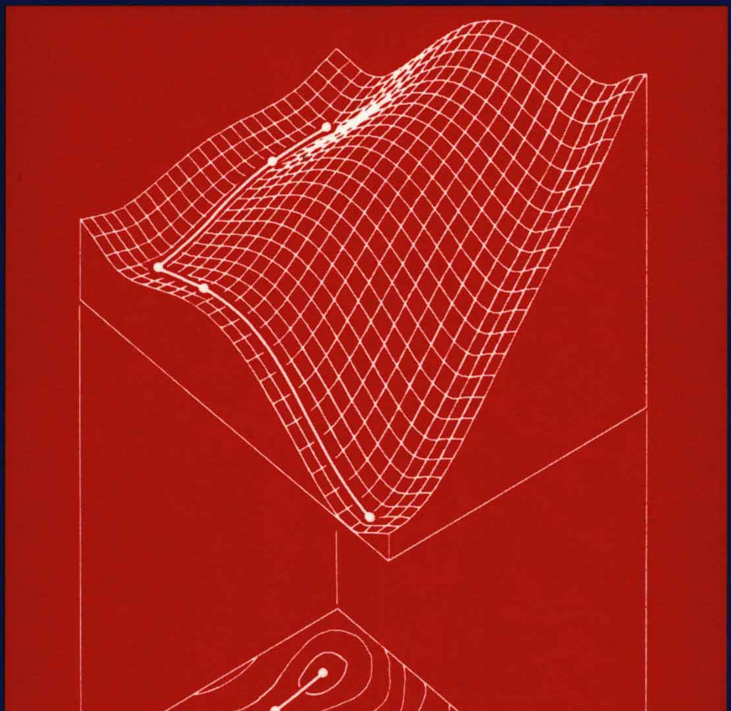
CHEMICAL KINETICS AND DYNAMICS

SECOND EDITION



Jeffrey I. Steinfeld · Joseph S. Francisco
William L. Hase

Chemical Kinetics and Dynamics

Second Edition

Jeffrey I. Steinfeld
Massachusetts Institute of Technology

Joseph S. Francisco
Purdue University

William L. Hase
Wayne State University

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Preface

The first edition of *Chemical Kinetics and Dynamics,* which appeared in 1989, was an attempt to combine the essential content of classical chemical kinetics with the new developments in molecular dynamics which had transformed both our understanding of and experimental approach to the study of chemical reaction dynamics. At that time, the principal focus of the study of chemical reactions had shifted from the macroscopic treatment of empirical kinetics to the microscopic, molecular viewpoint of chemical dynamics. The microscopic approach had stimulated new experimental and theoretical developments, making chemical dynamics one of the most active fields of physical chemistry. Most of the chemical kinetics textbooks then available emphasized either the macroscopic kinetics or microscopic dynamics aspect, often at the expense of the other. We set about to cover both older and newer aspects of chemical reaction processes as comprehensively as possible, with the aim of illustrating the interconnections between phenomenological chemical kinetics and molecular reaction dynamics. The treatment was intended to be accessible to advanced undergraduates who had completed an introductory course in physical chemistry and to beginning graduate students, while serving as an entry point into the large and ever-growing research literature on chemical kinetics and reaction dynamics.

This approach proved to be a successful one, as attested to by favorable reviews and several subsequent imitations. Since the first edition appeared, a number of significant developments have occurred in the study of chemical reaction dynamics, both at the fundamental molecular level and in applications to complex systems. One such development is vastly greater computational power, which makes possible accurate calculation of potential energy surfaces, solution of classical or quantum-mechanical equations of motion on such surfaces, and integration of large coupled sets of kinetic equations, such as are encountered in atmospheric chemistry. New experimental techniques include refinement of laser and molecular-beam techniques to probe state-to-state kinetics, reactant orientation, vector correlations of product molecule distributions, and the use of ultrashort laser pulses to obtain real-time information on chemical reactions, including attempts to characterize the elusive Transition State.

We have tried to incorporate a number of these new developments in the present edition, without, however, eliminating the core experimental and theoretical bases of chemical kinetics. The text begins with an exposition of the basic principles of chemical kinetics, followed by a description of current experimental and analytic techniques in kinetics. The treatment includes reactions in the gas phase, in liquids, and at catalytic surfaces. The transition to the microscopic level is made by introducing molecular scattering and potential energy surfaces. Following a treatment of statistical reaction rate theories (transition-state and RRKM treatments for bimolecular and unimolecular reactions, respectively), the analysis of multilevel and multicomponent kinetic systems is carried out using master equation and information-theoretical methods. The text concludes with a treatment of important, real-world complex kinetic systems, viz., atmospheric and combustion chemistry. In order to keep the revised edition at a manageable length, some of the topics considered in the first edition, such as Laplace Transforms and information theory, have been condensed (but not eliminated). New topics covered in this edition include experimental tests and theoretical models of the $H + H_2$ reaction; current understanding of stratospheric chemistry, including heterogeneous processes; and the aforementioned attempts at observation of the Transition State region by "Femtochemistry" and electron detachment spectroscopy.

The background assumed is a basic knowledge of physical chemistry and enough mathematics to be able to set up and solve systems of linear differential equations. When advanced techniques, such as Laplace Transforms, matrix methods, or information theory are utilized, a brief introduction is provided in the text. The book is intended to provide students with the necessary background to delve into current research topics using the journal and review literature. To this end, extensive chapter references and bibliographies are provided. There is also a large number of problems and exercises, some of which involve numerical procedures. Please note that an Instructor's Manual for this text is available, containing problem solutions, sample computer programs, and suggestions for optimal use of the text for several different course syllabi. The Instructor's Manual may be ordered directly from the publisher: request ISBN 0-13-080605-6.

This book is based on a series of lectures given over a number of years to students at the Massachusetts Institute of Technology, Wayne State University, and Purdue University. We would like to express our appreciation to the numerous reviewers, colleagues, and students who have provided material for incorporation into the text, as well as pointing out errors in the text, problems, and problem solutions of the first edition; all such corrections have been incorporated in the present version, we hope without introducing new errors. Some of these contributors are T. Baer, S. Chapman, B. J. Garrison, P. Gaspar, R. G. Gilbert, D. T. Gillespie, D. M. Hirst, J. T. Hynes, S. R. Leone, R. D. Levine, R. Lucchese, W. H. Miller, M. Molina, J. Parson, B. S. Rabinovitch, H. Rabitz, G. C. Schatz, D. G. Truhlar, and J. C. Tully. We would like to thank John Challice and Matthew Hart of Prentice Hall for their skillful management of the revision and publication process, and our colleagues, friends, and families for their forbearance while all this was going on.

J. I. STEINFELD
J. S. FRANCISCO
W. L. HASE

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CHAPTER 1

Basic Concepts of Kinetics

> "Nothing *is* in this world, because everything is in a state of becoming something else" —Heraclitus (540–480 B.C.E.), *Theaetetus*

Among the most familiar characteristics of a material system is its capacity for *chemical change.* In a chemistry lecture, the demonstrator mixes two clear liquids and obtains a colored solid precipitate. Living organisms are born, grow, reproduce, and die. Even the formation of planetary rocks, oceans, and atmospheres consists of a set of chemical reactions. The time scale for these reactions may be anywhere from a few femtoseconds (10^{-15} sec) to geologic times (10^9 years, or 10^{+16} sec).

The science of *thermodynamics* deals with chemical systems at equilibrium, which by definition means that their properties do not change with time. Most real systems are not at equilibrium and undergo chemical changes as they seek to approach the equilibrium state. *Chemical kinetics* deals with changes in chemical properties in time. As with thermodynamics, chemical kinetics can be understood in terms of a continuum model, without reference to the atomic nature of matter. The interpretation of chemical reactions in terms of the interactions of atoms and molecules is frequently called *reaction dynamics*. A knowledge of the dynamic basis for chemical reaction has, in fact, permitted us to design and engineer reactions for the production of an enormous number of compounds which we now regard as essential in our technological society.

We begin our study of chemical kinetics with definitions of the basic observable quantities, which are the concentrations of the chemical components in a system, and how these concentrations change with time.

1.1 DEFINITION OF THE RATE OF A CHEMICAL REACTION

Chemical kinetics may be described as the study of chemical systems whose composition changes with time. These changes may take place in the gas, liquid, or solid phase of a substance. A reaction occurring in a single phase is usually referred to as a *homogeneous* reaction, while a reaction which takes place at an interface between two phases is known as a *heterogeneous* reaction. An example of the latter is the reaction of a gas adsorbed on the surface of a solid.

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The chemical change that takes place in any reaction may be represented by a *stoichiometric equation* such as

$$aA + bB \rightarrow cC + dD \tag{1-1}$$

where *a* and *b* denote the number of moles of reactants A and B that react to yield *c* and *d* moles of products C and D. Various symbols are used in the expression which relates the reactants and products. For example, the formation of water from hydrogen and oxygen may be written as the balanced, irreversible chemical reaction

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1-2}$$

In this simple example, the single arrow is used to indicate that the reaction proceeds from the left (reactant) side as written: water does not spontaneously decompose to form hydrogen and oxygen. A double arrow in the stoichiometric equation is often used to denote a reversible reaction, that is, one which can proceed in either the forward or the reverse direction; an example is

$$H_2 + I_2 \rightleftarrows 2HI \tag{1-3}$$

While each of equations (1-2) and (1-3) describes an apparently simple chemical reaction, it so happens that neither of these reactions proceeds as written. Instead, the reactions involve the formation of one or more *intermediate* species, and include several steps. These steps are known as *elementary* reactions. An elementary reaction is one in which the indicated products are formed directly from the reactants, for example, in a direct collision between an A and B molecule; intuitively, they correspond to processes occurring at the molecular level. In the hydrogen-oxygen reaction, a key elementary reaction is the attack of oxygen atoms on hydrogen molecules given by

$$O + H_2 \rightarrow OH + H$$

while in the hydrogen-iodine reaction it is

$$2I + H_2 \rightarrow H_2I + I$$

The details of these reactions are discussed in sections 14.2 and 2.3.2, respectively. In the meantime, note here that they involve atoms (O, I), free radicals (OH), and/or unstable intermediates (H_2I); this is often the case with elementary reactions.

The change in composition of the reaction mixture with time is the *rate of reaction, R*. For reaction 1-1, the rate of consumption of reactants is

$$R = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} \tag{1-4}$$

A standard convention in chemical kinetics is to use the chemical symbol enclosed in brackets for species concentration; thus, [X] denotes the concentration of X. The negative signs in equation (1-4) indicate that during the course of the reaction the concentration of reactants decreases as the reactants are consumed; conversely, a positive sign indicates that the concentration of products increases as those species are formed. Consequently, the rate of formation of products C and D can be written as

$$R = +\frac{1}{c}\frac{d[\mathrm{C}]}{dt} = +\frac{1}{d}\frac{d[\mathrm{D}]}{dt} \tag{1-5}$$

The factors, a, b, c, and d in equations (1-4) and (1-5) are referred to as the *stoichiometric coefficients* for the chemical entities taking part in the reaction. Since the concentrations of reactants and products are related by equation (1-1), measurement of the rate of change of any one of the reactants or products would suffice to determine the rate of reaction R. In reaction (1-2), the rate of reaction would be

$$R = -\frac{1}{2}\frac{d[\mathrm{H_2}]}{dt} = -\frac{d[\mathrm{O_2}]}{dt} = +\frac{1}{2}\frac{d[\mathrm{H_2O}]}{dt} \tag{1-6}$$

A number of different units have been used for the reaction rate. The dimensionality of R is

$$[\text{amount of material}][\text{volume}]^{-1}[\text{time}]^{-1}$$

or

$$[\text{concentration}][\text{time}]^{-1}$$

The standard SI unit of concentration is mole per cubic decimeter, abbreviated mol dm^{-3}. In the older literature on kinetics, one frequently finds the equivalent unit mol liter^{-1} for reactions in solution, and mol cm^{-3} for gas phase reactions. The SI unit is preferred, and should be used consistently. Multiplying moles cm^{-3} by Avogadro's Number (6.022×10^{23}) gives the units molecules cm^{-3}, which is still extensively used and, indeed, is convenient for gas phase reactions.

A subcommittee of the International Union of Pure and Applied Chemistry chaired by Laidler has attempted to standardize units, terminology, and notation in chemical kinetics.[1] We have attempted to follow the subcommittee's recommendations in this text.

1.2 ORDER AND MOLECULARITY OF A REACTION

In virtually all chemical reactions that have been studied experimentally, the reaction rate depends on the concentration of one or more of the reactants. In general, the rate may be expressed as a function f of these concentrations,

$$R = f([\mathrm{A}],[\mathrm{B}]) \tag{1-7}$$

In some cases the reaction rate also depends on the concentration of one or more intermediate species, e.g., in enzymatic reactions (see chapter 5). In other cases the rate expression may involve the concentration of some species which do not appear in the stoichiometric equation (1-1); such species are known as *catalysts,* and will be discussed in chapter 5. In still other cases, the concentration of product molecules may appear in the rate expression.

The most frequently encountered functional dependence given by equation (1-7) is the rate's being proportional to a product of algebraic powers of the individual concentrations, i.e.,

$$R \propto [\mathrm{A}]^m[\mathrm{B}]^n \tag{1-8}$$

The exponents m and n may be integer, fractional, or negative. This proportionality can be converted to an equation by inserting a proportionality constant k, thus:

$$R = k[\mathrm{A}]^m[\mathrm{B}]^n \tag{1-9}$$

This equation is called a *rate equation* or *rate expression.* The exponent m is the *order* of the reaction with respect to reactant A, and n is the order with respect to reactant B. The proportionality constant k is called the *rate coefficient.* The overall order of the reaction is simply $p = m + n$. A generalized expression for the rate of a reaction involving K components is

$$R = k\prod_{i=1}^{K} c_i^{ni} \tag{1-10}$$

The product is taken over the concentrations of each of the K components of the reaction. The reaction order with respect to the ith component is n_i, $p = \Sigma_{i=1}^{K} n_i$ is the overall order of the reaction, and k is the rate constant.

In equation (1-10), k must have the units

$$[\text{concentration}]^{-(p-1)}[\text{time}]^{-1}$$

so for a second-order reaction, i.e., $m = n = 1$ in equation (1-8), the units would be $[\text{concentration}]^{-1}[\text{time}]^{-1}$, or $\mathrm{dm^3mol^{-1}sec^{-1}}$ in SI units. Note that the units of liter $\mathrm{mol^{-1}sec^{-1}}$ are frequently encountered in the older solution-kinetics literature, and $\mathrm{cm^3mol^{-1}sec^{-1}}$ or $\mathrm{cm^3molecule^{-1}sec^{-1}}$ are still encountered in the gas-kinetics literature.

Elementary reactions may be described by their *molecularity,* which specifies the number of reactants that are involved in the reaction step. If a reactant spontaneously decomposes to yield products in a single reaction step, given by the equation

$$\mathrm{A} \rightarrow \text{products} \tag{1-11}$$

the reaction is termed *unimolecular.* An example of a unimolecular reaction is the dissociation of N_2O_4, represented by

$$\mathrm{N_2O_4 \rightarrow 2NO_2}$$

If two reactants A and B react with each other to give products, i.e.,

$$\mathrm{A + B} \rightarrow \text{products} \tag{1-12}$$

the reaction is termed *bimolecular.* An example of a bimolecular reaction would be a metathetical atom-transfer reaction such as

$$\mathrm{O + H_2 \rightarrow OH + H}$$

or

$$F + H_2 \rightarrow HF + H$$

Both of these reactions are discussed in subsequent chapters.

Three reactants that come together to form products constitute a *termolecular* reaction. In principle, one could go on to specify the molecularity of four, five, etc., reactants involved in an elementary reaction, but such reactions have not been encountered in nature. The situation reflects the molecular bases of elementary reactions. A single, suitably energized molecule can decompose according to equation (1-11); such unimolecular processes are discussed in chapter 11. A collision between two molecules can lead to a bimolecular reaction according to equation (1-12); this is further discussed in chapters 8 and 10. At moderate to high gas pressures, termolecular processes can occur, such as three-body recombination, i.e.,

$$A + B + M \rightarrow AB + M \tag{1-13}$$

However, physical processes involving simultaneous interaction of four or more independent particles are so rare in chemical kinetics as to be completely negligible.

For an elementary reaction, the molecularity and the overall order of the reaction are the same. Thus, a bimolecular elementary reaction is second order, a termolecular reaction third order, and so on. The reverse is not always true, however. For example, the hydrogen-iodine reaction (1-3) is second order in both directions, but bimolecular reactions between H_2 and I_2, and between two HI molecules, are thought not to occur. Instead, the reaction consists of several unimolecular, bimolecular, and possibly termolecular steps (see chapter 2).

A further distinction between molecularity and reaction order is that, while molecularity has only the integer values 0, 1, 2, and 3, order is an experimentally determined quantity which can take on noninteger values. In principle, these values could be any number between $-\infty$ and $+\infty$, but values between -2 and 3 are usually encountered in practice. Negative orders imply that the component associated with that order acts to slow down the reaction rate; such a component is termed an *inhibitor* for that reaction. Fractional values of the reaction order always imply a complex reaction mechanism (see section 1.6). An example of a fractional-order reaction is the thermal decomposition of acetaldehyde given by

$$CH_3CHO \xrightarrow{300-800°C} CH_4 + CO \tag{1-14}$$

which has a 3/2 reaction order, i.e.,

$$\frac{d[CH_4]}{dt} = (\text{constant})[CH_3CHO]^{3/2} \tag{1-15}$$

Similarly, under certain conditions the reaction of hydrogen with bromine

$$H_2 + Br_2 \rightarrow 2HBr \tag{1-16}$$

has a 3/2 reaction order, first order in $[H_2]$ and 1/2 order in $[Br_2]$:

$$\frac{d[HBr]}{dt} = (\text{constant})[H_2]\,[Br_2]^{1/2} \tag{1-17}$$

Under other conditions, reaction (1-16) can display an even more complicated behavior, *viz.*,

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{(\mathrm{constant})[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{1 + (\mathrm{constant}')[\mathrm{HBr}]} \tag{1-18}$$

The constants in equation (1-15), (1-17), and (1-18) are clearly not identifiable with an elementary reaction, but instead are phenomenological coefficients obtained by fitting the rate expression to experimental data. Such coefficients are properly termed *rate coefficients,* rather than rate constants. The latter term should be reserved for the coefficients in rate expressions for elementary reactions, which follow a rate expression having the form of equation (1-10).

1.3 INTEGRATED REACTION RATE LAWS

Thus far, we have defined the rate of reaction in terms of concentrations, orders, and reaction rate constants. Next, we consider the time behavior of the concentration of reactants in reactions with simple orders. The time behavior is determined by integrating the rate law for a particular rate expression.

1.3.1 Zero-Order Reaction

The rate law for a reaction that is zero order is

$$R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k \tag{1-19}$$

Zero-order reactions are most often encountered in heterogeneous reactions on surfaces (see chapter 5). The rate of reaction for this case is independent of the concentration of the reacting substance. To find the time behavior of the reaction, equation (1-19) is put into the differential form

$$d[\mathrm{A}] = -kdt \tag{1-20}$$

and then integrated over the boundary limits t_1 and t_2. Assuming that the concentration for A at $t_1 = 0$ is $[\mathrm{A}]_0$, and at $t_2 = t$ is $[\mathrm{A}]_t$, equation (1-20) becomes

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = -k\int_{t_1=0}^{t_2=t} dt \tag{1-21}$$

Hence,

$$[\mathrm{A}]_t - [\mathrm{A}]_0 = -k(t - 0) \tag{1-22}$$

Consequently, the integrated form of the rate expression for the zero-order reaction is

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - kt \tag{1-23}$$

A plot of [A] versus time should yield a straight line with intercept $[\mathrm{A}]_0$ and slope k.

1.3.2 First-Order Reactions

A first-order reaction is one in which the rate of reaction depends only on one reactant. For example, the isomerization of methyl isocyanide, CH_3NC, is a first-order unimolecular reaction:

$$CH_3NC \rightarrow CH_3CN \tag{1-24}$$

This type of equation can be represented symbolically as

$$A \rightarrow B$$

and the rate of disappearance of A can be written as

$$R = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^1 \tag{1-25}$$

Note that the reaction is of order one in the reactant A. Thus, since only one A molecule disappears to produce one product B molecule, $a = 1$ and equation (1-25) becomes

$$-\frac{d[A]}{dt} = k[A] \tag{1-26}$$

Integration of equation 1-26 leads to

$$\begin{gathered} -\int \frac{d[A]}{dt} = k\int dt \\ -\ln[A]_t = kt + \text{constant} \end{gathered} \tag{1-27}$$

If the boundary conditions are such that at $t = 0$ the initial value of [A] is $[A]_0$, the constant of integration in equation (1-27) can be eliminated if we integrate over the boundary limits as follows:

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k\int_0^t dt \tag{1-28}$$

This gives

$$-(\ln[A]_t - \ln[A]_0) = kt \tag{1-29}$$

and hence

$$-\ln[A]_t = kt - \ln[A]_0 \tag{1-30}$$

Thus, the constant in equation (1-27) is just

$$\text{constant} = -\ln[A]_0 \tag{1-31}$$

Equation (1-30) can be written in various forms. Some that are commonly used are

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \tag{1-32a}$$

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