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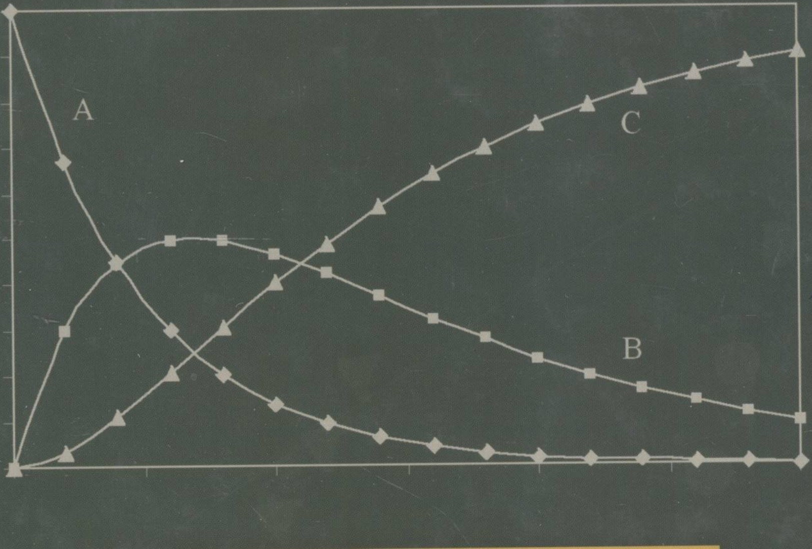

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JAMES E. HOUSE

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James E. House
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and
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Principles of Chemical Kinetics

Preface

Chemical kinetics is an enormous field that has been the subject of many books, including a series that consists of numerous large volumes. To try to cover even a small part of the field in a single volume of portable size is a difficult task. As is the case with every writer, I have been forced to make decisions on what to include, and like other books, this volume reflects the interests and teaching experience of the author.

As with the first edition, the objective has been to provide an introduction to most of the major areas of chemical kinetics. The extent to which this has been done successfully will depend on the viewpoint of the reader. Those who study only gas phase reactions will argue that not enough material has been presented on that topic. A biochemist who specializes in enzyme-catalyzed reactions may find that research in that area requires additional material on the topic. A chemist who specializes in assessing the influence of substituent groups or solvent on rates and mechanisms of organic reactions may need other tools in addition to those presented. In fact, it is fair to say that this book is not written for a *specialist* in any area of chemical kinetics. Rather, it is intended to provide readers an introduction to the major areas of kinetics and to provide a basis for further study. In keeping with the intended audience and purposes, derivations are shown in considerable detail to make the results readily available to students with limited background in mathematics.

In addition to the significant editing of the entire manuscript, new sections have been included in several chapters. Also, Chapter 9 "Additional Applications of Kinetics," has been added to deal with some topics that do not fit conveniently in other chapters. Consequently, this edition contains substantially more material, including problems and references, than the first edition. Unlike the first edition, a solution manual is also available.

As in the case of the first edition, the present volume allows for variations in the order of taking up the material. After the first three chapters, the

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remaining chapters can be studied in any order. In numerous places in the text, attention is drawn to the fact that similar kinetic equations result for different types of processes. As a result, it is hoped that the reader will see that the assumptions made regarding interaction of an enzyme with a substrate are not that different from those regarding the adsorption of a gas on the surface of a solid when rate laws are derived. The topics dealing with solid state processes and nonisothermal kinetics are covered in more detail than in some other texts in keeping with the growing importance of these topics in many areas of chemistry. These areas are especially important in industrial laboratories working on processes involving the drying, crystallizing, or characterizing of solid products.

It is hoped that the present volume will provide a succinct and clear introduction to chemical kinetics that meets the needs of students at a variety of levels in several disciplines. It is also hoped that the principles set forth will prove useful to researchers in many areas of chemistry and provide insight into how to interpret and correlate their kinetic data.

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CHAPTER 1

Fundamental Concepts of Kinetics

It is frequently observed that reactions that lead to a lower overall energy state as products are formed take place readily. However, there are also many reactions that lead to a decrease in energy, yet the rates of the reactions are low. For example, the heat of formation of water from gaseous H_2 and O_2 is −285 kJ/mol, but the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \tag{1.1}$$

takes place very slowly, if at all, unless the reaction is initiated by a spark. The reason for this is that although a great deal of energy is released as H_2O forms, there is no low energy pathway for the reaction to follow. In order for water to form, molecules of H_2 and O_2 must react, and their bond energies are about 435 and 490 kJ/mol, respectively.

Thermodynamics is concerned with the overall energy change between the initial and final states for a process. If necessary, this change can result after an infinite time. Accordingly, thermodynamics does not deal with the subject of reaction *rates*, at least not directly. The preceding example shows that the *thermodynamics* of the reaction favors the production of water; however, *kinetically* the process is unfavorable. We see here the first of several important principles of chemical kinetics. There is no necessary correlation between thermodynamics and kinetics of a chemical reaction. Some reactions that are energetically favorable take place very slowly because there is no low energy pathway by which the reaction can occur.

One of the observations regarding the study of reaction rates is that a rate cannot be calculated from first principles. Theory is not developed to the point where it is possible to calculate how fast most reactions will take place. For some very simple gas phase reactions, it is possible to calculate approximately how fast the reaction should take place, but details

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of the process must usually be determined experimentally. Chemical kinetics is largely an experimental science.

Chemical kinetics is intimately connected with the analysis of data. The personal computers of today bear little resemblance to those of a couple of decades ago. When one purchases a computer, it almost always comes with software that allows the user to do much more than word processing. Software packages such as Excel, Mathematica, MathCad, and many other types are readily available. The tedious work of plotting points on graph paper has been replaced by entering data in a spreadsheet. This is not a book about computers. A computer is a *tool*, but the user needs to know how to interpret the results and how to choose what types of analyses to perform. It does little good to find that some mathematics program gives the best fit to a set of data from the study of a reaction rate with an arctangent or hyperbolic cosine function. The point is that although it is likely that the reader may have access to data analysis techniques to process kinetic data, the purpose of this book is to provide the background in the principles of kinetics that will enable him or her to interpret the results. The capability of the available software to perform numerical analysis is a separate issue that is not addressed in this book.

1.1 RATES OF REACTIONS

The rate of a chemical reaction is expressed as a change in concentration of some species with time. Therefore, the dimensions of the *rate* must be those of concentration divided by time (moles/liter sec, moles/liter min, etc.). A reaction that can be written as

$$\mathrm{A} \rightarrow \mathrm{B} \tag{1.2}$$

has a rate that can be expressed either in terms of the disappearance of A or the appearance of B. Because the concentration of A is *decreasing* as A is consumed, the rate is expressed as $-d[\mathrm{A}]/dt$. Because the concentration of B is *increasing* with time, the rate is expressed as $+d[\mathrm{B}]/dt$. The mathematical equation relating concentrations and time is called the *rate equation* or the *rate law*. The relationships between the concentrations of A and B with time are represented graphically in Figure 1.1 for a first-order reaction in which $[\mathrm{A}]_o$ is 1.00 **M** and $k = 0.050\,\mathrm{min}^{-1}$.

If we consider a reaction that can be shown as

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{1.3}$$

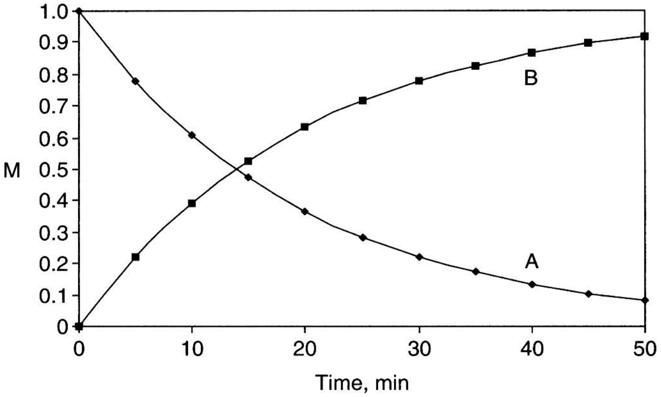


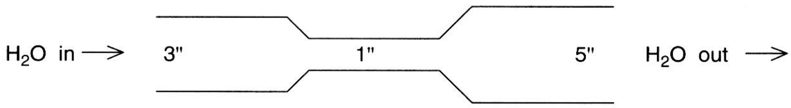
FIGURE 1.1 Change in concentration of A and B for the reaction A → B.

the rate law will usually be represented in terms of a constant times some function of the concentrations of A and B, and it can usually be written in the form

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y \tag{1.4}$$

where x and y are the exponents on the concentrations of A and B, respectively. In this rate law, k is called the rate constant and the exponents x and y are called the *order* of the reaction with respect to A and B, respectively. As will be described later, the exponents x and y may or may not be the same as the balancing coefficients a and b in Eq. (1.3). The overall order of the reaction is the sum of the exponents x and y. Thus, we speak of a second-order reaction, a third-order reaction, etc., when the sum of the exponents in the rate law is 2, 3, etc., respectively. These exponents can usually be established by studying the reaction using different initial concentrations of A and B. When this is done, it is possible to determine if doubling the concentration of A doubles the rate of the reaction. If it does, then the reaction must be first-order in A, and the value of x is 1. However, if doubling the concentration of A quadruples the rate, it is clear that [A] must have an exponent of 2, and the reaction is second-order in A. One very important point to remember is that there is no *necessary* correlation between the balancing coefficients in the chemical equation and the exponents in the rate law. They *may* be the same, but one can not *assume* that they will be without studying the rate of the reaction.

If a reaction takes place in a series of steps, a study of the rate of the reaction gives information about the slowest step of the reaction. We can see an analogy to this in the following illustration that involves the flow of water,



If we study the rate of flow of water through this system of short pipes, information will be obtained about the flow of water through a 1" pipe since the 3" and 5" pipes do not normally offer as much resistance to flow as does the 1" pipe. Therefore, in the language of chemical kinetics, the 1" pipe represents the *rate-determining step.*

Suppose we have a chemical reaction that can be written as

$$2\text{A} + \text{B} \rightarrow \text{Products} \tag{1.5}$$

and let us also suppose that the reaction takes place in steps that can be written as

$$\text{A} + \text{B} \rightarrow \text{C (slow)} \tag{1.6}$$

$$\text{C} + \text{A} \rightarrow \text{Products (fast)} \tag{1.7}$$

The amount of C (known as an *intermediate*) that is present at any time limits the rate of the overall reaction. Note that the sum of Eqs. (1.6) and (1.7) gives the overall reaction that was shown in Eq. (1.5). Note also that the formation of C depends on the reaction of one molecule of A and one of B. That process will likely have a rate that depends on $[\text{A}]^1$ and $[\text{B}]^1$. Therefore, even though the balanced overall equation involves *two* molecules of A, the *slow step* involves only one molecule of A. As a result, formation of products follows a rate law that is of the form $\text{Rate} = k[\text{A}][\text{B}]$, and the reaction is second-order (first-order in A and first-order in B). It should be apparent that we can write the rate law directly from the balanced equation only if the reaction takes place in a *single step.* If the reaction takes place in a series of steps, a rate study will give information about steps up to and including the slowest step, and the rate law will be determined by that step.

1.2 DEPENDENCE OF RATES ON CONCENTRATION

In this section, we will examine the details of some rate laws that depend on the concentration of reactants in some simple way. Although many complicated cases are well known (see Chapter 2), there are also a great many reactions for which the dependence on concentration is first-order, second-order, or zero-order.

1.2.1 First-Order

Suppose a reaction can be written as

$$A \rightarrow B \tag{1.8}$$

and that the reaction follows a rate law of the form

$$\text{Rate} = k[\text{A}]^1 = -\frac{d[\text{A}]}{dt} \tag{1.9}$$

This equation can be rearranged to give

$$-\frac{d[\text{A}]}{[\text{A}]} = k\,dt \tag{1.10}$$

Equation (1.10) can be integrated but it should be integrated between the limits of time $= 0$ and time equal to t while the concentration varies from the initial concentration $[\text{A}]_o$ at time zero to [A] at the later time. This can be shown as

$$-\int_{[\text{A}]_o}^{[\text{A}]} \frac{d[\text{A}]}{[\text{A}]} = k\int_0^t dt \tag{1.11}$$

When the integration is performed, we obtain

$$\ln\frac{[\text{A}]_o}{[\text{A}]} = kt \quad \text{or} \quad \log\frac{[\text{A}]_o}{[\text{A}]} = \frac{k}{2.303}t \tag{1.12}$$

If the equation involving natural logarithms is considered, it can be written in the form

$$\ln[\text{A}]_o - \ln[\text{A}] = kt \tag{1.13}$$

or

$$\begin{gathered} \ln[\text{A}] = \ln[\text{A}]_o - kt \\ y = b + mx \end{gathered} \tag{1.14}$$

It must be remembered that $[\text{A}]_o$, the initial concentration of A, has some fixed value so it is a constant. Therefore, Eq. (1.14) can be put in the form of a linear equation where $y = \ln[A]$, $m = -k$, and $b = \ln [A]_o$. A graph of $\ln[A]$ versus t will be linear with a slope of $-k$. In order to test this rate law, it is necessary to have data for the reaction which consists of the concentration of A determined as a function of time. This suggests that in order to determine the concentration of some species, in this case A, simple, reliable, and rapid analytical methods are usually sought. Additionally, one must measure time, which is not usually a problem unless the reaction is a very rapid one.

It may be possible for the concentration of a reactant or product to be determined directly within the reaction mixture, but in other cases a sample must be removed for the analysis to be completed. The time necessary to remove a sample from the reaction mixture is usually negligibly short compared to the reaction time being measured. What is usually done for a reaction carried out in solution is to set up the reaction in a vessel that is held in a constant temperature bath so that fluctuations in temperature will not cause changes in the rate of the reaction. Then the reaction is started, and the concentration of the reactant (A in this case) is determined at selected times so that a graph of $\ln[A]$ versus time can be made or the data analyzed numerically. If a linear relationship provides the best fit to the data, it is concluded that the reaction obeys a first-order rate law. Graphical representation of this rate law is shown in Figure 1.2 for an initial concentration of A of 1.00 **M** and $k = 0.020\,\text{min}^{-1}$. In this case, the slope of the line is $-k$, so the kinetic data can be used to determine k graphically or by means of linear regression using numerical methods to determine the slope of the line.

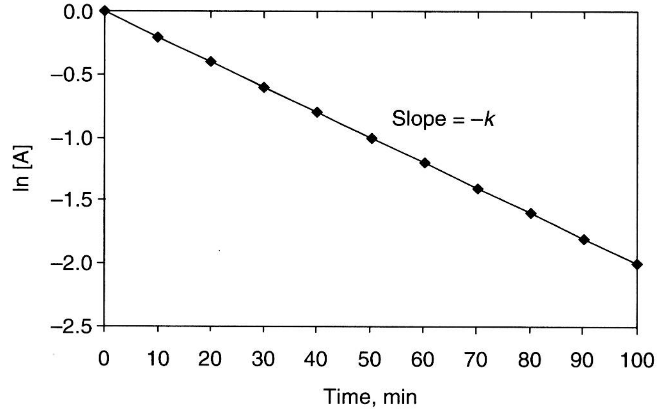


FIGURE 1.2 First-order plot for $A \rightarrow B$ with $[A]_o = 1.00\,\mathbf{M}$ and $k = 0.020\,\text{min}^{-1}$.

The units on k in the first-order rate law are in terms of time^{-1}. The left-hand side of Eq. (1.12) has [concentration]/[concentration], which causes the units to cancel. However, the right-hand side of the equation will be dimensionally correct only if k has the units of time^{-1}, because only then will kt have no units.

The equation

$$\ln [\mathrm{A}] = \ln [\mathrm{A}]_o - kt \tag{1.15}$$

can also be written in the form

$$[\mathrm{A}] = [\mathrm{A}]_o \, e^{-kt} \tag{1.16}$$

From this equation, it can be seen that the concentration of A decreases with time in an exponential way. Such a relationship is sometimes referred to as an *exponential decay*.

Radioactive decay processes follow a first-order rate law. The rate of decay is proportional to the amount of material present, so doubling the amount of radioactive material doubles the measured counting rate of decay products. When the amount of material remaining is one-half of the original amount, the time expired is called the *half-life*. We can calculate the half-life easily using Eq. (1.12). At the point where the time elapsed is equal to one half-life, $t = t_{1/2}$, the concentration of A is one-half the initial concentration or $[\mathrm{A}]_o/2$. Therefore, we can write

$$\ln \frac{[\mathrm{A}]_o}{[\mathrm{A}]} = \ln \frac{[\mathrm{A}]_o}{\dfrac{[\mathrm{A}]_o}{2}} = kt_{1/2} = \ln 2 = 0.693 \tag{1.17}$$

The half-life is then given as

$$t_{1/2} = \frac{0.693}{k} \tag{1.18}$$

and it will have units that depend on the units on k. For example, if k is in hr^{-1}, then the half-life will be given in hours, etc. Note that for a process that follows a first-order rate law, the half-life is independent of the initial concentration of the reactant. For example, in radioactive decay the half-life is independent of the amount of starting nuclide. This means that if a sample initially contains 1000 atoms of radioactive material, the half-life is exactly the same as when there are 5000 atoms initially present.

It is easy to see that after one half-life the amount of material remaining is one-half of the original; after two half-lives, the amount remaining is one-fourth of the original; after three half-lives, the amount remaining

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