



at a time, so it takes many measurements to determine a rate equation (i.e., the rate as a function of concentration). One can get useful data from a single run with an indirect measurement.

Still, the advantage of a direct method is that one measures the rate equation (i.e., the rate as a function of the reactant concentration) directly. One does not have to make any assumptions about the form of the rate equation to get an answer.

Generally direct measurements are much easier to fit to a rate equation than indirect measurements because, in a direct measurement, one determines the rate equation directly, while in an indirect measurement, one needs to infer the rate equation by fitting a curve to the data. The latter process can introduce some degree of error.

In my experience, when you are trying to determine kinetics for a new system, it is usually better to start with an indirect method. The indirect method gives you an approximate rate equation with a quick and easy experiment. That is often good enough. A direct method is required only when you need a precise rate equation. If you are designing a process where a 10% change in rate matters, you need to do direct rate measurements. If you can accept a 10% error and adjust the process accordingly, an indirect method will suffice. In my experience, direct measurements take 10–100 times longer than indirect measurements, so direct methods are useful only when a high degree of accuracy is needed.

3.5 EXAMPLES OF DIRECT AND INDIRECT METHODS

Indirect methods are the most common kinetic measurements in the older literature. You measure a concentration as a function of time and then fit the data to a rate equation. Direct measurements are harder. One has to find a way to measure the rate of reaction directly.

Most direct methods involve differentiating a rate equation. However, that is not a necessity. For example, in the reactor in Figure 3.8, one could measure how much arsine flows into the reactor and how much flows out. If one knows how many moles per hour of arsine flow into the reactor and how many moles per hour flow out of the reactor, one can calculate the rate from a mass balance:

$$R_{As} = \frac{1}{A_w} (F_{in} - F_{out}) \quad (3.9)$$

where R_{As} is the rate of arsenic deposition per unit area, A_w is the area of the wafer, F_{in} is the flow rate of arsine into the reactor in mol/hour, and, F_{out} is the flow rate of arsine out of the reactor in mole/hour.

Notice that one is still directly measuring the rate. Therefore, one would call the measurement a *direct method* or a *differential method*, even though you are not differentiating anything to get a direct measurement of the rate.

Note, however, that equation (3.9) applies only if the rate is constant across the wafer and there is no reaction anywhere else in the reactor. If there were a reaction somewhere else in the reactor, one would have to do analysis to eliminate those effects. One would call the measurement *integral methods* or *indirect methods* since one needs to do an analysis to determine the rate. Generally, one would only call a measurement a *direct determination* of the rate equation when one can directly measure the rate as a function of concentration. If one has to do some analysis, it will be an indirect method.

There are many variations of this idea. Today, most direct kinetic measurements are made in a continuously stirred tank reactor (CSTR). Figure 3.4 shows a diagram of a CSTR. Basically, you continuously feed reactants into the reactor. Some of the reactant molecules react, while other reactant molecules just flow through the reactor. You then measure the reactant concentration in the inlet and outlet of the reactor. The average reaction rate \bar{r}_A in the reactor is given by

$$\bar{r}_A = \frac{C_A^{in} - C_A^{out}}{\tau} \quad (3.10)$$

One then runs the reactor so that the mixture stays well mixed. In that case, the rate is constant throughout the reactor, so one can calculate the rate directly from equation (3.10).

Another important direct method is the **method of initial rates**. In the initial rate method, one runs the reaction in a batch reactor, as in an indirect measurement. However, one analyzes the rate differently. Consider the data in Figure 3.2. Figure 3.2 shows concentration–time data. Notice that according to equation (2.4), the rate at any time is the slope of the tangent to the line. Therefore, one can use the slope to get a rate.

In the initial rate method, one fits a (dashed) line to the initial part of the concentration versus the data. The rate is the slope of the line. One then changes the initial concentration, and generates the rate versus concentration data. The advantage of this approach is that one can operate direct data quickly, by running several small reactors at once.

3.6 EXAMPLES OF INDIRECT MEASUREMENTS

Indirect measurements are generally made in a batch system. Most of the rate measurements you did in your chemistry lab were indirect measurements. For example, you might have loaded some species into a beaker, measured the concentration versus time, and fit the data to a first-order or second-order rate law. That is an indirect measurement. The flash photolysis experiments that students sometimes do are also indirect measurements of the rate law. Direct measurements require that you actually measure the rate. The measurements are harder. They are seldom done in undergraduate labs. In Table 3.1, we briefly mentioned several techniques that one uses to measure rates of reaction. As an exercise, the reader should go back and decide whether each method is a direct or indirect one.

3.7 FITTING DATA TO EMPIRICAL RATE LAWS: SINGLE REACTANTS

At this point, we will be changing topics. We will assume that you have used either a direct or an indirect method to measure the rate data for a given reaction. We will now discuss how one fits the rate data to a rate equation.

The general scheme will be to

1. Determine the order of the reaction. (In a complicated case, one also has to determine the form of the rate equation.)
2. Fit the constants.

The hard part is to determine the order of the reaction.

3.8 ANALYSIS OF DATA FROM A DIFFERENTIAL REACTOR

The easiest data to analyze are data from a differential reactor. As noted above, in a differential reactor, one can measure the rate directly at a fixed concentration of reactants. One then varies the concentration of the reactants and measures the rate again. The data can then be fit to a rate equation using a regression technique.

If the data are simple, a log-log plot of the rate versus concentration can be used to infer the order of the reaction. In a more complex case, one needs to assume a form for the rate equation and then fit the data to constants. In Chapters 4 and 5, we will discuss how one can guess a suitable rate form for the rate equation. However, the analysis is easy once the data are obtained.

For example, copper and platinum have been suggested as components in memory chips. Steger and Masel (1994, 1998) have examined the rate that copper is etched in a mixture of oxygen and hexafluoroantipentadecane ($\text{CF}_3\text{COCH}_2\text{COCF}_3$). Steger and Masel found that the main reaction is



Steger and Masel loaded a copper disk into a flow reactor similar to the one shown in Figure 3.7. They then turned on the feed and measured the weight of the copper disk as a function of time to yield the data in Figure 3.9. The data were then plugged into equation (3.10) to calculate a rate. Steger and Masel then changed the O_2 concentration in the reactor and measured the rate again. After several runs, they were able to generate the data shown in Figure 3.10. The data are a little unusual in that Steger and Masel observed two different rate laws: one rate law when the copper is oxidized and a different rate law when the copper is reduced. Further, there is a change from one rate law to another as the oxygen pressure is increased in the reactor and the copper is oxidized. Still, the analysis of this data are simple. For example, Steger and Masel used a regression technique to fit the data on the unoxidized surface to the following rate form:

$$R_{\text{Cu}} = \frac{k_3 P_{\text{O}_2}^{1/2}}{1 + K_2 P_{\text{O}_2}^{1/2}} \quad (3.12)$$

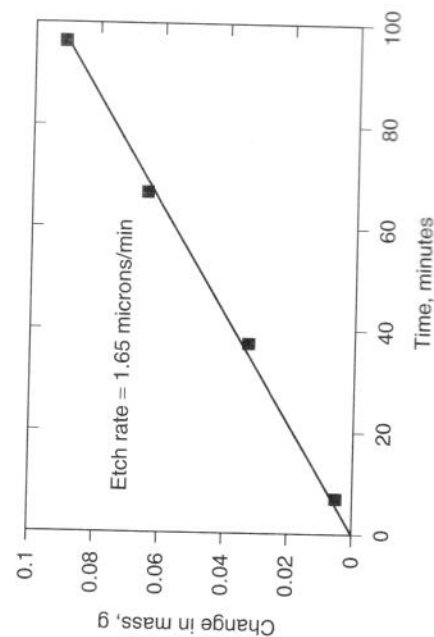


Figure 3.9 The weight of a copper disk as a function of time as measured by Steger and Masel.

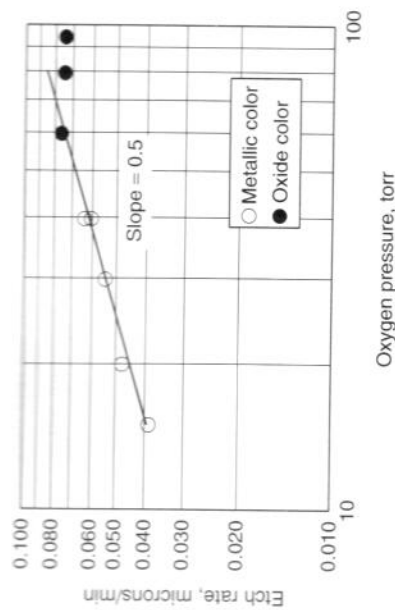


Figure 3.10 The rate of copper etching as a function of the oxygen concentration. [Data of Steger and Masel (1998).]

Notice how easy it is to do the analysis even though this is a very complex reaction. The technique can easily be generated. If one can measure a reaction in a differential reactor, one can get data for the rate as a function of the reactant concentration. One can then fit the rate data using a regression method. Detailed analysis of the data are given in Example 3.E. The result is a straightforward analysis of rate data.

3.8.1 Pitfalls in the Analysis of Rate Data from a Differential Reactor

There are a few pitfalls in analyzing the rate data from a differential reactor.

- It is not uncommon for more than one rate equation to fit the measured kinetics within the experimental uncertainties. One should not infer that the rate equation is correct just because the data fits.
- The quality of kinetic data varies with the equipment used and the method of temperature measurement and control. Data taken on one apparatus are seldom directly comparable to data taken on a different apparatus.
- It is not uncommon to observe 10–30% variations in rate taken in the same apparatus on different days. Usually, these variations can be traced to variations in the temperature, pressure, or flow rate in the reactor.
- The procedure used to fit the data can have a major effect on the values of the parameters obtained in the data analysis.
- The quality of the regression coefficient (r^2) does not tell you how well a model fits your data.

Examples 3.A to 3.C illustrate this effect. In the examples, we fit the parametric data in Figure 2.1 to two different rate equations:

$$\text{Rate} = \frac{k_1 K_2 [\text{par}]}{1 + K_2 [\text{par}]} \quad (3.13)$$

$$\text{Rate} = \frac{k_1 K_2 [\text{par}]}{1 + K [\text{par}]^{3/2}} \quad (3.14)$$

and three different fitting procedures.

then fits the resulting data to a universal curve to infer a rate equation. In this section, we will derive expressions for the universal curves. We will assume perfect mixing and kinetics of the form:

$$r_A = -k_n[A]^n \tag{3.15}$$

We will then derive a universal curve for the concentration versus time. We include the derivation for completeness. However, one can skip to equation (3.42) without loss of continuity.

Consider a reaction $A \Rightarrow B$ in the batch reactor shown in Figure 3.11. For the purpose of derivation, we will assume that the concentration of A is the same everywhere in the reactor, and that the reactor is sealed so no A evaporates, enters the reactor, or leaves the reactor.

If there is no flow in or out of the reactor, then all of the A that is generated in the reactor must accumulate in the reactor. Therefore

$$\left(\text{Rate of accumulation of A} \right) = \left(\text{Rate of generation of A} \right) \tag{3.16}$$

where

$$\left(\text{Rate of generation of A} \right) = \left(\begin{matrix} \text{moles of} \\ \text{A reacted} \\ \text{per unit time} \end{matrix} \right) \tag{3.17}$$

Substituting the definition of r_A into the right side of equation (3.17) yields

$$\left(\text{Rate of generation of A} \right) = r_A V \tag{3.18}$$

where V is the volume of liquid in the batch reactor. Similarly

$$\left(\text{Rate of accumulation of A} \right) = \frac{dN_A}{dt} \tag{3.19}$$

where N_A is the number of moles of A in the batch reactor.

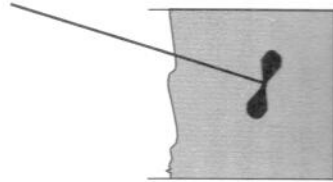


Figure 3.11 A batch reactor.

Table 3.3 Results of four different ways to fit the rate data

Rate Equation	Fitting Method	k_1	K_2	r^2	Total Error
(3.13)	Lineweaver-Burke	140	0.0370	0.901	9454
(3.13)	Eadie-Hofstee	246	0.0156	0.344	5647
(3.13)	Nonlinear least squares	204	0.0221	0.905	4919
(3.14)	Nonlinear least squares	—	—	0.908	4576

Table 3.3 illustrates the result of the analysis. Notice that the rate constants vary by a factor of 2 according to which fitting procedure is used. The Eadie-Hofstee fitting method gives a terrible r^2 but a reasonable error. The Lineweaver-Burke method gives a great r^2 , but a large error. Equations (3.13) and (3.14) fit the data almost equally well. The data show a small preference for equation (3.14). However, the analysis in Example 3.C shows that the differences are not statistically significant.

These examples illustrate the pitfalls in analyzing rate data. A rate equation can fit data poorly and still give a reasonable value of r^2 . A rate equation can fit well and give a poor value of r^2 . Different models can fit the data within the statistical noise in the data.

There is one other difficulty with direct measurements—the measurements are rather tedious. One needs to make a separate measurement for each set of conditions. Generally, each point in Figure 3.10 took about a day to take and a second day to reproduce. The entire plot took over a month. Further, we needed several plots: one for each hexafluoropentamethione concentration to determine a rate law. These measurements took months to complete. Also, differential reactors tend to be hard to operate. There were many bad runs. One does have to think about whether it is necessary to take such difficult data when one is planning the experiment.

3.9 ANALYSIS OF RATE DATA FROM AN INTEGRAL REACTOR

The alternative is to use an indirect method. The advantage of an indirect method is that one can generate a significant amount of data in a short time. The disadvantage is that the data are harder to analyze than data from a differential method and the uncertainty in the data analysis is large with differential data.

In the next several sections, we will discuss how one analyzes data from what is called an **integral reactor**, which is a reactor you use to do both indirect and direct rate measurements. The simplest integral reactor is a **batch reactor**. A batch reactor is a closed vessel like a flask with a stirrer. One loads the reactants into the batch reactor and measures the concentration of the reactants as a function of time. Typical data are shown in Figure 3.2. One then fits the data to a universal curve to infer the order of the reaction and the rate constant. We will derive an equation for the performance of the batch reaction in Section 3.9.1 and use the equation in Section 3.10. The actual derivation is not important. One could skip to Section 3.10 without loss of continuity.

3.9.1 Derivation of the Concentration versus Time for Batch Reactions

Generally, if one wants to use a batch reactor to determine kinetics, one loads the reactants into the reactor and runs the reaction while measuring the concentration versus time. One

Substituting equations (3.18) and (3.19) into equation (3.16) shows

$$r_A V = \frac{dN_A}{dt} \quad (3.20)$$

Integrating equation (3.20) yields

$$\int_{N_A^0}^{N_A^F} \frac{dN_A}{V} = \int_0^\tau dt = \tau \quad (3.21)$$

where N_A^0 is the initial concentration of A, N_A^F is the final concentration of A, and τ is the reaction time. Inverting the limits in equation (3.21) yields

$$\int_{N_A^F}^{N_A^0} \frac{dN_A}{V(-r_A)} = \tau \quad (3.22)$$

It is often useful to work in terms of quantity called the *conversion*, X_A , where X_A is defined by

$$X_A = \frac{N_A^0 - N_A}{N_A^0} \quad (3.23)$$

Physically, X_A is the fraction of the reactant A that has been converted into products. One should memorize this definition before proceeding.

Differentiating equation (3.23) and rearranging yields

$$dN_A = N_A^0(-dX_A) \quad (3.24)$$

Changing the integral in equation (3.22) from moles to conversion yields

$$\int_0^{X_A} \frac{N_A^0(-dX_A)}{V(-r_A)} = \tau \quad (3.25)$$

rearranging equation (3.25) yields

$$N_A^0 \int_0^{X_A} \frac{dX_A}{V(-r_A)} = \tau \quad (3.26)$$

Note that r_A is negative in equation (3.26), that is, $(-r_A)$ is positive. Consequently τ works out to be positive in equation (3.26). Equations (3.22) and (3.26) are the key equations for batch reactors.

Note that when a reaction proceeds, $(-r_A)$ decreases. $1/V(-r_A)$ increases as indicated in Figure 3.12. The time is proportional to the area under the curve in Figure 3.12. Initially, it takes little time to increase the conversion. However, as time proceeds, the curve in Figure 3.12 increases so it takes proportionally more time to get to higher conversion.

Another important idea is that the time to get to a certain conversion is proportional to the area under the curve in Figure 3.12. This idea is often used in reactor design.

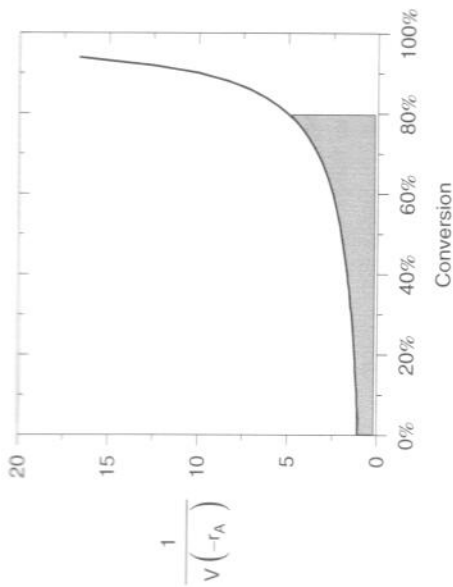


Figure 3.12 A plot of $\frac{1}{V(-r_A)}$ for a first-order reaction in a batch reactor.

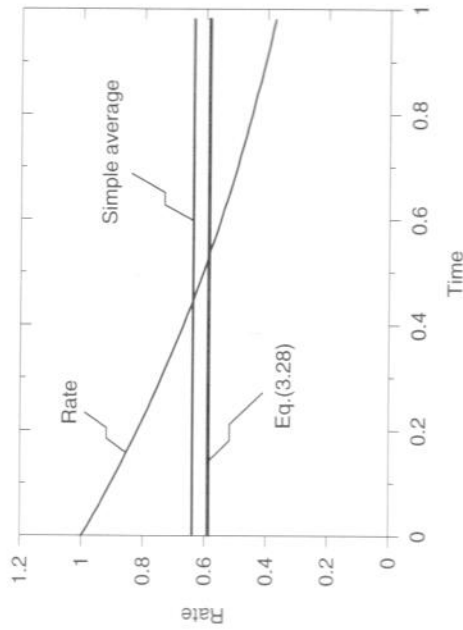


Figure 3.13 $\left(\frac{1}{r_A}\right)$ versus \bar{C} for a first-order reaction in a batch reactor. Notice that the rate decreases with time.

Next we will derive an approximation for constant density systems. Examples of constant density systems include

1. Liquid reactions in solution
2. Gas-phase reactions with no net change in moles, such as

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$$
3. Reactions in constant-volume closed-batch reactors

For constant density, we can remove V from the integral in equation (3.26):

$$\frac{N_A^0}{V} \int_0^{X_A} \frac{dX_A}{-r_A} = \tau \quad (3.27)$$

$$C_A^0 \int_0^{X_A} \frac{dX_A}{-r_A} = \tau \quad (3.28)$$

where C_A^0 is the initial concentration of the reactant A in the reactor. It is also useful to transform equation (3.28) as follows. Note that if we divide equation (3.23) by V , and rearrange, we find that for a constant-density system

$$C_A = C_A^0(1 - X_A) \quad (3.29)$$

where C_A is the concentration of A and, C_A^0 is the initial concentration of A. Substituting equation (3.29) into equation (3.28) yields

$$\int_{C_A^0}^{C_A} \frac{dC_A}{-r_A} = \tau \quad (3.30)$$

where C_A in the upper limit of the integral is the concentration after a time, τ . Switching the limits in equation (3.30) yields

$$\int_{C_A^0}^{C_A} \frac{dC_A}{-r_A} = \tau \quad (3.31)$$

Equations (3.28) and (3.31) form the basis of batch reactor design for constant-density systems.

Notice that according to equation (3.31), the time is given as an integral of the rate equation, which is why this type of analysis is called an *integral method*.

Equation (3.31) is different from equation (3.26) in that it considers a plot of $1/(-r_A)$. $1/(-r_A)$ decreases with increasing concentration as indicated in Figure 3.13. Note, however, that during the reaction you start with a high concentration of the reactants, and end up with a low concentration of reactions. Consequently, $1/(-r_A)$ increases as the reaction proceeds.

The time needed to obtain to a given is proportional to the area under the curve in Figure 3.14. The idea that time is proportional to an area under the curve is quite important to reactor design.

Next, it is useful to discuss how equation (3.31) relates to the definition of a reaction rate in Chapter 2. Recall that in Chapter 2 we defined the reaction rate to be a rate in molecules per hour per reactor volume. Next, we want to demonstrate that equation (3.31) implies that the production rate of species in the reactor is proportional to the average rate

In the reactor times the reactor volume, where the average reaction rate, \bar{r}_A is given by

$$\frac{1}{\bar{r}_A} = \frac{\int_{C_A^0}^{C_A} \frac{dC_A}{r_A}}{\int_{C_A^0}^{C_A} dC_A} \quad (3.32)$$

Note that during a reaction in a batch reactor, r_A is changing with time as indicated in Figure 3.13. The function \bar{r}_A is an average value of r_A over the course of the reaction. Performing the integral in the denominator of equation (3.32) and rearranging yields

$$\frac{(C_A^0 - C_A)}{\bar{r}_A} = \int_{C_A^0}^{C_A} \frac{dC_A}{r_A} \quad (3.33)$$

Substituting equation (3.31) into equation (3.32) yields

$$-\frac{C_A^0 - C_A}{\bar{r}_A} = \tau \quad (3.34)$$

Rearranging equation (3.34) yields

$$\frac{C_A - C_A^0}{\tau - t_0} = \bar{r}_A \quad (3.35)$$

where $t_0 = 0$. One can rewrite equation (3.35) as

$$\frac{\Delta C_A}{\Delta t} = \bar{r}_A \quad (3.36)$$

This compares to the corresponding equation for a differential reactor.

$$\frac{dC_A}{dt} = r_A \quad (3.37)$$

Notice that equations (3.36) and (3.37) are very similar. In a differential reactor, one measures an instantaneous rate. In contrast in an integral reactor, one measures an average rate where the average is defined by equation (3.32). When one averages, one washes out some of the details. Consequently, integral methods tend to be less accurate than differential methods.

3.9.2 Derivation of the Performance Equations for nth-Order Kinetics

Next, we will derive the performance equations for a first-order reaction and an nth-order reaction in a batch reactor. The derivation is included because many of our students need to see it again. However, I am assuming that most of our readers have already seen the derivation. Therefore, one could skip this section without loss of continuity.

Let's begin by considering first-order reactions. For a first-order reaction $A \Rightarrow B$

$$r_A = -k_1 C_A \quad (3.38)$$

Substituting equation (3.38) into equation (3.31) and integrating yields

$$\boxed{\frac{1}{k_1} \ln \left(\frac{C_A^0}{C_A} \right) = \tau} \quad (3.39)$$

Substituting equation (3.29) into equation (3.39) yields

$$\frac{1}{k_1} \ln \left(\frac{1}{1 - X_A} \right) = \tau \quad (3.40)$$

Similarly, for an n th-order reaction

$$r_A = -k_n (C_A)^n \quad (3.41)$$

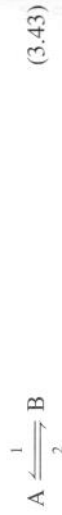
Substituting equation (3.41) into equation (3.31), integrating, and rearranging yields

$$\boxed{\frac{1}{(n-1)k_n(C_A^0)^{n-1}} \left[\left(\frac{C_A^0}{C_A} \right)^{n-1} - 1 \right] = \tau} \quad (3.42)$$

where C_A^0 is the initial A concentration; C_A is the concentration at time, τ ; n is the order of the reaction; and, k_n is the rate constant. As an exercise, the reader may want to show that equation (3.42) goes to equation (3.39) as n goes to 1.0.

3.9.3 Reversible Reactions

The derivations in Section 3.9.1 were for irreversible reactions. However, many reactions are reversible. Consider the reaction



which obeys

$$(r_A) = -k_1[A] + k_2[B] \quad (3.44)$$

From a mass balance

$$[B] = [A]_0 - [A] \quad (3.45)$$

Substituting (3.45) into (3.43) yields

$$\frac{d[A]}{dt} = (r_A) = -k_1[A] + k_2([A]_0 - [A]) \quad (3.46)$$

Table 3.4 Integrated rate laws for a number of reactions

Section	Reaction	Rate Law	Differential Equation	Integral Equation	See
3.9.1	$A \rightarrow \text{products}$	$r_A = k_A$	$\frac{dX_A}{dt} = k_A$	$X_A = \frac{r_A \tau}{k_A}$	3.9.1
3.9.1	$A + B \rightarrow \text{products}$	$r_A = k_A[A]$	$\frac{dX_A}{dt} = k_A X_A$	$k_A \tau = \frac{1}{k_A} \ln \left(\frac{1}{1 - X_A} \right)$	3.9.1
3.9.1	$A \rightarrow \text{products}$	$r_A = k_A[A]^n$	$\frac{dX_A}{dt} = k_A (C_A^0)^{n-1} X_A^n$	$k_A \tau = \frac{1}{k_A (C_A^0)^{n-1}} \left[\frac{1}{1 - X_A} \right]^{n-1} - 1$	3.9.1
3.9.2	$A + B \rightarrow \text{products}$	$r_A = k_A[A][B]$	$\frac{dX_A}{dt} = k_A(1 - X_A) \times (C_B^0 - C_A^0 X_A)$	$k_A \tau = \frac{1}{k_A} \ln \left(\frac{C_B^0(1 - X_A)}{C_B^0 - X_A C_A^0} \right)$	3.9.2
3.9.2	$A + 2B \rightarrow \text{products}$	$r_A = k_A[A][B]$	$\frac{dX_A}{dt} = k_A(1 - X_A) \times (C_B^0 - 2C_A^0 X_A)$	$k_A \tau = \frac{1}{k_A} \ln \left(\frac{C_B^0(1 - X_A)}{C_B^0 - 2X_A C_A^0} \right)$	3.9.2
3.9.2	$A \rightarrow B$ (reversible)	$r_A = k_1[A] - k_2[B]$	$\frac{dX_A}{dt} = k_A(1 - X_A) - k_2 X_A$	$(k_1 + k_2) \tau = \frac{1}{k_1} \ln \left(\frac{X_e - X_A}{1 - X_A} \right)$ where X_e is the equilibrium conversion	3.9.2

The reaction rate goes to zero when the rate reaches equilibrium. Let's define $[A]_e$ as the concentration of A when the system reaches equilibrium. By definition

$$0 = -k_1[A]_e + k_2([A]_0 - [A]_e) \quad (3.47)$$

Subtracting equation (3.47) from (3.46) yields

$$\frac{d[A]}{dt} = (k_1 + k_2)([A] - [A]_e) \quad (3.48)$$

The solution of equation (3.48) is

$$\tau = \frac{1}{(k_1 + k_2)} \ln \left(\frac{[A]_0 - [A]_e}{[A] - [A]_e} \right) \quad (3.49)$$

which looks just like a first-order approach to equilibrium. Table 3.4 shows several other examples. Derivations are given in later sections.

3.10 QUALITATIVE BEHAVIOR

Equations (3.39), (3.42), and (3.49) are the key performance equations for n th-order kinetics in a batch reactor.

It is interesting to plot these results as a function of time. Figure 3.14 shows a plot of the concentration as a function of time calculated from equations (3.39) and (3.42) for $n = \frac{1}{2}, 1, 2, 3$. All of the curves are qualitatively the same. The concentration starts out varying linearly with time and then levels off. Generally, the curve levels off more quickly with larger values of n , namely, higher-order reactions.

We plotted the results in two ways in Figure 3.14: first with $k(C_A) = 1$, and then with $k = 1$ and $C_A^0 = 1.5$. Notice that all of the plots are similar. The concentration of

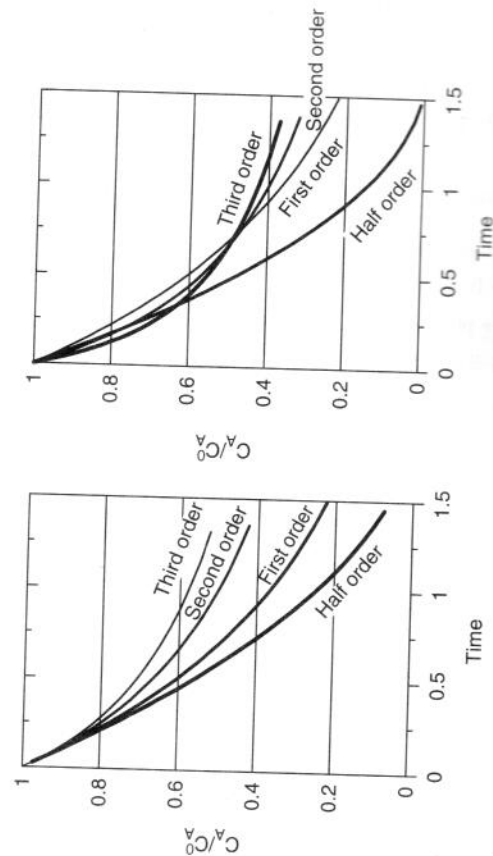


Figure 3.14 A plot of the concentration as a function of time calculated from equations (3.39) and (3.42).

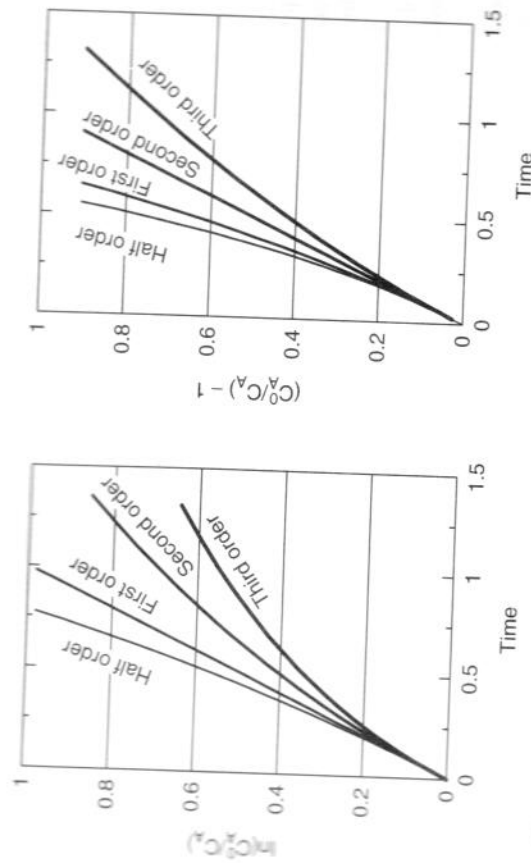


Figure 3.15 A replot of the data from Figure 3.14 as a function of $\ln(C_A^0/C_A)$ and $(C_A^0/C_A) - 1$.

the reactant, A, initially decays quickly with time. However, the rate of decay slowly decreases, giving an exponential-looking curve in all cases.

The key point that one needs to draw from Figure 3.14 is that the concentration-time plots for a batch reactor look qualitatively the same, independent of the order of the reaction. The concentration-time profiles are the same at low conversion independent of the order of the reaction. There are some quantitative differences, especially at high conversion. However, these differences are often subtle, especially when there is some error in the data.

There are two ways to look at this result. On one hand, the performance of a batch reactor does not vary that much with the order of the reaction, except at high conversion. Consequently, for many purposes, you are going to get the right answer even if you assume the wrong order for the reaction. On the other hand, it will be hard to use a batch reactor to determine the order of the reaction because the results are not going to vary that much with the reaction order. Consequently, there are some uncertainties in using batch reactor data to determine kinetics.

8.11 FITTING RATE DATA TO IDEAL BEHAVIOR

8.11.1 Essen's Method

In the literature, people say that one can get some useful information by replottting the data in Figure 3.14. For example, Figure 3.15 shows a plot of $\log(C_A/C_A^0)$ versus time and $[(C_A^0/C_A) - 1]$ versus time. Notice that a plot of $\log(C_A/C_A^0)$ is linear for a first-order reaction, while a plot of $(C_A^0/C_A) - 1$ is lightly curved. In contrast, the plot of $[(C_A^0/C_A) - 1]$ is linear for a second-order reaction and slightly curved for a first-order reaction. Therefore, in principle, one can distinguish between first- and second-order kinetics by preparing curves like those in Figure 3.15 and seeing which plot is the most linear.

Essen proposed that one could generalize these ideas to determine the order of the reaction. The idea is to

1. Measure the concentration versus time in a batch reactor.
2. Fit the data to the batch reactor equations [equation (3.39) for first-order, equation (3.42) for second-order].
3. Whichever fits best is assumed to be the correct rate equation for the reaction.

Note that according to equation (3.42), a plot of $(C_A)^{1-n}$ versus time should be linear for $n \neq 1$ while according to equation (3.39), a plot of $\ln(C_A^0/C_A)$ versus time should be linear for $n = 1$ (i.e., a first-order reaction).

Essen proposed that one can determine the order of a reaction by constructing plots of $\ln(C_A^0/C_A)$ and $[(C_A^0/C_A)^{n-1} - 1]$ versus time for various values of n , and then doing some analysis to check the results. See Harcourt and Essen (1865, 1866, 1867).

For example, in our undergraduate labs, we examine the reaction between Red Dye 4 and hydrogen peroxide to yield a yellow dye. Table 3.5 shows the concentration of Red Dye 4 as a function of time as measured in a batch reactor starting with equal dye and peroxide concentration. According to Essen, one should analyze this data by making a plot of $\ln(C_A^0/C_A)$ (for first-order reactions), $(C_A^0/C_A) - 1$ (for second-order reactions), and $(C_A^0/C_A)^2 - 1$ (for third-order reactions), and see which plot is the most linear.

The easiest way to do this is to put the data into a spreadsheet on a computer. One then uses the spreadsheet to plot $\ln(C_A^0/C_A)$, $(C_A^0/C_A) - 1$, $(C_A^0/C_A)^2 - 1$ versus time to see which plot is the most linear. Sample spreadsheets are given in Example 3.D. A linear regression process can be used to fit the rate constants.

Figure 3.16 shows the plots. The data are actually second-order, but you could not tell that from the figure. Notice that all of the plots look linear. If we exclude the first two points, then a plot of $\ln(C_A^0/C_A)$ is linear with a regression coefficient of 0.981, a plot of $(C_A^0/C_A) - 1$ is linear with a regression coefficient of 0.999, while a plot of $(C_A^0/C_A)^2 - 1$ is linear with a regression coefficient of 0.984. A regression coefficient of 0.981 is as good as the measurements.

There are two ways to look at this result. First, all the regression coefficients are reasonable, which means that you cannot accurately determine the order of the reaction from the data. On the other hand, the plot of (C_A^0/C_A) is more linear than the other plots. According to Figure 3.15, this is the expected behavior for a second-order reaction. Therefore, one might say that the data in Table 3.5 are as expected for a second-order reaction (i.e., $n = 2$).

My own opinion is that such an assertion is not valid. In the supplementary material we note that a regression coefficient measures the uncertainty in the parameters obtained

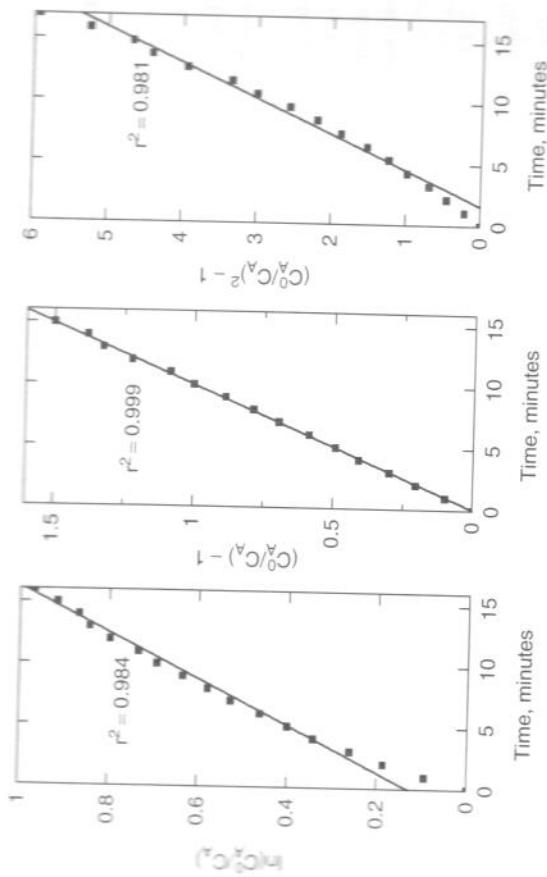


Figure 3.16 An Essen plot of the data in Table 3.5.

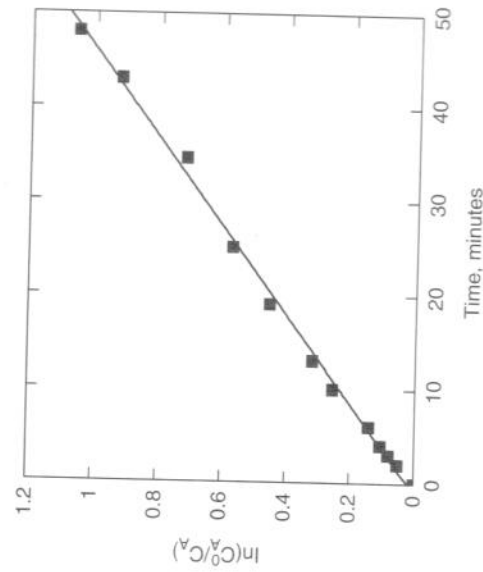


Figure 3.17 Essen Plot of the Data in Table 3.6.

from a linear fit to the data assuming that the model is correct. It does not tell you how well a model works. In Example 3.A, we show that the regression coefficient can vary by a factor of 2 according to how it is calculated. As a result, it is not useful to compare regression coefficients calculated for different models; each regression coefficient is calculated using a different model (i.e., a first-order model vs. a second-order model). As a result, comparisons of small differences in the regression coefficients are rarely meaningful. Still, that subtlety is often lost in the literature. You often see people making the mistake of saying that a rate equation fits better because the regression coefficient is closer to 1.0. That assertion is incorrect.

Table 3.5 The concentration of dye as a function of time

C_A , mmol/liter	τ , minutes	C_A , mmol/liter	τ , minutes	C_A , mmol/liter	τ , minutes
1	0	0.63	6	0.45	12
0.91	1	0.59	7	0.43	13
0.83	2	0.56	8	0.42	14
0.77	3	0.53	9	0.40	15
0.71	4	0.50	10	0.38	16
0.67	5	0.48	11	0.37	17

is not really first-order even though a plot of $\ln(C_A^0/C_A)$ versus τ is linear. Rather, the reaction follows a complicated rate equation.

Van't Hoff noted that one has to be very careful in using the Essen plots to analyze data because one can easily be fooled into thinking that a reaction with a complex rate equation follows simple first- or second-order kinetics. Van't Hoff asserted that it was important to check the results from Essen's analysis. To do the check, one computes k_1 from equation (3.51) for $n = 1$, or k_n from

$$k_n = \frac{1}{(n-1)\tau(C_A^0)^{n-1}} \left[\left(\frac{C_A^0}{C_A} \right)^{n-1} - 1 \right] \quad (3.52)$$

for $n \neq 1$. One then makes a plot to check that k_n is constant. k_n should always work out to be constant within experimental error. If k_n varies in any sort of systematic way, then the reaction is not really first- or second-order. Instead, a complex rate equation will be needed to fit the rate data.

In my experience, Van't Hoff's method is much more accurate than Essen's. I find it useful to plot what I call a *Van't Hoff plot*, which is a plot of k_n versus τ for various values of n , and see if it is constant. For example, Figure 3.18 is a Van't Hoff plot of the dye data in Table 3.5. Notice that k_2 is constant, which means that the reaction really is second-order. On the other hand, k_1 is not constant for the chloroacetic acid data in Table 3.6, which means that the reaction is not first- or second-order. We give further examples in the solved problems. In my experience, Van't Hoff plots are much more revealing than Essen plots. Surprisingly, though, you usually see Essen plots, not Van't Hoff plots, in most textbooks. Example 3.D illustrates this method more carefully. One should carefully examine this example before proceeding.

3.11.3 Powell's Method

There are many other ways to analyze kinetic data. A particularly powerful method that was used mainly before computers were available is called **Powell's method**. Powell's method is derived from equations (3.39) and (3.42).

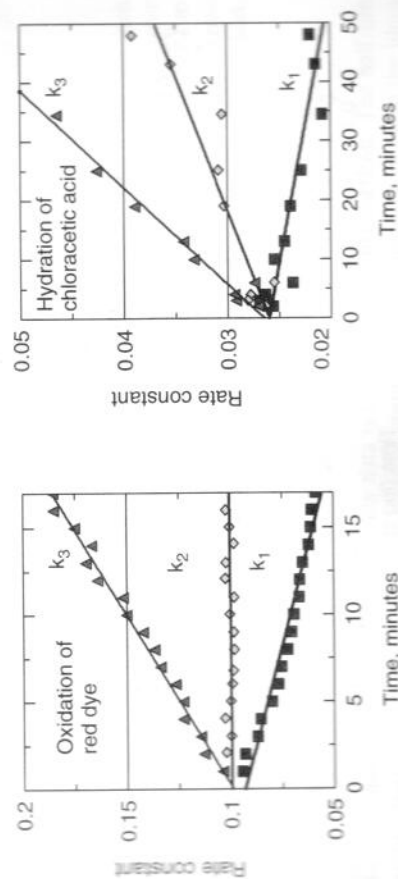


Figure 3.18 Van't Hoff Plot of the data from Tables 3.5 and 3.6.

I do not want to imply that the results in Figure 3.16 are useless. The one advantage of Figure 3.16 is that one can calculate the rate constant for the reaction from the slope of the line in Figure 3.16. According to equation (3.42), the slope of the curve is given by

$$\text{Slope} = (n-1)k_n(C_A^0)^{n-1} \quad (3.50)$$

For the data in Figure 3.17, $n = 2$. Therefore, if we know the slope and C_A^0 , we can calculate k_n .

Essen and Harcourt (1865) and Van't Hoff (1884) showed that one can use this method to analyze data for a wide variety of simple reactions. The advantage of this approach is that it is conceptually simple and it is easy to assess the goodness of the fit. The disadvantage of the method is that it requires many plots, although that is not a problem if one has a spreadsheet available.

3.11.2 Van't Hoff's Method

Van't Hoff (1884) used Essen's method to analyze a variety of rate data. He found that it usually worked. However, there were some examples where the method did not work well.

Table 3.6 shows data for the reaction of chloroacetic acid and water at 100 K. Figure 3.17 shows a plot of $\ln(C_A^0/C_A)$ versus τ . The plot is very linear, which suggests that the reaction is first-order. However, Van't Hoff examined the reaction in more detail and noted that if one rearranges equation (3.39), one can show that a first-order reaction should obey

$$k_1 = \frac{1}{\tau} \ln \left(\frac{C_A^0}{C_A} \right) \quad (3.51)$$

Table 3.6 shows values of k_1 computed in this way. Notice that k decreases slightly as the reaction proceeds. Schwab (1883) examined this effect in some detail, and proved that the rate constant varied with the product HCl concentration. Therefore, the reaction

Table 3.6 Buchanan's (1871) data for the reaction $\text{ClCH}_2\text{COOH} + \text{H}_2\text{O} \Rightarrow \text{HOCH}_2\text{COOH} + \text{HCl}$ at 100°C

Time, hours	$[\text{ClCH}_2\text{COOH}]$, grams/liter	$k_1 = \ln \left(\frac{[\text{ClCH}_2\text{COOH}]^0}{[\text{ClCH}_2\text{COOH}]} \right)$, hour ⁻¹
0	4	—
2	3.80	0.026
3	3.69	0.026
4	3.60	0.023
6	3.47	0.025
10	3.10	0.024
13	2.91	0.023
19	2.54	0.022
25	2.26	0.021
34.5	1.95	0.020
43	1.59	0.021
48	1.39	0.021

Rearranging equation (3.42) and taking the logarithm of both sides yields

$$\log_{10} \left\{ \frac{1}{n-1} \left[\left(\frac{C_A^0}{C_A} \right)^{n-1} - 1 \right] \right\} = \log_{10} [k(C_A^0)^{n-1}] + \log_{10}(\tau) \quad (3.53)$$

Similarly, taking the logarithms of both sides of equation (3.39) yields

$$\ln \left(\ln \left(\frac{C_A^0}{C_A} \right) \right) - \ln(k) = \ln(\tau) \quad (3.54)$$

Figure 3.19 shows a plot of (C_A/C_A^0) versus $\log(\tau)$ calculated from equation (3.53) for various values of $k(C_A^0)^{n-1}$ and n . Notice that all of the curves calculated for a first-order reaction have an identical shape. They are just shifted to the right or left of each other. In contrast, the curves for second-order reactions have a decidedly different shape. Consequently, one should be able to distinguish first-order reactions from second-order reactions by plotting C_A/C_A^0 versus $\log(\tau)$ and looking at the general shape of the plot.

The easiest way to use Powell's method is to employ a spreadsheet on a computer. The general procedure is to

1. Make a plot of C_A/C_A^0 versus $\log_{10}(\tau)$.
2. Program the spreadsheet to calculate ideal curves for C_A^0/C_A versus $\log_{10}(\tau)$ for $n = \frac{1}{2}, 1, 2, 3$.
 - (a) Use equations (3.53) and (3.54) to calculate the values of $\log(\tau)$ for each value of C_A/C_A^0 .
 - (b) Treat $\log_{10}(k(C_A^0)^{n-1})$ as a variable (i.e., \$B\$). Set the variable initially to zero.
3. Vary $\log_{10}(k(C_A^0)^{n-1})$ to see which curve fits.

Example calculations are given in solved Example 3.D.

Powell actually proposed his method before computers were available, and so he did not use a spreadsheet. Instead, Powell used a set of universal curves for zero-, first-, second-, and third-order reactions to see how data fit. Figure 3.20 is a suitable set of

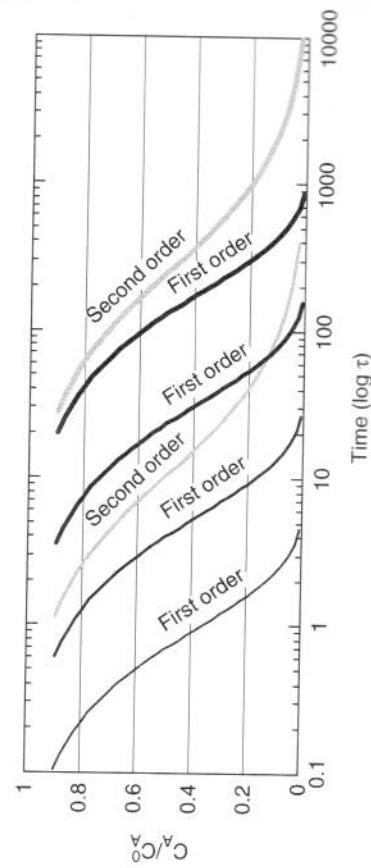


Figure 3.19 A plot of (C_A/C_A^0) versus $\log \tau$ calculated for a series of first-order and second-order reactions.

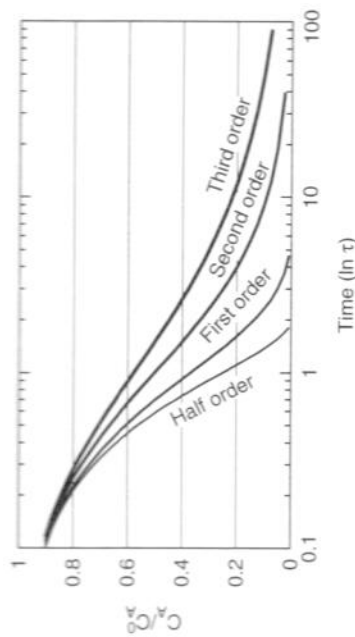


Figure 3.20 Powell's universal curves for half-, first-, second-, and third-order reactions.

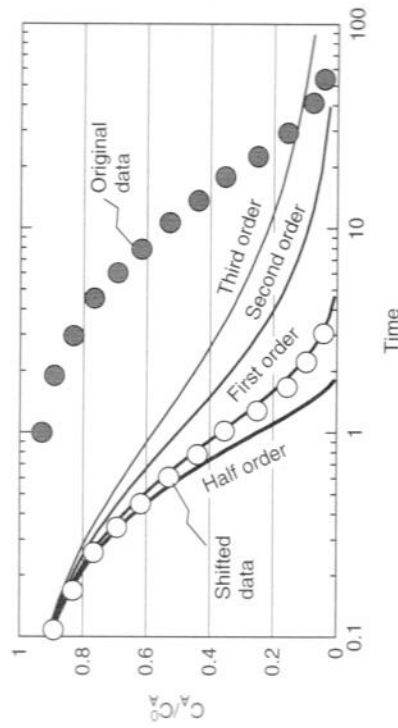


Figure 3.21 An illustration of a Powell plot for data taken for a second-order reaction.

universal curves. One can use these curves to calculate the order of a reaction. The general scheme is to

1. Make a plot of C_A/C_A^0 versus $\ln(\tau)$ as shown in Figure 3.20, making sure that the scales on each of the axes are the same as in Figure 3.20.
2. Slide the data to the left and right to see which curve in Figure 3.20 fits best.

Figure 3.21 illustrates this method. We took data and plotted it on the Powell plot. We then shifted the data to the right to see which curve fits best. In this case, the second-order curve fits better than the rest, so we conclude that the reaction is second-order. We do need to go back and make a table of k_1 versus τ as described in Section 3.12 to calculate the rate constant. Example 3.A gives additional examples of analysis of data with Powell's method.

3.12 THE HALF-LIFE METHOD

Another indirect method to analyze rate data is called the **half-life method**. The half-life method was quite popular before the days of computers. We include it because the ideas are useful even if the method is not used very much anymore.

The half-life, $\tau_{1/2}$, is defined as the time to get to 50% conversion. In the half-life method, one makes a log-log plot of the half-life versus time and calculates the order from the slope of the plot.

Next, we will derive an expression for the half-life as a function of C_A^0 for a first-order reaction and an n th-order reaction. Rearranging equation (3.39) shows that for a first-order reaction

$$\frac{1}{k_1} \ln \left(\frac{C_A^0}{C_A} \right) = \tau \quad (3.55)$$

at 50% conversion ($C_A^0/C_A = 2$). Therefore, $\tau_{1/2}$, the half-life, is given by

$$\tau_{1/2} = \frac{\ln(2)}{k_1} \quad (3.56)$$

Similarly, rearranging equation (3.42) shows that for an n th-order reaction:

$$\frac{1}{(n-1)k_n(C_A^0)^{n-1}} \left[\left(\frac{1}{1-X_A} \right)^{n-1} - 1 \right] = \tau \quad (3.57)$$

$X_A = 0.5$ at $\tau_{1/2}$. Therefore, for an n th-order reaction:

$$\tau_{1/2} = \frac{1}{(n-1)k_n(C_A^0)^{n-1}} (2^{n-1} - 1) \quad (3.58)$$

Figure 3.22 shows a plot of the half-life versus concentration calculated for half-order, a first-order, second-order, and third-order reactions. Notice that in all cases, one should observe a linear plot on a log-log scale where the slope of the plot is proportional to

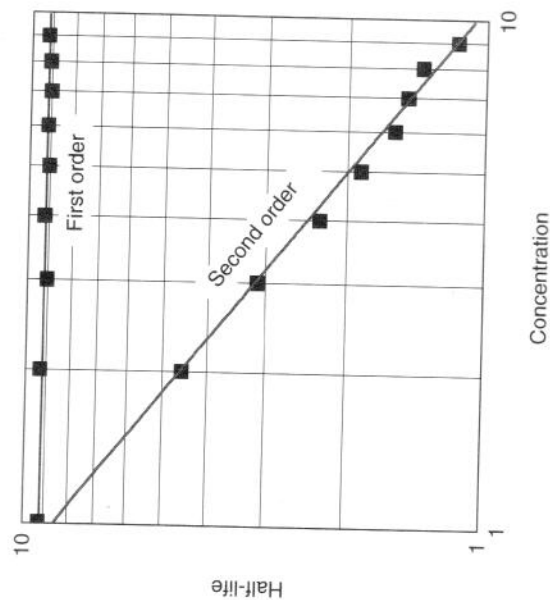


Figure 3.22 A plot of the half-life versus C_A^0 for a first-order reaction and a second-order reaction.

$(n-1)$. The fact that we get linear plots on a log-log scale is a great advantage because it allows one to calculate the order directly even for fractional order systems. Consequently, the half-life method was quite popular before computers were readily available. It is used less now because Van't Hoff's method and Essen's method are so easy to put in a spreadsheet that they have replaced most other methods.

Still, the half-life method is very useful in getting a very rough idea about the kinetics of a reaction. One loads reactants into the reactor and measures how long it takes to convert about half the reactants into products. One then dilutes the reactants by a factor of 10 and runs the reaction again.

If the time is about constant in the two experiments, the reaction is probably first-order. If the time increases markedly with each data run, the reaction is most likely second-order. One can then get a very rough value of the rate constant from equation (3.57) or (3.58).

If one needs to know only an approximate rate constant, one does not have to actually run to exactly 50% conversion. Rather, one can run to any fixed conversion and get useful information.

Now, if one needs to get an exact rate constant, one needs to add some extra work. One will have to run the reaction versus time and calculate an exact time to 50% conversion. Note that one can calculate $\tau_{1/2}$ versus C_A^0 from data for a single run. Figures 3.23 and 3.24 illustrate the process.

Let's start the experiment at $\tau = 0$. If we start at $\tau = 0$, $C_A^0 = 1$ mol/liter, then $\tau_{1/2}$ in the time to get to $C_A = 0.5$ as shown in the left part of Figure 3.23. Now imagine starting the experiment at $\tau = 0.3$. At $\tau = 0.3$, $C_A^0 = 0.9$. Therefore, the half-life is the time it takes to go from $C_A = 0.9$ to $C_A = 0.45$. Similarly, we can imagine starting the experiment at any value of C_A in Figure 3.23 and calculate the half-life for that value of C_A . The result is that one can construct a half-life plot from a single run.

Figure 3.24 shows data generated in this way. Notice that the half-life decreases linearly with $\ln(C_A^0)$. The slope of the plot is -1.0 , which implies that $1-n = -1.0$ or $n = 2$.

In my experience, half-life plots were the easiest way to analyze batch reactor data before computers were readily available. The biggest advantage of the half-life method is

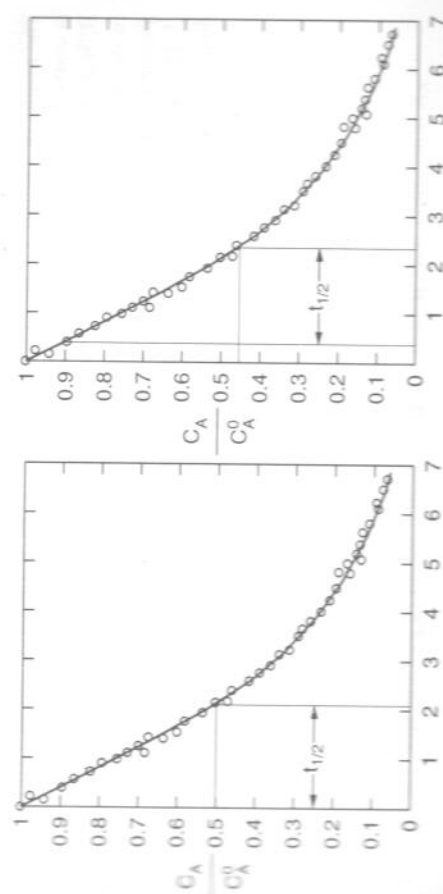


Figure 3.23 An illustration of how one can calculate the half-life from a single data set.

assuming that we run the reaction in a constant-volume batch reactor and that the rate equation for the reaction is of the form

$$r_B = -k_B C_B C_C \quad (3.60)$$

where C_B is the benzoquinone concentration, C_C is the cyclopentadiene concentration, r_B is the rate of formation of benzoquinone and k_B is a constant.

According to equation (3.31)

$$\tau = C_B^0 \int_0^{X_B} \frac{dX_B}{(-r_B)} \quad (3.61)$$

where X_B is the conversion, and τ is the reaction time.

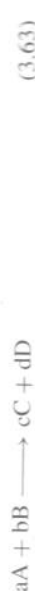
Combining equations (3.60) and (3.61) yields

$$\tau = C_B^0 \int_0^{X_B} \frac{dX_B}{k_B C_B C_C} \quad (3.62)$$

In order to use equation (3.62), we need an expression for C_B and C_C in terms of X_B . In the next section, we will describe how to get it.

3.13.1 The Stoichiometric Table

Consider a general reaction



where $-a$, $-b$, c , and d are the stoichiometric coefficients for species A, B, C, and D, respectively. Assume that N_A^0 moles of A and N_B^0 moles of B are loaded into a closed isothermal vessel. Next, we will derive a relation between the concentrations of all of the species as a function of the concentration of a single species, A. To simplify the algebra, it is useful to work in terms of a new variable, X_A , the fractional conversion of A, where X_A is defined as

$$X_A = \frac{N_A^0 - N_A}{N_A^0} \quad (3.64)$$

Physically X_A is the fraction of the reactant A that has been converted into products. One should memorize this definition before proceeding.

Next, it is useful to calculate the concentrations of each of the species in the reactor as a function of X_A . Fogler [1998] has a neat trick that makes it easier to keep track of this. The trick is called a **stoichiometric table**.

The stoichiometric table is a table where the following information is presented (for a batch system):

- Column 1: The particular species
- Column 2: The number of moles of each species initially present
- Column 3: The change in the number of moles due to reaction
- Column 4: The number of moles remaining in the reactor after conversion X_A

Table 3.7 is a stoichiometric table for reaction (3.63) with some of the information missing. Next, let's calculate the changes in moles of each of the species as a function of X_A . Assume that we load N_A^0 moles of A and N_B^0 moles of B into the reactor. Then we run

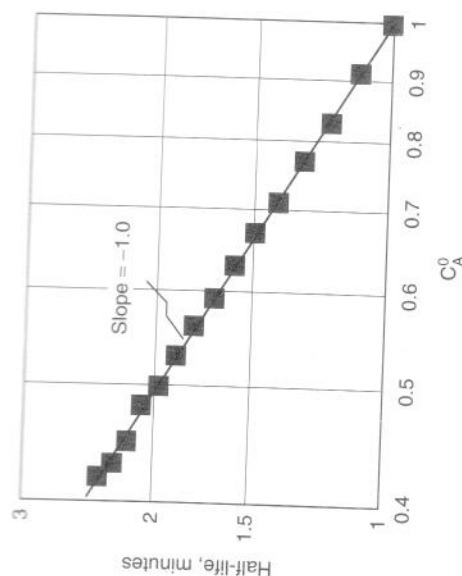


Figure 3.24 The half-life as a function of C_A for the data in Table 3.5 (with some extra points added).

that there are large differences between, for example, first- and second-order data. Further, if one takes data on a system that does not follow a simple rate equation, one knows it because the half-life plot is curved on a log-log scale. Still, the half-life method is difficult to automate. Consequently, half-life plots are now rarely seen in the literature.

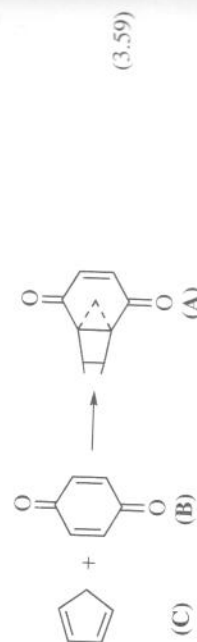
Equations (3.56) and (3.58) are very useful, however. One can use these equations to decide how to run experiments, or to estimate activation barriers from very little data. See Section 2.5.1 for more information.

There are other methods in the literature, including the Gugenheim method. These methods have largely disappeared as computers made their appearance. For an older review, see Roseveare (1931).

3.13 FITTING DATA TO EMPIRICAL RATE LAWS: MULTIPLE REACTANTS

The results in Section 3.7 are useful only in the case of a reaction where a single reactant is converted into products. In a more typical reaction, two reactants, for example, C and B, react to form products. One needs a more complex analysis to consider those cases. In the work that follows, we will derive an expression for the conversion versus time of a system with multiple reactions. However, we need some further information first.

For example, consider the Diels-Alder reaction of benzoquinone (B) and cyclopentadiene (C) to yield an adduct (A):



It is useful to consider what data we need to analyze rate data for reaction (3.59). Next, we will derive an expression for the conversion of benzoquinone as a function of time

Table 3.7 The start of a stoichiometric table for reaction (3.63)

Species	Initial Moles	Change in Moles	Final Moles
A	N_A^0		N_A^f
B	N_B^0		N_B^f
C	N_C^0		N_C^f
D	N_D^0		N_D^f
Inerts	N_I^0		N_I^f
Total	$N_T^0 = N_A^0 + N_B^0 + N_C^0 + N_D^0 + N_I^0$		N_T^f

the reaction for a time, t , so that the conversion of species A is X_A . From the definition of the conversion we obtain

$$\text{Moles of A converted} = N_A^0 X_A \quad (3.65)$$

From the stoichiometry of the reaction, the number of moles of B converted is given by

$$\text{Moles of B converted} = \left(\frac{b}{a}\right) N_A^0 X_A \quad (3.66)$$

Similarly:

$$\text{Moles of C formed} = \left(\frac{c}{a}\right) N_A^0 X_A \quad (3.67)$$

$$\text{Moles of D formed} = \left(\frac{d}{a}\right) N_A^0 X_A \quad (3.68)$$

It is important to keep track of the sign. During the reaction, the concentrations of A and B decrease while the concentrations of C and D rise. Consequently, the change in moles of B is:

$$\Delta N_B = - \left(\frac{b}{a}\right) X_A N_A \quad (3.69)$$

while the change in moles of C is

$$\Delta N_C = + \left(\frac{c}{a}\right) X_A N_A \quad (3.70)$$

Therefore, the stoichiometric table is as given in Table 3.8:
One can slightly simplify Table 3.8 by noting

$$-a - b + c + d = \sum_v \beta_v = \Delta \text{mol} \quad (3.71)$$

where Δmol is the change in moles when reaction (3.63) goes one time. Substituting equation (3.67) into Table 3.8 yields Table 3.9.

3.13.2 Derivation of the Performance Equation for Reaction (3.59)

Now it is useful to go back and derive a performance equation for reaction (3.59). Let's go back to equation (3.62). Equation (3.62) was a performance equation for reaction (3.59).

Table 3.8 The stoichiometric table for reaction (3.63)

Species	Initial Moles	Change in Moles	Final Moles
A	N_A^0	$-N_A^0 X_A$	$N_A^0(1 - X_A)$
B	N_B^0	$-\left(\frac{b}{a}\right) N_A^0 X_A$	$N_B^0 - \left(\frac{b}{a}\right) N_A^0 X_A$
C	N_C^0	$+\left(\frac{c}{a}\right) N_A^0 X_A$	$N_C^0 + \frac{c}{a} N_A^0 X_A$
D	N_D^0	$+\left(\frac{d}{a}\right) N_A^0 X_A$	$N_D^0 + \frac{d}{a} N_A^0 X_A$
Inerts	N_I^0	0	N_I^0
Total	N_T^0	$\left(\frac{-a - b + c + d}{a}\right) N_A^0 X_A$	$N_T^0 + N_A^0 \left(\frac{-a - b + c + d}{a}\right) X_A$

Table 3.9 An alternative stoichiometric table for reaction (3.63)

Species	Initial Moles	Change in Moles	Final Moles
A	N_A^0	$-N_A^0 X_A$	$N_A^0(1 - X_A)$
B	N_B^0	$-\left(\frac{b}{a}\right) N_A^0 X_A$	$N_B^0 - \left(\frac{b}{a}\right) N_A^0 X_A$
C	N_C^0	$+\left(\frac{c}{a}\right) N_A^0 X_A$	$N_C^0 + \frac{c}{a} N_A^0 X_A$
D	N_D^0	$+\left(\frac{d}{a}\right) N_A^0 X_A$	$N_D^0 + \frac{d}{a} N_A^0 X_A$
Inerts	N_I^0	0	N_I^0
Total	N_T^0	$+N_A^0 \left(\frac{\Delta \text{mol}}{a}\right) X_A$	$N_T^0 + N_A^0 \left(\frac{\Delta \text{mol}}{a}\right) X_A$

However, we needed an expression for C_C as a function of C_B so that we can integrate the equation. We can get the needed expression from a stoichiometric table. Table 3.10 shows a general stoichiometric table, while Table 3.11 shows the specific stoichiometric table for the case considered here.

Substituting results from Table 3.11 into equation (3.60) yields

$$(-r_B) = K_B \{C_B\} \{C_C\} = K_B \{C_B^0(1 - X_B)\} \{C_C^0 - X_B C_B^0\} \quad (3.72)$$

According to equation (3.30)

$$\tau = C_B^0 \int_0^{X_B} \frac{dX_B}{(-r_B)} \quad (3.73)$$

Table 3.10 The stoichiometric table for the reaction $bB + cC \Rightarrow aA$

Species	Initial Concentration	Change	Final Concentration
B	C_B^0	$-C_B^0 X_B$	$C_B^0(1 - X_B)$
C	C_C^0	$-(c/b)C_B^0 X_B$	$C_C^0 - (c/b)C_B^0 X_B$
A	C_A^0	$(a/b)C_B^0 X_B$	$C_A^0 + (a/b)C_B^0 X_B$

Table 3.11 The stoichiometric table for the reaction $C + B \rightarrow A$

Species	Initial Concentration	Change	Final Concentration
B	C_B^0	$-C_B^0 X_B$	$C_B^0(1 - X_B)$
C	C_C^0	$-C_B^0 X_B$	$C_C^0 - C_B^0 X_B$
A	C_A^0	$C_B^0 X_B$	$C_A^0 + C_B^0 X_B$

Substituting equation (3.72) into equation (3.73) yields

$$\tau = C_B^0 \int_0^{X_B} \frac{dX_B}{(k_B C_B^0 (1 - X_B)(C_C^0 - X_B C_B^0))} \quad (3.74)$$

The integral equation (3.74) looks imposing. Fortunately, I was able to look it up in Gradshteyn and Ryzhik (1965).

$$\tau = \frac{\left[\ln \left(\frac{C_B^0}{C_C^0} \left(\frac{C_C^0 - X_B}{1 - X_B} \right) \right) \right]}{k_B (C_C^0 - C_B^0)} \quad (3.75)$$

Equation (3.75) has two interesting limits: the limit where $C_C^0 \gg C_B^0$ and the limit where $C_C^0 = C_B^0$. The first limit, called the "swamping limit," corresponds to running the reaction with a huge excess of cyclopentadiene (C). If C_C^0 is in large excess, $C_C^0/C_B^0 \gg 1 \geq X_B$. Therefore, the X_B term in the numerator of the log term in equation (3.75) will be negligible. Similarly, C_B^0 in the denominator of equation (3.75) will be negligible. Consequently, when there is a large excess of cyclopentadiene, equation (3.75) reduces to

$$\tau = \frac{1}{k_B C_C^0} \ln \left(\frac{1}{1 - X_B} \right) \quad (3.76)$$

A comparison of equations (3.76) and (3.39) shows that equation (3.76) is a first-order rate equation with

$$k_1 = k_B C_C^0 \quad (3.77)$$

Physically, what is happening is that when $C_C^0 \gg C_B^0$, the concentration of cyclopentadiene does not change significantly during the reaction. The C_C is constant in the rate equation. Therefore, the reaction appears as if it were first-order.

The other key limit is when $C_B^0 = C_C^0$. Note that during reaction (3.59), benzoquinone (B) and cyclopentadiene (C) are used up at the same rate. Consequently, if initially $C_B^0 = C_C^0$, then

$$C_B = C_C \quad (3.78)$$

everywhere during the reaction. Consequently, the rate equation for reaction (3.59) will reduce to the equation for a second-order reaction.

One can derive the same result by letting C_B^0 approach C_C^0 in equation (3.84), and using l'Hôpital's rule to do the limit. The result is

$$\tau = \frac{1}{k_B C_B^0} \left(\frac{C_B^0}{C_B} - 1 \right) \quad (3.79)$$

Equation (3.79) is equivalent to equation (3.42), with $n = 2$. Equations (3.75) and (3.79) are used to plan experiments. First, one swamps the reactor with one species, say, C, and measures the concentration of B as a function of time, and uses Essen's method or Powell's method to see if the reaction follows equation (3.76). One then runs the reaction with equal B and C concentrations, and uses Powell's method or Essen's method to see if equation (3.79) works. If both equations fit the data, then one can be assured that the rate data follows equation (3.60). If either equation (3.76) or (3.79) fails, one needs a more complex procedure to fit the data. Such procedures are beyond the scope of the discussion here.

3.14 SEQUENTIAL REACTIONS

There is one other example that we will need to consider later in this book, which is the limit where a reactant A is first converted into an intermediate, I, and then into a product, P:



Next, we will derive equations for the concentrations of A, B, and C versus τ assuming that reactions 1 and 2 are both first-order.

If reaction 1 is first-order, then

$$\frac{dC_A}{d\tau} = r_A = -k_1 C_A \quad (3.81)$$

where C_A is the concentration of A. Solving equation (3.81) yields

$$C_A = C_A^0 e^{-k_1 \tau} \quad (3.82)$$

If reactions 1 and 2 are first-order, then

$$\frac{dC_I}{d\tau} = k_1 C_A - k_2 C_I \quad (3.83)$$

where C_I is the concentration of I.

Combining equations (3.82) and (3.83) and integrating yields

$$C_I = \frac{k_1 C_A^0}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) + C_I^0 e^{-k_2 \tau} \quad (3.84)$$