

ANALYSIS OF RATE DATA

PREFACE

At this point, we will be changing our focus. In Chapter 2, we discussed general principles that can be applied to a variety of reactions. In this chapter, we will be discussing some of the techniques one uses to fit rate data to a rate equation. First, we will briefly discuss experimental techniques. Then we will discuss how to analyze rate data.

When this book was written, it was assumed that our readers had seen this material before. Maybe they had measured a rate in freshman chemistry or integrated a rate equation in their physical chemistry or reactor design course. However, people seldom know where to start when presented with a new problem. What needs to be measured, and how does one analyze the data? The objective of the material that follows is to summarize the key ideas that one needs to understand in order to measure rate data for a new system.

1.1 INTRODUCTION

Studies of rates of chemical reactions date back to Wilhelm's (1850) measurement of the rate of sugar conversion in the grapejuice used to make wine. They have been improved ever since.

In this chapter we will discuss how one actually determines a rate equation. First we will briefly discuss some of the experimental techniques that one uses to determine a rate equation. In particular, we will distinguish between direct and indirect methods, and describe the properties of each. Then we will discuss the data analysis. Our approach is a little nonstandard, in that we point out that some common data analysis schemes are subject to some uncertainty. Understanding the uncertainty is as important as understanding the methods.

The outline of the material is as follows:

- In Sections 3.2–3.4 we will briefly review the experimental techniques. The experimental techniques are evolving all of the time, and we had to keep up with the latest advances. Still, we wanted to give a picture of how the data are taken, and in particular to distinguish between direct and indirect methods.
- In Sections 3.5–3.8 we will examine the analysis of the data. We will derive the key equations and explain how they are used.
- Then we will include solved examples. The solved examples are a key part of this chapter, and one should be sure to examine them carefully.

I have focused the discussion to make it most understandable to a senior undergraduate. Please refer to your physical chemistry or reaction engineering text for a less advanced treatment.

3.2 BACKGROUND

Studies of the kinetics of chemical reactions began in earnest in the middle part of the nineteenth century. At the time, winemaking was one of the key chemical industries, so many of the studies used wine, and winemaking equipment.

One of the key issues in a winery is controlling how sweet the wine tastes. Generally, sweeter grapes will produce a sweeter wine, so it is very important to control the sugar content of the grapes used to produce the wine.

In the 1600s, it was discovered that the refractive index of sugar solutions varied linearly with the sugar concentration. Consequently, one can measure the refractive index of a grape squeezing and use that measurement to estimate the sugar content of the grapes. If you have been to a winery, you will know that when the grapes are delivered, people use a refractometer to measure the sugar concentration of the grape juice.

There is a problem with that measurement, however. Sometimes when you let grape juice sit, the sucrose in the grape juice is converted to fructose and lactose via reaction (2.7). The refractive index of a fructose/lactose solution is quite different from the refractive index of a sucrose solution. Consequently, if some of the sucrose in grape juice has been converted to fructose and lactose, one will not get an accurate sugar measurement with a refractometer.

In 1850, Wilhelmy did some measurements to try to understand how quickly the sucrose was converted to lactose and fructose. He started with a sucrose solution and used a polarimeter to measure the sucrose concentration as a function of time. Wilhelmy also added various acids because it had previously been found that acids would speed the spoilage of wine or grape juice.

Figure 3.1 shows some of Wilhelmy's results. Notice that the sucrose concentration decays with time. Later in this chapter, we will show that for a first-order reaction, the sucrose concentration, C_S , should follow

$$C_S = C_S^0 \exp(-k_S \tau) \quad (3.1)$$

where C_S^0 is the initial sucrose concentration, τ is time, and k_S is the rate constant. Ostwald (1885) fit Wilhelmy's data to equation (3.1) and then inferred a rate equation for the conversion of sucrose to lactose and fructose.

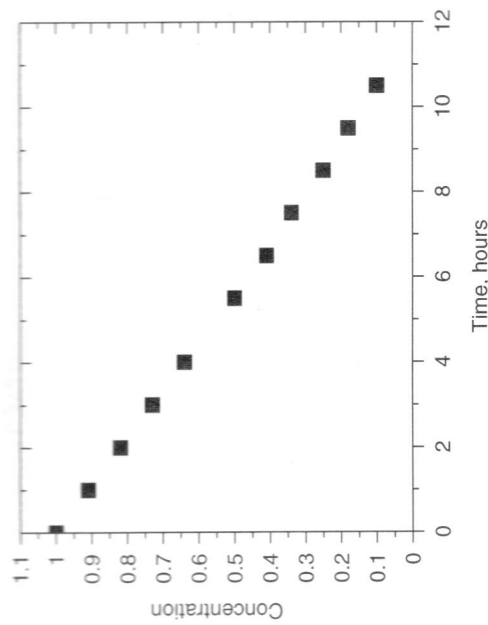


Figure 3.1 Wilhelmy's (1850) measurements of the changes in sucrose concentration in grape juice after acid is added.

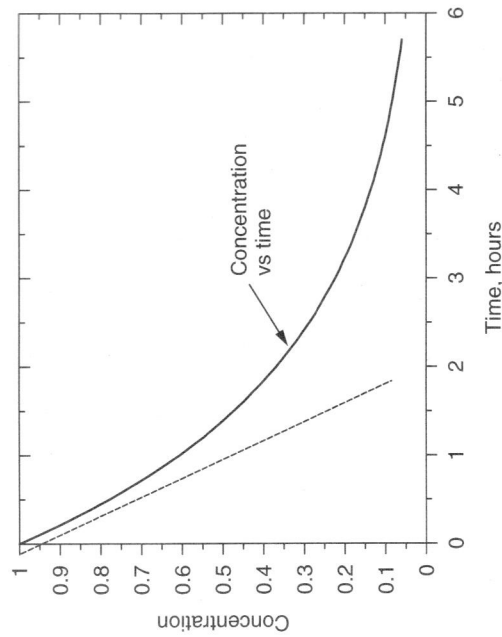


Figure 3.2 Concentration versus time for a simple reaction.

Most simple kinetic measurements are done using a technique that is very similar to those pioneered by Wilhelmy. One finds a way to initiate the reaction and then measures the concentration of some key species as a function of time. Typical data are shown in Figure 3.2. One then uses the data to infer the order of the reaction and the rate constant. Over the years, the details have changed. However, one still induces a change in the system and then uses spectroscopy to measure the concentration as a function of time.

In the next several sections we briefly describe the techniques, and mention how they are used.

3.3 BRIEF OVERVIEW OF THE EXPERIMENTAL TECHNIQUES

Most kinetics books talk about the various methods one uses to measure rates of reaction. Generally, the methods discussed in most books are similar. One finds a way to initiate a reaction and then uses some sort of spectroscopic technique to measure the concentration of a key species as a function of time. One then fits the data to an equation to infer a rate law.

There are lots of schemes to initiate the reaction. If the reaction is slow, you can simply mix the reactants together. If the reaction is fast, you might start the reaction by mixing the reactants at low temperature and then quickly heating the mixture. People also use spark plugs and lasers to initiate reactions. For a really fast reaction, one uses a molecular beam system to measure rates.

Table 3.1 summarizes the methods discussed in most textbooks. The simplest method, called the *conventional method*, is to mix the reactants in a beaker, and then measure concentrations as a function of time. Generally, this is a very easy technique. However, it usually, takes several seconds to mix the reactants, and possibly several seconds to make a concentration measurement. As a result, the conventional methods are useful only for reactions that are slow enough that the reactants can be mixed and measurements made before there is significant conversion of reactants to products. In Table 3.1, we say that the reaction must take 10 seconds or more. That is because it usually takes several seconds to pour the reactants into a beaker and thoroughly mix them.

The next method is the *stopped-flow method*. In the stopped flow, one runs the reaction in a flow cell in a spectrophotometer. You start the experiment by flowing the reactants into the flow cell, and increase the velocity of the reactants until the conversion of the reactants is negligible. You wait for everything to be well mixed, and then you stop the flow and measure the concentrations of the reactants as a function of time. The stopped-flow method avoids the difficulties of the conventional method, since the reactants are already mixed at the start of the reaction. Still, it takes time to stop the flow. As a result, the stopped-flow method is limited to reactions that take 10^{-3} seconds or more.

The third method is the *temperature-jump method*. In this method, one mixes the reactants at a low enough temperature that the reaction rate is negligible and then zaps the mixture with a CO_2 laser to suddenly heat the reactants to the desired reaction temperature. Again, mixing problems are avoided, but there is the difficulty that one can heat things only so fast. In practice, the temperature-jump method is usually limited to reactions that take 10^{-6} seconds or more, although people are developing techniques to heat liquids as fast as 10^{-9} seconds.

The *shock tube* is a way to examine fast reactions in gases. One constructs a long tube, with a thin membrane in the middle. One then puts one reactant on one side of the membrane, and a second reactant on the other side of the membrane. One adds an atmosphere or two of an inert gas, to ensure that there is a large pressure difference between the two sides of the membrane. One then ruptures the membrane, and allows the gases to suddenly mix. Generally, a shock wave forms at the interface between the high-pressure and low-pressure gas. The shock wave heats the reactants and allows them to mix. One can generally observe reactions that take between 10^{-3} and 10^{-5} seconds in this way. One cannot study faster reactions with the technique because of the finite mixing times. One cannot study slower reactions because the gas cools off after the shock wave has passed.

Flash photolysis is the fastest method. One zaps a mixture with a laser, and uses a variety of spectroscopic techniques to observe the resultant reactants. Generally, one

Table 3.1 Some techniques used to measure rates of reaction

Method	Description	Timescale, seconds
<i>Batch Methods</i>		
Conventional	1) Mix reactants together in a batch reactor 2) Measure concentration versus time	≥ 10
Stopped flow	1) Set of continuous-flow systems where reactants are fed into the reactor, and flow out again so quickly that there is negligible reaction 2) Stop the flow so that the reactants can react 3) Measure conversion versus time	$\geq 10^{-1}$
Temperature jump	1) Mix reactants at such a low temperature that the reaction rate is negligible 2) Use CO_2 laser to suddenly heat reaction 3) Measure concentration vs. time	$\geq 10^{-6}$
Shock tube	1) Put 10^{-1} atm of one reactant and 10 atm at helium on one side of a diaphragm 2) Put 10^{-3} atm of the other reactant on the other side of the diaphragm 3) Suddenly break the diaphragm so that the gas flows from the high-pressure side to the low-pressure side Measure the reactant concentration vs. time	$10^{-3}-10^{-5}$
Flash photolysis	1) Put the reactants into a vessel under conditions where reaction is negligible 2) Pulse a laser or flash lamp to start reaction 3) Measure the reactant concentration vs. time	$10^{-9}-10^{-1}$
NMR ^a	1) Initiate a change with a magnetic pulse 2) Measure the decay of spins by NMR	$10^{-2}-10^{-9}$
<i>Flow Methods</i>		
Conventional flow system	1) Continuously feed reactants into a reactor (CSTR ^b or plug flow)	$\geq 10^{-3}$
Molecular beam	1) Measure the steady-state reaction rate 1) Direct beams of reactants toward each other in a vacuum system 2) Measure the steady-state reaction rate	$10^{-13}-10^{-9}$

^aNuclear magnetic resonance.

^bContinuously stirred tank reactor.

can use the laser to examine the reactions of radicals or other reactive intermediates by creating the intermediates with a laser and watching how they react. Generally, laser methods are limited to reactions that take 10^{-9} seconds or more because laser pulses usually last perhaps 10^{-10} seconds. However, people are working on femtosecond lasers to get around those difficulties.

The methods described in the preceding paragraphs are called *batch experiments*. In a batch experiment, one mixes a batch of reactants in a reactor and then allows the reactants to react. One can also run reactions in a flow reactor where one continuously

feeds reactants into the reactor. There are two kinds of flow reactors, continuously stirred tank reactors (CSTRs) and plug-flow reactors. In either case, one flows reactants into the reactor and measures the concentration of the products as a function of the residence time in the reactor τ , where τ is given by

$$\tau = \frac{\text{(reactor volume, liters)}}{\text{(volumetric flow rate of reactants, liters/hour)}} \quad (3.2)$$

The CSTR is the simplest reactor. The CSTR consists of a mixing tank with flow in and out, as indicated in Figure 3.3. Later in this chapter, we will show that when the general reaction $A \Rightarrow B$ occurs in a CSTR, the reaction rate, r_A , in the CSTR is related to the residence time in the CSTR by

$$r_A = \frac{C_A^{\text{in}} - C_A^{\text{out}}}{\tau} \quad (3.3)$$

where C_A^{in} is the concentration of A in the inlet to the reactor, C_A^{out} is the concentration in the outlet of the pipe, and τ is the residence time. Plug-flow reactors are basically pipes with baffles to prevent backward mixing. One feeds reactants into the pipe and takes products at the end. One can show that the residence time for a plug-flow reactor is related to the reaction rate by

$$\tau = \int_{C_A^0}^{C_A^f} \frac{dC_A}{-r_A} \quad (3.4)$$

Plug-flow reactors (Figure 3.4) can be used to measure kinetics, although they are used less often than CSTRs.

One last experimental technique, that is especially important, is called *molecular beam*. Molecular beam measurements are fundamentally different than all of the other measurements in Table 3.1. Figure 3.5 shows a schematic of the molecular beam system

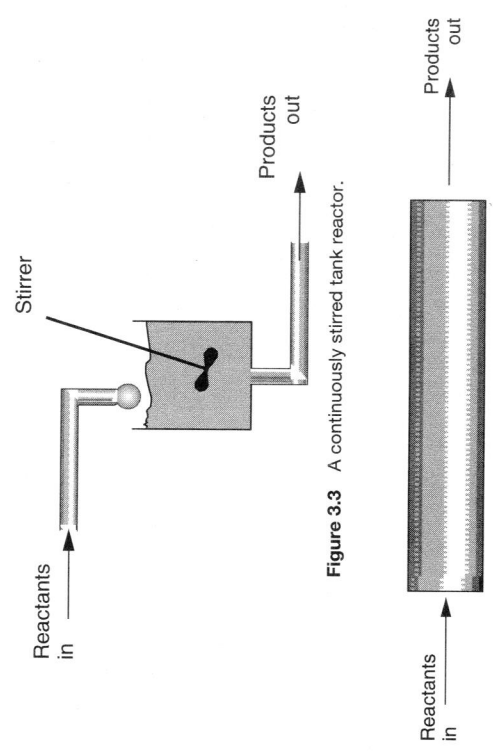


Figure 3.3 A continuously stirred tank reactor.

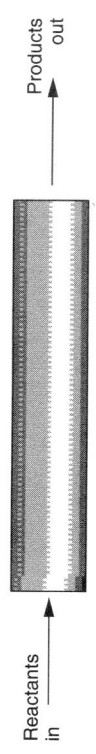


Figure 3.4 A plug-flow reactor.

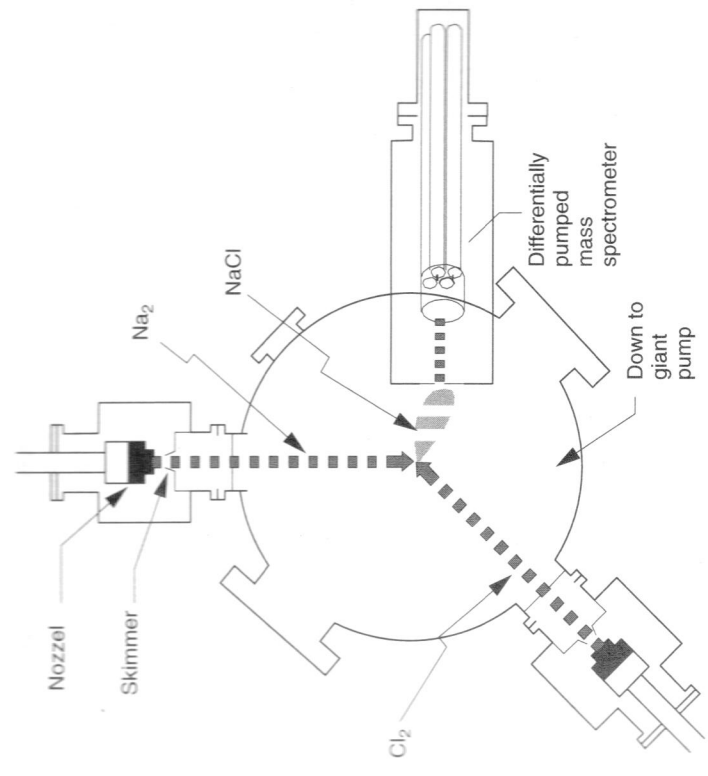
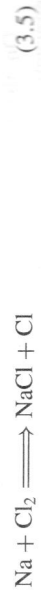


Figure 3.5 A molecular beam system used to measure the rate of the reaction $\text{Na} + \text{Cl}_2 \Rightarrow \text{NaCl} + \text{Cl}$. After Cloustan et al (1968), and Lee et al (1968).

being used to examine the rate of the reaction:



Sodium atoms are generated in the sodium source and flow into a vacuum system. The sodium atoms collide with the stream of chlorine, and the NaCl and Cl products are detected with a mass spectrometer. A laser can also be used to measure the properties of the reactant and product molecules. The system is designed so that the unreacted sodium atoms and chlorine molecules are pumped away.

The advantage of a molecular beam system is that the sodium atoms are in close proximity to the Cl_2 molecules for perhaps only 10^{-11} seconds. Consequently, very fast processes can be studied via molecular beam techniques. Further, one can catch the product NaCl molecules before the products collide with the walls or other molecules. One can directly measure the properties of the molecules that have reacted, and simultaneously determine all of the properties of the product molecules that form. Therefore, one can get more information about what happens during the reaction than with conventional techniques.

In practice, the beam systems have allowed people to examine much faster processes than could be examined with conventional techniques. Also, many of the details of a reaction can be probed only by using molecular beam techniques. Consequently, molecular beam techniques have been popular in the literature.

Unfortunately, there is insufficient room for us to discuss molecular beam techniques here. One should refer to Herglbauh (1966) Levine and Bernstein (1987) or Scoles (1988) for a discussion of molecular beam techniques and how they contribute to kinetics. We also do not have room to discuss all of the experimental techniques in Table 3.1 in detail. Several older books, including the books by Moore and Pearson (1981) and Laidler (1987), discuss the experimental techniques.

Still, there is one other important point to recognize in the table—one needs to use a different experimental method for a fast reaction than for a slow reaction. If a reaction takes 10^{-2} seconds, one needs to initiate the reaction within 10^{-3} seconds. A fast measurement system is needed. A much slower measurement technique can be used if the reaction takes several minutes. Table 3.1 indicates which methods can be used to measure rates for fast reactions and which ones are limited to slow reactions. Consequently, the reader should memorize the information in Table 3.1 before proceeding.

3.4 DIRECT AND INDIRECT METHODS

The listing in Table 3.1 separates the experimental methods according to the timescale of the measurement. However, there is another key distinction: whether the technique produces a **direct** or **indirect** measurement of the rate equation. I am assuming that the reader probably is not familiar with the terms *direct* and *indirect methods*. Therefore, I thought that I would define them before proceeding.

Recall that, by definition, the rate equation is an expression for the rate as a function of the concentration of the reactants. One can measure the rate as a function of concentration directly or indirectly. The experimental methods in Section 3.2 were mainly indirect measurements. If one loads a reactant into a reactor and measures the reactant concentration as a function of time, one is not measuring the rate as a function of concentration. Instead, one is measuring the concentration as a function of time, and fitting that data to infer a rate law. This is an indirect measurement of the rate law, so I will refer to it as an *indirect method*.

On the other hand, it is possible to directly measure the rate as a function of concentration. In that case, one can fit the rate equation directly. I will call such a measurement a *direct rate measurement*. More precisely, I will define a direct method as any experimental method where one actually measures the rate of reaction as a function of the concentrations in the reactor. I will define an indirect method as a method where one does not actually measure the rate. Instead, one measures some other property, for example, a concentration as a function of time, and fits that data to infer a rate law.

In the literature, it has become common to refer to a direct method as a **differential method**, while an indirect method is referred to as an **integral method**.

It is useful to consider an example, the decomposition of arsine (AsH_3), to illustrate the difference between direct and indirect measurements. The decomposition of arsine on silicon or gallium arsenic is quite important to semiconductor device manufacture. During the reaction, the arsine decomposes to yield an arsenic film and liberate hydrogen:



Reaction (3.6) is used to deposit arsenic as a dopant for silicon in the manufacture of integrated circuits. Reaction (3.6) is also used as an arsenic source in gallium arsenide production for light-emitting diodes (LEDs), flat-panel displays, and compact-disk (CD) players.

Figure 3.6 shows a typical reactor used for this reaction. The reactor consists of a quartz tube in a tube furnace. You load silicon wafers into the reactor, evacuate, turn on the oven, and let the wafers heat to 1000°C . You then feed arsine onto the hot wafers. The arsine decomposes, depositing arsenic onto the wafer.

Now, let's consider trying to measure the rate of reaction (3.6). One can measure the rate of reaction (3.6) using the apparatus in Figure 3.7. The apparatus consists of a reactor containing a very sensitive balance called a 'microbalance.' During a kinetic measurement, one loads a microchip onto the microbalance, runs the reaction, and then weighs the chip as a function of time. The change in weight of the chip is equal to the weight of the arsenic that is deposited. Therefore, one can use the change in weight of the chip to determine how much arsenic is deposited.

There are two ways to run the reactor. First, one could continuously feed arsine into the reactor, ensure a constant concentration of the arsine in the reactor and then determine the weight of the chip as a function of time. In that case, one would get a steady-state reaction rate. Second, one could load a fixed amount of arsine into the reactor and determine how much arsine is deposited as a function of time. In that case, one would determine a transient reaction rate.

In the first case, arsine would be continuously deposited onto the chip. If one measured the weight of the chip as a function of time, one could calculate R_D , the arsenic deposition

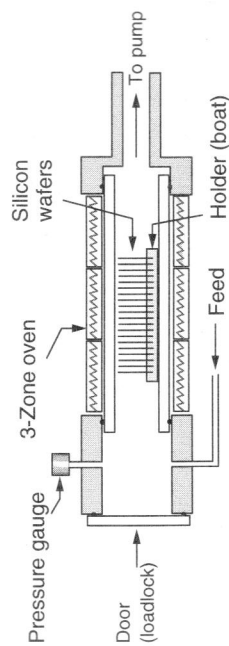


Figure 3.6 A typical arsine decomposition reactor.

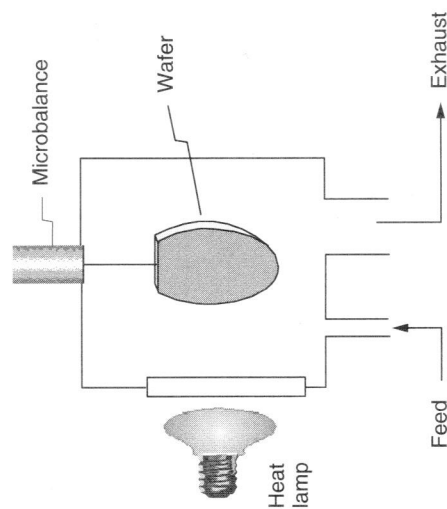


Figure 3.7 A possible apparatus to examine the decomposition of arsine (AsH_3) on silicon.

rate in mol/(hour-cm²), from

$$R_D = \frac{1}{(A_w) MW_{As}} \frac{dW_{\text{chip},w}}{dt} \quad (3.7)$$

where A_w is the area of the chip, MW_{As} is the molecular weight of arsenic, and $W_{\text{chip},w}$ is the weight of the chip. In this way, one could measure the rate of arsenic deposition at any arsenic concentration directly.

If one wanted to use this method to determine a rate law, one would repeat the measurements dozens of times, varying the arsine and hydrogen concentration within the reactor. Eventually, one could get a plot of the rate of reaction as a function of the arsine and hydrogen concentration within the reactor. Notice that during such an experiment, one is directly measuring a rate of reaction as a function of the concentration in the reactor. Therefore, I like to call such a measurement a **direct method** because of the rate equation. In the literature, people also call it a **differential method** because one generally has to differentiate data to calculate a rate.

An alternate experiment is to load a fixed amount of arsine into the reactor and measure the arsine pressure as a function of time while the arsine is deposited. Figure 3.8 shows typical data. In this case, the rate varies with time because the arsine is being used up. One could still differentiate the data to get the rate as a function of time. However, an alternative is to derive a theoretical equation for the pressure versus time, and compare the theoretical equation to the data.

Later in this chapter, we will integrate the rate equation to show that, for a first-order reaction, the weight of the chip will vary as follows:

$$P_{\text{AsH}_3} = P_{\text{AsH}_3}^0 \times e^{-k_1 t} \quad (3.8)$$

where P_{AsH_3} is the measured pressure of arsine, which varies with time; $P_{\text{AsH}_3}^0$ is the initial arsine pressure; k_1 is the rate constant for arsine decomposition; and t is time. One could measure the weight as a function of time and fit the data to equation (3.8) to calculate

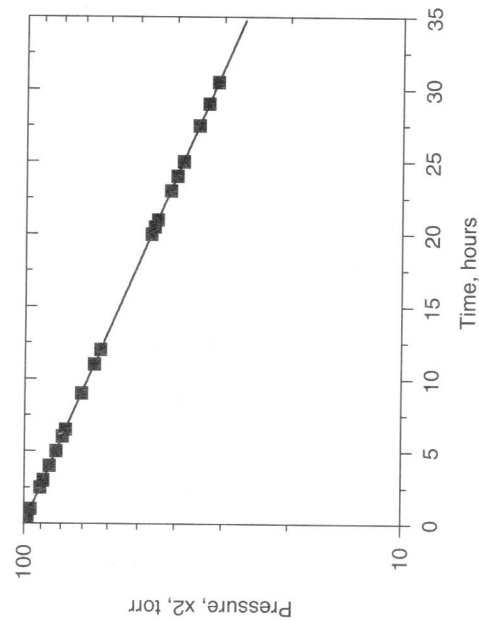


Figure 3.8 Typical batch data for reaction (3.7). [Data of Tamaru et al. (1955).]

the rate constant. In the literature, people call such an analysis an **integral method** since one derived equation (3.8) by integrating the rate equation.

I like to instead call it an **indirect method** because one is not measuring the rate as a function of concentration directly. Instead, one is determining how the rate varies with concentration indirectly by fitting the measurements to a theoretical expression.

Now one might ask, "How are the direct method and the indirect method fundamentally different?" Notice that when one uses the direct method, one is actually measuring the rate law directly. In other words, when one differentiates the weight versus time data, one gets a direct measurement of the rate for each arsine concentration. One does not have to make any assumptions about the form of the rate equation to calculate a rate; one just has to fit data. Alternatively, with the indirect method, the concentration is varying, so one has to make an assumption about the form of the rate equation to derive equation (3.8). That is less accurate. However, the advantage is that one does not need to differentiate data to get useful information.

In the literature, it has become common to refer to any method where one gets a direct measurement of the rate at each concentration a **direct method** or **differential method**, even if one does not have to actually differentiate data to calculate a rate. Alternatively, one refers to any method where one gets an indirect measurement of the rate as an **indirect method** or **integral method**, even though one would not necessarily need to integrate a rate equation to analyze the data.

3.4.1 Advantages of Direct and Indirect Methods

When one plans an experiment to determine the rate equation for a given reaction, one first needs to do is to decide whether to use a direct or indirect method.

Table 3.2 compares the advantages and disadvantages of direct and indirect methods. Generally, indirect measurements require easier experiments than do direct measurements, but the resulting rate equations are less accurate. With an indirect method, one simply loads reactants into a reactor and measures concentration versus time. Those are usually relatively easy measurements. In contrast, direct measurements generally require a flow system and a very sensitive measurement device to directly measure the rate. Consequently, the actual experiments are harder with a direct method than with an indirect method. The experiments are impossible with very fast or very slow reactions. Also, one doing a direct measurement gets only one point on the rate versus concentration curve

Table 3.2 Comparison of the advantages and disadvantages of direct and indirect methods

Direct Method	Indirect Method
Advantages	Disadvantages
Get rate equation directly	Must infer rate equation
Easy to fit data to a rate law	Hard to analyze rate data
High confidence on final rate equation	Low confidence on final rate equation
Disadvantages	Advantages
Difficult experiment	Easier experiment
Need many runs	Can do a few runs and get important information
Not suitable for very fast or very slow reactions	Suitable for all reactions including very fast or very slow ones

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 target 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.