). From that time on, \( B \) disappears more quickly than it is formed, and \( c_B \) decreases. Since \( P \) is formed at a rate proportional to \( c_B \), \( P \) accumulates steadily, and its rate of accumulation is largest when \( c_B \) is largest.

Analytical solutions to the mass balances on \( B \) and \( P \) for \( c_B(0) = c_P(0) = 0 \) can be derived by integration of the corresponding rate expressions, yielding:

\[
c_B(t) = \frac{k_A c_A(0)}{k_B - k_A} \left( \exp(-k_A t) - \exp(-k_B t) \right) \tag{53}
\]

\[
c_P(t) = \frac{c_A(0)}{k_B - k_A} \left( k_B \left\{ 1 - \exp(-k_A t) \right\} - k_A \left\{ 1 - \exp(-k_B t) \right\} \right) \tag{54}
\]

The concentration profiles for all three species in a system with \( c_A(0) = 100 \, \mu\text{mol/L} \) and \( c_B(0) = c_P(0) = 0 \, \mu\text{mol/L} \), and with \( k_A = k_B = 0.1 \, \text{min}^{-1} \) are shown in Figure 3.4. The results are consistent with the discussion above. In particular, \( B \) accumulates in the system until approximately \( t = 10 \, \text{minutes} \), at which time the rates of formation and destruction of \( B \) are equal, and its concentration is approximately \( c_B = 36 \, \mu\text{mol/L} \). Continuously thereafter, \( B \) reacts more rapidly than it forms, so its concentration decreases. The overall reaction is
substantially complete \( (c_P = 90 \, \mu\text{mol/L}) \) in about 40 minutes. This result is consistent with what one might expect based on the characteristic times, which are 10 minutes for each of the constituent reactions. In this case, because the characteristic time is identical for the two reactions, neither reaction can be said to be rate limiting.

**Figure 3.4.** Concentration vs. time profiles for a sequential irreversible reaction \( A \rightarrow B \rightarrow P \) in a batch reactor, with \( c_A(0) = 100 \, \mu\text{mol/L} \), and \( c_B(0) = c_P(0) = 0 \, \mu\text{mol/L} \), and with \( k_A = k_B = 0.1/\text{min} \).

Figures 3.5a and 3.5b show the corresponding concentration profiles for systems with the same initial composition as in Figure 3.4, but with one of the rate constants larger than the other by a factor of 100. In the system with \( k_A >> k_B \) (Figure 3.5a), almost all the \( A \) is converted to \( B \) before significant amounts of \( B \) are converted to \( P \). As a result, \( c_B \) increases rapidly to a value near \( c_A(0) \), after which the only relevant reaction is decay of \( B \) to \( P \). That is, after a relatively short reaction time (representing several characteristic reaction times for the reaction \( A \rightarrow B \), but much less than one characteristic reaction time for the reaction \( B \rightarrow P \)), the composition of the system can be approximated as \( c_A \approx 0 \, \mu\text{mol/L}, \ c_B \approx c_A(0), \ c_P = 0 \, \mu\text{mol/L} \). Thereafter, the first reaction can be ignored, and the only reaction of relevance is the first-order decay of \( B \) to \( P \).
The same conclusions can be reached by evaluating Equations 53 and 54 with \( k_A \gg k_B \). In such a case, \( \exp(-k_A t) \ll \exp(-k_B t) \), and the expressions simplify to:

\[
c_B(t) = c_A(0)\exp(-k_B t) \tag{55}
\]

\[
c_P(t) = c_A(0)\{1 - \exp(-k_B t)\} \tag{56}
\]

As expected, the resulting equations are those that would apply for a first order, irreversible reaction in which \( P \) is formed from \( B \), if the initial concentration of \( B \) were \( c_A(0) \). In this case, conversion of \( B \) to \( P \) is the rate limiting step, and the characteristic time for the overall reaction (i.e., the characteristic time for formation of \( P \)) is \( k_B^{-1} \).

On the other hand, if \( k_B \gg k_A \) (Figure 3.5b), then \( A \) decays quite slowly to form \( B \), and \( B \) decays almost immediately to form \( P \). As a result, the general pattern of \( c_B \) observed in the previous cases still applies (i.e., \( c_B \) increases, passes through a maximum when \( k_A c_A = k_B c_B \), and then decreases), but the absolute value of the concentration of \( B \) at any time is always small. The equations characterizing the concentrations of \( B \) and \( P \) in this case are as shown below. In this case, the conversion of \( A \) to \( B \) is the rate limiting step in the overall reaction so, as we might expect, the characteristic time for formation of \( P \) is \( k_A^{-1} \).

\[
c_B = \frac{k_A}{k_B} c_A(0)\exp(-k_A t) \tag{57}
\]

\[
c_P = c_A(0)\{1 - \exp(-k_A t)\} \tag{58}
\]
Figure 3.5. Concentration profiles for species $A$, $B$, and $C$ for the same reaction sequence as characterized in Figure 3.4, except with different rate constants: (a) $k_A = 1.0/\text{min}$, $k_B = 0.01/\text{min}$; (b) $k_A = 0.01/\text{min}$, $k_B = 1.0/\text{min}$.
Generalizing the above result, in any reaction sequence, the characteristic time of the overall sequence is at least as long as that of the rate limiting step. If the characteristic time of the rate limiting step is significantly greater than that of any other step in the sequence, that the characteristic time of the overall reaction is approximately that of the rate limiting step. Although this point is made by considering only first order reactions in the example system described above, it applies equally regardless of the detailed reaction rate expressions of the individual reactions in the sequence.

To review, then, when a reaction sequence is initiated, material starts passing through all the steps, and some material accumulates upstream of each point of resistance; i.e., some of each intermediate species accumulates, providing the driving force for the next reaction in the sequence. In an irreversible reaction sequence occurring in a batch reactor, the concentration of each intermediate increases steadily until the driving force is sufficient to push material through that step as rapidly as it is arriving from the upstream step. Thereafter, as the rate at which material arrives declines (because the initial supply of reactant becomes depleted), the concentration of the intermediate decreases, decreasing the rate at which the subsequent reaction proceeds. This process continues until essentially all the material has passed through the whole sequence, and only the ultimate product of the reaction sequence is present.

If the same reaction sequence occurred in a reactor system with a continuous input of the initial reactant (e.g., a CFSTR with the reactant present in the influent at some steady concentration), each intermediate would be generated continuously, and the whole system would reach a steady state in which material was flowing through each reaction at the same rate. To achieve that steady-state condition, the concentration of each intermediate would be large if it preceded a high-resistance reaction, and small if it preceded a low-resistance reaction. Again, the analogy to water flow through a series of tanks is apt.

Regardless of whether the reaction sequence occurs in a batch reactor or a reactor with flow, the greatest resistance (or, colloquially, the tightest bottleneck), the longest characteristic time, and the greatest accumulation of material are all associated with the rate limiting step. In many reaction sequences, the resistance associated with the rate limiting step is so much greater than that of any other step in the sequence that it is reasonable to treat the system as though none of the other reactions impose any resistance at all. In such a case, the initial reactant in the sequence is depleted at a rate that is determined solely by the rate constant for its disappearance. Intermediate species that precede the rate-controlling step are formed and then depleted relatively rapidly compared to formation of ultimate product, while those that follow the rate controlling step attain concentrations that change slowly, allowing the reactions involving those species to proceed at approximately the same rate as the rate controlling step. As a result, the ultimate product is formed continuously at that rate as well.

The preceding summary indicates that material moves through the rate controlling step and all subsequent steps at approximately the same rate. Thus, it is not correct to state that the rate controlling step is the slowest one in the sequence. What is true is that the rate controlling is the major impediment to speeding up the reaction; i.e., material
could move through the rest of the system faster, if the rate-limiting step were not holding everything up.

EXAMPLE 14

Two reactions proceed in sequence. In the first, reactants A and B are converted to a product C and an intermediate D. In the second, D reacts with water to form product E. Both reactions can be treated as irreversible. The reaction between species A and B is first order with respect to each of those species and second order overall, with a rate constant of \(10^{-3} \text{ L/mol-s}\). The subsequent reaction forming species E is pseudo-first order, with \(k = 10^{-2} \text{ s}^{-1}\).

\[
A + B \rightarrow C + D \quad r_A = -(10^{-3} \text{ L/mol-s}) \ c_A c_B
\]
\[
D + \text{H}_2\text{O} \rightarrow E \quad r_D = -(10^{-2} \text{ s}^{-1}) \ c_D
\]

(a) Determine the rate limiting step for this reaction sequence in a system in which the initial concentrations of A and B are both \(10^{-2} \text{ mol/L}\), and the system initially contains no C, D, or E.

(b) Verify your conclusion by comparing the production rates of species E in the initial system and in systems in which \(k_{AB \rightarrow CD}\) or \(k_{D \rightarrow E}\) is increased by a factor of ten. (The hypothetical cases where the rate constant is multiplied by ten might be accomplished by adding catalysts to the system.)

Solution. (a) The characteristic time of the first reaction can be computed using the expressions in Table 3.3, since the initial concentrations of A and B are identical. Using the first definition for \(t_{\text{char}}\), we find:

\[
t_{\text{char}} = \frac{e^n - 1}{n - 1} \frac{1}{k_n c_A^n(0)} = e - 1 \frac{1}{k_n c_A(0)} = 172,000 \text{ s} = 47.8 \text{h}
\]

The characteristic time of the second reaction is simply the inverse of the rate constant, or 100 s. The first reaction is therefore expected to be rate-limiting and to provide almost all the resistance to formation of product.

(b) The conclusion reached in part a is confirmed by the simulations shown in the Figure Ex14-1. Increasing the rate constant of the initial reaction increases the rate of formation of E dramatically, while increasing the rate constant of the second reaction has a much smaller effect.
Figure Ex14-1. Concentration of species $E$ as a function of time in the two-step, irreversible reaction described in the example problem statement, for various values of the forward rate constants $k_{AB}$ and $k_D$. Values shown for $k_{AB}$ are in L/mol-s, and those for $k_D$ are in s$^{-1}$.

Reversibility in a Reaction Sequence

Qualitatively, the effect of reversibility on a consecutive reaction network is easy to predict. Considering the irreversible sequence as the base case, the effect of each reverse reaction is to drive material back upstream in the sequence, thereby slowing the net generation of product. That is, the reverse reaction recycles material that has already passed through part of the network, forcing it to pass through some of the steps again. If the final reaction in the sequence has a sufficiently large equilibrium constant that the overall reaction goes to completion, almost all the initial reactant is eventually converted to product, but with each additional reverse reaction that must be considered, and with each increase in the magnitude of a reverse rate constant, the time required before the reaction is complete increases.

Clearly, reversibility will have the greatest effect on a reaction network if it alters the rate at which material passes through the forward rate determining step. That is, if we consider only the forward reactions in the sequence, we can identify the rate limiting step as described above. A reverse reaction that causes material to pass through that step more than once will have a significant effect on the overall rate of reaction. Similarly, if a reverse reaction significantly slows the rate at which material accumulates upstream of
the rate controlling step, it will slow the overall reaction dramatically. On the other hand, reversibility that forces material to pass through a rapid forward step more than once and does not alter the concentration of reactants driving the rate controlling forward step is not likely to affect the overall rate dramatically.

A Note on the Thermodynamics of Sequential Reactions

The extent of disequilibrium of various reactions is quantified above by the ratio of the activity quotient to the equilibrium constant \( Q/K_{eq} \). Although this ratio is a perfectly valid measure of the extent of disequilibrium, the more conventional thermodynamic measure of disequilibrium is the molar Gibbs energy of the reaction, \( \Delta G_r \) (kJ/mol of reaction). This quantity is related to \( Q/K_{eq} \) by:

\[
\Delta G_r = RT \ln(Q/K) \tag{59}
\]

Thus, the farther a reaction is from equilibrium (i.e., the closer it is to being irreversible), the larger is its negative molar Gibbs energy of reaction.

In a sequence of reactions, the Gibbs energies of the individual reactions are additive, so \( \Delta G_r \) for the overall reaction is the sum of the \( \Delta G_r \) values of the individual reactions. Thus, one can say that, in a reaction sequence, the Gibbs energy of the overall reaction is expended little by little in pushing material through the various steps. Extending the metaphor, other things being equal, the larger is the (negative) Gibbs energy required to push material through an individual step, the larger is the resistance with which that step opposes the overall reaction. The idea that the reaction farthest from equilibrium provides the greatest resistance to the overall reaction is based on this argument, in conjunction with Equation 59.

Since reactions always proceed toward equilibrium, they always proceed in the direction that causes \( \Delta G_r \) to approach zero (and \( Q/K \) to approach 1.0). Thus, it is not possible for the Gibbs energy released from one step in a reaction sequence to allow another step to proceed “uphill” or to “overcome a Gibbs energy barrier.” Such a statement implies that a chemical reaction proceeds in a non-thermodynamic direction (i.e., away from equilibrium) because it somehow knows that the energy cost of doing so can be paid by another reaction. What is possible is that a product from one reaction can be depleted so rapidly by a subsequent reaction that its concentration is maintained at a very low level. In this way, the Gibbs energy change for the first step can be held at a negative value, so that the driving force for that reaction is in the forward direction. Such relationships are the core feature of sequential reactions.

Steady-State: Definition and Comparison with Chemical Equilibrium

A species whose concentration at a given location is not changing over time is said to be at steady state, and, if the concentrations of all chemical species in a reactor are unchanging over time, then the reactor is said to be at steady state. (Note that the concentrations might change from point to point in the reactor; the definition of steady
state requires only that they be constant at each point over time.) In reactors with flow, true steady state conditions can be established, in which case \( dc/dt \) is zero and \( r_i \) is constant indefinitely. Although the reactant concentrations in a reaction sequence proceeding in a batch reactor do change over time, the rates of change of some intermediates that are simultaneously being formed and destroyed can be relatively small. In such cases, an approximation is often made that those intermediates are at steady-state during most of the time the reaction is proceeding. A classic example of the use of this approximation is provided in the next section of this chapter.

Comparing the definition of steady state to that of chemical equilibrium, one might say that steady state describes a condition for a particular species that is analogous to the condition that chemical equilibrium describes for a reaction: in both cases, an overall process is poised at a stable condition as a result of on-going, balanced sub-processes. Because both concepts are central to analysis of physical/chemical treatment systems, and because the distinctions between them are sometimes subtle, it is worth considering a few situations in which each concept is applied independently.

It is noted above that the equilibration of water molecules with \( H^+ \) and \( OH^- \) is so rapid at near-neutral pH that it can be considered instantaneous. If a slow reaction is proceeding in an aqueous system, \( H^+ \) or \( OH^- \) might be generated slowly in the water. For instance, biological processes might consume or generate acidity in a waste treatment system. In such a case, the concentrations of \( H^+ \) and \( OH^- \) could be changing steadily, so they are not at steady state, but they would nevertheless be in continuous equilibrium with one another and with \( H_2O \) via the association/dissociation reaction for water.

On the other hand, as noted above, a species can be at steady state in a reactor if it is formed and destroyed at equal rates by different chemical reactions, or if the summation of the rates at which it is formed by all reactions and the rate at which it enters the reactor by advection, diffusion, and dispersion equals the summation of the rates at which it is destroyed and/or removed from the reactor by those same processes. In many systems, even though one or more individual species are at steady state, the chemical reactions in which those species participate are not at equilibrium.

Thus, a reaction can be at equilibrium even if the concentrations of the reactants and products in the system are changing, and a species can be at steady state even if all the reactions in which it participates are far from equilibrium. Additional important examples of steady state systems are presented in Chapter 4, where the effects of fluid flow and dispersion on the concentration are considered in addition to those of chemical reaction.

**Derivation of the Michaelis-Menten Expression from a Hypothesized Mechanism**

The usefulness of the steady state approximation can be illustrated by the development of the classical Michaelis-Menten relationship describing the enzyme-catalyzed conversion of organic substrates to cell parts. This mechanism was postulated by Michaelis and Menten in 1913 and is still used as the basis for most mathematical modeling of biological reactions in wastewater treatment. The analysis would be quite
complex if the variation in the concentration of intermediates over time had to be considered, but it is greatly simplified if the steady state assumption is made, as shown below.

Michaelis and Menten hypothesized the following set of elementary equations:

\[
E + S \xrightleftharpoons[k_{ES}]{k_{S \rightarrow ES}} ES^* \\
ES^* \xrightleftharpoons[k_{P \rightarrow ES}]{k_{ES^* \rightarrow P}} P + E
\]

where \( E = \) enzyme, \( S = \) substrate, \( P = \) product, and \( ES^* = \) a reaction intermediate. Key assumptions of the model are that:

(i) the concentration of \( ES^* \) reaches an approximate steady state value (note that this value is not the concentration required for equilibrium with \( S \) and \( E \)).
Thus, \( \frac{dC_{ES^*}}{dt} = 0 \).

(ii) for the given steady state concentration of \( ES^* \), \( k_{ES^* \rightarrow P}C_{ES^*} \gg k_{P \rightarrow ES}C_P \), i.e., the reaction \( ES^* \rightarrow P \) is far from equilibrium, and so is essentially irreversible.

Assumption (ii) is usually considered applicable for any steady state concentration of \( ES^* \), implying that the reaction \( ES^* \rightarrow P \) goes to completion. Note that, since the reaction forming \( ES^* \) is assumed to have a significant reverse rate while the reaction forming \( P \) is approximately irreversible, \( Q/K_{eq} \) is much smaller and \( -\Delta G_r \) is much larger for the second step, i.e., most of the energy driving the reaction is released in the second step.

In accord with these assumptions, the expressions for the net formation rates of the enzyme-substrate complex (\( ES^* \)) and the product are:

\[
r_{ES^*} = 0 = k_{S \rightarrow ES}C_EC_S - k_{ES^* \rightarrow S}C_{ES^*} - k_{ES^* \rightarrow P}C_{ES^*} \quad (60)
\]

\[
r_p = k_{ES^* \rightarrow P}C_{ES^*} \quad (61)
\]

The feature of the biological system that is not typical of other reactions is that one of the reactants (\( E \), is consumed in the first reaction step but is then regenerated in the second step. Therefore, in a batch reactor, the total amount of \( E \) in the system (the sum of the concentrations of \( ES^* \) and unbound \( E \)) is constant, regardless of how much \( S \) reacts. The enzyme is thus a catalyst, i.e., a substance that participates in a reaction and affects the overall reaction rate, but is neither generated nor consumed by the overall reaction. Thus, defining \( c_{E,tot} \) as the total concentration of enzyme, we can write:
\[ c_{E,\text{tot}} = c_E + c_{ES^*} \quad (62) \]

Substituting Equation 62 into Equation 60 and then solving for the concentration of \( ES^* \) yields:

\[ 0 = k_{S \rightarrow ES^*} \left( c_{E,\text{tot}} - c_{ES^*} \right) c_S - \left( k_{ES^* \rightarrow S} + k_{ES^* \rightarrow p} \right) c_{ES^*} \quad (63) \]

\[ c_{ES^*} = \frac{k_{S \rightarrow ES^*} c_{E,\text{tot}} c_S}{k_{S \rightarrow ES^*} c_S + k_{ES^* \rightarrow S} + k_{ES^* \rightarrow p}} \quad (64) \]

Finally, inserting Equation 64 into Equation 61 yields, after some manipulation:

\[ r_p = \frac{k_{ES^* \rightarrow p} c_{E,\text{tot}} c_S}{k_{ES^* \rightarrow S} + k_{ES^* \rightarrow p} + c_S} \quad K_m + c_S \quad (65) \]

where \( K_m = \left( \frac{k_{ES^* \rightarrow S} + k_{ES^* \rightarrow p}}{k_{S \rightarrow ES^*}} \right) \) has units of concentration and is known as the Michaelis constant or the half-velocity constant. Assuming the total enzyme concentration is proportional to the microorganism concentration \( c_X \), i.e., \( c_{E,\text{tot}} = k_X c_X \), and letting \( k_X k_{ES^* \rightarrow p} = k_{\text{max}} \), Equation 65 can be rewritten as follows:

\[ r_p = \frac{k_{\text{max}} c_S c_X}{K_m + c_S} \quad (66) \]

Equation 66 is commonly evaluated in terms of the relative values of \( K_m \) and \( c_S \). If \( c_S \ll K_m \), the rate expression reduces to:

\[ r_p = \frac{k_{\text{max}} c_S c_X}{K_m} \quad (67) \]

That is, for fixed \( c_{E,\text{tot}} \) or \( c_X \), the rate of formation of product (new cell parts) is proportional to the concentration of substrate \( (c_S) \), and the reaction is said to be substrate-limited. Under these conditions, there is a significant amount of free enzyme available. As a result, the steady state concentration of \( ES^* \), and hence the rate at which product is formed, can be increased by increasing the substrate concentration.

At the opposite extreme, if \( c_S \gg K_m \), the rate expression reduces to:

\[ r_p = k_{\text{max}} c_X \quad (68) \]
Under these conditions, the reaction is *enzyme-limited*. The system contains a negligible steady state concentration of free enzyme, so adding more substrate cannot increase the concentration of $ES^*$ or the rate of product formation. Using the terms defined earlier in this chapter, the first reaction is poised at a condition of near completion, in which almost all the enzyme is in the form of product ($ES^*$).

The terms substrate-limited and enzyme-limited can be somewhat misleading, since Equations 67 and 68 indicate that the rate of product formation is proportional to the total enzyme concentration in both cases. More descriptive terms would be substrate-and-enzyme-limited and enzyme-only-limited, respectively, but the shorter terms have been universally adopted. The rate under both limiting conditions and under intermediate conditions can be seen in a plot of $r_p$ versus $c_S$ (Figure 3.6).

**Figure 3.6.** Production rate of $P$ as a function of substrate ($S$) concentration for a Michaelis-Menten type reaction. $k_{\text{max}} = 2 \times 10^{-3}$ mol/L-min, $K_m = 0.012$ mol/L.

Derivations such as that shown above played an important role in the historical development of kinetics modeling. The need to make simplifying assumptions to analyze the kinetics of complex networks has diminished as high-speed computing equipment has been used to model the progress of all the steps in such reactions. Nevertheless, the steady-state assumption is still useful for developing simplified conceptual models of these systems and for interpreting the results of the computer simulations.
THE RATE EXPRESSION: MOLECULAR LEVEL INTERPRETATIONS AND TEMPERATURE DEPENDENCE

As noted above, empirical investigations have shown that the rate of formation of products in all elementary reactions, as well as some non-elementary reactions, can be modeled as the product of the rate constant and the concentrations of the reacting species. The dependence of the reaction rate on reactant concentrations is universally attributed to the direct relationship between concentration and collision frequency. The nature of this dependence is the same for all reactions, independent of the identities of the reactants. The rate constant, on the other hand, depends on the specific chemical reaction under study, the chemical conditions in the system, and the temperature.

The effects of temperature on reaction rates are important in environmental engineering because many industrial wastes are generated at elevated temperatures, and in some cases the flow rate of a waste stream is small enough that increasing its temperature in an effort to increase the reaction rate (or, in the case of biological processes, to provide a selective advantage for growth of certain microbes) is an economically and technically attractive option. In addition, temperature is an important parameter to consider when comparing treatment processes in different climates, and seasonal changes in temperature can have a large effect on reaction rates in many natural and engineered aquatic systems. Investigations of the effect of temperature on reaction rates can also provide insight into the mechanisms controlling those rates.

The earliest successful attempt to describe the temperature dependence of reaction rate constants was by Arrhenius, who derived the relationship:

\[ k = k_{Ar} \exp \left( -\frac{E_{Ar}}{RT} \right) \]  

(69)

where \( E_{Ar} \) is an empirical constant, unique to a particular reaction, with units of energy per mole, \( R \) is the universal gas constant \(^{10}\), and \( T \) is the absolute temperature. The value of \( E_{Ar} \) can be related to certain energy changes defined for mechanistic models of elementary reactions. However, Arrhenius’s result was strictly empirical and was based on studies of both elementary and non-elementary reactions.

The effect of temperature on the rate constant, according to the Arrhenius equation, is seen most easily by separating the temperature term from the others in the argument of the exponential and taking the logarithm of both sides of Equation 69:

\[ \ln k = \ln k_{Ar} - \frac{E_{Ar}}{RT} \]  

(70)

\(^{10}\) \( R \) has dimensions of energy per mole per degree (temperature). Values of \( R \) in some common units are 1.987 cal/mol-K, 8.314 J/mol-K and 0.0821 L-bar/mol-K.
Defining $k_{r_1}$ and $k_{r_2}$ as the reaction rate constants at temperatures $T_1$ and $T_2$, Equation 70 can be manipulated as follows:

$$\ln k_{r_2} - \ln k_{r_1} = \ln \frac{k_{r_2}}{k_{r_1}} = -\frac{E_A}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$  \hspace{1cm} (71)

Equation 70 indicates that a plot of $\ln k$ vs. $1/T$ should be a straight line with slope $-\frac{E_A}{R}$ and intercept $\ln k_{A_r}$, as shown in Figure 3.7. By preparing such a plot, one can determine these values and use them to compute the rate constant at other temperatures, either graphically or by inserting the constants into Equation 71.

Recall that the maximum (diffusion-controlled) rate of reaction between two dissolved substances can be estimated based on their encounter rate, as given by Equation 7. By substituting an expression to describe the approximate dependence of $\mu$ on temperature into that equation, the diffusion-controlled rate constant for a reaction between two given species can be described as a function of temperature only. Comparison of such an equation with the Arrhenius expression (Equation 69) allows one to estimate an apparent $E_{A_r}$ of 12 to 20 kJ/mol for diffusion-controlled reactions between uncharged molecules.

---

**Figure 3.7.** Characteristic plot of the rate constant vs. inverse absolute temperature, from which the values of $k_{A_r}$ and $E_{A_r}$ can be computed. ($\ln k_{A_r}$) is found by extrapolating the straight line to the hypothetical condition $1/T = 0$.)

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71
A Molecular-Level Picture of an Elementary Reaction, and its Relationship to the Components Of the Reaction Rate Expression

The Arrhenius model for the dependence of the reaction rate constant on temperature has held up remarkably well over the years. However, more modern representations of reaction kinetics are based on mechanistic models of the relevant molecular interactions, and both the rate constant and the concentration dependence of the reaction rate are interpreted in the context of these models. Since these models attempt to represent the progress of individual reactions at the molecular level, the results are directly applicable only to elementary reactions and not to more complex situations. The following discussion provides a conceptual model describing the progress of an elementary reaction; the translation of this model into a mathematical framework is then described.

When reactant molecules approach one another, interactions between their electric fields cause the bonds in each molecule to become strained, a process that increases the chemical potential energy of the molecules. The strain increases dramatically with decreasing separation. Since energy is conserved during the interaction, this increase in chemical potential energy must somehow be balanced by a corresponding decrease in energy elsewhere in the system. In this case, the dominant conversion process is from molecular kinetic energy into chemical potential energy: the molecules slow down as the distance between them decreases (some of the molecular energy associated with intramolecular vibrations and rotation may also be affected). In the absence of other factors, the molecules would eventually stop their mutual approach and then begin moving away from each other, thereby relieving the strain and re-converting the chemical energy into kinetic energy. The process is identical to that represented by a ball rolling up an incline, stopping, and reversing itself.

However, it is possible that, as the original molecular structures adjust in response to the strain, some bonds will weaken and others will begin to form. At some critical point, the original bonds may become sufficiently distorted, and the new bonds may form to a sufficient extent, that the strain can be more easily relieved by rearrangements that form product molecules rather than the original reactants. The amount of energy necessary to bring molecules from far apart (no interaction) to the critical point (the point where the strain is equally likely to be relieved by formation of products or re-formation of reactants), or, equivalently, to increase the chemical potential energy from the condition of no interaction to the critical point, is called the activation energy. Similarly, the process of reaching the critical condition is sometimes referred to as overcoming the activation energy barrier. At the critical point, the molecules are not identifiable as either the reactants or the products, but are an intermediate species of negligible stability known as an activated complex.

In addition to the energy of the colliding molecules, the orientation of the molecules when they collide might be important in determining whether a reaction occurs. If the molecules are not spherically symmetric, only a fraction of all collisions can cause the bonds to distort in a way that leads to the formation of product, even if the collisions involve an amount of energy greater than the activation energy. Thus, the overall rate of reaction depends on the frequency with which reactant molecules interact, the likelihood
that colliding molecules are properly oriented and have sufficient kinetic energy to form the activated complex, and the rate at which the activated species is converted to products.

Catalysts operate by providing an alternative mechanism by which a reaction can occur. In terms of the current discussion, they allow reactants to be converted to products via a route that has a lower activation energy than the route that is taken in their absence. The path that reactants follow as they convert to products is sometimes compared to a landscape, in which energy is initially required to bring the reactants to the top of a hill before they can progress down the other side to form the product. Based on that analogy, a catalyst might be viewed as a substance that opens an alternative path that does not require quite so much of a climb before arriving at a point on the downhill slope. In some cases, catalysts can increase the rate of an overall reaction by a factor of many orders of magnitude.

Sometimes, the product of the reaction itself can act as a catalyst. For instance, during the oxidation of ferrous ion (Fe\(^{2+}\)), ferric hydroxide solids (Fe(OH)\(_3\)(s)) are often formed. The surfaces of such oxides can catalyze the oxidation of the ferrous ions remaining in solution, so the effective rate constant increases as the reaction proceeds. Such reactions are called auto-catalytic. In other cases, the products of the reaction may combine with a reactant to form a species that does not participate in the original reaction. In those cases, the net result is that as product forms, the overall (apparent) rate constant decreases, and the reaction is said to be auto-retardant.

Note that, since the reactants and ultimate products are the same in the presence or absence of catalysts, catalysts cannot change the energetics of an overall reaction (e.g., they cannot change \(\Delta G^{\circ}\)) or the equilibrium constant for the reaction. Since the equilibrium constant for an elementary reaction is the ratio of the forward and reverse reaction rate constants, this ratio cannot change when a catalyst is added to the system, so catalysts must increase the reverse reaction rate constant by exactly the same factor as they increase the forward rate constant.

Two mathematical models for the overall reaction rate expression have been developed based on the conceptual picture described above. The models are called the collision model and the activated complex or transition state model, although the names may be somewhat misleading since both rely on the conceptual framework of collisions causing molecules to pass through an activated state which decays to product. The key difference between the models relates to how molecules are envisioned to approach and pass through the activated state. In the collision model, this passage is treated as an instantaneous process, like passing through an infinitely thin gate: at any instant, no molecules can be said to be in the gate; each molecule in the system can be identified as either a reactant or a product.

In the transition state model, the passage from reactants to products is viewed more as a continuum. The mathematical formalism of the model involves a representation of the energy path that reactant molecules follow during the process, a path that, as noted above, is often likened to passage over a mountain pass. While the concentration of molecules at
the exact peak of the path is essentially zero at any instant, a finite concentration of molecules is envisioned to be on the flat part of the pass near the peak, and all of these molecules are considered to be activated complexes. For a generic bimolecular reaction between $A$ and $B$, the activated complexes are commonly represented as $AB^*$, i.e., the reaction is $A + B \rightarrow AB^* \rightarrow P$. A schematic of the energy relationships in the transition from reactants through the high-energy state to products according to the two models is shown in Figure 3.8.

![Figure 3.8. Schematic representation of the transition from reactants to products according the collision and activated complex (transition state) models.](image)

Currently, the activated complex model is the dominant model for characterizing the progress of reactions. In the following section, some key mathematical relationships that define or have been derived from this model are presented. Additional information on both the conceptual underpinnings of the model and its implications are available in a number of water chemistry books as well as in virtually all physical chemistry textbooks.\(^{11}\)

SUMMARY

This chapter describes the techniques commonly used to analyze rate data from batch, well-mixed, homogenous (one-phase) systems. Such systems are often used for the study of reaction kinetics, because the mass balance reduces to a very simple form. Reaction kinetics studies are also sometimes studied in reactors with flow, either as a matter of preference or for more fundamental reasons. Such systems are discussed and the relevant mass balances are solved in the following chapter. Subsequent chapters extend the analysis to multi-phase systems, e.g., systems where transfer of a substance into a gas or onto a solid adsorbent is an important process.

Chemical reactions generally occur via collisions among molecules. Reactions that result from a single collision are called elementary reactions, and their rates are given by the product of a temperature-dependent rate constant and the concentrations of the colliding species. However, many overall reactions reflect the result of two or more elementary reactions. In such cases, the rate expression can take many mathematical forms, sometimes containing more than one constant and the concentrations of the reacting species raised to various powers.

Elucidation of rate expressions generally involves collection of experimental data and attempts to fit the data to potentially appropriate equations. Both integral and differential methods are used to test hypothesized rate expressions. The identification of an appropriate rate expression is reasonably straightforward in cases where the data can be fit with a power law expression. If the rate expression is not of the power law type, its identification is more problematic. If a reaction rate depends on the concentrations of several different species, the effect of individual species can be isolated by adding a relatively great excess of all species except one. By repeating the process and changing the species that is not added in excess, information about the rate dependence on each species can be obtained.

All reactions are reversible, at least in theory, and are therefore characterized by an equilibrium constant. For elementary reactions, the equilibrium constant can be identified as the ratio of the forward and reverse rate constants. The extent of disequilibrium of a reaction is quantified by the ratio $Q/K_{eq}$, a quantity that is also related to the amount of Gibbs free energy that is released as a reaction proceeds. Reactions that are far from equilibrium can be approximated as being irreversible.

The characteristic reaction time provides a rough idea of the time frame over which a reaction proceeds. If the time available for reaction is far less than the characteristic time, negligible reaction occurs, and if the time available is far greater, the reaction proceeds almost to its endpoint (completion or equilibrium). The characteristic reaction time is also a qualitative indicator of how much a particular reaction resists conversion of reactants into products: the longer the characteristic time, the greater the resistance.

Many overall reactions of interest consist of a sequence of approximately irreversible reactions. If one of the reactions in the sequence has a much longer characteristic time than the others, then it generates almost all the resistance to the progress of the reaction.
Such a reaction is called the rate limiting, rate determining, or rate controlling step. This step represents a bottleneck in the overall process, and it limits the overall rate of product formation. Reactants upstream of the rate controlling step are depleted relatively quickly, and those downstream (other than the ultimate product) attain gradually changing concentrations that allow them to proceed at approximately the same rate as the rate-controlling step.

Reversible reactions in the middle of a reaction sequence slow the overall rate of product formation. The effect of reversibility is particularly significant if it decreases the driving force for the rate limiting step in the sequence, or if it causes material to pass through that step more than once.

Mathematical analysis of reaction networks can be complex even when the networks include only a few reactions. Approximations that some constituents are at steady state, or that some reactions are irreversible, rapidly equilibrated, or complete are sometimes made to reduce the mathematical and conceptual complexity of such systems. The Michaelis-Menten expression is a well known and historically important example of the application of such simplifications. The proposed mechanism associated with that expression also shows how catalysts can participate in an overall reaction, even though they do not appear in the overall reaction stoichiometry.

Attempts to predict the rates of elementary reactions from first principles have led to development of the collision and activated complex models of reaction progress. The models represent reactions as requiring collisions among molecules that have enough energy and are properly oriented to overcome an activation energy barrier, after which conversion into product molecules is spontaneous. In aqueous solutions, the maximum rate at which reactions can proceed is limited by the rates of diffusion of the reacting molecules. Although some reactions seem to proceed at the maximum rate, most proceed more slowly, indicating that the activation energy barrier is significant.

No matter how persistent or determined the investigator, some reaction rate expressions seem to defy efforts to represent them in reasonably tractable mathematical forms. In such cases, it must be remembered that the study of kinetics is inherently empirical, and that, in the absence of simple mathematical relationships describing rate expressions, empirical data describing the reaction rate as a function of the concentrations of various constituents of the system can serve the same function.
HOMEWORK PROBLEMS

1. The following table gives the rate of product formation from a reaction between $A$ and $B$, for various concentrations of both reactants. Deduce the values of $x$ and $y$ and of the rate constant $k$, if the reaction rate expression is known to be $r = k (A)^x (B)^y$.

<table>
<thead>
<tr>
<th>$c_A$, mol/L</th>
<th>$c_B$, mol/L</th>
<th>$-r_A$, mol/L-s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.3 \times 10^{-4}$</td>
<td>$3.1 \times 10^{-5}$</td>
<td>$5.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$4.6 \times 10^{-4}$</td>
<td>$6.2 \times 10^{-5}$</td>
<td>$4.16 \times 10^{-3}$</td>
</tr>
<tr>
<td>$9.2 \times 10^{-4}$</td>
<td>$6.2 \times 10^{-5}$</td>
<td>$1.66 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

2. An enzyme-mediated reaction is described by the Michaelis-Menten equation with $K_m$ of $3 \times 10^{-3}$ mol/L, $c_E$ of $10^{-4}$ mol/L, and $k_{S \rightarrow IS^*}$ of $10$ min$^{-1}$. How long would it take to convert 99% of the initial substrate $S$ to product $P$ in a batch process if the initial concentration of $S$ is $10^{-2}$ mol/L? Compare the result based on an analytical solution to the problem (by integrating the relevant equation) with that obtained if the assumption is made that $c_S \gg K_m$.

3. Oliver and Schindler (EST 14, 12, 1502 (1980)) presented the data shown below for chloroform (CHCl$_3$) production from the chlorination of aquatic algae.

Time Course of Production of CHCl$_3$ from Chlorination of Anabaena oscillarioides. Reaction Conditions: chlorine, 10.3 mg/L; algae, 3.6 mg dry weight/L; T, 20°C.

<table>
<thead>
<tr>
<th>Time, h</th>
<th>pH 7</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>22</td>
<td>16</td>
<td>68</td>
</tr>
<tr>
<td>47</td>
<td>35</td>
<td>125</td>
</tr>
<tr>
<td>76</td>
<td>48</td>
<td>171</td>
</tr>
<tr>
<td>95</td>
<td>65</td>
<td>212</td>
</tr>
</tbody>
</table>
Effect of Chlorine Dose on CHCl₃ Production from *Anabaena oscillarioides*. Reaction conditions: algae, 3.6 mg dry weight/L; T, 20°C; reaction time, 24 h.

<table>
<thead>
<tr>
<th>Chlorine Dose, mg/L</th>
<th>CHCl₃, µg/L at pH 7</th>
<th>CHCl₃, µg/L at pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>72</td>
</tr>
<tr>
<td>20</td>
<td>23</td>
<td>143</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>180</td>
</tr>
<tr>
<td>75</td>
<td>24</td>
<td>205</td>
</tr>
<tr>
<td>150</td>
<td>30</td>
<td>230</td>
</tr>
</tbody>
</table>

(a) What do you think the reaction order is with respect to chloroform? Explain briefly how you reached your conclusion.

(b) Assuming the reaction is first order with respect to algal dry weight concentration, derive a conditional rate expression for the reaction at pH 7.0 and 20°C. Note: You will have to develop the expression based on your own interpretation of the data; there is no single correct rate expression that can be identified based on the given information. However, you should be able to identify an expression that is at least reasonably consistent with the trends shown.

(c) According to your expression in part (b), how much chloroform would be generated in a batch system containing 8 mg/L dry weight algae exposed to 5.0 mg/L Cl₂ for 2 hours at pH 7?

4. Based on data obtained by Lee (199x), the following data characterize the oxidation of acetic acid by hydrogen peroxide under supercritical conditions (*T* > 374°C, *P* > 218 bar) in a batch system. The first table contains data collected at *T* close to 500°C, and the second table contains data over a range of temperatures. (Note: these data are messy; considering the implicit data point at time zero in addition to the reported data will aid in the analysis.)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>(c(0)), mmol/L</th>
<th>(c(t)), mmol/L</th>
<th>Time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>502.7</td>
<td>2.925</td>
<td>0.313</td>
<td>13.7</td>
</tr>
<tr>
<td>501.0</td>
<td>2.822</td>
<td>0.468</td>
<td>14.1</td>
</tr>
<tr>
<td>502.3</td>
<td>2.815</td>
<td>0.152</td>
<td>20.2</td>
</tr>
<tr>
<td>503.7</td>
<td>2.804</td>
<td>0.056</td>
<td>26.0</td>
</tr>
</tbody>
</table>
(a) Use integral methods to determine whether the data are best described by zero, first, or second order reaction kinetics with respect to acetic acid, and estimate the rate constant for the chosen rate expression.

(b) Based on the reaction order determined in part (a), estimate the value of the rate constant $k$ for each experiment, and estimate the value of $E_a$ for the reaction.

5. Revise the rate expression in Example 6 so that it is given as a function of $c_{CN^-}$ rather than as $c_{CN_{tot}}$. The acidity constant for HCN is $pK_a = 9.2$. 

\[
\begin{array}{cccc}
\text{Temp (°C)} & c(0), \text{mmol/L} & c(t), \text{mmol/L} & \text{Time, s} \\
450.9 & 3.877 & 1.935 & 29.3 \\
449.0 & 5.369 & 3.425 & 20.7 \\
461.7 & 3.509 & 1.323 & 27.6 \\
462.7 & 3.239 & 1.189 & 26.0 \\
473.9 & 3.250 & 0.546 & 32.1 \\
474.9 & 3.242 & 0.486 & 32.2 \\
502.3 & 2.815 & 0.152 & 20.2 \\
503.7 & 2.804 & 0.056 & 26.0 \\
523.9 & 1.555 & 0.023 & 14.1 \\
525.5 & 1.528 & 0.015 & 20.6 \\
\end{array}
\]