

When you read the book you should pay attention to a few key things.

- Look for equations in boxes. They are the most important equations in the chapter, and you should probably memorize them.
- Be sure to look at the solved examples. I put the solved examples at the end of the chapter so that you can find them easily when you are doing the homework. Be sure to look at them.
- Read the chapter twice. I usually recommend that students (1) read the chapter through once, skipping the derivations, (2) go through the solved examples, and then (3) read the chapter a second time to concentrate on the details.
- Download the computer programs. I have posted computer programs for many of the examples on my Website, <http://www.utuc.edu/~r-masel/>. Be sure to download them and try them out.
- Remember to read the words as well as the equations. I know that students often use a book to help figure out how to solve their homework. Still, in my experience a qualitative understanding of kinetics is more important than knowing how to put numbers into the equations. Be sure to read the words as well as the equations.
- Do not trust everything in the textbook. I know that the statement "Do not trust everything in the textbook" sounds strange to a student, but remember that kinetics is an evolving field. If I look back to 10 years ago, things that I was sure then were right are now known to have serious limitations. I expect that 10 years from now, some of the ideas that I discuss here will be known to not work as well as I thought when I wrote this book. Evolution of knowledge is part of science; and in 10 years something in this book is bound to be wrong.

I have tried to make this book as useful of a teaching tool as possible given the length limitations. I hope that you enjoy it.

In Chapters 3–14, I will list a series of bibliographic works for further information. Reviews of the history of kinetics include:

- V. A. Kritisman, G. E. Zaikov, and M. M. Emanuel, *Chemical Kinetics and Chain Reactions: Historical Aspects*, Nova Science Publishers, 1995.
- K. J. Laidler, *The World of Physical Chemistry*, Oxford University Press, New York, 1996.
- M. C. King, Experiments with time, progress and problems in the development of chemical kinetics. *Ambix* **28**, 70 (1981).
- M. C. King, *Ambix* **29**, 49 (1982).

Specific references mentioned in this chapter are given at the end of this book.

REVIEW OF SOME ELEMENTARY CONCEPTS

PREFACE

The objective of this chapter is to provide some background material that will be used throughout the rest of the book. Specifically, we review the definition of the reaction rate, the stoichiometric coefficient, the rate equation, the order of reaction, the preexponential, and the activation energy. We will then discuss empirical rate laws, and the effect of temperature and catalysts on rates. Discussions of these topics are necessarily brief, since most of the readers of this book will already be familiar with these topics. However, the objective of this chapter is to bring the student's understanding of these topics to the next level. We will provide precise definitions of terms that were defined loosely in freshman chemistry. We will point out the historical basis for ideas, and describe how the ideas can be applied to nonstandard problems. We will also give real examples. There is necessarily some review material in the chapter. However, we directed the chapter toward someone who already has seen the material and who wants to understand it better, rather than to someone learning the material for the first time.

2.1 DEFINITIONS

To start off, it is useful to define some key terms. In this section we will define

- The stoichiometric coefficient
- The rate of reaction
- Homogeneous reactions
- Heterogeneous reactions

First, it is useful to start with some history. Chemical reactions were first studied in detail at the end of the eighteenth century. The initial work was done before people knew that

there were atoms or molecules and the idea that there were chemical compounds was still in dispute. It was clear that chemical reactions did occur. However, the nature of the reactions was still unclear.

One of the difficulties in the early work was that when one did an experiment, everything seemed to change. For example, Lavoisier [1789] did a series of experiments where he oxidized tin to tin-calx (SnO_2). The volume of the tin changed during the reaction and the mass changed during reaction. All of the properties of the tin seemed to change during the reaction. Lavoisier initially had trouble finding anything that was constant. However, in a series of famous experiments, Lavoisier oxidized the tin in a sealed flask and weighed the flask as the reaction proceeded. The experiment required the most sensitive balance that had ever been constructed, and the work was possible only because the French Academy of Science decided to finance the work. Lavoisier found that the weight of the sealed flask did not change during reaction. Instead, the weight change occurred only when air was able to rush into the vessel. This work showed, for the first time, that mass was conserved during chemical reactions.

Lavoisier also found that a fixed amount of air reacted with a fixed amount of tin. This work led to the law of fixed proportions, which states that chemicals react in fixed proportions during chemical reactions.

Finally, Lavoisier found that only part of the air was reactive. This finding led Lavoisier to propose that air was made up of different elements: a reactive element and an unreactive element.

Lavoisier called the reactive element in the air the "atmospheric principle". Later, Joseph Priestley visited France at Lavoisier's invitation. Lavoisier and Priestley discussed Priestley's discovery [1790] of 'dephlogogenated air', which was liberated when mercury oxide was heated. Lavoisier quickly recognized that the dephlogogenated air was the reactive element in the air. Lavoisier renamed the reactive element *oxygen*. This work led to the idea that air, and all mixtures and chemical compounds are made up of fundamental components called elements. Lavoisier also showed that reactions happen when an element moves from one chemical compound to another chemical compound.

Lavoisier then did a series of experiments where he reacted oxygen with a series of metals, and found that in most cases, a fixed amount of oxygen reacted with a fixed amount of metal to yield a fixed amount of oxide. Soon thereafter, Lavoisier proposed that **molecules react in fixed proportions**. That is, if one has a given reaction between A and B, one can define coefficients α_1 and α_2 such that during a given reaction, α_1 molecules of A always react with α_2 molecules of B to yield α_3 molecules of C and α_4 molecules of D:



In Lavoisier's case, he said that 1 kilogram (kg) of air would always react with 0.78 kg of tin to yield 0.99 kg of tin-calx and leave 0.79 kg of inerts. Lavoisier decided to call the study of these fundamental proportions **stoichiometry**, from the Greek word *stoichio-*, which means fundamental. Lavoisier also proposed that one could write an equation for each chemical reaction by balancing the production of all of the essential elements in the reaction. In other words, during the reaction between oxygen and tin, the number of kilograms of oxygen used up during the reaction would be equal to the number of kilograms of oxygen in the product calx.

Lavoisier also defined the **stoichiometric coefficient** β_n for molecule n participating in a given reaction, where Lavoisier defined the stoichiometric coefficient as the number of molecules of n *produced* when the given reaction goes once. Lavoisier's definition

is different from the one you are used to in freshman chemistry. The stoichiometric coefficient is negative for the reactants and positive for the products. For example, in the reaction



$\beta_{\text{CO}} = -2$, $\beta_{\text{O}_2} = -1$, $\beta_{\text{CO}_2} = 2$. The advantage of this definition is that it is much easier to use in a computer program and a spreadsheet than a definition where all stoichiometric coefficients are positive. Later in this book, we will find that this definition also allows you to simplify the equations for a complex reaction pathway. The disadvantage of the definition is that you have to watch out for the negative numbers.

One thing to be careful about is that the value of the stoichiometric coefficient changes according to how one writes the equation. For example, reaction (2.2) can be rewritten



In reaction (2.3), $\beta_{\text{CO}} = -1$, $\beta_{\text{O}_2} = -\frac{1}{2}$, and $\beta_{\text{CO}_2} = 1$.

Dalton [1805] extended Lavoisier's idea with his atomic theory. Dalton proposed that each of Lavoisier's elements were composed of tiny particles called *atoms*. Dalton showed that the number of each type of atom was conserved during chemical reactions. Each particle had a fixed weight. Although Dalton could not weigh each atom, he could define a relative scale by arbitrarily defining the relative weight of hydrogen to be one atomic mass unit (1 amu), and then calculating the weights of all of the elements accordingly. Dalton's calculations were not particularly accurate, but they did allow Lavoisier to calculate stoichiometric coefficients for many reactions.

Inspired by Lavoisier and Dalton's findings, many gentlemen-scientists set out to explore the nature of molecules. A particularly famous person at that time was Louis Thénard, [1818] who discovered hydrogen peroxide. Thénard thought that hydrogen peroxide was a wondrous molecule. It was composed of hydrogen and oxygen—the same components as ordinary water. Yet hydrogen peroxide behaved much differently than ordinary water. It could change the colors of dyes and would convert alcohol to vinegar. Thénard, being a wine connoisseur, was particularly interested in how hydrogen peroxide could convert alcohol into vinegar. He studied the reaction and measured the rate. Thénard found that when he diluted the alcohol, the rate went down. Additional hydrogen peroxide made the reaction go faster. Thénard then showed that by eliminating peroxides, he could make wine last longer. Thénard never quantified his findings, but his work showed for the first time that rates of chemical reactions varied with the concentrations of the reactants.

Many people expanded on Thénard's findings. In 1869, Guldberg and Waage proposed that rates of reaction were proportional to the "active masses" of the reactants, where in most cases the active mass roughly corresponded to the concentration of the species. Many other rate laws were proposed between 1860 and 1880. Still, it was not until Van't Hoff published his famous book, *Etudes de Dynamique Chimie* in 1884 that rates were put into a quantitative framework.

Van't Hoff was considered to be the greatest chemist of his day. Van't Hoff started the field *physical chemistry* and was the first person to really push the idea that quantitative reasoning was useful to a chemist. Van't Hoff wrote several influential books, including *Theoretische Chemie*, which set out the field of physical chemistry for the first time, and *Etudes de Dynamique Chimie*, which established chemical kinetics as a separate subdiscipline.

In *Etudes de Dynamique Chimie*, Van't Hoff quantified his ideas about rates of chemical reactions. Van't Hoff (1878) noted is that if one wants to compare rates of different reactions, one has to do so on a consistent basis. At that time, people had used all different kinds of reactors to examine rates of reactions. Some people had worked in tiny reactors, while other people had worked on big reactors. Generally, big reactors produced products faster than did small reactors, independent of what reaction was occurring in the reactor. Van't Hoff asserted that if one wanted to understand reactions, one would have to remove the effects of the size of the reactor from the analysis. For example, Van't Hoff noted that if a reaction is occurring uniformly over the volume of a vessel, then if one doubles the size of the vessel, one will produce twice as many moles of products in a given time. Consequently, Van't Hoff noted that it was not very useful to compare the total number of moles of product produced in one reactor to the number of moles of a different product produced in a different-sized reactor. Rather, it was important to consider how the rate per unit volume varied from one reaction to the next. Van't Hoff defined r_A , the rate that a given molecule *A* reacts as the rate of *production* of *A* in moles per volume per time. With this definition, the reaction rate, r_A , for a species *A* is negative if *A* is a reactant and positive if *A* is a product. Van't Hoff showed that if a reaction is run in a closed vessel with perfect mixing, one can determine r_A by measuring C_A , the concentration of *A*, as a function of time, *t*, and then substituting into the following equation:

$$r_A = \frac{dC_A}{dt} \quad (2.4)$$

Van't Hoff also noted that equation (2.4) is useful only when a reaction is occurring uniformly over the volume of a reactor. Van't Hoff considered several reactions that were instead occurring on the surface of his reactor. In that case, it is useful to define R_A , a rate per unit surface (i.e., mol/(cm²·second)).

In the work that follows, we will use a small *r* to indicate a rate per unit volume and a capital *R* to indicate a rate per unit area. We will also define **heterogeneous reactions** as reactions that take place on the walls of the reactor or on other surfaces within the reactor. We will also define **homogeneous** reactions as reactions that occur in the gas phase, in liquids, or throughout the bulk at a solid.

Again, these definitions are slightly different from the definitions you learned in freshman chemistry. In freshman chemistry, one usually talked about homogeneous reactions occurring in the same phase as the reactants and heterogeneous reactions as occurring in the interface between two phases. Note, however, that the freshman chemistry definition is not accurate. For example, consider the hydrogenation of ethylene:



One can run ethylene hydrogenation by bubbling ethylene and hydrogen through a liquid containing rhodium atoms or by bubbling the same mixture through a reactor containing a solid platinum catalyst. In the former case, the ethylene and hydrogen absorb (i.e., dissolve) into the liquid and react while they are in solution. In the latter case, the ethylene and hydrogen adsorb onto (i.e., bind to) the surface of the catalyst and react on the surface. Therefore, both processes are very similar. Still, we call the former case a *homogeneous* reaction because the reaction is occurring in a liquid. We call the latter case a *heterogeneous* reaction because the reaction is occurring on a surface. Nevertheless, in both cases the reaction is occurring in the same phase as the absorbed or adsorbed

Table 2.1 Summary of the key definitions

Stoichiometric coefficient	The amount of product produced when the reaction goes once; the stoichiometric coefficient is positive for a product and negative for a reactant
r_A	The net rate of production of a species <i>A</i> ; r_A is positive for a product and negative for a reactant
Rate of reaction $1, r_1$	$r_1 = \frac{1}{\beta_A} r_A$ for any species <i>A</i> participating in reaction 1.
Homogeneous reaction	A reaction that happens throughout the reacting mixture.
Heterogeneous reaction	A reaction that happens near the boundary of a reacting phase

reactants, so one cannot distinguish between homogeneous and heterogeneous reactions by looking to see if the reaction occurs in the same phase as do the reactants.

For the material later in this book, we will have to distinguish between r_A , the rate of production of species *A*; and, r_1 , the rate of reaction 1. Van't Hoff defined r_1 , the rate of reaction 1, as

$$r_1 = \frac{1}{\beta_A} r_A \quad (2.6)$$

where r_1 is the rate of reaction 1, r_A is the rate of formation of *A* during reaction 1, and β_A is the stoichiometric coefficient of *A*. Note in general that $r_A \neq r_1$. Again this definition is slightly different from the one you learned in freshman chemistry. In Example 2.A at the end of this chapter, we show how to use measurements on a simple reactor to calculate r_A and r_1 . The reader may want to look at this solved example before proceeding.

Table 2.1 summarizes the key definitions so far in this chapter. The reader should memorize these definitions before proceeding.

2.2 VARIATION IN RATE WITH CONDITIONS

Next we want to discuss how rates of reaction vary with conditions. Van't Hoff showed that generally rates vary with

- Concentrations of all of the reactants, products, and other species in the system
- Temperature
- The presence of solvents
- The presence of catalysts

In the next several sections, we will discuss the effects of concentration and temperature at length. The role of solvents and catalysts will be discussed in Chapters 12–14.

2.3 EMPIRICAL RATE LAWS

We will first consider the role of concentration on the rate of reaction. Our objective is to define the rate equation and the order of a reaction.

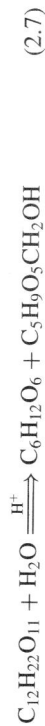
Studies of the role of concentration on rates of chemical reactions started in the middle part of the nineteenth century. Van't Hoff summarized the effects in his 1896 book.

Van't Hoff reported data on many different reactions, and showed how to correlate the measurements to the concentrations of the various species. Van't Hoff proposed that the rate was a function of only the temperature of the reactor, the concentration of all of the species, the concentration of solvents or catalysts, and the total pressure. Further, Van't Hoff asserted that if one fixed the temperature and solvent, one could formulate an equation for the rate as a function of concentration. An equation that describes the relationship between the rate of reaction and the concentration of all of the species in the reactor is called a **rate equation**.

Van't Hoff published the findings described above in a series of books that were classics for the day. The interest generated by Van't Hoff's books and the fact that he won the first Nobel Prize in chemistry stimulated many other scientists to examine the effect of concentration on rates of reactions.

The most famous person to follow in Van't Hoff's footsteps was Friedrich Wilhelm Ostwald. Ostwald had a very strong character. On one hand, he argued vehemently that while atoms were useful theoretical constructions, atoms do not really exist. On the other hand, Ostwald was the first person to propose that ions formed when species dissolve in solution. Ostwald created electrochemistry and did much of the early work on thermodynamics of solutions.

Ostwald was fascinated with rates of reaction in solution. A particularly interesting example was the hydration of (+)sucrose ($C_{12}H_{22}O_{11}$) to glucose ($C_6H_{12}O_6$), and fructose, ($C_5H_9O_5CH_2OH$):



Reaction (2.7) is a common natural process called *sugar inversion*. Honeybees use sugar inversion to convert sugar from plants into honey. Humans invert sucrose as part of digestion.

Experimentally, sucrose is stable in water for months. Still, if one adds a small amount of either an acid such as HCl, or an enzyme called *invertase*, the sucrose is quickly converted into glucose and fructose.

Wilhelmy [1850] and Berthelot (1862) examined the reaction in some detail and found that it obeyed a simple rate law as follows:

$$r_G = -r_S = k_3 C_S C_A \quad (2.8)$$

where r_G is the rate of formation of glucose, r_S is the rate of production of sucrose, C_S is the sucrose concentration, C_A is the acid concentration, and k_3 is a constant.

Ostwald reexamined reaction (2.7) and found that he could catalyze the reaction with a wide range of acids. Equation (2.8) did not explain his data very well. Still, he could fit the data with the following rate form:

$$r_G = k_6 C_S C_{H^+} \quad (2.9)$$

where C_{H^+} is the concentration of hydrogen ions in solution.

Ostwald also generalized his results by noting that if one takes an arbitrary reaction of the form $A \Rightarrow B$, one might be able to fit the data to a form like equation (2.8). Thus r_A , the rate of production of A, is given by

$$r_A = -k_1 C_A \quad (2.10)$$

where C_A is the concentration of the species A that is being reacted away; r_A is the rate of production of A, and k_1 is a constant. Note that r_A is negative.

Ostwald did extensive measurements of rates of many reactions in solution. He also reanalyzed all of the rate data that had appeared prior to 1890 and found that the rate equation given by equation (2.10) sometimes works great. However, more often than not equation (2.10) is a poor representation of the rate of reaction. Ostwald also noted that a slightly modified equation could represent a wide range of data:

$$r_A = -k_n (C_A)^n \quad (2.11)$$

where n is a fitting constant.

Table 2.2 illustrates some rate data that one might fit to equation (2.11). In the data in Table 2.2 the rate doubles when the concentration doubles. Consequently, $n = 1$. One can also plug the data in Table 2.2 back into equation (2.11) to calculate k_n . k_n works out to be 0.5/min.

Ostwald called n the **order** of the reaction, and k_n the **rate constant**. The relationship between the rate and the concentrations of the reactants is called the **rate equation**. The definition of a rate equation as *the rate as a function of concentration* is quite important. The reader should memorize this definition before proceeding.

Ostwald also proposed that heterogeneous reactions could also be fitted by a similar rate form

$$R_A = k_n (C_A^s)^n \quad (2.12)$$

where C_A^s is the surface concentration of A in mol/cm².

For future reference, we note that reactions that obey equation (2.11) with $n = 1$ are called **first-order** reactions, reactions that obey equation (2.11) with $n = 2$ are called **second-order** reactions, while reactions that obey equation (2.11) with $n = 3$ are called **third-order** reactions. The terms *rate constant*, *rate equation*, *first-order*, and *second-order* are quite important. The reader should memorize the definitions before proceeding.

As an exercise, the reader might want to show that the rate constant for a homogeneous or heterogeneous first-order reaction has the dimension (time)⁻¹ (e.g., hour⁻¹), the rate constant for a homogeneous second-order reaction has the dimensions volume/(molecule or mole)/time [e.g., liter/(mol·hour)], while the rate constant for a heterogeneous second-order reaction has dimensions of area/(molecule or mole)/time [e.g., cm²/(mol·hour)]. Similarly, the rate constant for a homogeneous third-order reaction has the dimensions volume²/(molecule or mole)²/time [e.g., liters²/(mol²·hour)]. While the rate constant for a third-order heterogeneous catalyst has dimensions of area²/time/(moles or molecule)³ [e.g., cm⁴/(mol²·minute)].

The idea that there was a rate equation was a sizable advance. At the time this work was going on, people did not know whether chemical processes would be amenable to quantitative analysis. The fact that the rate could be written as a function (i.e., equation)

Table 2.2 Sample rate data to illustrate equation (2.11)

C_A , mol/liter	Rate, (mol-liter/hour)	C_A , (mol-liter)	Rate, (mol-liter)/hour
0.25	0.13	1	0.5
0.5	0.25	2	1.0

of the concentrations of all of the species in the reactor meant that many chemical processes would be amenable to quantitative analysis. Most students do not realize that the observation that the rate can be written as a rate equation is important. In fact, however, this observation forms the basis of all studies of kinetics.

In 1896, it was not obvious that the rate was a *function* of the concentration where we use the word *function* in a mathematical sense. Recall from freshman calculus, that certain criteria must be satisfied before it is mathematically correct to say that one variable is a function of another. However, Van't Hoff (1884, 1896) examined all of the reactions that had been studied prior to 1896, and found that in all cases, he could express the rate as a function of the concentration. Therefore, Van't Hoff asserted that one could write a rate equation for any reaction.

More recent data show that Van't Hoff is usually correct; one can usually fit rate data to a rate equation. However, there are some exceptions where the rate is not a mathematical function of just the temperature, pressure, and composition (see Section 2.8). Still, those are rare exceptions. In most cases, the rate is a function of the temperature, pressure, and composition.

Rate equations, of the form in equation (2.11), apply only to cases where there is only one reactant. When there are two reactants, A and B, one often finds rate equations such as:

$$r = k_m(C_A)^p(C_B)^m \quad (2.13)$$

In the case of reaction (2.13), one defines the **overall order of the reaction** to be $n + m$. If $n = 1$ and $m = 2$, the reaction will be third-order. One might also say that the reaction is first-order in A and second-order in B.

Table 2.3 illustrates some data that one might fit to equation (2.13). In the data in the table, the rate goes up a factor of 2 when C_A doubles, so $n = 1$. However, the rate goes up by a factor of approximately $2^2 = 4$ when C_B doubles. Therefore, $m = 2$. If one plugs back into equation (2.13), one finds k_m equals 0.5 liter/(mol-minute).

Table 2.4 summarizes the definitions in this section; one should memorize these definitions before proceeding.

Table 2.3 Sample data to illustrate equation (2.12)

C_A , mol/liter	C_B , mol/liter	Rate, (mol-liter)/minute	C_A , mol/liter	C_B , mol/liter	Rate, (mol-liter)/minute
1	0.25	0.031	0.25	1	0.13
1	0.5	0.13	0.5	1	0.25
1	1	0.5	1	1	0.5
1	2	2.0	2	1	1.0

Table 2.4 The key definitions from Section 2.3

Rate equation	The rate as a function of the concentration of the reactants
Order	The exponent n is the expression
First-order reaction	A reaction whose rate is preparation to the reactant concentration to the first power [e.g., $n = 1$ in equation (2.11)]
Second-order reaction	A reaction whose rate is proportional to the reactant concentration to the second order
Overall order of reaction	The sum of the orders for all of the reactants

2.3.1 Notation

In the next section, we will be discussing the rate equations for a variety of reactions. Before we do so, we will need to define some notation. We will define small k with a subscript as being the rate constant for a reaction; so k_1 , k_2 , k_3 , and k_{-1} will be the rate constants for reactions 1, 2, 3, and -1 , respectively. Similarly, large K with a numerical subscript will be an equilibrium constant for a reaction; so K_1 , K_2 , and K_3 will be the equilibrium constants for reactions 1, 2, and 3. k_B , where the k has a tail, will be Boltzmann's constant where Boltzmann's constant equals the gas law constant (R) divided by Avogadro's number. We will use two different notations for a concentration of a species A: C_A , and $[A]$ (concentration of A), where:

$$[A] \equiv C_A \quad (2.14)$$

We will use the $[A]$ notation mainly where we have a molecule reacting. In the later notation, equation (2.9) will be rewritten

$$r_G = k_6[\text{sucrose}][\text{H}^+] \quad (2.15)$$

Again, we note that we define r_A as the rate per unit volume of a homogeneous reaction while R_A is the rate per unit surface area of a heterogeneous reaction. The reader should memorize this notation before proceeding.

2.4 THE EXPERIMENTAL SITUATION

Now that we have the notation out of the way, it is interesting to go back and compare equation (2.13) to the data. Our key point will be that equation (2.13) works for a wide variety of reactions provided the data are being taken over a limited range of concentration. To start, it is useful to recall that Ostwald first proposed equation (2.13) in 1890. At the time there were reliable data for three gas-phase reactions and six reactions in solution. Table 2.5 shows the rate equations for these reactions as cited by Van't Hoff (1896). Notice that all of these rate equations are of the general form of equation (2.13). Since 1896, thousands of reactions have been examined. Most follow simple first- or second-order rate laws over moderate concentration ranges. There are some exceptions. Generally, the rate equation is different or there are concentrations of 0.001 and 10 mol/liter. However, equation (2.13) works for 95% of the reactions that have been examined so far. The main exceptions are catalytic reactions. They will be discussed later in this chapter.

Equation (2.13) has also proved to be useful in a wide range of systems outside of chemistry. For example, Figure 2.1 shows data for the reproduction rate of *E. coli* (a common bacterium) in a sugar solution. Notice that the reproduction rate of *E. coli* follows

$$r_{COI} = k_{COI}[E. coli][\text{sugar}] \quad (2.16)$$

where r_{COI} is the rate of production of *E. coli*, $[E. coli]$ is the *E. coli* concentration, [sugar] is the sugar concentration, and k_{COI} is a constant. The plot is linear over most of the range, indicating that the reproduction of *E. coli* is first-order in the sugar concentration.

Similarly, Figure 2.1 shows how the reproduction rate of paramecium varies with the population of the paramecium. Notice that at paramecium concentrations below

Table 2.5 Some of the rate equations that were discovered before 1880^a

Reaction	Rate equation
$4\text{PH}_3 \longrightarrow \text{P}_4 + 6\text{H}_2$	$r_{\text{PH}_3} = -k_3[\text{PH}_3]$ (2.T.1)
$2\text{AsH}_3 \longrightarrow \text{As}_2 + 3\text{H}_2$	$r_{\text{AsH}_3} = -k_4[\text{AsH}_3]$ (2.T.3)
$2\text{PH}_3 + 4\text{O}_2 \longrightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$	$r_{\text{PH}_3} = -k_5[\text{PH}_3][\text{O}_2]^{1/2}$ (2.T.5)
$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$	$r_{\text{S}} = -k_6[\text{sucrose}][\text{H}^+]$ (2.T.7)
$\text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_3\text{H}_9\text{O}_3\text{CH}_2\text{OH}$	
$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{ROH}$	$r_{\text{Ac}} = +k_7[\text{CH}_3\text{COOH}][\text{H}^+]$ (2.T.9)
$\text{CH}_3\text{COOH} + \text{ROH} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOR} + \text{H}_2\text{O}$	$r_{\text{Ac}} = -k_8[\text{CH}_3\text{COOH}][\text{ROH}][\text{H}^+]$ (2.T.12)
$\text{C}(\text{CH}_2\text{COOH})_4 + \text{H}_2\text{O}$	$r_{\text{C}_2\text{H}_5\text{CO}_2} = -k_9[\text{C}_2\text{H}_5\text{ClO}_2]$ (2.T.14)
$\xrightarrow{\text{H}^+} \text{HOCH}_2\text{COOH} + \text{HCl}$	
$2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$	$r_{\text{Fe}^{3+}} = -k_{10}[\text{Fe}^{3+}]^2[\text{Sn}^{2+}]$ (2.T.15)
$\text{KClO}_3 + 6\text{FeO} \longrightarrow \text{KCl} + 3\text{Fe}_2\text{O}_3$	$r_{\text{Fe}^{3+}} = k_{11}[\text{Fe}^{2+}][\text{ClO}_3^-]$ (2.T.17)

^aIn these equations, r_{PH_3} , r_{AsH_3} , r_{S} , r_{Ac} , $r_{\text{C}_2\text{H}_5\text{CO}_2}$, and $r_{\text{Fe}^{3+}}$ are the rates of formation of phosphine, arsine, sucrose, acetic acid, chloroacetic acid, and Fe^{3+} , respectively; $[\text{PH}_3]$, $[\text{AsH}_3]$, $[\text{O}_2]$, $[\text{sucrose}]$, $[\text{H}^+]$, $[\text{CH}_3\text{COOH}]$, $[\text{ROH}]$, $[\text{Sn}^{2+}]$, $[\text{ClO}_3^-]$, and $[\text{C}_2\text{H}_5\text{ClO}_2]$ are the concentrations of phosphine, arsine, oxygen, sucrose, hydrogen ion, acetate, acetic acid, alcohol, Sn^{2+} , ClO_3^- , and chloroacetic acid, respectively; and k_3 , k_4 , k_5 , k_6 , k_7 , k_8 , k_9 , k_{10} , and k_{11} are constants.

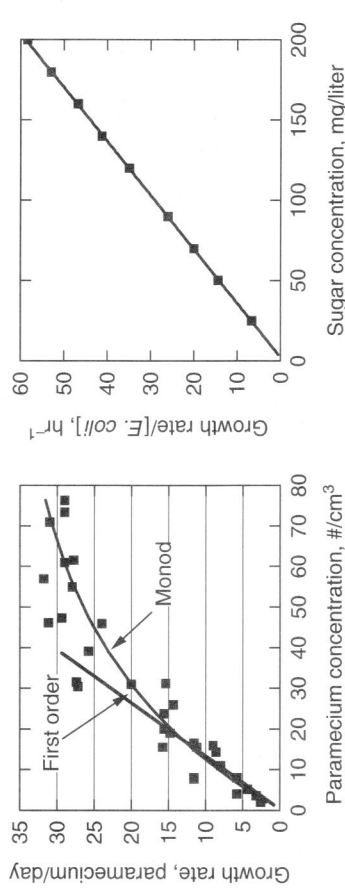


Figure 2.1 The reproduction rate of paramecium as a function of the paramecium concentration and the rate of *Escherichia coli* growth in sugar solutions as a function of the sugar concentration. [Paramecium data of Meyers (1927) 1; *E. coli* data from Monod (1942).]

$20/\text{cm}^3$ the reproduction rate of the paramecium increases linearly with the paramecium population:

$$r_{\text{par}} = k_{\text{par}}[\text{par}] \quad (2.17)$$

where r_{par} is the rate of paramecium reproduction, $[\text{par}]$ is the concentration of paramecium, and k_{par} is a constant. Consequently, the reproduction of paramecium is a first-order process. Equation (2.13) fits data in a wide variety of systems, which is why it has proved to be so useful.

Of course, data taken over a wider range of concentrations show that reactions do not follow equation (2.13). For example, the growth of *E. coli* follows so-called **Monod** (after Jacques L. Monod, biochemist) kinetics:

$$r_{\text{ecoli}} = \frac{k_1 K_2 [E. coli] [\text{sugar}]}{(1 + K_2 [\text{sugar}])} \quad (2.18)$$

where k_1 and K_2 are constants.

According to equation (2.18), the rate goes up and then saturates as shown in Figure 2.2. If one plots the log of the rate versus concentration, one gets a characteristic S-shaped curve. The one special feature of reaction (2.16) is that as the reaction proceeds, more bacteria are born, so the rate increases. In the usual case, the rate decreases as the reaction proceeds because the reactants are used up. One calls reactions where the rate increases as products build up **autocatalytic reactions**. In autocatalytic reactions the product catalyses (i.e., speeds up) the reaction. Many biological processes are autocatalytic.

Rate data for most biological growth processes can fit to equation (2.13) when concentrations are small. Such a result shows the power of equation (2.13). Still, equation (2.13) seldom fits at high concentrations. Instead, one needs a more complex rate equation like that in equation (2.18).

In the previous paragraph, we noted that the *E. coli* growth curve does not follow equation (2.13) at high concentrations. Similar effects are seen in most chemical reactions. Figure 2.3 shows a plot of the rate of CH_3NC isomerization as a function of pressure. To keep the plot in perspective, if we take the log of equation (2.11), we obtain

$$\ln(-r_A) = \ln(K_n) + n \ln(C_A) \quad (2.19)$$

Therefore, the plot of the log of the rate versus the log of the pressure should be linear with a slope of 1 for a first-order reaction and linear with a slope of 2 for a second-order reaction. Notice that the slope is a 1.0 at high pressure, implying a first-order reaction. However, the reaction changes to second-order at low pressure. Experimentally, changes in the order of a reaction with pressure are quite common. In fact, it is unusual to see a change in the kinetics of a gas-phase reaction when one works over a wide range of pressures.

It is also common to find that the rate data for a given reaction *cannot* be fit to a rate equation of the form in equation (2.13). For example, the rate of the reaction

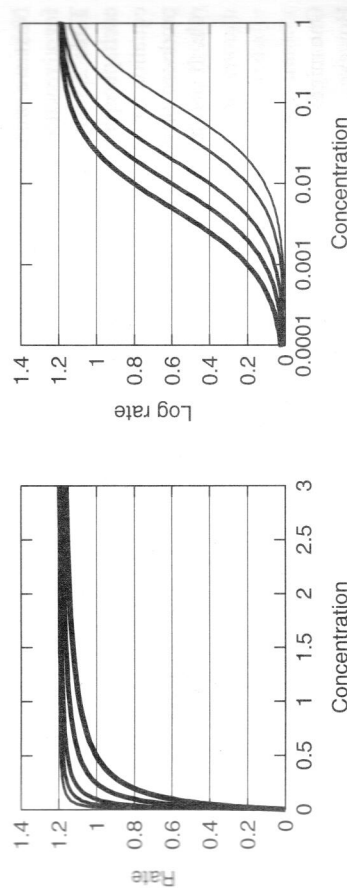


Figure 2.2 A plot of the rate for Monod kinetics, for $k_1 = 1, 2$ and $K_2 = 10, 20, 50, 100, 200$.

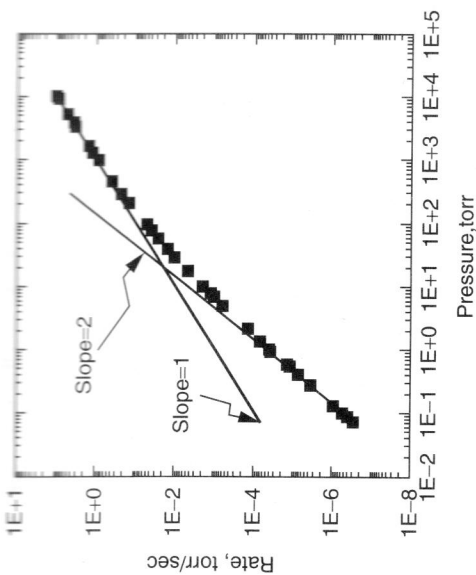


Figure 2.3 The rate of CH₃CN isomerization to CH₃CN as a function of the CH₃CN pressure. [Data of Schneider and Rabinovitz (1962).]

is thought to obey a complex rate equation, as follows:

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]}{1 + K_2[\text{Br}_2]} \quad (2.21)$$

where r_{HBr} is the rate of formation of HBr, $[\text{H}_2]$ is the H₂ concentration, $[\text{Br}_2]$ is the Br₂ concentration, $[\text{HBr}]$ is the HBr concentration, and, k_1 and K_2 are constants. One cannot fit HBr rate data to equation (2.13).

Note also that one cannot easily define a reaction order when one has a complex rate equation such as that in equation (2.21). In my experience, equation (2.13) works great most of the time. However, it can fail, especially when the kinetic data are taken over a wide range of concentration.

2.4.1 The Relationship between Stoichiometry and Rate

Next we want to consider whether there is any relationship between the rate equation for a reaction and the stoichiometry of the reaction. The experimental data shown in Table 2.3 say no. Notice that in reaction (2.T.5), (in Table 2.5), two oxygens react with each phosphine. Yet reaction (2.T.5) is only half-order in oxygen. Similarly, the rate equation for reaction (2.T.7) is first-order in the H⁺ concentration, even though no H⁺ is produced or consumed in the reaction. Reaction (2.T.1) seems to be an exception to the rule. If one rewrites reaction (2.T.1) as



One might say that the kinetics of the reaction bear some relationship to the stoichiometry. However, the data in Figure 2.3 show that the first-order behavior does not persist over a wide range of conditions. *Experimentally, there is seldom any relationship between the*

rate of a reaction and the stoichiometry of the reaction. Consequently, stoichiometry does not seem to have an important influence on the form of the rate equation.

We will discuss this point further in Chapter 4. However, the key thing to remember for now is that rate data can often be fit to a rate equation but that the rate equation may not be related to the stoichiometry of the reaction in a simple way.

2.4.2 Summary of the Effect of Composition on Rates

In summary, then, so far in this chapter we have considered how rates of reaction vary with concentration. We found that in most cases the rate of reaction varies in a simple way with composition. We often observe first- or second-order data. There are some exceptions, especially when we take data over a wide range of conditions. However, we can usually find a rate equation that works even over a wide temperature range.

2.5 TEMPERATURE EFFECTS

At this point, we will be changing topics. So far, we have been talking about the dependence of rate on composition. Now, we want to change topics and discuss how reaction rates depend on temperature. Our objective will be to present Arrhenius' law, and the Harcourt-Essen equation.

Studies of the influence of temperature effects in reactions date back to the medieval alchemists. The alchemists mixed substances together and saw what happened. One of the things that was discovered was that many reactions turn on suddenly over a modest temperature range. For example, the alchemists discovered that oil will suddenly ignite when the oil is heated to 320°C. Similarly, a hydrogen-oxygen mixture is stable at 400°C, but ignites suddenly at about 440°C. In a series of important experiments, Meyer and Raum (1895) showed that if they held a mixture of hydrogen and oxygen at 300°C for 65 days, 1–5% of the hydrogen and oxygen is converted into water. Therefore, it was concluded that reactions do not really turn on suddenly. Instead, rates of reaction change with temperature.

People explored the effects of temperature on rates of reaction in the latter part of the nineteenth century. The studies were usually limited to a modest temperature range (50°C). The variations in rate were so small that no one was able to accurately test models for the temperature dependence of rates. Still, considerable data were generated.

In 1893, Kooij and Van't Hoff examined the decomposition of phosphine between 310 and 510°C. This was the first time that the kinetics of a single reaction was measured over a wide temperature range. Figure 2.4 shows a plot of the rate of phosphine decomposition via reaction (2.T.1) (in Table 2.2) as measured by Kooij and Van't Hoff. Notice that the rate increases rapidly with temperature, doubling once every 35 K.

Prior to Kooij and Van't Hoff's work, there were two competing models in the literature on the effects of temperature on rates: Perrin's model and Arrhenius' model. Perrin (1919) had proposed that reactions were activated because the reactants had to accumulate enough energy to break bonds before reaction could occur. Perrin noted that the energy transfer could come from radiation or convection. If one calculates the rate of energy transfer to a cold molecule, the rate of energy transfer from the walls of the vessel can be approximated by

$$E_T = E_T^0 T^n \quad (2.23)$$

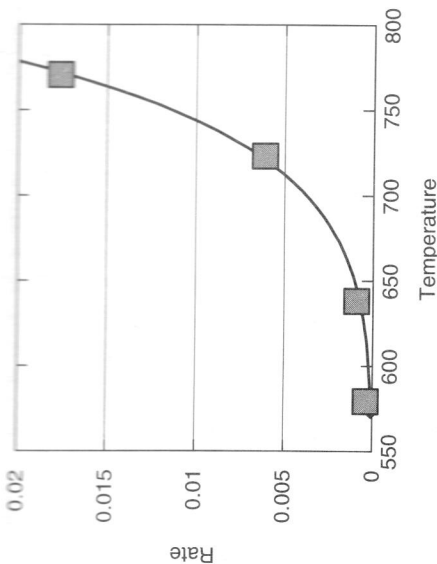


Figure 2.4 The rate of PH_3 decomposition as a function of temperature. [Data of Kooij (1893).]

where E_T is the rate of energy transfer, T is the absolute temperature, E_T^0 is a constant, and n is a constant that varies from 1 (when forced convection dominates) to 4 (when radiation dominates). Consequently, Perrin suggested that if the rate of energy transfer from the walls of a vessel controls the rate of reaction, the rate constant for a given reaction k_1 can be written as

$$k_1 = k_1^0 T^n \quad (2.24)$$

where k_1^0 is a constant. Equation (2.24) was also proposed by Harcourt and Esson on empirical grounds (the model worked).

An alternative model was proposed by Arrhenius. Arrhenius suggested molecules needed to go over a barrier before reaction could occur. Wigner [1932] and Polanyi [1931] later represented the barrier as a hill between reactants and products as seen in Figure 2.5. Only hot molecules (i.e., molecules with a total energy greater than E_a) can react, and there are more hot molecules at higher temperatures. Consequently, rates increase with temperature.

Arrhenius quantified his ideas by assuming that the hot molecules were in equilibrium with the reactants. At equilibrium, F_{E_A} , the fraction of the molecules that are hotter than

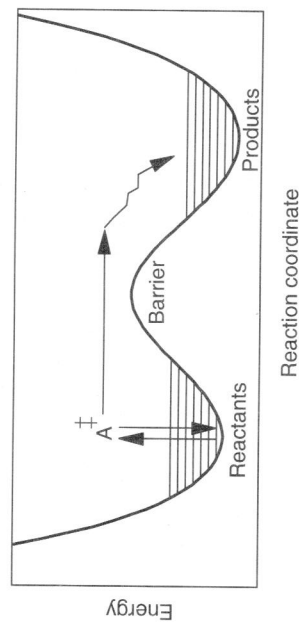


Figure 2.5 Wigner and Polanyi's representation of Arrhenius' model of activation barriers to reactions.

E_A , is given by

$$F_{E_A} = e^{-E_A/k_B T} \quad (2.25)$$

where E_A is called the *activation energy*, k_B is Boltzmann's constant, and, T is the absolute temperature. Note that Boltzmann's constant is just the ideal-gas law constant (R) divided by Avogadro's number. Also note the notation k_B . We use the tail on the k to indicate that k_B is not a rate constant.

The rate constant becomes

$$k_1 = k_1^0 e^{-E_a/k_B T} \quad (2.26)$$

where k_1^0 is called the *preexponential*. Equation (2.26) is called *Arrhenius' law*. It is a key equation for the remainder of this book.

Equation (2.28) is correct for the case when the activation energy is measured in kilocalories per molecule. If you measure activation barriers in kilocalories per *mole*, then the following equation should be used:

$$k_1 = k_1^0 \exp\left(-\frac{E_a}{RT}\right) \quad (2.27)$$

where again R is the gas law constant.

Van't Hoff (1896) compared equations (2.24) and (2.26) to his phosphine data and found that at low pressure, equation (2.24) worked best. However, when he examined a wider data set, equations (2.24) and (2.26) worked equally well much of the time. Still, Van't Hoff found it hard to believe that radiation played an important role in chemical reactions. Later, Langmuir [1920] showed that the emissivity of the walls did not affect chemical reaction rates, so energy transfer from the walls of the vessel does not affect reactions. As a result, Perrin's equation was discarded in the literature. Arrhenius' equation on the other hand is seen in most textbooks.

Still, Dunbar and McMahon (1998) have shown that radiation from the walls can have an important influence on the rate of unimolecular reactions. Later in this book, we will find that energy transfer barriers to reactions are just as important as activation barriers. The energy transfer barriers are not barriers to energy transfer to the walls. Rather, they are barriers to energy transfer within a molecule. Reactions with energy transfer barriers do not follow Arrhenius' law [equation (2.26)]. Instead, they follow

$$k_1 = k_m^0(T)^m e^{-E_A/k_B T} \quad (2.28)$$

where k_1 is the rate constant, E_A is the activation barrier, k_B is Boltzmann's constant, T is temperature, and m and k_m^0 are constants. According to Arrhenius' law, a plot of the log of the rate versus $1/T$ should be linear. However, Figure 2.6 shows some data for a typical reaction, and one observes significant curvature. Equation (2.28) fits the data in Figure 2.6 much better than does Arrhenius' law. Nevertheless, Arrhenius' law equation (2.26) is cited much more often than equation (2.24) or (2.28). Therefore, the reader should memorize equation (2.26) before proceeding.

In my experience, Arrhenius' law works great when one is working over perhaps a 50–100 K temperature range. It only fails when one measures data over a much wider temperature range.

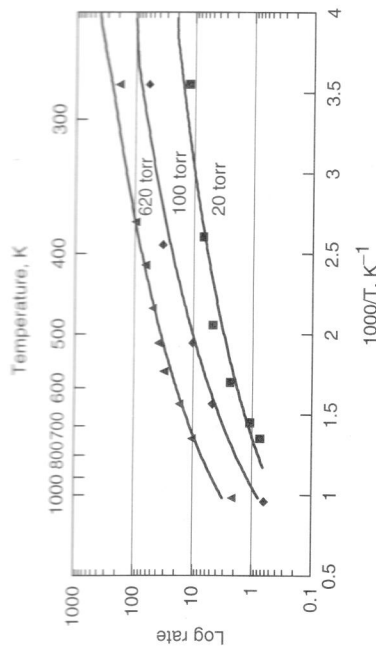


Figure 2.6 The rate of the reaction $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$ as a function of the temperature. [Data of Becker, et al. (1996).]

2.5.1 Implications of Arrhenius' Law

In freshman chemistry, you learned that Arrhenius' law can be used to calculate activation barriers. The idea is to measure the rate of reaction as a function of temperature, and then make a plot of the log of the rate versus one over the temperature. The slope of the plot is proportional to the activation barrier. Figure 2.7 shows an example of that. Arrhenius' law equation (2.26) fits the data okay, although not as well as does equation (2.28).

In my view, if the only thing you could do with Arrhenius' law were to fit data, Arrhenius' law would not be as important. After all, equation (2.28) fits data much better. However, the real strength of Arrhenius' law is that it allows one to make predictions without doing very many experiments. In this section, we will show how Arrhenius' law can be used to make useful predictions from very little data.

According to Arrhenius' law, the rate constant for a reaction, k_1 , will be given by

$$k_1 = k_1^0 e^{-E_a/\xi_B T} \quad (2.29)$$

where k_1^0 is the preexponential, E_a is the activation energy, ξ_B is Boltzmann's constant, and T is temperature.

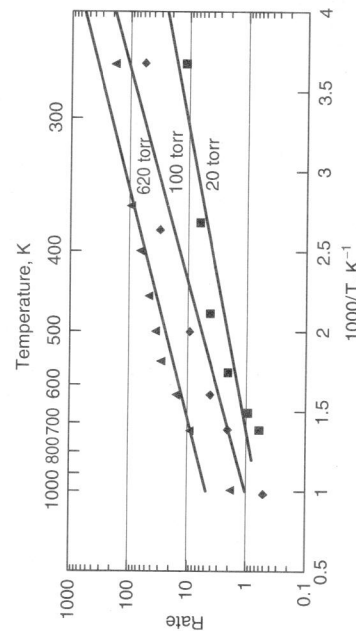


Figure 2.7 A fit of the data in Figure 2.6 to Arrhenius' law.

In Chapter 7, we will find that for an elementary reaction, k_1^0 is usually about $10^{14.5}$ /second for first-order reactions, $10^{13.2}$ \AA^2 /molecule-second for second-order reactions; and $10^{13.2}$ \AA^6 /molecule²-second for third-order reactions. The reader should memorize these typical values of the preexponentials before proceeding.

Now, let's consider a first-order reaction $A \Rightarrow B$. In Chapter 3, we will find that if we load A into a beaker and let it react, then 50% of the A will be reacted after a time $\tau_{1/2}$, given by

$$\tau_{1/2} = \frac{\ln 2}{k_1} \quad (2.30)$$

Figure 2.8 shows a plot of $\tau_{1/2}$ versus E_a calculated from equation (2.30) for $k_1^0 = 10^{13}$ /second. Notice that at 300 K, a reaction with an activation barrier of 14 kcal/mol takes about one millisecond (1 ms) to go to 50% completion. A reaction with an activation barrier of 18 kcal/mol takes about 1 second to go to 50% completion. A reaction with an activation barrier of 20.4 kcal/mol takes about 1 minute to go to 50% completion. A reaction with an activation barrier of 23 kcal/mol takes about an hour to go to 50% completion. A reaction with an activation barrier of 24.8 kcal/mol will take a day to go to 50% completion. A reaction with an activation barrier of 28 kcal/mol will take about a year to go to 50% completion. A reaction with an activation barrier of 31 kcal/mol will take a century to go to 50% completion. A reaction with an activation barrier of 36 kcal/mol will take about a million years to go to 50% completion.

Physically, this is very important because it means that if you run a reaction at room temperature and the rate is easily measurable (i.e., the reaction takes between 1 second and 1 hour), the activation barrier for the reaction will usually be 20 ± 6 kcal/mol.

In Professor Masel's lab, students often do experiments where they slowly heat a system and watch for reaction. Generally, if one observes a reaction taking a minute at some temperature T_{minute} , then the activation energy for the reaction will be approximately

$$E_a = (1/15 \text{ kcal/mol} \cdot \text{K}) T_{\text{minute}} \quad (2.31)$$

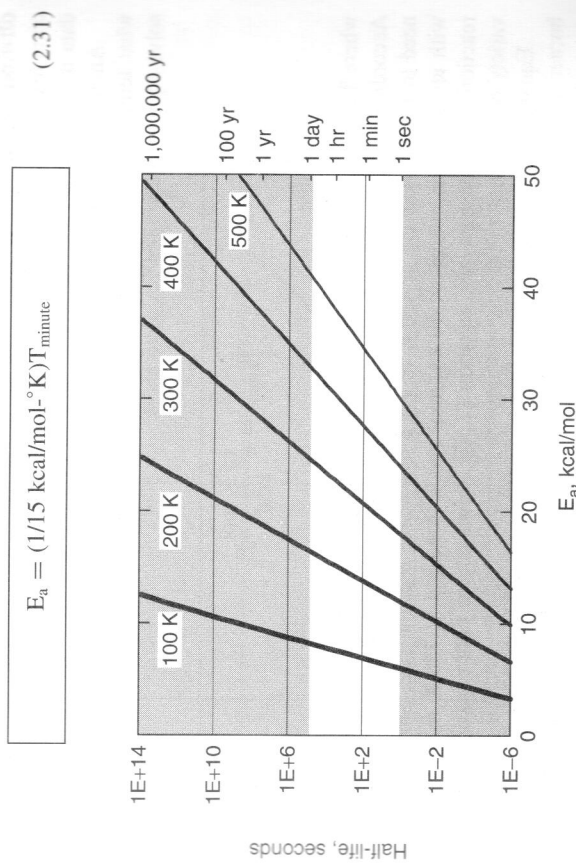


Figure 2.8 A plot of $\tau_{1/2}$ versus E_a at 100, 200, 300, 400, and 500 K.

Note that T_{minute} in equation (2.31) is temperature in degrees Kelvin. Similarly, if the reaction takes a second at some temperature, T_{second} , then the activation barrier is approximately

$$E_a = [(0.06 \text{ kcal}\cdot\text{mol})\text{K}]T_{\text{second}} \quad (2.32)$$

We use the expression "the reaction takes a second" very loosely in equations (2.31) and (2.32). The equations were derived using the time where 50% of the product is used up. However, if you would instead consider the time it takes for 10% to be used up, or the time it takes for 90% to be used up, you could derive almost the same expression, except that the constant would change by perhaps 10%. Equations (2.31) and (2.32) are very important because they allow one to get a rough estimate of the activation energy from very little data. If you see a reaction at room temperature, you know that the reaction probably has a barrier of 20 ± 6 kcal/mol, independent of the details of the reaction. As an example, most of the chemical reactions occurring in the metabolic processes in living cells have activation barriers of 15–25 kcal/mol. So do the reactions involved with digesting your food or bleaching your clothes in a clothes washer. One can use equations (2.31) and (2.32) to get a reasonable value of the activation barrier for reaction for a wide variety of reactions without knowing much about the reaction. That makes equations (2.31) and (2.32) very powerful (although sometimes inaccurate).

Still, equations (2.31) and (2.32) are approximations that assume that there is only one reaction occurring. If you have two competing reactions, or other complicated effects, then equations (2.31) and (2.32) will not work.

In my experience, equations (2.31) and (2.32) work in about 90% of the cases. In most of the other cases, there is something complicated going on, either there are competing reactions, or some other complexities. If you measure an activation barrier and it is way off from that predicted from equations (2.31) and (2.32), it is safe to assume that some complex process is happening during the reaction. You need to be very careful with your data in such a case.

Another application of equations (2.31) and (2.32) is to solve the equations to see at what temperature a given reaction will have a measurable rate. For example, one can solve equation (2.31) for T_{minute} to show

$$T_{\text{minute}} = \frac{15 \text{ K}\cdot\text{mol}}{\text{kcal}} E_a \quad (2.33)$$

where T_{minute} is the temperature you would have to go to get a half-life of about a minute. According to equation (2.33), if a reaction has an activation barrier of 30 kcal/mol, you need to run the reaction at 450 K to get a reasonable reaction rate. Similarly, a reaction with an activation energy of 50 kcal/mol needs to be run at 750 K to get a reasonable reaction rate. Consequently, equation (2.33) allows one to plan experiments for a wide variety of systems.

Equation (2.33) can also be used to estimate ignition temperatures. If you have a gas burner in your kitchen, the gas usually stays in the flame for about a tenth of a second. If the ignition process has an activation barrier of 50 kcal/mol, then, according to equation (2.33), you need to heat the system to about 800 K before ignition will occur.

Equations (2.31)–(2.33) are very useful in estimating activation barriers and planning experiments. The reader should memorize these equations before proceeding.

2.6.2 Changes in Rate with Temperature

Next, it is useful to quantify the extent to which rates go up with increasing temperature. Consider a reaction occurring at a rate r_1 , at temperature T_1 . According to equation (2.26), for an n th-order reaction

$$r_1 = k_1^0 \exp\left(\frac{-E_a}{k_B T_1}\right) (C_A)^n \quad (2.34)$$

Now consider changing the temperature to T_2 . At that temperature, the rate is given by

$$r_2 = k_2^0 \exp\left(\frac{-E_a}{k_B T_2}\right) (C_A)^n \quad (2.35)$$

dividing equation (2.34) by equation (2.35) and rearranging yields

$$r_2 = r_1 \exp\left(\frac{E_a}{k_B} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \quad (2.36)$$

Equation (2.36) allows one to calculate how the rate of a given reaction changes with changing temperature.

Figure 2.9 shows the fractional change in the rate of an n th-order reaction when the temperature is changed from 25 to 35°C as a function of the activation energy of the reaction. The increase varies from a factor of 1.1 to a factor of 10 for reasonable values of the activation barrier. To put the plot in perspective, according to equation (2.32), a reaction that takes about a second at room temperature should have an activation energy of about 20 kcal/mol. Plugging into equation (2.36) shows that the rate of a reaction with a 20-kcal/mol barrier should go up about $2\frac{1}{2}$ times for every 10°C.

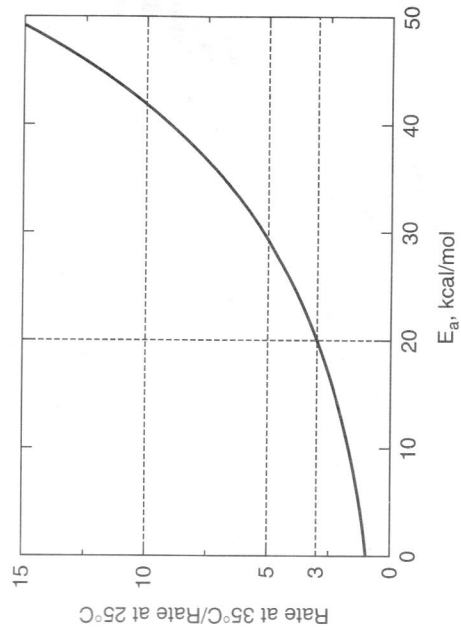


Figure 2.9 The fractional change in the rate of an n th-order reaction when the temperature is changed from 25 to 35°C.

Table 2.6 The variation in rate of a series of reactions with a 10-K change in temperature

Reaction	Temperature range, °C	Rate Change with a 10-K Temperature Change
$\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}$	3.6–30.4	2.03
$\text{CH}_3\text{CH}_2\text{Cl} + \text{NaOH} \xrightarrow{\quad} \text{H}_2\text{C}=\text{CH}_2 + \text{NaCl} + \text{H}_2\text{O}$	23.5–43.6	2.87
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaOH} \xrightarrow{\quad} \text{CH}_3\text{CH}=\text{CH}_2 + \text{NaCl}$	24.5–43.6	2.68
$\text{HPO}_3 + \text{H}_2\text{O} \xrightarrow{\quad} \text{H}_3\text{PO}_4$	0–61	3.0

Source: Data from Van't Hoff (1884).

Table 2.6 shows how the rates of several room-temperature reactions actually vary with temperature. Notice that the rate of room-temperature reactions increase by a factor of 2 or 3 for every 10 K increase in temperature, just as you learned in freshman chemistry. This happens because all room-temperature reactions have activation barriers of 20 ± 6 kcal/mol, and when the activation barrier is 20 ± 6 kcal/mol, the rate doubles or triples every 10°C.

You probably did not learn this in freshman chemistry, but the fact that rates double every 10°C is a very universal phenomenon. Plant growth follows Arrhenius' law. Growth of yeast or bacteria follows Arrhenius' law. Many other processes in nature also follow Arrhenius' law.

For example, Clausen (1890) examined the respiration rate of plants. He found that the respiration rate of wheat went up 2.47 times every 10°, lilac went up 2.48 times; and lupine (a blue flower) went up 2.46 times (see Table 2.7). Bailey and Ollis (1977) report the rate of *E. coli* (bacteria) growth as a function of temperature. Figure 2.10 shows their results. Notice that again, the rate of *E. coli* growth goes up about 2.5 times every 10 K until the yeast begins to die at 40°C.

A different example is the chirping of crickets. Male crickets chirp to attract mates, and the chirping rate changes as their temperature changes. Figure 2.11 shows how the rate of cricket chirping varies with temperature. Again the rate doubles every 10°C.

There are similar data on the growth of insects, lizards, and other cold-blooded animals. Even the speed at which ants walk doubles every 10°C. Another example includes the fact that bleach cleans clothes twice as fast when one raises the water temperature by 10°C. These examples show the idea that the rate of room temperature reactions goes up by about a factor of 2–3 for every 10°C increase in temperature; this rate change applies to a wide range of systems, and is not limited to things that happen in a chemical reactor.

Another application of Arrhenius' law is to learn how to control the rate of a chemical reaction. If you have a reaction that is too slow, the easiest way to speed it up is to increase the reaction temperature. Heating up a room temperature reaction usually doubles

Table 2.7 The variation in the respiration rate of plants with a 10° change in temperature

Wheat	2.47
Lilac	2.48
Lupine	2.46

Source: Data from Clausen (1890).

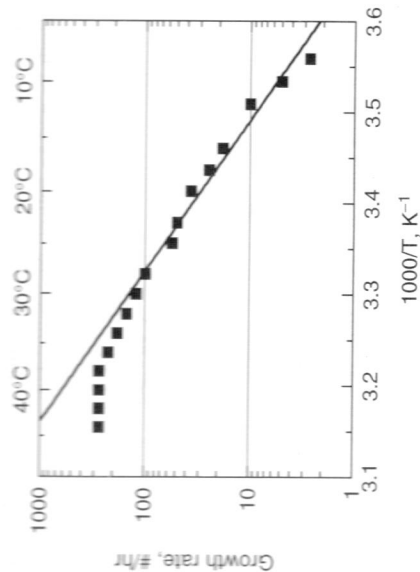


Figure 2.10 The rate of *E. coli* growth as a function of temperature. [Adapted from Bailey and Ollis (1977).]

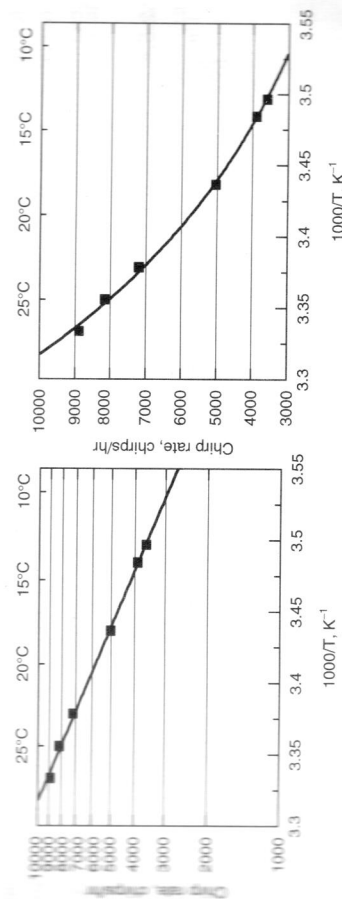


Figure 2.11 The rate that crickets chirp as a function of temperature. Data for field crickets (*Gryllus pennsylvanicus*). From Heinrich (1993).

or triples the rate of reaction. When you are running a reactor in industry, you often adjust the temperature to control the rate. Equation (2.33) will allow you to estimate the required temperature.

2.5.3 Exceptions to Arrhenius' Law

There is one key subtlety in Arrhenius' law, in that it applies only to elementary reactions, not overall reactions. The terms *elementary reactions* and *overall reactions* will be defined in Chapter 3.) If you consider a complex reaction, Arrhenius' law will work for each of the elementary reactions. However, the overall reaction might not show Arrhenius behavior. In this section, we want to work out a simple example, to illustrate the fact that overall rates might not show Arrhenius behavior even though elementary rates do.

Consider a reversible reaction $A \rightleftharpoons B$. In Chapter 3 we will find

$$r_B = k_2[A] - k_1[B] \quad (2.37)$$

where k_1 is the rate constant for the forward reaction and k_2 is the rate constant for the reverse reaction. Both k_1 and k_2 follow Arrhenius' law:

$$k_1 = k_1^0 \exp\left(\frac{-E_a^1}{k_B T}\right)$$

$$k_2 = k_2^0 \exp\left(\frac{-E_a^2}{k_B T}\right)$$

where k_1^0 and k_2^0 respectively are the preexponentials for the forward and reverse reactions and E_a^1 and E_a^2 are the activation barriers for each reaction.

In Chapter 3 we will show that for a reversible reaction

$$E_a^2 = E_a^1 + \Delta H_r$$

where ΔH_r is the heat at reaction.

Figure 2.12 shows a plot of the rate calculated from equation (2.37) as a function of temperature. Notice that the overall rate of the endothermic reaction shows significant deviations from Arrhenius' law even though k_1 and k_2 follow Arrhenius' law. This example illustrates that Arrhenius' law applies only to elementary reactions.

2.5.4 Important Exceptions to Arrhenius' Law

The example in the previous section was not a typical example, but in fact all reactions that follow complex rate laws do not also follow Arrhenius' law. Instead, a plot of the log of the overall rate versus one over temperature shows nonlinear behavior.

For example, earlier in this chapter we noted that the growth of bacteria follows Monod kinetics:

$$r_{\text{ecoli}} = \frac{k_1 K_2 [E. coli]}{(1 + K_2 [E. coli])} \quad (2.38)$$

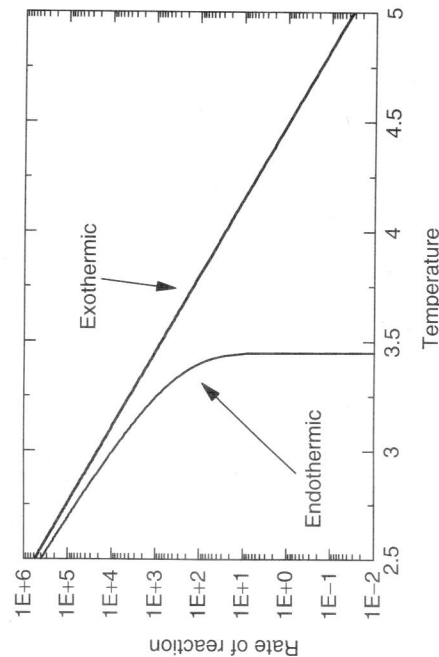


Figure 2.12 The rate of the reaction $A \rightleftharpoons B$ with $k_1^0 = k_2^0 = 10^{13}$ /second, $E_a = 15$ kcal/mol, $\Delta H = +3$ kcal/mol, and $[A] = 1$ mol/liter $[B] = 0.01$ mol/liter.

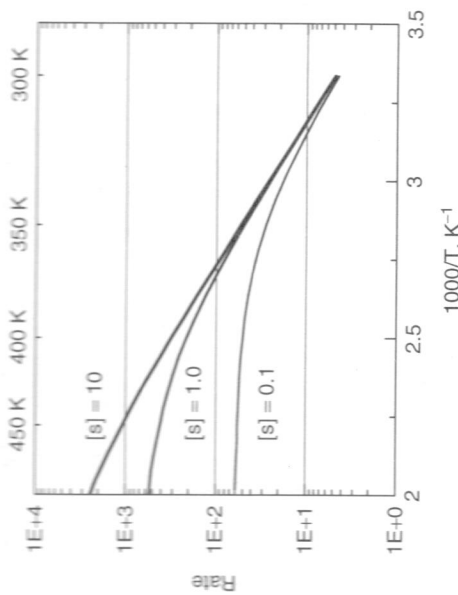


Figure 2.13 The temperature dependence of a reaction that follows Monod's law $r_S = k_1 K_2 [S] / (1 + K_2 [S])$ with $k_1 = 10^{13}$ /second -20 (kcal/mol)/ $k_B T$ and $K_2 = 6 \times 10^{-6}$ (10 kcal/mol)/ $k_B T$.

In equation (2.38), k_1 and k_2 follow Arrhenius' law. However, *E. coli* shows nonlinear behavior.

Figure 2.13 shows a plot of the rate versus temperature calculated from Monod's law with some typical values of the parameters. Notice that the rate shows no linear behavior with temperature. Our rules of thumb from Section 2.14 do not work in this example.

In my experience, most simple reactions follow Arrhenius' law. However, the overall rate of most industrially important reactions cannot be accurately fit with Arrhenius' law. Again, we note that each elementary reaction will follow Arrhenius' law. It is just the rate at overall reaction that shows derivations from Arrhenius' law.

2.6 CATALYSTS

Industrially, the deviations from Arrhenius' law are quite important. Recall that most industrial reactions are run with catalysts. Well, most catalytic reactions do not follow Arrhenius' law. These exceptions are so important that I wanted to highlight them early in this book. In the remainder of this chapter, I want to discuss catalytic reactions, and show how the kinetics at catalytic reactions are different from the kinetics of simple reactions in solution.

To start, it is useful to review some background material on catalysis. Ostwald defined a catalyst as "a substance one adds to a chemical reaction to speed up the reaction without the catalyst undergoing a chemical change itself." Later in this book, we will find that this definition is not quite accurate. Catalysts do undergo chemical changes during the course of reaction. It is just that the changes are reversible, so that the catalyst is not consumed as the reaction proceeds. Examples of catalysts include the acids in your stomach that you use to break down food, and the enzymes that people put in detergents to make the detergent work better. Most chemical processes use catalysts at some stage in the production process.

There are two kinds of catalysts: **homogeneous catalysts** and **heterogeneous catalysts**. Homogeneous catalysts are things that one dissolves in a liquid or a gas to promote a

reaction. Homogeneous catalysts include acids and bases, enzymes, transition metal ions, and alkyls. In some cases, solvents can act as homogeneous catalysts.

A **heterogeneous catalyst** is a solid that one adds to a reaction mixture. The solid does not dissolve in the mixture, but still is able to promote a desired reaction or a series of desired reactions. Typical heterogeneous catalysts include transition metals (e.g., platinum on alumina) or solid acids such as silica/alumina.

Heterogeneous and homogeneous catalysts are fundamentally different. A homogeneous catalyst dissolves into the gas phase or solution and acts uniformly throughout the liquid or gas mixture. On the other hand, heterogeneous catalysts do not dissolve. Instead, the reaction occurs on the surface of the catalyst.

Table 2.8 shows some typical homogeneous catalysts. Generally, homogeneous catalysts consist of transition metal atoms, peroxoradicals, and acids or bases. Industrially, one uses homogeneous catalysts in most polymerization and carbonylation reactions, and in some partial oxidations.

Homogeneous catalysts are also used in the home. For example, most detergents contain enzymes to allow the oxidation and depolymerization of stains (i.e., dissolved proteins). Cleansers contain metal atoms to speed up the action of bleach. Most biological reactions are also controlled by homogeneous catalysts, such as enzymes or RNA.

Heterogeneous catalysts are more important industrially. Figure 2.14 shows some typical heterogeneous catalysts. Heterogeneous catalysts are generally powders or pellets that one can add to a reacting mixture to speed up the reaction. Heterogeneous catalysts are used extensively in chemical processing because heterogeneous catalysts are easier to separate from the products of a reaction mixture than a homogeneous catalyst. Table 2.9 shows some typical heterogeneous catalysts. Over 90% of all bulk chemicals and petroleum products are made via catalytic processes.

Heterogeneous catalysts are also used in people's homes. For example, people used to sell catalytic igniters that one could use to start a gas range or fireplace. Now the most common heterogeneous catalyst in your possession is the catalytic converter in your car. The catalytic converter reduces the pollution and toxic emissions produced by your car. People also make catalytic converters to destroy pollutants in homes or in woodstove chimneys. Heterogeneous catalysts are not as common as homogeneous catalysts in the home but they are equally important.

Catalysts are so important because they make tremendous differences in reaction rate. For example, a hydrogen/oxygen mixture may be stable for years at 25°C. However, if one adds a platinum wire to the mixture, the mixture explodes. Table 2.10 shows some

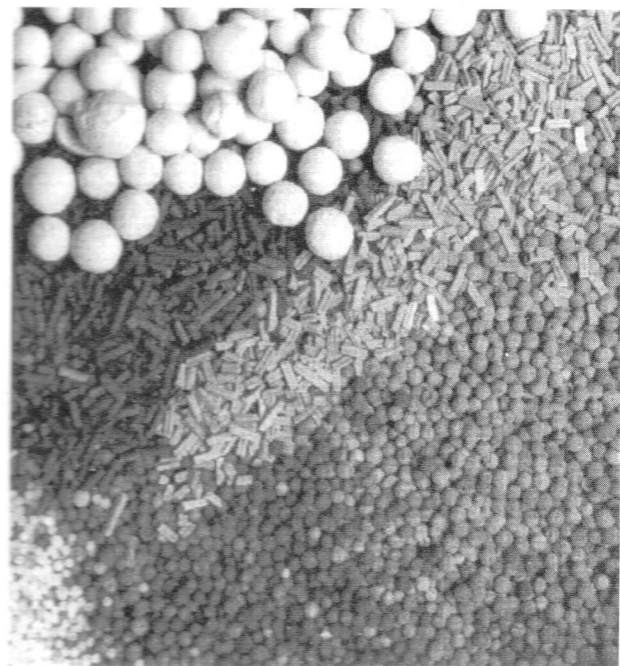


Figure 2.14 Photographs of some heterogeneous catalysts. (From Wijngaarden and Westertep, 1998).

Table 2.9 Common Heterogeneous Catalysts

Catalyst	Reaction
Platinum on alumina, nickel on alumina	Hydrogenation/dehydrogenation
Platinum/tin on acidic alumina	Reforming
Solid acids (zeolites)	Hydrocarbon isomerization, cracking
Silver	$C_2H_4 + \frac{1}{2}O_2 \rightarrow$ ethylene oxide
$(H_2O)_x(MO_3)_y$	$CH_2=CHCH_3 + \frac{3}{2}O_2 + NH_3 \rightarrow CH_2CH-CHO + H_2O$
V_2O_5	$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
Platinum gauze	$2NH_3 + 4O_2 \rightarrow N_2O_5 + 3H_2O$

other examples. Notice that in the examples shown, the catalyst lowers the activation barrier for the reaction by 19–30 kcal/mol. It is not unusual for a catalyst to lower the barrier for a reaction by 19–30 kcal/mol, and Masel (1996) gives some special examples where the catalyst lowers the activation barrier for a reaction by more than 50 kcal/mol. A 19–30-kcal/mol change in the barrier for a reaction changes the rate tremendously. The examples in Table 2.10 show rate enhancements of 10^8 – 10^{13} . Similar changes in rate are quite common. Masel (1996) reports some special cases where the rate enhancements are as large as 10^{21} .

From a practical standpoint, one of the key roles of a catalyst is to lower the temperature where a reaction takes place. According to Table 2.10, the reaction



Table 2.8 Some Common Homogeneous Catalysts

Reaction	Catalyst
Ethylene \rightarrow polyethylene (polymerization)	$TiCl_4/Al(C_2H_5)_3$ (Ziegler–Natta catalyst)
Ethylene \rightarrow polyethylene, styrene \rightarrow polystyrene	Peroxides
$C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3(C=O)H$ (Wacker process)	$PdEt_3$
Olefins + CO + H ₂ \rightarrow aldehydes (hydroformylation)	$Co(CO)_6$
$CH_3OH + CO \rightarrow CH_3COOH$	$RhCl_3$
$SO_2 \rightarrow SO_3$ (lead chamber process)	NO/NO_2
$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$ (sucrose \rightarrow glucose + fructose)	Acids or bases; invertase

Table 2.10 The change in rate of some typical reactions seen when a catalyst is added to the reaction mixture

Reaction	Catalyst	E_a , kcal/mol		Rate of Enhancement Calculated at 500 K
		Uncatalyzed,	Catalyzed,	
$H_2 + I_2 \rightarrow 2HI$	Pt	44	14	10^{13}
$2N_2O \rightarrow 2N_2 + O_2$	Au	58	29	10^{13}
$(C_2H_5)_2O \rightarrow 2C_2H_4 + H_2O$	I ₂	53	34	10^8

Source: Table adapted from data in Bond (1987).

has an activation barrier of 53 kcal/mol in the absence of a catalyst and 38 kcal/mol in the presence of a catalyst. According to equation (2.33), you need to run a reaction with an activation barrier of 53 kcal/mol at about 800 K. While you can run a reaction with an activation barrier of 38 kcal/mol at 600 K, that temperature difference is huge if you need to pay the heating costs. Besides, there is an explosion hazard at the higher temperature. In industry, one hardly ever runs a reaction without a catalyst, which is why catalysis is so important. In 1995, almost 700 billion dollars of products were made with catalysts in the United States.

2.7 CATALYTIC KINETICS

One of the key features of catalysts is that they change the form of the rate equation. Over the years, there have been many attempts to determine how rates of reactions on heterogeneous catalysts vary with the partial pressure of the reactants. One of the things that has been discovered is that rates of catalytic reactions do not bear any simple relationship to the stoichiometry. In the gas phase, rates of reactions are often proportional to the reactant concentrations to some simple powers. However, catalytic reactions follow much more complex rate equations. It is common for the rate of a catalytic reaction to be constant or even go down as the concentration of one of the reactants increases. This is quite different from gas-phase reactions, where rates generally increase with increasing reactant pressure.

For example, Figure 2.15 shows data on the rate of CO oxidation on a catalyst called Rh(111). Notice that the rate increases linearly with the CO concentration up to a CO partial pressure of 10^{-7} torr. However, then the rate decreases again. One cannot fit data with a rate equation like that in equation (2.11). However, one can fit them with a more complex rate form:

$$r_{CO} = \frac{k_1 P_{CO} P_{O_2}}{(1 + K_2 P_{CO} + K_3 P_{O_2})^2} \quad (2.40)$$

where r_{CO} is the rate of reaction; P_{CO} is the CO pressure; P_{O_2} is the oxygen pressure; and, k_1 , K_2 , and K_3 are constants.

In the discussion that follows, we will provide examples of this effect for two separate cases: unimolecular surface reactions, where a single reactant rearranges or decomposes to yield products; and bimolecular surface reactions, where two or more reactants combine and rearrange to form products.

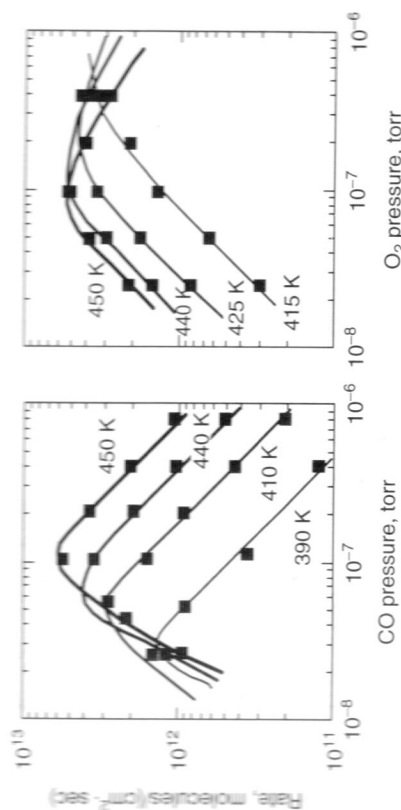


Figure 2.15 The influence of the CO pressure on the rate of CO oxidation on Rh(111). [Data of Schwartz, et al. (1966).]

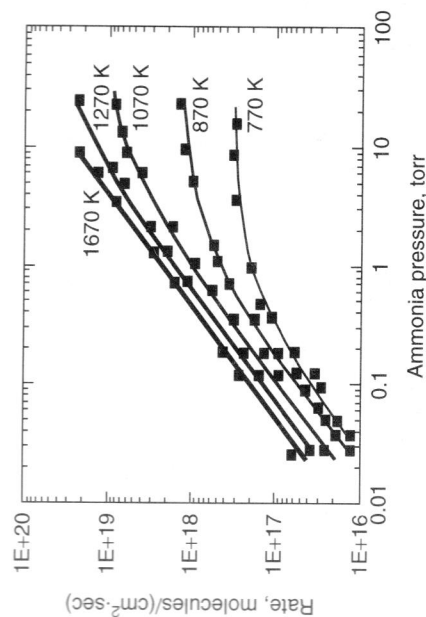


Figure 2.16 The rate of the reaction $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$ over a platinum wire catalyst. [Data of Loffler and Behnmidt (1976a,b).]

Figure 2.16 shows some data for the rate of a simple unimolecular surface reaction; the decomposition of ammonia over a polycrystalline platinum wire catalyst.



Notice that at moderate temperatures, the rate of reaction increases with increasing ammonia pressure and then levels off. At higher temperatures the rate continues to increase over the pressure range shown. However, other data show that the rate will eventually level off at sufficiently high pressures.

Figure 2.17 shows how the reaction rate varies with temperature at a series of fixed pressures. Notice that the rate increases with increasing temperature and then begins to level off.

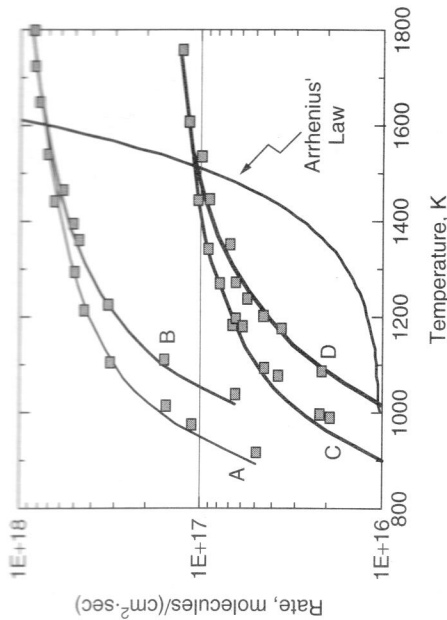


Figure 2.17 The variation in the rate of the reaction in Figure 2.16 with temperature: (a) $P_{\text{NH}_3} = 0.3$, $P_{\text{H}_2} = 0.15$; (b) $P_{\text{NH}_3} = 0.3$, $P_{\text{H}_2} = 0.44$; (c) $P_{\text{NH}_3} = 0.05$, $P_{\text{H}_2} = 0.15$; (d) $P_{\text{NH}_3} = 0.05$, $P_{\text{H}_2} = 0.45$. [Data of Löffler and Schmidt (1976a,b).]

The fact that the data do not follow Arrhenius' law shows that there is some complication during the reaction. Later in this book, we will find that the ammonia sticks onto the platinum, and then there are two competing pathways: (1) reaction and (2) desorption back into the gas-phase. The presence of two competing pathways causes the curvature in Figure 2.17.

The results in Figures 2.16 and 2.17 are typical of those for unimolecular reactions on heterogeneous catalysts. Generally, one observes rates that increase with increasing temperature and pressure. However, the rate seldom increases monotonically with pressure. Rather, the rate increases with increasing pressure, and eventually plateaus at high pressures. The rate also increases with temperature. However, the slope of the curve decreases with increasing temperature.

Note that gas-phase reactions show behavior very different from that seen in Figures 2.16 and 2.17. In the gas-phase, the rate of a simple unimolecular reaction increases continuously with increasing pressure and never levels off. The rate also increases continuously with increasing temperature. According to Arrhenius' law

$$\text{Rate} = r_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.42)$$

According to equation (2.42), the slope of the rate-temperature curve should increase with increasing temperature. However, Figure 2.17 shows that the slope actually decreases. Therefore, it seems that the kinetics of unimolecular catalytic reactions are quite different from the kinetics of unimolecular reactions in the gas-phase.

Even larger differences are seen for bimolecular reactions. For example, Figure 2.18 shows how the rate of the reaction



varies with temperature over a Rh(111) catalyst. Notice that at fixed reactant pressure, the rate reaches a maximum with increasing temperature and then declines. Figure 2.15 shows the pressure dependence of the reaction rate. Notice that the rate first increases with

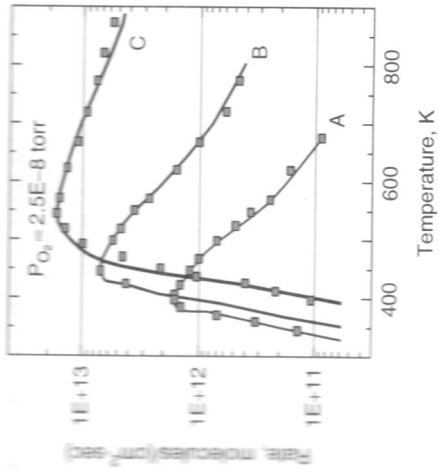
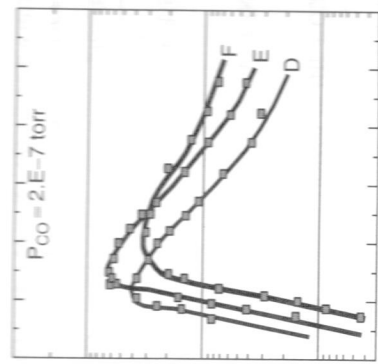


Figure 2.18 The rate of the reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ on Rh(111): (a) $P_{\text{CO}} = 2.5 \times 10^{-8}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-6}$ torr; (b) $P_{\text{CO}} = 1 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-6}$ torr; (c) $P_{\text{CO}} = 8 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-6}$ torr; (d) $P_{\text{CO}} = 2 \times 10^{-7}$ torr, $P_{\text{O}_2} = 4 \times 10^{-7}$ torr; (e) $P_{\text{CO}} = 2 \times 10^{-7}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-6}$ torr; (f) $P_{\text{CO}} = 2.5 \times 10^{-6}$ torr, $P_{\text{O}_2} = 2.5 \times 10^{-6}$ torr. Data of Schwartz et al. (1986).



increasing CO pressure and then declines. At lower temperatures, the rate continuously decreases with increasing CO pressure, while at higher temperatures the rate increases with increasing CO pressure.

The behavior in Figures 2.15 and 2.18 is typical of that for a bimolecular reaction on a heterogeneous catalyst. The reaction rate generally shows complex behavior with temperature and concentration. The behavior is usually quite different than that of bimolecular gas-phase reactions.

Typically, one fits data for the rate of a surface reaction with a complex rate equation. Table 2.11 shows a selection of the rate equations that have been fit to data on supported catalysts. The table is extracted from a longer compilation of Mezaki and Inoue (1991). Note that the rate equations are often quite complex and the rate can go up or down with increasing reactant pressure.

For example, the rate of the reaction $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ increases with increasing CO pressure and then reaches a plateau. However, the rate continuously increases with a continuous increase in H_2 pressure. In contrast, the rate of the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ plateaus as the partial pressure of either reactant increases while the rate of the reaction $4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$ reaches a maximum with increasing reactant pressure and then declines. Generally, the kinetics of reactions on surfaces are quite different from the kinetics of reactions in the gas-phase or in solution, so much different rate equations are generally used.

Table 2.11 shows several other examples. Notice that the rate equations for surface reactions are generally more complex than the rate equations for typical gas-phase reactions. Generally, the rate equation has a term for each reactant in both the numerator and the denominator. The term in the numerator can cause the rate to decrease with increasing reactant concentration. By comparison, the rate of gas-phase reactions always increases with increasing concentration.

This unusual behavior arises because catalytic reactions are generally surface reactions. The reactants adsorb on the surface of the catalyst. Then there is a reaction between the reactants to form products.

Table 2.11 A selection of some of the rate equations for some common catalytic reactions extracted from the compilation of Mezaki and Inoue (1991)

Reaction	Catalyst	Rate Equation
$\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$	V_2O_5	$\frac{k_1 K_3 K_4 P_{\text{SO}_2} P_{\text{O}_2}^{1/2} - k_2 K_5 P_{\text{SO}_3}}{1 + K_3 P_{\text{O}_2}^{1/2} + K_4 P_{\text{SO}_2} + K_5 P_{\text{SO}_3}}$
$\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$	$\text{Fe}/\text{Al}_2\text{O}_3$	$k_1 P_{\text{N}_2} \left(\frac{P_{\text{H}_2}}{P_{\text{NH}_3}} \right)^a - k_2 \left(\frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3} \right)^{1-a}$
$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	$\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$	$\frac{k_1 P_{\text{CO}} P_{\text{H}_2}^2 - k_2 P_{\text{CH}_3\text{OH}}}{1 + k_3 P_{\text{H}_2} + k_4 P_{\text{CO}} + k_5 P_{\text{CO}} P_{\text{H}_2}^{3/2}}$
$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	$\text{Ni}/\text{Al}_2\text{O}_3$	$\frac{k_1 K_2 K_3 P_{\text{H}_2} P_{\text{C}_2\text{H}_4}}{(1 + K_2 P_{\text{H}_2} + K_3 P_{\text{C}_2\text{H}_4})^2}$
$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$	$\text{Ag}/\text{Al}_2\text{O}_3$	$\frac{k_1 K_2 P_{\text{O}_2} P_{\text{C}_2\text{H}_4}}{1 + K_2 P_{\text{O}_2} + P_{\text{C}_2\text{H}_4}}$
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$	$\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$	$\frac{k_1 K_3 K_4 P_{\text{CO}} P_{\text{H}_2\text{O}} - k_2 K_5 K_6 P_{\text{H}_2} P_{\text{CO}_2}}{(1 + K_3 P_{\text{CO}} + K_4 P_{\text{H}_2\text{O}} + K_5 P_{\text{CO}_2} + K_6 P_{\text{H}_2})^2}$
$4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$	Pt	$\frac{k_1 K_2 K_3 P_{\text{NO}} P_{\text{NH}_3}^{1/2}}{(1 + K_2 P_{\text{NO}} + K_3 P_{\text{NH}_3}^{1/2})^2}$

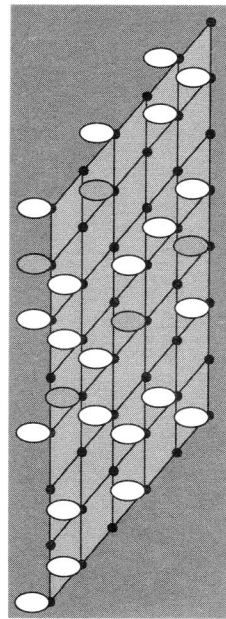


Figure 2.19 Langmuir's model for the adsorption of gas on a solid catalyst. The light gray area represents the surface of the catalyst. The black dots are the sites on the catalyst are sites that are available to adsorb gas. The white ovals are the adsorbed A molecules. The dark ovals are adsorbed B molecules.

Figure 2.19 is a snapshot of what the surface during the reaction $A + B \Rightarrow C$. The light gray area represents the surface of the catalyst. The black dots are the sites on the catalyst are sites that are available to adsorb gas. The white ovals are the adsorbed A molecules. The dark ovals are adsorbed B molecules. During the reaction, an adsorbed A molecule reacts with an adsorbed B molecule to produce products. The rate of the reaction is proportional to the surface concentration of A and B.

An important detail is that the surface has a finite capacity to adsorb A and B. When you put more A on the surface, there is not as much room to hold B. Consequently, the B concentration will decrease.

Now consider a simple reaction $A + B \Rightarrow C$ that follows

$$R_C = 1 \text{ \AA}^2 / (\text{molecule}\cdot\text{second}) [A_{(\text{ad})}][B_{(\text{ad})}] \quad (2.44)$$

In this equation R_C is the rate of formation of C, and $[A_{(\text{ad})}]$ and $[B_{(\text{ad})}]$ are the surface concentrations of A and B, in molecules/per square angstrom.

Table 2.12 The changes in the rate of production of C as $[A_{(\text{ad})}]$ varies, assuming $[A_{(\text{ad})}] + [B_{(\text{ad})}] = 1 \text{ molecule}/\text{\AA}^2$, $R_C = 1 \text{ \AA}^2 / (\text{molecule}\cdot\text{second}) [A_{(\text{ad})}][B_{(\text{ad})}]$

$[A_{(\text{ad})}]$, molecule/ \AA^2	$[B_{(\text{ad})}]$, molecule/ \AA^2	R_C , (molecule $\cdot\text{\AA}^2$)/second
0.1	0.9	0.09
0.2	0.8	0.16
0.5	0.5	0.25
0.8	0.2	0.16
0.9	0.1	0.09

Calculated from Equation (2.44)

Table 2.12 shows how the rate of formation of C changes as $[A_{(\text{ad})}]$ varies, assuming $[A_{(\text{ad})}] + [B_{(\text{ad})}] = 1 \text{ molecule}/\text{\AA}^2$. Notice that initially the rate goes up as the A concentration is increased. But then the rate reaches a maximum and decreases again with further increases in A. The decrease in rate causes the unusual behavior in Figure 2.18.

We will derive a qualitative equation for this effect in Section 12.17.1. The thing to remember for now is that rates of catalytic reactions show complex behavior because whenever the concentration of one reactant goes up, the surface concentrations of the other reactants go down.

The other thing that is special about a heterogeneously catalyzed reaction is that the reaction rate scales as the surface area of the catalyst, not the volume of the reactor. The rate is often measured as R, a rate in (mol $\cdot\text{cm}^2$)/min. That is different than the rate of a reaction in a fluid, where r is the rate in (mol $\cdot\text{cm}^3$)/min or (mol $\cdot\text{liter}$)/hour.

Experimentally, the rate of a heterogeneously catalyzed reaction is proportional to the surface area of the catalyst. A catalyst with a surface area of 1000 m^2 will produce twice as much product as a catalyst with a surface area of 500 m^2 .

People often call reactions on heterogeneous catalysts **surface reactions** since the reaction occurs on the surface of the catalyst.

People have developed a number of special materials to squeeze as much surface area as possible in as little volume as possible. Figure 2.20 shows some of the materials. Generally, it is possible to squeeze the surface area of 5000 m^2 (a football field) into 100 cm^3 or less of material!

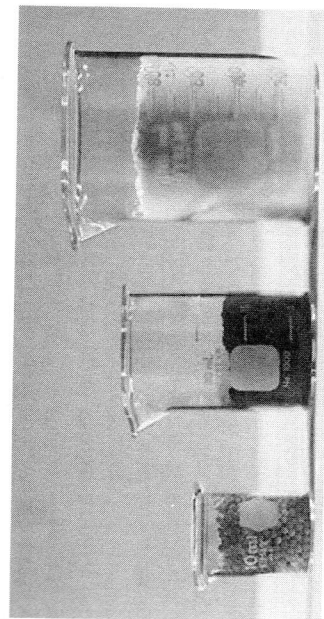


Figure 2.20 The amount of Linde molecular sieve, activated carbon, and γ -alumina needed to get a surface area of about 5000 m^2 (i.e., about the area of a football field). [From Masel (1996).]

For a typical catalytic reaction, one might have a catalyst with an effective surface area of $10^4 \text{ m}^2/\text{liter}$ of catalyst and a reaction rate of $10^{-6} \text{ (mol}\cdot\text{m}^2/\text{second})$.

In the literature, people rarely report a reaction rate in $(\text{mol}\cdot\text{m}^2/\text{second})$. Instead, they use a unit called a **turnover number**, T_N , or turnover frequency. The turnover number is defined as the rate that molecules are converted per atom in the surface of the catalyst per second. One can calculate the turnover number from

$$T_N = \frac{R_A}{N_S} \quad (2.45)$$

where R_A is the rate that molecules are converted in $(\text{molecule}\cdot\text{cm}^2/\text{second})$ and N_S is the number of surface atoms/ cm^2 . One usually sees turnover numbers expressed in units of reciprocal seconds (second^{-1}).

Figure 2.21 shows some typical values of the turnover numbers for some typical catalytic reactions. Note that typically, the turnover numbers are on the order of $1/\text{second}$ (i.e., 1 second^{-1}). Rates of $1/\text{sec}$ are also seen in semiconductor growth.

Students usually have trouble relating to a turnover number of $1/\text{second}$. Just to give you an idea, a liter of a typical catalyst might have an effective surface area of 10^4 m^2 . If you run a reaction over that catalyst, then, at a turnover rate of $1/\text{second}$, you would produce about 10 mol/minute of product. If you had 2 liters of catalyst, you would produce 20 mol/minute of product. In general, we can write the reaction rate as $1 \text{ (mol}\cdot\text{minute)/liter}$ of catalyst.

Now think back to your organic chemistry days and recall the reactions you ran in organic chemistry lab. It might have taken 30 minutes to 0.1 mol of product in a 200-cm flask. A production of 0.1 mol in 30 minutes in a 200-cm vessel corresponds to a reaction rate of

$$r_A = \frac{0.1 \text{ mol}}{(30 \text{ minutes})(0.2 \text{ liter})} = 0.0167 \frac{\text{mol}}{\text{liter}\cdot\text{min}} \quad (2.46)$$

Catalytic reactions generally go 1000–10,000 times faster than the reactions you ran in organic chemistry lab. Further, they will speed up reactions that are too slow to run in a chemistry lab. As a result, catalysts are very useful.

We will be discussing catalysts in detail in Chapter 12 in this book. For now, the key thing to remember is that catalysts tremendously change rates and also change the rate equation for a reaction.

2.2 MULTIPLE STEADY STATES, OSCILLATIONS, AND OTHER COMPLEXITIES

There is one other subtler with catalytic reactions: sometimes, one cannot write a rate equation for a catalytic reaction. All of the examples so far in this chapter had relatively simple rate equations. The rate could be written as a function of easily measured variables such as the concentrations of the reactants and products and perhaps a catalyst concentration (e.g., $[\text{H}^+]$). There were no other variables in the rate equation. In most reactions, one can write the rate of reaction as a function of a series of easily measurable concentrations. There are some exceptions. In this section, we will discuss the exceptions. There are two kinds of systems that do not follow simple rate equations: those that show something called *multiple steady states*, and those that show something called *oscillations*. We will discuss multiple steady states first.

Figure 2.22 shows some data for the rate of CO oxidation:



over a rhodium catalyst. In the experiment, Schwartz et al. (1986) fed a fixed amount of CO and O_2 over a rhodium catalyst in a well-stirred reactor. Then the rate of CO_2 production was measured as a function of temperature. The conversion of the system was low, so the concentrations of CO and O_2 were constant within the reactor. Schwartz et al. found that when they heated the surface from a low temperature, the reaction rate followed the lower curve in the figure. In contrast, when they cooled from a high temperature, the rate followed the higher curve in the figure. Notice that at temperatures between 500 and 600 K, the rate is about an order of magnitude lower when the system is being heated up than when the system is being cooled down. Yet the concentration of all of the species and the temperature is constant.

Now, think about how to write a rate equation for the data in Figure 2.22. One can imagine expressing the rate as a function of the reactant concentration, the product concentration, and temperature. However, that will not work for the data in Figure 2.22. After all, one observes two different rates at what are nominally the same conditions. As a result, one cannot write a simple rate equation for the data in Figure 2.22.

Gray and Scott (1990) review several examples showing two different rates at what are nominally the same conditions. The feature that all of these systems have in common is that while the compositions are constant, some other internal variable is different when

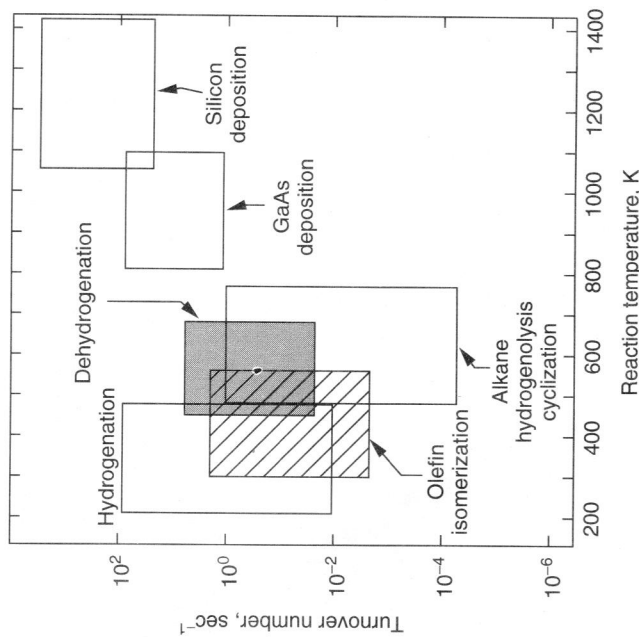


Figure 2.21 Turnover numbers for some typical reactions. [From Masel (1996).]

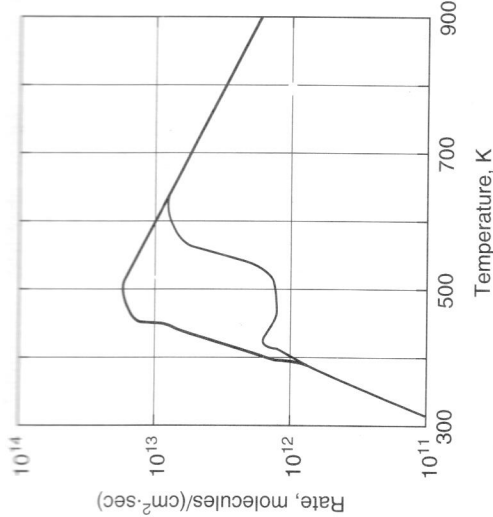


Figure 2.22 Rate data for CO oxidation on Rh(100) catalyst. [Data of Schwartz et al. (1986).]

the rate is high than when the rate is low. The fact that you have an extra variable complicates the rate equation. For example, the rhodium catalyst in Figure 2.22 shows two different crystal structures. One crystal structure is more reactive than the other. The crystal structure then becomes another variable that one needs to consider in the rate equation. A surface with 30% of the first crystal structure and 70% of the second will have a reactivity quite different from that of a sample, which has 70% of the first crystal structure and 30% of the second crystal structure.

One can define a new internal variable, the percentage of the catalyst in each crystal structure. The different crystal structure is an internal variable which alters the rate. The presence of the extra internal variable makes the analysis of rate data difficult.

Some other examples have other complications. For example, Figure 2.23 shows data for the rate of the Belousov-Zhabotinskii (BZ) reaction:

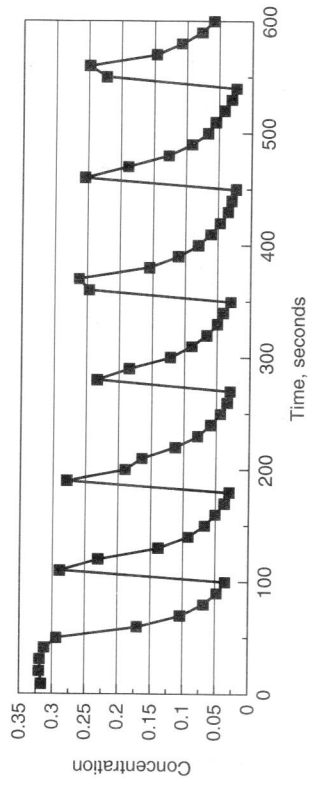
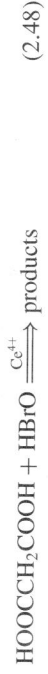


Figure 2.23 The concentration versus time measured during the Belousov-Zhabotinskii reaction. (Unpublished data of G. E. Poisson, D. A. Tuchman, and R. I. Masel.)

as a function of time. This reaction is special because if one loads a fixed amount of HBrO and maleic acid into the reactor, the reactor does not come to steady state. Instead, the composition in the reactor oscillates with time. The rate never reaches steady state.

The oscillations in rate seen with the BZ reaction are more complex versions of the same physics that is causing the CO oxidation reaction to exhibit multiple steady states. The rate depends on the oxidation state of the cerium catalyst. The cerium can be +3 or +4 state, and the reactivity is different for the +3 and +4 states. In addition, there are at least three reaction pathways that occur simultaneously.

One can write a rate equation for reaction (2.48). However, the rate is a function of the Ce^{3+} , Ce^{4+} , and maleate concentration. One cannot express the rate as a simple function of the concentrations of the reactants and products. The result is a very complex rate equation. See Gray and Scott (1990) for details.

The key point to remember for the discussion in this book is that in a complex case, the rate of reaction can depend on variables other than the concentration of the reactants and products and the temperature. The additional variables make any kinetic analysis difficult.

Generally, Van't Hoff's assumption that the rate is a function of the concentration works for 99.9% of the reactions which have been studied so far. However, there are a few exceptions.

2.9 SUMMARY

In summary, then, in this chapter, we reviewed some of the elementary concepts in kinetics that most of our readers had seen before. We defined the rate of reaction, the rate equation and the rate constant. We saw what rate equations are like, and we defined first- and second-order reaction. We described how temperature affects rates and how to use that information. We briefly discussed catalysis. Most of the material was qualitative. We will quantify the material in the next several chapters.

2.10 SOLVED EXAMPLES

Example 2.A Illustration of Some of the Concepts from Section 2.1 Ethane emissions from cars are one of the major sources of air pollution in the United States. Most cars today are equipped with a catalytic converter, which, among other things, oxidizes ethane to CO_2 and water. Consider the oxidation of ethane in the 10 liter catalytic converter shown in Figure 2.A.1. The overall reaction is

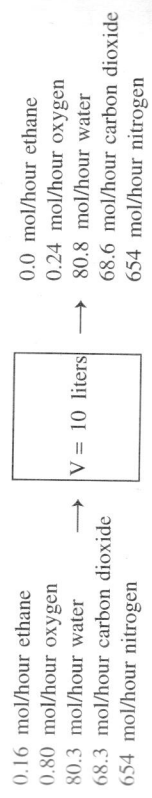


Figure 2.A.1 The flow rates into and out of a catalytic converter for the complete combustion of ethane.

- (a) Use a mass balance to show that the average rate of production of any species A in the reactant r_A is

$$r_A = \frac{(\text{mol/hour of A out of reactor}) - (\text{mol/hour of A into the reaction})}{\text{volume of the reactor}} \quad (2.A.2)$$

- (b) Calculate r_A for all of the species in the reactor.
 (c) Calculate all of the stoichiometric coefficients (i.e., β_A values).
 (d) Calculate the rate of the reaction from the equation

$$r_{2,A} = \frac{1}{\beta_A} r_A$$

Do a separate calculation for each species.

- (e) How do the calculations compare?

Solution

- (a) A mass balance on species A in the reactor is

$$\begin{aligned} \text{Moles of A out per hour} - \text{moles of A in per hour} \\ = \text{moles of A produced per hour} \end{aligned} \quad (2.A.2)$$

The definition of r_A the rate of production of species A is

$$r_A = \frac{\text{moles of A produced per hour}}{\text{volume of reactor}} \quad (2.A.3)$$

Combining (2.A.2) and (2.A.3) yields

$$r_A = \frac{\text{moles of A out per hour} - \text{moles of A in per hour}}{\text{volume of reactor}} \quad (2.A.4)$$

- (b) Equation (2.A.4) is the key equation for this problem plugging in the numbers.

$$\begin{aligned} r_{\text{ethane}} &= \frac{0 \text{ mol/hr} - 16 \text{ mol/hr}}{10 \text{ liters}} = -0.016 \text{ mol/(liter-hour)} \\ r_{\text{O}_2} &= \frac{0.24 \text{ mol/hour} - 0.80 \text{ mol/hour}}{10 \text{ liters}} = -0.056 \text{ mol/(liter-hour)} \\ r_{\text{H}_2\text{O}} &= \frac{80.8 \text{ mol/hour} - 80.3 \text{ mol/hour}}{10 \text{ liters}} = 0.05 \text{ mol/(liter-hour)} \\ r_{\text{CO}_2} &= \frac{68.6 \text{ mol/hour} - 68.3 \text{ mol/hour}}{10 \text{ liters}} = 0.03 \text{ mol/(liter-hour)} \\ r_{\text{N}_2} &= \frac{654 \text{ mol/hour} - 654 \text{ mol/hour}}{10 \text{ liters}} = 0 \text{ mol/(liter-hour)} \end{aligned}$$

- (c) $\beta_{\text{O}_2} = -7$, $\beta_{\text{C}_2\text{H}_6} = -2$, $\beta_{\text{CO}_2} = +4$, $\beta_{\text{H}_2\text{O}} = +6$.

- (d) Next calculate $r_{2,A}$ the rate of reaction 2.A.1. According to equation (2.6)

$$r_A = \frac{1}{\beta_A} r_{2,A} \quad (2.A.5)$$

$$r_{2,A,1} = \frac{1}{\beta_{\text{O}_2}} r_{\text{O}_2} = \frac{1}{(-7)} [-0.056 \text{ mol/(liter-hour)}] = 0.008 \text{ mol/(liter-hour)}$$

$$r_{2,A,1} = \frac{1}{\beta_{\text{C}_2\text{H}_6}} r_{\text{C}_2\text{H}_6} = \frac{1}{(-2)} [-0.016 \text{ mol/(liter-hour)}] = 0.008 \text{ mol/(liter-hour)}$$

$$r_{2,A,1} = \frac{1}{\beta_{\text{CO}_2}} r_{\text{CO}_2} = \frac{1}{4} [0.03 \text{ mol/(liter-hour)}] = 0.0075 \text{ mol/(liter-hour)}$$

$$r_{2,A,1} = \frac{1}{\beta_{\text{H}_2\text{O}}} r_{\text{H}_2\text{O}} = \frac{1}{6} [0.05 \text{ mol/(liter-hour)}] = 0.0083 \text{ mol/(liter-hour)}$$

- (e) Notice that all of the values of $r_{2,A,1}$ are the same to within the measurement error.

Example 2.B Comparing First- and Second-Order Reactions Consider a first-order reaction and a second-order reaction: How much would the rate change if you diluted the reactants by a factor of 3?

Solution For a first-order reaction

$$r = k_A C_A \quad (2.B.1)$$

Consider two different concentrations C_A and C_A^1 . The rates are

$$r_A = k_A C_A \quad (2.B.2)$$

$$r_A^1 = k_A C_A^1 \quad (2.B.3)$$

Dividing (2.B.2) by (2.B.3) yields

$$\frac{r_A^1}{r_A} = \frac{C_A^1}{C_A} \quad (2.B.4)$$

Therefore, if we dilute the reactants by a factor of 3, the rate will go down by a factor of 3:

$$\frac{r_A^1}{r_A} = \left(\frac{1}{3} \right) = \frac{1}{3}$$

If instead we have a second-order reaction, then

$$r_A = k_2 (C_A)^2 \quad (2.B.5)$$

$$r_A^1 = k_2 (C_A^1)^2 \quad (2.B.6)$$

$$\frac{r_A^1}{r_A} = \left(\frac{C_A^1}{C_A} \right)^2 \quad (2.B.7)$$

Therefore, if we dilute the reactants by a factor of 3, the rate will go down by a factor of 9:

$$\frac{r_A^1}{r_A} = \left(\frac{1}{3}\right)^2 = \frac{1}{9}$$

The difference between these results gives one a quick way to determine the order of a reaction.

Example 2.C Using Equation (2.32) to Estimate Ignition Temperatures How hot would you need to heat a methane-oxygen mixture before the mixture ignites? Assume that the activation barrier for the reaction is half the bond energy of the weakest bond in the methane molecule (bond energy = 104 kcal/mol).

Solution Ignition is a complex problem to solve exactly because one needs to consider the increases in temperature during ignition, how much heat is lost to the walls, and other effects. However, one can approximate the autoignition temperature from equation (2.34) assuming an ignition time of about 1 second.

$$T_{\text{sec}} = \frac{E_a}{0.06 \text{ (kcal/mol}\cdot\text{K)}}$$

If we assume $E_a = 52 \text{ kcal/mol}$ (i.e., half the C-H bond energy), we calculate

$$T_{\text{sec}} \left(\frac{52 \text{ kcal/mol}}{0.06 \frac{\text{kcal}}{\text{mol}\cdot\text{K}}} \right) = 866 \text{ K}$$

By comparison, the experimental value is 810 K.

Example 2.D Fitting Data to Equation 2.28 In Section 2.6, we noted that if one measures rate data over a wide temperature range, it is often necessary to fit the data to

$$k_1 = k_1^0 T^N \exp\left(\frac{-E_a}{k_B T}\right) \quad (2.D.1)$$

rather than Arrhenius' law. The objective here is to do an example of the fitting procedure. Yang et al. (1995) examined the rate of the reaction



As a function of temperature. Their data are given in Table 2.D.1. In the table, the apparent rate constant is defined as $\text{rate}/([\text{NCO}][\text{NO}])$ and is measured in units of $10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{second})$.

Fit the data in Table 2.D.1 to equation (2.D.1).

Solution The easiest way to solve this problem is to use the linear regression tool in Microsoft Excel or Lotus 1-2-3. I used Excel.

Table 2.D.1 The rate of reaction 2.C.2 as a function of temperature

Temperature, K	Apparent Rate Constant	Temperature, K	Apparent Rate Constant
293	3.8	432	2.92
344	3.36	538	2.28
		632	1.72
		836	1.28

I rearranged equation (2.D.1) as follows:

$$\ln(k_1) = \ln(k_1^0) + N \ln(T) - \frac{E_a}{k_B T} \quad (2.D.3)$$

Equation (2.D.3) is a linear equation, with two variables, $\ln(T)$ and $1/T$. Therefore, a linear regression package can be used to fit the unknown parameters $\ln(k_1^0)$, N , and E_a/k_B . I decided to solve the equation in Microsoft Excel.

I set up my spreadsheet as shown in Table 2.D.2. The temperature is listed in column A; the rate constant K is listed in column B. I want to do a linear fit of $\ln(k)$ versus $\ln(T)$ and $1/T$. Column C gives $\ln(k)$, column D gives $\ln(T)$, and column E gives $1/T$.

I then used the regression analysis tool (under analysis tools) in Excel. I called c2 through e7 Y, and d2 through e7 X. I then used the analysis tool to solve for the coefficients. The analysis tool gives lots of output. The key part of the output is

	Coefficients	Standard Error
Intercept	14.362	1.07
X variable 1	-2.0136	0.1486
X variable 2	-469.29	70.0

Therefore the best fit of the line is

$$\ln(k) = (14.4 \pm 1.0) - (2 \pm 0.15) \ln T + \frac{(-469 \pm 70)}{T}$$

Therefore

$$k = \exp(14.4) T^{-2} \exp\left(\frac{-469}{T}\right)$$

Table 2.D.2 The formulas used to solve Example 2.D.1

	A	B	C	D	E
1	Temp	k	$\ln k$	$\ln(T)$	$1/T$
2	293	3.8	$=\text{LN}(\$B2)$	$=\text{LN}(A2)$	$=1/\$A2$
3	344	3.36	$=\text{LN}(\$B3)$	$=\text{LN}(A3)$	$=1/\$A3$
4	432	2.92	$=\text{LN}(\$B4)$	$=\text{LN}(A4)$	$=1/\$A4$
5	538	2.28	$=\text{LN}(\$B5)$	$=\text{LN}(A5)$	$=1/\$A5$
6	632	1.72	$=\text{LN}(\$B6)$	$=\text{LN}(A6)$	$=1/\$A6$
7	836	1.28	$=\text{LN}(\$B7)$	$=\text{LN}(A7)$	$=1/\$A7$

There is one other detail of note. Different spreadsheet programs give different results. For example, Quatrpro gives

	Coefficient	Error
Intercept	13.634	0.0467
X variable 2	-1.92033	0.3562
X variable 2	-408.09	166.479

This difference arises because of a bug in Excel.

Example 2.E Determining Reaction Order Under some conditions the platinum-catalyzed reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$ follows the rate equation

$$r_{\text{CO}_2} = \frac{k_1[\text{CO}][\text{O}_2]^{1/2}}{(1 + K_2[\text{CO}])^2} \quad (2.E.1)$$

- (a) What is the order of the reaction?
 (b) If $K_2[\text{CO}] \gg 1$, what is the order of the reaction?
 (c) If $K_2[\text{CO}] \ll 1$, what is the order of the reaction?

Solution

- (a) No general order.
 (b) If $K_2[\text{CO}] \gg 1$, the rate equation becomes

$$r_{\text{CO}_2} = \frac{k_1[\text{CO}][\text{O}_2]^{1/2}}{(1 + K_2[\text{CO}])^2} = \frac{k_1[\text{CO}][\text{O}_2]^{1/2}}{(K_2)^2[\text{CO}]^2} = \frac{k_1}{(K_2)^2} [\text{CO}]^{1/2} [\text{O}_2]^{1/2}$$

Therefore, half order in O_2 ; negative one order in CO ; negative half-order overall.

- (c) If $K_2[\text{CO}] \ll 1$, then

$$r_{\text{CO}_2} = \frac{k_1[\text{CO}][\text{O}_2]^{1/2}}{(1 + K_2[\text{CO}])^2} = k_1[\text{CO}][\text{O}_2]^{1/2}$$

Thus, first-order in $[\text{CO}]$; half-order in O_2 ; $\frac{3}{2}$ -order overall.

Examples of fitting catalytic rate constants will be given in Chapter 3.

Example 2.F Numerical Integration of a Rate Equation Assume that you are running a reaction $\text{A} \Rightarrow \text{B}$ that follows

$$r_{\text{A}} = -(1 \times 10^{13}/\text{second}) \exp\left(\frac{-20 \text{ kcal/mol}}{k_{\text{B}}T}\right) [\text{A}] \quad (2.F.1)$$

where r_{A} is the rate of reaction, T is temperature, k_{B} is Boltzmann's constant, and $[\text{A}]$ is the A concentration. The temperature varies during the course of the reaction according to:

$$T = 300 \text{ K} + 10 \text{ K} \sin\left(\frac{t}{10 \text{ seconds}}\right) \quad (2.F.2)$$

where t is time. How long will it take to reduce the A concentration from 1 mol/liter to 0.1 mol/liter?

Solution According to equation (2.4)

$$\frac{d[\text{A}]}{dt} = r_{\text{A}} \quad (2.F.3)$$

Combining equations (2.F.1)–(2.F.3) yields

$$\frac{d[\text{A}]}{dt} = -(1 \times 10^{13}/\text{second}) \exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t/10 \text{ seconds}))}\right] [\text{A}] \quad (2.F.4)$$

Rearranging and integrating

$$-\int_{C_{\text{A}}^0}^{C_{\text{A}}^t} \frac{d[\text{A}]}{[\text{A}]} = (1 \times 10^{13}/\text{second}) \int_0^t \exp\left[-\frac{20 \text{ kcal/mol}}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t/10 \text{ seconds}))}\right] dt \quad (2.F.5)$$

where C_{A}^0 is the initial concentration of A and C_{A} is the concentration at time t . Performing the integral on the left-hand side yields

$$\ln\left(\frac{C_{\text{A}}^t}{C_{\text{A}}^0}\right) = (1 \times 10^{13}/\text{second}) \int_0^t \exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t/10 \text{ seconds}))}\right] dt \quad (2.F.6)$$

The right-hand side can be integrated with the trapezoidal rule. In the trapezoidal rule, you divide time into small segments Δt , then approximate the integral as a sum. For example, if you want to integrate a function $F(t)$, you say

$$\int_0^t F(t) dt = \sum_{i=0}^{n-1} F(t_i) \Delta t - \frac{1}{2} (F(t_0) + F(t_n)) \Delta t \quad (2.F.7)$$

Consequently, according to the trapezoidal rule

$$\begin{aligned} & \int_0^t \exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t/10 \text{ seconds}))}\right] dt \\ &= \sum_{i=1}^n \exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t_i/10 \text{ seconds}))}\right] \Delta t \\ & \quad - 0.5 \left(\exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t_0/10 \text{ seconds}))}\right] \Delta t \right. \\ & \quad \left. + \exp\left[-\frac{(20 \text{ kcal/mol})}{k_{\text{B}}(300 \text{ K} + 10 \text{ K} \sin(t_n/10 \text{ seconds}))}\right] \Delta t \right) \end{aligned} \quad (2.F.8)$$

where t_i is the time at time increment i , t_0 is the initial time, and t_n is the final time. Combining (2.F.6) and (2.F.8) yields

$$\ln\left(\frac{C_A^0}{C_A}\right) = \sum_i (1 \times 10^{13} / \text{second}) \exp\left[-\frac{20 \text{ kcal/mol}}{k_B(300 \text{ K} + 10 \text{ K} \sin(t_i/10 \text{ seconds}))}\right] \Delta t - 0.5 \times 10^{13} \left(\exp\left[-\frac{(20 \text{ kcal/mol})}{k_B(300 \text{ K} + 10 \text{ K} \sin(t_0/10 \text{ seconds}))}\right] \Delta t + \exp\left[-\frac{(20 \text{ kcal/mol})}{k_B(300 \text{ K} + 10 \text{ K} \sin(t_n/10 \text{ seconds}))}\right] \Delta t\right) \quad (2.F.9)$$

It is useful to simplify this expression by defining the temperature at time t_i by

$$T_i = 300 \text{ K} + 10 \text{ K} \sin(t_i/10 \text{ seconds}) \quad (2.F.10)$$

Combining equations (2.F.9) and (2.F.10) yields

$$\ln\left(\frac{C_A^0}{C_A}\right) = \sum_i (1 \times 10^{13} / \text{second}) \exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_i}\right) \Delta t - 0.5 \times 10^{13} \left[\exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_0}\right) \Delta t + \exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_n}\right) \Delta t\right] \quad (2.F.11)$$

Rearranging

$$C_A = C_A^0 \exp\left\{-\sum_i (1 \times 10^{13} / \text{second}) \exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_i}\right) \Delta t + 0.5 \times 10^{13} \left[\exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_0}\right) \Delta t + \exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_n}\right) \Delta t\right]\right\} \quad (2.F.12)$$

Therefore, I can integrate equation (2.F.12) numerically to calculate the concentration versus time. I used a Microsoft Excel worksheet to solve the problem. Table 2.F.1 shows the formulas in my worksheet; Table 2.F.2 shows the numerical values. I named cell b1 to be dt so I could set delta time. I also named cell D1 Ca0. I made column A time and column B, temperature. I defined column C as the term I needed to sum

$$\text{Term} = (1 \times 10^{13} / \text{second}) \exp\left[-\frac{(20 \text{ kcal/mol})}{k_B T_i}\right] \Delta t \quad (2.F.13)$$

Next I want to compute the integral from 0 to t_n where n varies. I defined column E to be the approximation to the integral

$$\text{Integral} = \left\{-\sum_i (1 \times 10^{13} / \text{second}) \exp\left(-\frac{20 \text{ kcal/mol}}{k_B T_i}\right) \Delta t + 0.5 \times 10^{13} \left[\exp\left(-\frac{(20 \text{ kcal/mol})}{k_B T_0}\right) \Delta t + \exp\left(-\frac{(20 \text{ kcal/mol})}{k_B T_n}\right) \Delta t\right]\right\} \quad (2.F.14)$$

Table 2.F.1 The formulas in the spreadsheet to calculate C_A

1	dt=	2	Ca0=	1
2	time	temp	term	sum
3	0	=300 + 10*SIN(A3 / 10)	=EXP(-20/0.00198/B3)*1.e13*dt	=SUM(C\$3:C3)
4	=A3 + dt	=300 + 10*SIN(A4 / 10)	=EXP(-20/0.00198/B4)*1.e13*dt	=SUM(C\$3:C4)
5	=A4 + dt	=300 + 10*SIN(A5 / 10)	=EXP(-20/0.00198/B5)*1.e13*dt	=SUM(C\$3:C5)
6	=A5 + dt	=300 + 10*SIN(A6 / 10)	=EXP(-20/0.00198/B6)*1.e13*dt	=SUM(C\$3:C6)
7	=A6 + dt	=300 + 10*SIN(A7 / 10)	=EXP(-20/0.00198/B7)*1.e13*dt	=SUM(C\$3:C7)
8	=A7 + dt	=300 + 10*SIN(A8 / 10)	=EXP(-20/0.00198/B8)*1.e13*dt	=SUM(C\$3:C8)
9	=A8 + dt	=300 + 10*SIN(A9 / 10)	=EXP(-20/0.00198/B9)*1.e13*dt	=SUM(C\$3:C9)
10	=A9 + dt	=300 + 10*SIN(A10 / 10)	=EXP(-20/0.00198/B10)*1.e13*dt	=SUM(C\$3:C10)
11	=A10 + dt	=300 + 10*SIN(A11 / 10)	=EXP(-20/0.00198/B11)*1.e13*dt	=SUM(C\$3:C11)
12	=A11 + dt	=300 + 10*SIN(A12 / 10)	=EXP(-20/0.00198/B12)*1.e13*dt	=SUM(C\$3:C12)
13	=A12 + dt	=300 + 10*SIN(A13 / 10)	=EXP(-20/0.00198/B13)*1.e13*dt	=SUM(C\$3:C13)
14	=A13 + dt	=300 + 10*SIN(A14 / 10)	=EXP(-20/0.00198/B14)*1.e13*dt	=SUM(C\$3:C14)
				=0.5*(C\$3 + C14) - D14
				=Ca0*EXP(E14)

Table 2.F.2 The numerical values in the spreadsheet to calculate Ca

A	B	C	D	E	F
1	dt=	2	1		
2	time	temp	sum	integral	Ca
3	0	300	0.047678	0	1
4	2	301.9867	0.0595	-0.107179	0.947821
5	4	303.8942	0.073401	-0.180579	0.886885
6	6	305.6464	0.088809	-0.269388	0.817794
7	8	307.1736	0.104667	-0.374055	0.742389
8	10	308.4147	0.119477	-0.493532	0.663681
9	12	309.3204	0.131501	-0.625033	0.58541
10	14	309.8545	0.139115	-0.764148	0.511324
11	16	309.9957	0.141197	-0.905345	0.444454
12	18	309.7385	0.137427	-1.042772	0.386656
13	20	309.093	0.128379	-1.171152	0.338537
14	22	308.085	0.115361	-1.286513	0.299694
spreadsheet continues					
38	70	306.5699	0.098104	2.295655	-2.22276
39	72	307.9367	0.113554	2.409208	-2.32859

I summed all of the terms from 0 to t and subtracted that sum from the second term in equation (2.F.14). I defined column F to be the concentration at time t. I used equation (2.F.12) to calculate it.

Therefore it takes between 70 and 72 seconds to get to 90% conversion.

Additional information about Arrhenius' law is given in

- K. J. Laidler, The development of Arrhenius's equation, *J. Chem. Educ.* **61**, 494 (1984).
 B. Heinrich, *Hot Blooded Insects*, Harvard University Press, Cambridge, MA, (1993).
 J. R. Heulett, Deviations from the Arrhenius equation, *Q. Rev., Chem. Soc.* **18**, 277 (1964).

2.11 PROBLEMS

2.1 Define the following terms in three sentences or less:

- (a) Rate equation
 (b) Order
 (c) Rate constant
 (d) Preexponential
 (e) Activation barrier
 (f) Arrhenius' law
 (g) Catalysis
 (h) Oscillating reaction
 (i) Multiple steady state
 (j) Catalyst
 (k) Stoichiometric coefficient
 (l) First order
 (m) Second order
 (n) Half order
 (o) Heterogeneous reaction
 (p) Homogeneous reaction

2.3 What did you learn that was new to you in this chapter? Were you aware of all of the definitions? Was the historical information new? Were you aware of the limitations of the Arrhenius equation and of representing data by a rate law? Were you aware that Arrhenius' law applies to so many practical situations? Did you know that you could estimate an activation barrier without doing many experiments? What else did you learn that was new?

2.4 Find 20 examples of kinetic processes in your home, such as cooking different kinds of meals, washing clothes, you digesting different types of food, or plants growing on your window sill.

2.5 Identify the units for

- (a) r_A , the rate per unit volume
 (b) R_A , the rate per unit surface area
 (c) A first-order gas-phase reaction
 (d) A first-order surface reaction
 (e) A second-order gas-phase reaction
 (f) A second-order surface reaction

2.6 A first-order reaction has a rate constant of 0.15/minute.

- (a) Calculate the rate of reaction at a reactant concentration of 0.57 mol/liter.
 (b) Repeat for a second-order reaction with a rate constant of 0.73 liter/(mol-minute).
 2.6 Calculate the activation barrier for a reaction whose rate exactly doubles from

- (a) 100 to 110 K
 (b) 200 to 210 K
 (c) 300 to 310 K
 (d) 500 to 510 K
 (e) 750 to 760 K
 (f) 1000 to 1010 K

2.7 According to Table 2.3, the oxidation of phosphine (PH_3) obeys

$$r_{\text{PH}_3} = k_5[\text{PH}_3][\text{O}_2]^{1/2}$$

(P2.7.1)

- (a) What is the overall order of the reaction?
 (b) What is the order with respect to phosphine?
 (c) What is the order with respect to oxygen?

(d) How much will the rate increase if you double the oxygen pressure keeping the phosphine pressure constant?

(e) How much will the rate increase if you double the phosphine pressure?

(f) How much will the rate increase if you double the total pressure constant?

Hint: First define $x_{\text{PH}_3} = P_{\text{PH}_3}/P_{\text{Total}}$. Show $P_{\text{O}_2} = P_{\text{Total}} - P_{\text{PH}_3} = P_{\text{Total}}(1 - x_{\text{PH}_3})$. Then substitute into equation (P2.7.1).

2.8 Later in this book, we will provide some methods to estimate the preexponentials and activation barriers for reactions. Assume that we solve a problem and make a mistake, and calculate a 25 kcal/mol barrier for a reaction that actually has a barrier of 30 kcal/mol. The preexponential was calculated accurately.

- (a) If you need to calculate the rate constant at 500 K, how large an error in the rate will you make?
- (b) How much would you have to change the temperature to compensate for the error (i.e., to increase the rate to the rate you calculate)?

2.9 Milk goes sour because bacteria in the milk converts the lactose in the milk into lactic acid.

- (a) The reaction goes 40 times faster at 25°C than at 4°C. Estimate the activation barrier.
- (b) How does your estimate compare to that from Figure 2.9? Assume a half-life of 12 hours.
- (c) How do you account for the differences?

2.10 Your taste buds work by a complex pathway. First the receptors in your tongue bind to some of the components in food. That sets off a complex chain reaction leading to a change in polarity of the cell, and eventually the sensation of taste. The object of this problem is to use the material in this chapter to guess how changes in the temperature of your tongue will affect the perception of taste.

- (a) How much would you expect the sensitivity of your tongue to change when you change the temperature of your taste buds by 10°C?
- (b) Guess or measure how much the temperature of your tongue changes when you drink a glass of soda pop (carbonated beverage).
- (c) Guess or measure how much the temperature of your tongue changes when you eat a dish of ice cream.
- (d) Ice cream manufacturers say that they need about twice as much sugar to sweeten ice cream as to sweeten soda pop to the same perceived level of sweetness. Are your expectations consistent with these findings?
- (e) Try an experiment to verify that this works. Take a sample of ice cream and store it in a sealed container in your refrigerator overnight. Let the ice cream warm up to 10°C. Now do a taste test. Taste the frozen ice cream. Taste the melted ice cream. Which tastes sweeter?

2.11 When you cook rice, you hydrolyze the cellulose in the rice to starch via the following chemical reaction:



Brown rice takes twice as long to cook as white rice because there is twice as much cellulose to hydrolyze. What does that tell you about the kinetics of the hydrolysis reaction?

- (a) If you had a first-order reaction, how would the cooking time vary with the cellulose concentration?
- (b) What does the fact that the cooking time doubles as the cellulose concentration doubles tell you about the kinetics of the reaction?
- (c) How would the cooking time vary if you were working at an altitude of 10,000 feet (ft)? (*Hint:* The boiling point of water at 10,000 feet is 92°C.)

2.13 The reaction $4\text{PH}_3 \longrightarrow \text{P}_4 + 6\text{H}_2$ follows:

$$r_1 = 0.08/\text{second} [\text{PH}_3]$$

- (a) Calculate r_{PH_3} , r_{P_4} , and r_{H_2} at 500°C, and a PH_3 partial pressure of 5 torr. [*Note:* 760 torr = 1 atm. (atmosphere of pressure).]

(b) How many milligrams of phosphorous do you deposit in 100 seconds?

2.14 In Section 2.1, we reported that Lavoisier found that 1 kg of air always reacted with 0.78 kg of tin to yield 0.99 kg of tin calx (SnO) and leave 0.79 kg of inerts.

- (a) Did Lavoisier measure things correctly? Does 1 kg of air react with 0.79 kg of tin to yield 0.99 kg of tin calx?
- (b) How many kilograms of the following substances will react with 1 kg of air: aluminum forming Al_2O_3 , iron forming Fe_2O_3 , Ni forming NiO , silicon forming SiO_2 ?
- (c) What are the stoichiometric coefficients in the reaction to form tin calx? Assume a basis of one mole of tin.

2.14 In Section 2.1, we noted that Lavoisier showed that mass is conserved during chemical reactions by sealing a flask filled with tin and air and measuring the weight change as the oxygen in the air reacted with the tin.

- (a) If you have a sealed 1 liter flask filled with air and 10 grams of tin, how much SnO_2 can you produce if you use up all of the oxygen in the air?
- (b) By much would the weight of the sealed flask change?
- (c) By much would the weight change if you opened the flask?
- (d) Now think about doing this in the year 1796. How would you measure the weight change?

2.15 Consider the reaction $4\text{PH}_3 \longrightarrow \text{P}_4 + 6\text{H}_2$. (P2.15)

- (a) What are the stoichiometric coefficients of each of the species in the reaction (P2.15)?
- (b) If we load 2 mol of PH_3 into a reactor, and convert 50% of the PH_3 into products, how much P_4 and H_2 would be produced?
- (c) Assume that we are using reaction (P2.15) to deposit phosphorous onto a silicon wafer. Assume that we deposit 10^{-4} mol/(hour-cm²) of P_4 on our wafer. Calculate

(1) The rate of reaction (P2.15)

(2) The rate of hydrogen production

(3) The rate of phosphine (PH_3) production

- (d) If we write the reaction $\text{PH}_3 \xrightarrow{2.15a} \frac{1}{4}\text{P}_4 + \frac{3}{2}\text{H}_2$, how will the stoichiometric coefficients change?

2.16 Are the following reactions homogeneous or heterogeneous?

- (a) Cooking a steak (i.e., converting the collagen to glycogen and oxidizing the myoglobin)
- (b) Bleaching your clothes (i.e., reactions of bleach with dirt)

- (c) Buildup of rust on you car (i.e., reacting oxygen with iron)
 (d) Combustion in your car's engine (i.e., burning gasoline)
 (e) Burning a candle
 (f) Digesting the sugar in a glass of beer (i.e., turning sucrose to glucose in your stomach)

2.17 In Example 2.A we considered the oxidation of ethane in a catalytic converter. However, another important reaction is the oxidation of ethanol:



Assume that you measure the oxidation of ethanol in a catalytic converter and the data in Table P2.17 are obtained.

- (a) Calculate the rate of formation of each species.
 (b) Calculate the overall rate of reaction.
 (c) Notice that the nitrogen and oxygen do not quite balance. This indicates that another reaction is occurring. What is the stoichiometry of other reaction? (*Hint*: How much excess oxygen and nitrogen are in the exit? What other species could decompose or react to form the excess oxygen and nitrogen?)
- 2.18** In Problem 2.D we fit the data in Table 2.D.1 to equation (2.D.1).
- (a) Set up the problem yourself and see if you can reproduce the findings. The spreadsheet is available from Professor Masel's website, <http://www.uiuc.edu/~rl-masel> or Wiley's website.
 (b) What is the activation energy (with error bars)?
 (c) By much would the activation barrier change if the point at 293 K were misrecorded so $k(273) = 3.08$?
 (d) What does the result in (c) tell you about the importance of experimental error in the measurement of activation barriers?

2.19 In Example 2.F we used a numerical procedure to integrate a rate expression.

(a) Set up the problem yourself and see if you can reproduce the findings. The spreadsheet is available from Professor Masel's website.
 (b) Assume that the temperature instead varies as $T = 300 \text{ K} + 5 \text{ K sin}(t/10 \text{ seconds})$. How will your answer change?

Table P2.17 The inlet and outlet flow rates (in mol/hour) from an experimental catalytic converter with a volume of 10 liters

Species	Inlet Flow Rate	Exit Flow Rate
Ethanol	0.21	0.01
Oxygen	0.80	0.30
Water	80.5	81.1
Carbon dioxide	60.9	61.3
Nitrogen	637	637.1

- (e) Assume that the temperature instead varies as $T = 300 \text{ K} + 1 \text{ K sin}(t/10 \text{ seconds})$. How will your answer change?
 (d) Assume that the temperature instead varies as $T = 300 \text{ K} + 0.1 \text{ K sin}(t/10 \text{ seconds})$. How will your answer change?
 (e) What do these results tell you about the importance of temperature control in kinetics measurements?

2.20 Fit the data in Figures 2.7 and 2.10 to Arrhenius' law. How well do the data fit in each case? (*Hint*: Draw a line on the graph. Do not use a spreadsheet.)

2.21 Figure P2.21 shows V. Van Spaendonk and R. I. Masel's unpublished data for the pyrolysis of a mixture of ethylene and hydrogen over a platinum catalyst. During the experiment, Van Spaendonk and Masel adsorbed ethylene and hydrogen onto the catalyst and then heated the catalyst and looked for reaction. Each of the peaks in Figure P2.21 corresponds to a different reaction pathway. For instance, the ethane peak at 310 K corresponds to a reaction where two adsorbed species react to form ethane.

(a) From the data shown, how many chemical reactions do you see? (*Hint*: Each chemical reaction will produce one peak.)

(b) Use the data in Figure P2.21 to estimate the activation barrier for each of these chemical reactions. Assume that the peak temperature corresponds to the temperature where the half-life is one second.

2.22 The objective of this problem is to use a spreadsheet (e.g., Lotus or Excel) to examine the implications of Arrhenius' law.

(a) Assume that you are running a first-order reaction in a batch reactor, and that the reaction has a half-life of 1 minute at some temperature T. Calculate

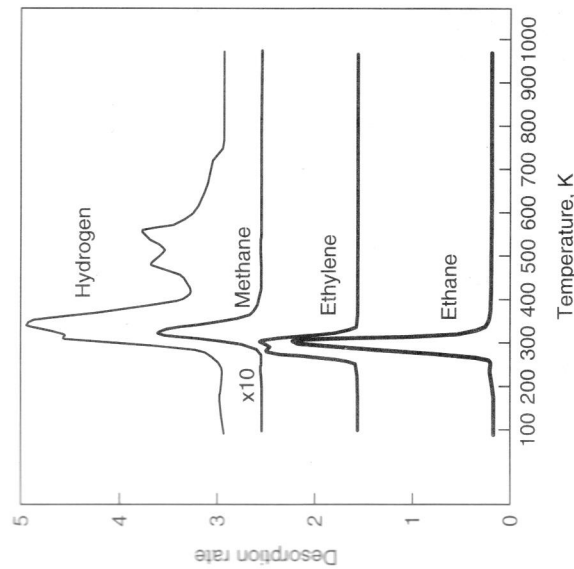


Figure P2.21 Van Spaendonk and Masel's data.

the activation energy of the reaction as a function of T , assuming that the reaction follows Arrhenius' law with a preexponential of 10^{13} /second. For the purposes of this problem, consider T to range between 100 and 1000 K.

- (b) Vary the preexponential from 10^{11} to 10^{15} /second. To what extent do your estimates of the activation barrier change?
- (c) Change your estimate of the half-life from a minute to an hour. By how much do your estimates of the activation barrier change?
- (d) Now go back to your estimate of the activation barrier in part (a). At each temperature, calculate how much you would have to increase the temperature in order to double the rate. (*Hint*: At 500 K you would need to increase the temperature to perhaps 514 to double the rate.)
- (e) Use your results to see if the idea that rates double every 10 K works for this example.

2.23 Yang, Lee and Wang, *International J. Of Chemical Kinetics*, **27**, (1995), 1111 examined the rate of the reaction



as a function of temperature. Their data are given in Table P2.23. In the table, the rate constant is defined as $\text{rate}/([\text{NCO}][\text{NO}_2])$ and is measured in units of $10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{second})$.

- (a) Are the units of the rate constant correct?
- (b) Fit the data to Arrhenius' law. How well do they fit?
- (c) Is the fit improved with equation (2.28)? Use the methods in Example 2.D.
- (d) How do you interpret the sign of the activation barrier?
- (e) On the basis of your fits and the error bars in Excel, how much confidence do you have in the value of the activation barrier?

2.24 Eberhard and Howard, *International J. Of Chemical Kinetics*, **28**, (1996) 731 examined the rate of the reaction



as a function of temperature. Their data are given in Table P2.24. In the table, the rate constant is defined as $\text{rate}/([\text{CH}_3\text{CH}_2\text{OO}][\text{NO}])$ and is measured in units of $10^{-12} \text{ cm}^3/(\text{molecule}\cdot\text{second})$.

Table P2.23 The rate of reaction (P2.23) as a function of temperature

Temperature, K	Apparent Rate Constant	Temperature, K	Apparent Rate Constant
294	2.68	384	2.08
320	2.43	431	2.02
351	2.57	493	1.58
		579	1.14
		665	1.12
		774	1.05

Table P2.24 The rate of reaction (P2.24) as a function of temperature

Temperature, K	Apparent Rate Constant	Temperature, K	Apparent Rate Constant
206	16.9	252	11.9
208	17.9	261	11.6
223	14.0	298	9.06
244	14.1	298	9.67
		325	9.2
		355	8.02
		402	6.76
		403	6.58

- (a) Are the units of the rate constant correct?
- (b) Fit the data to Arrhenius' law. How well do they fit?
- (c) Is the fit improved with equation (2.28)? Use the methods in Example 2.D.
- (d) How do you interpret the sign of the activation barrier?
- (e) On the basis of your fits, how much confidence do you have in the value of the activation barrier?

2.25 As noted earlier in this chapter, crickets chirp to attract mates; the cricket's metabolic rate varies with the cricket's body temperature, so the chirping rate also varies with the cricket's temperature. [Walker, *Evolution* **16**, (1962) 407.] measured the rate that a group of crickets chirped and obtained the following data:

Temperature, °F	Chirp rate, chirps/minute	Temperature, °F	Chirp rate, chirps/minute
55	60	64	122
58	65	73	136
		77	136
		81	148

- (a) Estimate the activation energy for the process leading to chirping.
- (b) A cricket often chirps from dusk to dawn. Assume that during the course of the night, the temperature varied as follows:

Time	Temperature, °F	Time	Temperature, °F
9 P.M.	80	12 P.M.	73
10 P.M.	77	1 A.M.	68
11 P.M.	75	2 A.M.	67
		3 A.M.	67
		4 A.M.	67
		5 A.M.	67

How many chirps would a cricket make from 9 P.M. to 5 A.M.? (*Hint*: Set up a problem as an integral that needs to be solved, then use the methods in Example 2.F to do the integration.)

- (c) Next time you are walking at night, listen for the crickets. How fast are they chirping? Does the chirp rate agree with the data above? Can you use the rate at which crickets chirp to estimate the air temperature? How accurate is your measurement?

2.26 A.M. Smith, *Environ, Entomol.* **21**, (1992), 314 examined the speed that pea weevil (*Brochus pisorum*) eggs matured as a function of temperature. The following data were obtained:

