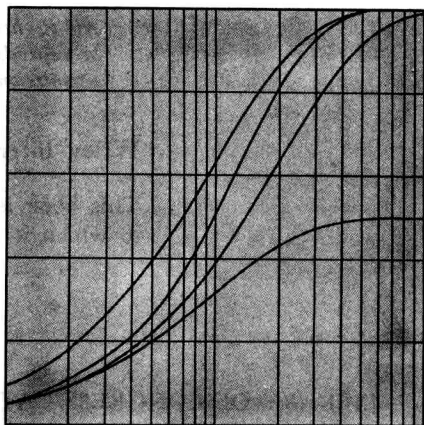Second Edition

Kinetics and Mechanism

A Study of Homogeneous
Chemical Reactions

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and
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PREFACE

This revision was made necessary by the substantial advances in chemical kinetics made during the last eight or nine years. The most important gains have been made in the areas of elementary reactions in the gaseous phase and the study of very rapid chemical reactions. The new edition attempts to do justice to these topics at an introductory level.

Since A. A. F. has succumbed to the siren call of quantum mechanics, the revision is almost entirely the work of R. G. P., who must be blamed for its shortcomings.

Thanks are due Dr. E. W. Schlag for reading much of the revised manuscript and for many helpful suggestions.

RALPH G. PEARSON

Evanston, Illinois
January, 1961

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PREFACE TO THE FIRST EDITION

When we started to write this book we were particularly struck by the fact that the existing textbooks on kinetics treated reaction mechanisms in a rather perfunctory style. There are, of course, excellent books on mechanisms particularly of organic reactions in which some mention of the use and value of kinetics is made. However, there seemed to be no work which showed enough of the intimate relationship between kinetics and mechanism to enable the student to understand exactly how much detail of reaction mechanism can be found from reaction kinetics and to understand what the limitations of the kinetic method of studying mechanism are.

A study of the recent literature will show that the great majority of the work on reaction velocities now being done is primarily concerned with trying to find out exactly in what manner the reactions are proceeding. Thus, while the theories of kinetics, mathematical and experimental details, and the calculation of energetics are all of great importance and, we hope, have not been neglected in this book, a neglect of mechanism would be to ignore the most important application of kinetics. Consequently we have included a great deal of rather detailed stereochemical discussion of the reaction steps.

We have not tried to include a catalogue of all the chief kinds of reactions that may be encountered, but we have tried to select a number of varied and fairly typical examples. Even in this we were regretfully forced to forego discussing a number of topics which might properly be included in a course in reaction kinetics, such as heterogeneous reactions and photochemistry, for example.

We hope that the absence of several such topics will be compensated

for by the added material on mechanism and that we are presenting a work which will be useful as a textbook for courses in kinetics on the graduate level, and as a reference book for those interested in the study of the mechanisms of chemical reactions.

We should like to take this opportunity to thank the following persons who contributed in one way or another to the writing and completion of this book: Professors R. L. Burwell, Jr., L. Carroll King, Ronald P. Bell, Louis P. Hammett, Richard E. Powell, Frank H. Seubold, Frank J. Stubbs, Lars Melander; Misses Elaine Strand, Marianne Fält, Mrs. Lenore Pearson, and Mrs. Faye Frost.

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Evanston, Illinois
*November, 1952*

CONTENTS

1.

INTRODUCTION

Kinetics is a part of the science of motion. In physics the science of motion is termed dynamics and is subdivided into kinematics, which treats of the motion of bodies, and kinetics, which deals with the effect of forces on motion. In chemistry, no such distinction is made. Kinetics deals with the rate of chemical reaction, with all factors which influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism. Chemical kinetics might very well be called chemical dynamics.
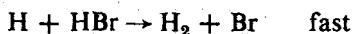
Chemical kinetics with its dynamic viewpoint may be contrasted with thermodynamics with its static viewpoint. Thermodynamics is interested only in the initial and final states of a system; the mechanism whereby the system is converted from one state to another and the time required are of no importance. Time is not one of the thermodynamic variables. The most important subject in thermodynamics is the state of equilibrium, and, consequently, thermodynamics is the more powerful tool for investigating the conditions at equilibrium. Kinetics is concerned fundamentally with the details of the process whereby a system gets from one state to another and with the time required for the transition. Equilibrium can also be treated in principle on the basis of kinetics as that situation in which the rates of the forward and reverse reactions are equal. The converse is not true; a reaction rate cannot be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more fundamental science than thermodynamics. Unfortunately, the complexities are such that the theory of chemical kinetics is difficult to apply with accuracy. As a result, we find that thermodynamics will tell with precision the extent of reaction, but only kinetics will tell (perhaps crudely) the rate of the reaction.

Underlying both chemical kinetics and thermodynamics are the more detailed theories of statistical mechanics and the kinetic-molecular theory, which provide alternative viewpoints for understanding microscopic phenomena in terms of atomic and molecular structure and dynamics. Because of the greater rigor of thermodynamic methods, there has been considerable effort in the last thirty years to approach kinetics from the thermodynamic viewpoint, particularly combined with the methods of statistical mechanics. The important feature of this effort is to treat reaction rates as involving an equilibrium between average molecules and high-energy molecules which are aligned and activated ready for reaction, or between molecules in the initial state and in the so-called "transition state" or "activated complex." Even in such a treatment a fundamental problem remains: calculating the rate of decomposition of the activated complex. Only quantum mechanics seems to offer a complete answer.† In both thermodynamics and kinetics, recourse must eventually be had to quantum mechanics for a calculation of the various energy levels involved.

The science of chemical kinetics may be of interest in itself, as, for example, in determining how changes in environment change the rate of a given reaction. Or, from a practical point of view, one may be interested in the rate of reaction, as in chemical engineering applications. However, of greatest interest to most chemists is the fact that kinetics provides the *most general method of determining the mechanism of reaction.* From a classical point of view (developed chiefly by physical chemists), mechanism of reaction is understood to mean all the individual collisional or other elementary processes involving molecules (atoms, radicals, and ions included) that take place simultaneously or consecutively in producing the observed overall reaction. Compare the mechanism of the two following similar reactions as carried out in the gas phase at elevated temperatures:

$$H_2 + I_2 = 2HI$$
$$H_2 + Br_2 = 2HBr$$
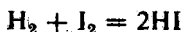
The reaction between hydrogen and iodine is known to take place at bimolecular collisions involving a single molecule of each kind. The reaction of hydrogen and bromine, however, is much more complicated, involving first the dissociation of bromine molecules into atoms followed by reactions between atoms and molecules, as follows:

$$Br_2 \rightleftharpoons 2Br$$
$$Br + H_2 \rightarrow HBr + H \qquad slow$$
$$H + Br_2 \rightarrow HBr + Br \qquad fast$$
$$H + HBr \rightarrow H_2 + Br \qquad fast$$
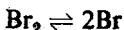
† See for example references 1, 2, and 3 at end of chapter.

From the above examples, it is obvious that the mechanism cannot be predicted from the overall reaction alone. Consider the formation of water from its elements:

$$2H_2 + O_2 = 2H_2O$$
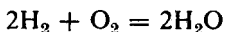
This reaction is often naively assumed to involve reaction at collisions of two hydrogen molecules and one oxygen molecule. This is definitely not true, the mechanism being sufficiently complicated so that it is not yet completely understood.

The above facts concerning the steps involved in the formation of hydrogen bromide and hydrogen iodide, respectively, are examples of the conclusions that can be drawn from kinetic studies. It must not be inferred, however, that kinetics will invariably give a definite answer concerning the individual steps of a chemical reaction. In general, the experimental results of studying the rate of a reaction as a function of concentrations, temperature, and other operating variables can be interpreted in several ways; that is, there are several conceivable mechanisms consistent with the data. Further experimentation may sometimes eliminate certain of these. However, if one mechanism remains which is in agreement with all the known facts, there is no assurance that it is unique or that new experiments will not add evidence discrediting it.

The difficulty is due to the fact that all such postulated mechanisms are essentially theories. The results of kinetic measurements (and other experiments) furnish facts. The mechanism is a mental model devised to explain the facts. Like any theory, a reaction mechanism currently in vogue may be eliminated later by newer facts or by newer concepts of the structure of matter. In spite of this difficulty, many reactions studied kinetically can be explained by a particular set of simple processes which are so reasonable and so in accord with all chemical experience that we accept them as essentially true. The justification for this becomes apparent when it is observed that a mechanism can successfully predict reaction products or the optimum conditions for running a chemical reaction.

There is, in addition to the classical definition already mentioned, a newer concept of reaction mechanism, developed chiefly by organic chemists. This newer concept includes not only a knowledge of all the individual steps in the overall reaction, but also a *detailed stereochemical picture* of each step as it occurs. This implies a knowledge not only of the composition of the activated complex in terms of the various atoms or molecules of reactants, but also of the geometry of the activated complex in terms of interatomic distances and angles. For example, in the conversion of

hypochlorite ion to chlorate it can be shown that the reaction consists of two steps

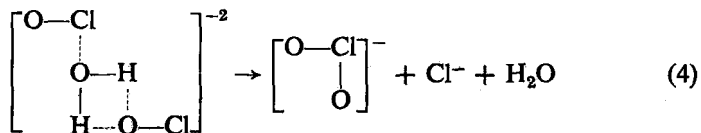$$ClO^- + ClO^- \xrightarrow{slow} ClO_2^- + Cl^- \tag{1}$$

$$ClO_2^- + ClO^- \xrightarrow{fast} ClO_3^- + Cl^- \tag{2}$$
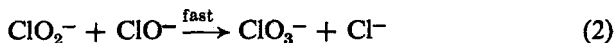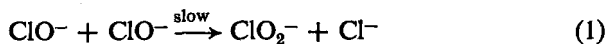
with the formation of chlorite ion the slower, or rate-determining, step, and the formation of chlorate ion a rapid process.[4] This can be deduced from kinetic evidence since the rate of formation of chlorate ion is proportional to the square of the hypochlorite concentration. Furthermore, the chlorite ion can be prepared separately and its rate of reaction with hypochlorite shown to be fast. These facts would have sufficed to fix a probable mechanism according to the older definition. The newer approach adds to the mechanism a picture such as (3) for the transfer of an oxygen atom between ions.

$$\begin{bmatrix} Cl\cdots O-Cl \\ | \\ O \end{bmatrix}^{-2} \rightarrow \begin{bmatrix} Cl-O \\ | \\ O \end{bmatrix}^{-} + Cl^- \tag{3}$$
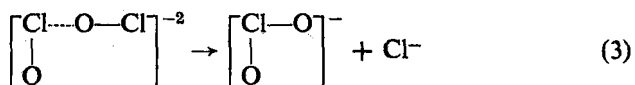
This stereochemical representation is guessed at from chemical intuition and experience. It enables the reaction to be classified as a member of a large class of similar reactions, a nucleophilic displacement of one base (Cl^-) by another (ClO^-). This classification encourages us to focus attention on what is going on and to understand such phenomena as the effect of pH on the rate of reaction, the effect of changing the halogen from chlorine to, say, bromine. We can better understand any one reaction, in other words, by drawing on a large body of information on similar reactions.[5] The stereochemical picture also suggests the possibility that the mechanism may be more complex in that the oxygen atom which leaves one hypochlorite ion may not be the same as that which appears on the other. Thus the solvent might be involved in the oxygen transfer[6] in some such way as shown in (4). In this particular example the products are the

$$\begin{bmatrix} O-Cl \\ \vdots \\ O-H \\ | \quad \vdots \\ H\cdots O-Cl \end{bmatrix}^{-2} \rightarrow \begin{bmatrix} O-Cl \\ | \\ O \end{bmatrix}^{-} + Cl^- + H_2O \tag{4}$$

same whether the solvent is involved or not, and whether (3) or (4) is more accurate may be of theoretical importance only. When we reflect, however, that the hydrolysis of an organic halide may lead to an alcohol with an inversion of original configuration, retention of configuration, or

a mixture of the two, then the necessity for a detailed and pictorial representation of a mechanism becomes more apparent.

Whereas kinetics is very useful in determining the individual steps of a reaction, it is rather limited in giving stereochemical details. Therefore, it is usually necessary to refer to other methods of obtaining information about mechanisms, which are incomplete in themselves and are best used in combination with kinetic evidence. Some of these other methods will be mentioned briefly now with further and more complete illustrations to be given later in the text.

The Products of Reaction

The most important circumstantial evidence as to reaction mechanism is the identity of the products formed. This seems so obvious that it is difficult to believe that kinetic studies have frequently been reported in which the exact nature of the products was unknown. Such, however, is the case. As an example of the type of reasoning involved after the products have been identified, consider the alkaline hydrolysis of a simple ester such as ethyl acetate. The formation of alcohol and an acetate ion indicates reaction of a hydroxide ion with an ester molecule breaking one C—O bond

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + OH^- \rightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + C_2H_5OH \qquad (5)$$
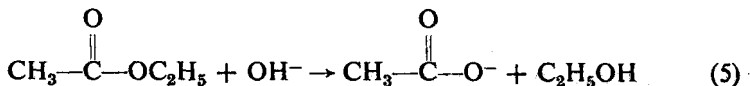
That the reaction goes as indicated could be proved by a kinetic study which shows that the rate of formation of acetate ion is proportional both to the concentration of ester and to the concentration of hydroxide ion.

Stereochemical Evidence

It is to be expected that considerable information as to the intimate details of a mechanism can be gained from the stereochemical evidence, that is, by examining the stereochemistry of the substances reacting and the substances formed. In the reaction above, if an optically active alcohol, RR'CHOH, is used instead of ethyl alcohol in forming the ester, the fact that the original alcohol can be recovered without racemization or inversion after hydrolysis[7] suggests strongly that in both the formation of ester and in its hydrolysis the C—O bond which is involved is the one in which the oxygen atom of the alcohol remains unchanged. It may be said at this point that, so far as reaction mechanism is intended to mean intimate, detailed mechanism, stereochemistry is as important an investigational tool as kinetics.
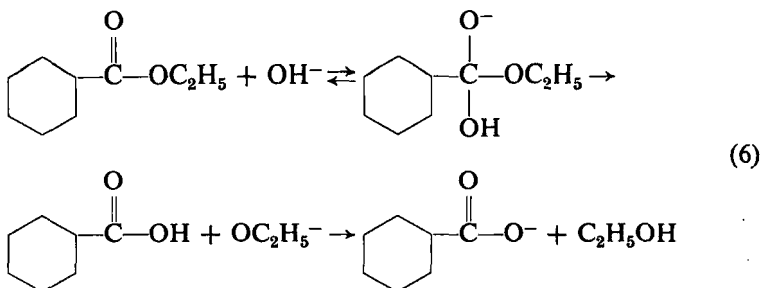
Use of Isotopes

The above conclusion that the bond is broken between the oxygen and the carbonyl carbon is confirmed by the use of hydroxide ion enriched with O^{18}. The heavy oxygen is then found in the anion of the acid rather than in the alcohol.[8] The increased production of isotopes of the more common elements has led to an increasing application of this technique in studying reactions where mechanisms are not easily determined by other means. Thus the question of solvent participation in the hypochlorite-ion reaction could be approached by the use of heavy oxygen water.[6] To be successful in this case it would be necessary to show that oxygen exchange between hypochlorite ion and the solvent was not so rapid as the rate of formation of chlorite ion.

Detection of Short-Lived Intermediates

A method that has been applied chiefly to reactions involving free atoms or radicals which are extremely reactive, and hence short-lived, is the actual demonstration of their existance. This can be done by adding substances (e.g., NO or I_2) to trap the radicals as stable compounds or by observing some specific physical or chemical property (e.g., mass spectrogram, absorption spectrum, or removal of metallic mirrors). A recent and very powerful tool for the study of free radicals is electron paramagnetic resonance (EPR), which measures directly the concentration of radicals and also supplies specific information about their structure. Closely related are photochemical techniques to produce the suspected atoms or radicals and simultaneous study of the reaction rate.

Refinements of Kinetic Methods

Actually no different in method from ordinary kinetic studies, but supplying additional information as to mechanisms, are such devices as studying the effect of substituents on the rate of a given reaction, or the effect of changing the solvent, ionic strength, etc. For example, in the alkaline hydrolysis of esters mentioned earlier, if a series of substituted ethyl benzoates is studied kinetically the influence of substituents on the rate can be used to elucidate the mechanism. It is found that electron-attracting substituents such as the nitro group increase the rate of hydrolysis, whereas electron-repelling substituents such as methoxyl decrease the rate.[9] The interpretation is that increased positive charge on the carbonyl carbon facilitates the addition of the hydroxide ion whose close approach then pushes off the ethoxide ion.

$$\text{(C}_6\text{H}_{11}\text{)}-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + OH^- \rightleftarrows (\text{C}_6\text{H}_{11})-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-OC_2H_5 \rightarrow$$

$$(\text{C}_6\text{H}_{11})-\overset{\overset{\displaystyle O}{\|}}{C}-OH + OC_2H_5^- \rightarrow (\text{C}_6\text{H}_{11})-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + C_2H_5OH$$

(6)

In a similar way, the effect of changing the dielectric constant of the solvent or the ionic strength can be used in conjunction with modern theories to give strong evidence that the reaction is between a negative ion and a neutral, but polar, molecule. Although the mechanism of basic hydrolysis of an ester seems clear enough from the discussion given, the subject will be taken up again in a later chapter. It will then be seen that certain ambiguities still exist, and that in particular the results mentioned above *cannot* be generalized to cover all cases of ester hydrolysis under basic conditions. This is a general result when a type reaction of a class of compounds is being studied unless the reaction type and the class are quite narrowly defined.

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2.

EMPIRICAL TREATMENT
OF REACTION RATES

Kinds of Systems

A closed system, sometimes called static, is one in which no matter is gained or lost, as in a typical reaction in a liquid phase in a flask or in a closed bomb, or in a gas-phase reaction taking place in a reaction vessel of constant volume. An open system, or flow system, involves gain or loss of matter and is exemplified by reactions of a flowing gas in a heated tube or at a solid catalyst, by a flame, and by living organisms where nutrients and metabolic products are exchanged with the surroundings. Closed systems are more convenient in general than open systems, both for precise rate measurements and for theoretical interpretation. It is to be understood in what follows that closed systems are always being considered unless an open system is explicitly indicated. The theory of the open system may be obtained by generalization of the theory of the closed system. There has been an increasing interest in open systems in recent years.†

A closed or an open system may be either homogeneous or heterogeneous, but the open system is usually heterogeneous and may have concentration gradients in the reaction zone which make such reactions quite different from typica. homogeneous reactions. Heterogeneous closed systems are of particular interest in connection with surface catalysis, but, because of their more fundamental value to chemical kinetic theory, homogeneous closed systems will be the principal subject of this treatise.

Isothermal systems are of most significance because temperature can then be considered an independent variable. However, non-isothermal or

† See Chapter 11.

approximately adiabatic systems are sometimes of interest as in connection with rapid exothermic reactions such as flames and explosions where the heat of reaction cannot be conducted away rapidly enough.

Definition of Reaction Rate

The reaction rate is usually defined as the rate of change of concentration of a substance involved in the reaction with a minus or plus sign attached, depending on whether the substance is a reactant or a product. In a general reaction with stoichiometric equation

$$a\text{A} + b\text{B} = g\text{G} + h\text{H}$$
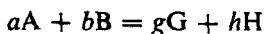
the rate may be expressed by

$$-d[\text{A}]/dt, \quad -d[\text{B}]/dt, \quad +d[\text{G}]/dt, \quad \text{or} \quad +d[\text{H}]/dt$$

where t is time and brackets mean concentration. The sign is attached so that the rate will be positive numerically. A derivative is used because the rate almost invariably changes as time goes on. The use of concentration in the definition rather than the amount of a substance makes the rate an intensive property, that is, independent of size of system.

In stating numerical values of reaction rate, not only must the time and concentration units be given, but also the particular substance whose concentration is involved must be stated because the reaction may use or produce different numbers of moles of the various reactants or products. For example, in the reaction

$$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$$

since two moles of hydrogen react for each mole of oxygen,

$$-d[\text{H}_2]/dt = -2d[\text{O}_2]/dt$$

For the general reaction above it is easily seen that

$$\frac{1}{a}\left(-\frac{d[\text{A}]}{dt}\right) = \frac{1}{b}\left(-\frac{d[\text{B}]}{dt}\right) = \frac{1}{g}\left(\frac{d[\text{G}]}{dt}\right) = \frac{1}{h}\left(\frac{d[\text{H}]}{dt}\right)$$

It is possible to avoid such integral conversion factors in relating different derivative rate expressions by defining rate in terms of equivalent concentration rather than molar concentration. If x is the equivalents per liter that have reacted in time t, then dx/dt is a convenient expression for the rate. The definition of the equivalent must be explicitly stated. Such a variable as x may be called the *reaction variable*.†

Variables other than concentration may be used in defining rate,

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† "Umsatzvariabel" of A. Skrabal, *Homogenkinetik*, Steinkopff, Dresden, 1938.

for examples, pressure as in a gas reaction or optical rotation as in a racemization, inversion, oɪ mutarotation reaction. Such variables are always related to one or more concentrations, usually linearly, and so may be treated as equivalent to concentrations for this purpose. A detailed discussion of such relations is given in the next chapter.

Effect of Concentration on Reaction Rate—Empirical Rate Expressions

The reaction rate at a fixed temperature is a function of the concentrations of some or all of the various components of the system, but usually of only the reactants. If the concentration of a product affects the rate, this effect is called either autoinhibition or autocatalysis. If a substance, neither a reactant nor a product, affects the rate it is called an inhibitor, retarder, sensitizer, or a catalyst, depending on the nature of the effect. The functional relation between rate and concentration is called a rate expression. In general it is not possible to predict the rate expression for a given reaction by just knowing the stoichiometric equation. Although the reactions of hydrogen with iodine and bromine follow similar stoichiometric equations, the rate expressions are of quite different form:

$$\text{For} \quad H_2 + I_2 = 2HI \qquad \frac{d[HI]}{dt} = k[H_2][I_2]$$

$$\text{For} \quad H_2 + Br_2 = 2HBr \qquad \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{\frac{1}{2}}}{1 + k'[HBr]/[Br_2]}$$

This striking difference is accounted for by the different mechanisms of the two reactions mentioned in Chapter 1, the rate expressions being the principal evidence for the postulated mechanisms.

Order of Reaction and Molecularity

Rate expressions that are of the form of a product of powers of concentrations such as

$$-dc_1/dt = kc_1{}^{n_1}c_2{}^{n_2}c_3{}^{n_3}$$

are easier to handle mathematically than expressions of a more complex type, such as that given above for the hydrogen-bromine reaction. For this restricted type of rate expression, and for this type only, there is defined the concept of *order of reaction*, n, where

$$n = n_1 + n_2 + n_3 + \cdots$$

the sum of all the exponents of the concentrations. Also each individual

exponent is called the *order with respect to that component*. For example, the hydrogen-iodine reaction is a second-order reaction, and the order with respect to each reactant separately is one. For the hydrogen-bromine reaction the concept of order does not apply since its rate expression is not of the restricted form required for this concept.

If conditions for a given reaction are such that one or more of the concentration factors are constant or nearly constant during a "run," these factors may be included in the constant k. In this case the reaction is said to be of *pseudo-nth order* or *kinetically of the nth order* where n is the sum of the exponents of those concentration factors which change during the run. This is the situation for catalytic reactions with the catalyst concentration remaining constant during the run, or if there is a buffering action that keeps a certain concentration such as that of the hydrogen ion nearly constant, or if one reactant is in large excess over another so that during the run there is only a small percentage change in the concentration of the former. Take, for example, the inversion of sucrose† catalyzed by strong acids. The rate is given by

$$-d[S]/dt = k[S][H_2O][H^+]$$

where S stands for sucrose. The reaction is third-order. However, since H^+ is a catalyst and its concentration remains constant during a run and also since $[H_2O]$ is essentially constant when water is the solvent, the reaction is pseudo-first-order. If some inert solvent is used and water is present only as a reactant, the reaction would be pseudo-second-order.

The exponents are usually simple positive integers, but occasionally they may be fractional or even negative, depending on the complexity of the reaction. When the order is one, two, or three, there is some confusion in the older literature with the terms unimolecular, bimolecular, and termolecular. These terms, examples of the *molecularity* of a reaction, are intended to indicate the number of molecules involved in a simple collisional reaction process. Molecularity is a theoretical concept, whereas order is empirical. They are generally different numerically. However, as will be shown later, a bimolecular reaction is usually second-order and a termolecular reaction third-order, but the reverse of these statements is less often true.

The k is called the rate constant, or the specific reaction rate. It is seen from the equation that it has dimensions of

$$[\text{conc.}]^{1-n}[\text{time}]^{-1}$$

Commonly used concentration units are moles/liter, moles/cc, molecules/cc,

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† This reaction is of historical interest as it is considered to be the first one studied kinetically. See reference 1 at end of chapter.