PRINCIPLES OF
CHEMICAL KINETICS

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PREFACE

This work is based on an earlier book, "Chemical Kinetics: Principles and Selected Topics," by I. Amdur and myself. The untimely death of I. Amdur has prevented a joint revision, but the present book retains the same philosophy of presentation and organization. However, the many recent innovations in chemical kinetics, especially in gas-phase dynamics, have required rather extensive revision of the earlier book. I am greatly indebted to Mrs. Alice Amdur and to the McGraw-Hill Book Company for permission to use portions of the older text.

The purpose of this book is to present the principles of chemical kinetics along with modern applications. Thus the student will learn not only the basic formulations but also will be stimulated (hopefully) by the exciting current research in chemical kinetics. Obviously a complete description of modern chemical kinetics would require a volume (or volumes) considerably larger than this one. Therefore, only a selection of topics is possible. Many extremely interesting aspects are not covered, but I believe that a student who understands the material presented will have no trouble in going directly to the literature for further information. The phenomenology and commonly used theories of chemical kinetics are presented in a critical manner, with particular emphasis on collision dynamics. How and what mechanistic information can be obtained from various experimental approaches is stressed throughout the book.

The concise presentation is designed to stimulate both students and teachers, and it is expected that the references cited at the end of each chapter will have to be consulted. Most of the problems are quite challenging and are designed both to test the students' comprehension of the subject matter and to complement the textual material.

The material in this book has been used as the basis for a one-semester course offered to seniors and graduate students at Cornell University. I firmly believe that at this level a general course in chemical kinetics, covering reactions in both

gases and liquids, is needed. Students all too soon reach the stage where their interests are confined to more specialized topics. Although some introductory material is reviewed, this text is intended for students with a general college background in chemistry, physics, and mathematics, and with a typical under-graduate course in physical chemistry.

I am indebted to my colleagues at Cornell for many stimulating discussions of chemical kinetics, especially S. Bauer and B. Widom. I am particularly grateful to P. Houston for his critical comments and many references related to the application of lasers to kinetic problems. I also would like to thank Miss Connie Wright, not only for typing several drafts of the manuscript, but for patiently correcting many errors and for organizing much of the material associated with this project.

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EMPIRICAL ANALYSIS
OF REACTION RATES

1-1 INTRODUCTION

Chemical kinetics is concerned with the dynamics of chemical reactions. In particular, it deals with the rates of chemical reactions and how these rates can be explained in terms of a reaction mechanism. Ideally, a complete reaction mechanism would involve a knowledge of all the molecular details of the reaction, including the energetics and stereochemistry, e.g., interatomic distances and angles throughout the course of the reaction, of the individual molecular steps involved in the mechanism. In practice, experiments involve the determination of an average rate of reaction of a large number of molecules; therefore proposed mechanisms usually present a sequence of steps in which the molecules are presumed to be in some sort of average energy and stereochemical state. Throughout its historical development, however, chemical kinetics has become increasingly concerned with presenting a more detailed molecular picture, although the ultimate goal has not yet been achieved, even for relatively simple reactions.

Thermodynamics gives little information about the mechanism of chemical reactions, but chemical kinetics provides an approach for obtaining a reaction mechanism. In principle, kinetic properties should be predictable from quantum and statistical mechanics and kinetic theory; however, the difficulty of treating time-dependent problems, in general, and of knowing the nonequilibrium energy distributions has made it extremely difficult to develop a rigorous and a generally usable theory of chemical kinetics. Several useful approximate theories have been developed, but the elucidation of reaction mechanisms proceeds almost exclusively through experimental work at the present time.

In this book we shall be concerned with two problems:

(1) a critical (but concise) presentation of currently accepted methods of proceeding from rate measurements to mechanisms and of interpreting the results in terms of existing theories, and

(2) a presentation of some of the currently active research topics in chemical kinetics.

These selected topics should provide a firm foundation for further study of modern chemical kinetics.

1-2 DEFINING KINETIC SYSTEMS

Before the rate of a reaction can be meaningfully discussed, the system under consideration must be precisely defined. In particular, the system can be either open or closed. In a closed system, matter is neither gained nor lost, while in an open system, matter may be exchanged with the surroundings. For the most part, we shall be concerned with closed constant-volume systems both because they are much easier to handle experimentally and theoretically and because they are most frequently encountered in the laboratory.

Another factor to be considered is the thermal state of the system. In practice, an effort is usually made to work with isothermal systems; however, if the reaction of interest is sufficiently exothermic, it may be impossible to maintain an isothermal state. In the extreme case of rapid exothermic reactions, e.g., flames, explosions, etc., the system is best described as adiabatic rather than isothermal.

A final factor to be considered is the homogeneity of the system. Although heterogeneous reactions are of considerable interest, e.g., surface catalysis, they will not be discussed here. The experimental problem of establishing the homogeneity of a system is not trivial, since often the walls of the vessel containing the reaction mixture can cause heterogeneous effects to be of importance.

1-3 REACTION RATES AND RATE LAWS

In a closed constant-volume system the rate of a chemical reaction can be defined simply as the rate of change with time of the concentration of any of the reactants or products. The concentration can be expressed in any convenient units of quantity per unit volume, e.g., moles per liter, moles per cubic centimeter, or grams per cubic centimeter. The rate will be defined as a positive quantity, regardless of the component whose concentration change is measured. As an example, consider the generalized chemical reaction

$$a\mathrm{A} + b\mathrm{B} \to c\mathrm{C} + d\mathrm{D} \tag{1-1}$$

The rate can be expressed as $-dA/dt$, $-dB/dt$, dC/dt, or dD/dt, where A, B, C, and D designate the concentrations in arbitrary units. (The parentheses usually used to designate concentrations will be omitted if no confusion is caused by this omission; for the sake of convenience, we shall usually use the units of moles per liter.) For the rate of a reaction to be independent of the component used to describe the rate, the stoichiometry of the reaction must be considered. Thus a unique rate of reaction consistent with the specified stoichiometry can be readily defined for reaction (1-1) as

$$R = -\frac{1}{a}\frac{dA}{dt} = -\frac{1}{b}\frac{dB}{dt} = \frac{1}{c}\frac{dC}{dt} = \frac{1}{d}\frac{dD}{dt} \qquad (1\text{-}2)$$

Although this definition of reaction rate has not been universally adopted, it will be used throughout this book.

If the restriction of constant volume is removed, two additional effects (neglecting convection) cause the concentration c to change: diffusion through the system and a change in volume V of the system. This can be expressed mathematically by the equation

$$dc = \left(\frac{\partial c}{\partial t}\right)_{V,D} dt + \left(\frac{\partial c}{\partial t}\right)_{V,R} dt + \left(\frac{\partial c}{\partial V}\right)_{R,D} dV \qquad (1\text{-}3)$$

where the subscripts V, D, and R designate no volume change, no diffusion, and no chemical reaction, respectively. If c is the number of moles per unit volume n/V,

$$\frac{dc}{dt} = \frac{1}{V}\frac{dn}{dt} - \frac{n}{V^2}\frac{dV}{dt} \qquad \text{and} \qquad \left(\frac{\partial c}{\partial V}\right)_{R,D} = -\frac{n}{V^2}$$

From the definition of reaction rate in a closed system

$$\left(\frac{\partial c}{\partial t}\right)_{V,D} = \pm aR$$

where a is the stoichiometric coefficient from the equation for the overall chemical reaction [cf. Eqs. (1-1) and (1-2)], and where the plus sign applies to products, the minus sign to reactants. Also, Fick's second law states that

$$\left(\frac{\partial c}{\partial t}\right)_{R,V} = \nabla^2(Dc)$$

where D is the diffusion coefficient. Combining all these equations, we obtain

$$\frac{1}{V}\frac{dn}{dt} = \pm aR + \nabla^2(Dc) \qquad (1\text{-}4)$$

In the case of a constant-volume system without diffusion,

$$\frac{1}{V}\frac{dn}{dt} = \frac{dc}{dt} = \pm aR$$

exactly as previously given. For a flow system of constant cross-sectional area A, the specific volume is certainly not constant in gaseous systems, and even in liquids it is not necessarily constant. Therefore for a steady state in which the mass flow docs not change with time,

$$\frac{dn}{dt} = \frac{dn}{dx}u$$

and

$$\frac{1}{V}\frac{dn}{dx}u = \frac{1}{Ax}\frac{dn}{dx}u = \pm aR + \nabla^2(Dc) \qquad (1\text{-}5)$$

where u is the linear flow velocity. In such a system with no diffusion, n can be measured at various values of x, and R can be calculated directly from the value of dn/dx at a fixed value of x. Alternatively, if the dependence of R on the concentrations of reactants and products is known, Eq. (1-5) can often be integrated. Flow experiments are frequently used for kinetic studies in both liquids and gases.

In general, the reaction rate can be a function of all the species present in a reaction mixture. Thus

$$R = f(c_1, c_2, \ldots, c_j) \qquad (1\text{-}6)$$

This equation is called the rate law for a given reaction. In general, the form of the rate law is determined by experiment and cannot be predicted from the stoichiometric equation for the overall reaction. For example, the rate law for the reaction [1]

$$H_2 + Br_2 \rightarrow 2HBr$$

is
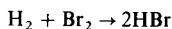
$$R = \frac{1}{2}\frac{d}{dt}(HBr) = \frac{\ell(H_2)(Br_2)^{1/2}}{1 + \ell'(HBr)/(Br_2)} \qquad (1\text{-}7)$$

One of the objectives of experimental kinetics is to propose a reasonable mechanism which will conform to the experimentally observed rate law.

In many cases, the rate equation takes the particularly simple form of a constant times the product of powers of concentrations so that

$$R = f(c_1, c_2, \ldots, c_j) = \ell c_1^{n_1} c_2^{n_2} \cdots c_j^{n_j} \qquad (1\text{-}8)$$

In such cases the reaction order is defined as the sum of the exponents ($\sum_{i=1}^{j} n_i$), and the reaction order with respect to any one component is simply the exponent associated with the particular component in question. Of course, the order of the reaction gives no information per se concerning the molecularity or number of molecules involved in the various steps in the reaction mechanism. The constant k appearing in the rate equation (1-8) is called the rate constant, and simple dimensional analysis shows that it must have the units of concentration$^{1-\Sigma n_i}$ time^{-1}. For example, if $\sum n_i = 1$, the units of the rate constant are time^{-1} (sec^{-1}, min^{-1}, etc.); if $\sum n_i = 2$, the units are concentration^{-1} time^{-1} (M^{-1} sec^{-1}, etc.).

The reaction order is not necessarily an integer. For example, under certain conditions, the reaction

$$CH_3CHO \rightarrow CH_4 + CO$$
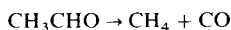
has a rate law with reaction order $\frac{3}{2}$ [2]:

$$-\frac{d}{dt}(CH_3CHO) = k(CH_3CHO)^{3/2}$$

In the case of the H_2–Br_2 reaction, the concept of reaction order is clearly without meaning, except under limiting conditions where one or the other of the terms in the denominator of the rate law [Eq. (1-7)] is dominant.

The rate of a chemical reaction is usually not measured directly; instead, the concentration of one of the reactants or products is determined as a function of time. A common procedure for determining the reaction order is to compare the experimental results with integrated rate equations for reactions of different orders. This can be best illustrated by integrating several particular rate equations as examples.

For a first-order rate equation,

$$-\frac{dc}{dt} = kc \tag{1-9}$$

This equation can be integrated easily by separating the variables and using integration limits such that at $t = 0$, $c = c_0$ and at $t = t$, $c = c$. The result is

$$\ln(c_0/c) = kt \tag{1-10}$$

If the reaction being studied is first order, a plot of $\ln c$ versus time should be a straight line with a slope of $-k$. Often the dependent variable chosen is the decrease in concentration of reactant. If this variable is designated as x and c_0 is the initial concentration,

$$\frac{dx}{dt} = k(c_0 - x) \qquad \text{and} \qquad \ln \frac{c_0}{c_0 - x} = kt$$

For a reaction second order with respect to one component,

$$-\frac{dc}{dt} = kc^2 = \frac{dx}{dt} = k(c_0 - x)^2 \tag{1-11}$$

and the integrated rate equation is

$$\frac{1}{c} - \frac{1}{c_0} = kt = \frac{1}{c_0 - x} - \frac{1}{c_0} \tag{1-12}$$

so that a plot of $1/c$ versus t should be linear for a second-order reaction. If the reaction is second order overall but first order with respect to each of two reactants consumed in equimolar amounts, that is, $A + B \to$ products,

$$\frac{dx}{dt} = k(A_0 - x)(B_0 - x) \tag{1-13}$$

For $A_0 = B_0 = c_0$, the integrated equation is exactly the same as given above, and for $A_0 \neq B_0$

$$\frac{1}{B_0 - A_0} \ln \frac{A_0(B_0 - x)}{B_0(A_0 - x)} = kt \tag{1-14}$$

In this particular case, the advantage of using the dependent variable x is clearly indicated. In a similar manner, integrated rate equations can be obtained for more complex reaction orders. For example, a reaction of nth order ($n > 0$, $\neq 1$) with respect to a single reactant has the rate law

$$\frac{dx}{dt} = k(c_0 - x)^n \tag{1-15}$$

and integration yields

$$\frac{1}{n-1} \left[\frac{1}{(c_0 - x)^{n-1}} - \frac{1}{c_0^{n-1}} \right] = kt \tag{1-16}$$

An alternative method of determining the reaction order is to measure the half-life $t_{1/2}$ as a function of initial concentrations. The half-life is simply the time necessary for x to become equal to one-half the initial concentration. (Any other fraction of the initial concentration would serve equally well.) From the integrated rate equations, it can be seen that for a first-order reaction [cf. Eq. (1-10)]

$$t_{1/2} = (\ln 2)/k \tag{1-17}$$

while for reactions of order n with $n > 1$ [cf. Eq. (1-16)]

$$t_{1/2} = \frac{1}{k(n-1)} \frac{2^{n-1} - 1}{c_0^{n-1}} \tag{1-18}$$

Thus the dependence of $t_{1/2}$ on the initial concentration determines the reaction order directly.

Still another method of determining reaction order is the method of initial rates. This method involves the direct measurement of the derivative dx/dt as the corresponding ratio of finite increments $\Delta x/\Delta t$. The fraction reacted is kept as small as possible, usually 0.1 or less. If a measurement is made at two different initial concentrations of any one component, the concentrations of the other reactants being held constant, the reaction order with respect to that component can be determined. For example, if the two rates and corresponding initial concentrations are designated as $(\Delta x/\Delta t)_1$, $(\Delta x/\Delta t)_2$, and (A_1), (A_2), then for a rate law of the form given in Eq. (1-8),

$$\left(\frac{\Delta x}{\Delta t}\right)_1 = k A_1^{n_1} B^{n_2} C^{n_3} \cdots, \qquad \left(\frac{\Delta x}{\Delta t}\right)_2 = k A_2^{n_1} B^{n_2} C^{n_3} \cdots$$

Solving for n_1, we obtain

$$n_1 = \frac{\log(\Delta x/\Delta t)_1 - \log(\Delta x/\Delta t)_2}{\log A_1 - \log A_2} \qquad (1\text{-}19)$$

The procedure outlined above can be used to determine all the exponents $n_1, n_2, n_3, \ldots$, and the rate constant can be evaluated. The advantage of this method is that complex rate equations, which may be difficult to integrate, can be handled in a convenient manner. Also, the reverse reaction can be completely neglected, provided that initial velocities are actually measured or are obtained by an appropriate extrapolation. For reactions having a simple rate law, i.e., first order, second order, etc., the methods discussed previously are more precise.

Another useful approach for determining the experimental rate law is the isolation method. With this method all of the reactants except one are present in excess. The apparent order of the reaction will be with respect to the one "isolated" reactant since the concentrations of those present in excess will be essentially constant during the course of the reaction. The reaction order with respect to each reactant can be determined by this technique. The primary shortcoming of the isolation method is that for a complex mechanism, the mechanism itself may be altered by the large changes in concentration required for "isolation" of each reactant. Other methods exist for determining the rate law but are not discussed here.

## 1-4 EXPERIMENTAL METHODS

Although general discussions of experimental methods are seldom profitable, some mention of this subject should be made. Throughout the history of kinetics, the development of ingenious new experimental techniques has

produced many of the great advances. Some recent examples will be discussed in considerable detail later in this book. The most desirable analytical methods are those which give a continuous and rapid measurement of the concentration of a specific component. However, it is really necessary only to be able to measure some property of the system which indicates the extent of the chemical reaction occurring. Thus, for example, changes in total pressure and volume can be frequently utilized in kinetic studies. In fact, any property linearly related to the concentration can be conveniently used. This can easily be seen by introducing the concept of the fraction reacted y which is equal to $(c_0 - c_t)/(c_0 - c_\infty)$, where the subscripts refer to the time. For example, $y = x/c_0$ and $\ln(1 - y) = -\ell t$ for an irreversible first-order reaction. Now if the property measured P_t is equal to $mc_t + q$, where m and q are constants, then it can be readily seen that

$$y = (P_0 - P_t)/(P_0 - P_\infty) \tag{1-20}$$

Examples of suitable properties P are conductance, absorbance, and optical rotation.

Often all the concentrations of reactants and products are linear functions of the same physical property, e.g., pressure, conductance. In this case, detailed analysis can become somewhat complex. As a particular example consider the following prototype reaction, which goes to completion:

$$aA + bB \rightarrow gG$$
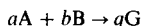
For the reaction mixture,

$$P_t = m_A c_{At} + m_B c_{Bt} + m_G c_{Gt} + q_A + q_B + q_G$$

If we now introduce the reaction variable x and the initial concentrations of A and B, setting that of G equal to zero,

$$P_t = m_A(A_0 - ax) + m_B(B_0 - bx) + m_G gx + q_A + q_B + q_G$$

and

$$P_\infty = m_B\left(B_0 - \frac{bA_0}{a}\right) + \frac{m_G gA_0}{a} + q_A + q_B + q_G$$

assuming A is the limiting reagent. Then

$$y = \frac{P_0 - P_t}{P_0 - P_\infty} = \frac{m_A ax + m_B bx - m_G gx}{m_B bA_0/a - m_G gA_0/a + m_A A_0/a} = \frac{x}{A_0/a}$$

Applications to other reaction mechanisms can be carried out in a similar manner.