

**INVESTIGATION OF  
RATES  
AND MECHANISMS  
OF REACTIONS  
PART I  
3RD EDITION**

**EDWARD S. LEWIS  
EDITOR**

**TECHNIQUES  
OF CHEMISTRY  
VOLUME VI**

# TECHNIQUES OF CHEMISTRY

VOLUME VI

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## INVESTIGATION OF RATES AND MECHANISMS OF REACTIONS

*Third Edition*

*Edited by*

EDWARD S. LEWIS

Department of Chemistry  
Rice University  
Houston, Texas

PART I

*General Considerations and Reactions at  
Conventional Rates*

A WILEY-INTERSCIENCE PUBLICATION

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ARNOLD WEISSBERGER, *Editor*

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VOLUME VI

## INVESTIGATION OF RATES AND MECHANISMS OF REACTIONS

*Third Edition*

# TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

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# INTRODUCTION TO THE SERIES

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Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can easily be recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

*Research Laboratories  
Eastman Kodak Company  
Rochester, New York*

ARNOLD WEISSBERGER



# PREFACE

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This book is to some extent a successor to Part I of Volume VIII of *The Technique of Organic Chemistry*. A new edition was appropriate for several reasons. The first, of course, is that kinetics and mechanisms are continually developing and neither the techniques nor the concepts are static. The new title, which eliminated the restriction to organic chemistry, prompted some changes and additions. Also, a somewhat different editorial philosophy was applied within the severe restriction of applying any editorial philosophy to a multiauthor volume. The thorough review of applications of the various techniques which characterized earlier editions seemed now impossible. The current aim, therefore, has been to select only a few relevant examples illustrative of the various techniques and ideas; some of these are new, some have acquired the status of classics. Comprehensive reviews have been deliberately avoided. We thereby hope to make the chapters more concise, more readable, and of more lasting value. There is a wide spectrum from discussion of detailed experimental techniques to consideration of fairly abstruse theoretical ideas. We trust that each will be of value to someone undertaking work in the area of kinetics and mechanisms.

*Houston, Texas*  
*November 1973*

EDWARD S. LEWIS

**Chapter IV**

Temperature-Jump Methods

GORDON G. HAMMES

**Chapter V**

Pressure-Jump Methods

WILHELM KNOCHE

**Chapter VI**

Electric Field Methods

LEO DE MAEYER and A. PERSOONS

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### Chapter II

Rapid Flow Methods BRITTON CHANCE
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### Chapter III

Theoretical Basis of Relaxation Spectrometry M. EIGEN and LEO DE MAEYER
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# GENERAL METHODS OF RATE AND MECHANISM STUDY

E. S. Lewis

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## 1 COVERAGE OF THIS PART

Among the ways of categorizing chemistry, the one pertinent to this volume is that of dividing chemistry into two areas, in the first of which time is not an important variable and in the second of which time is an essential variable. The familiar time-independent areas of chemistry include problems of molecular structure, both experimental and theoretical; the fields of thermodynamics and of chemical equilibria; and the study of the mechanical, electrical, and optical properties of pure and mixed substances. Among time-dependent areas are studies of transport and—the largest area—the study of the course of chemical reactions. This latter area is the primary subject of this volume.

This distinction becomes less clear when a given area is examined in detail. For example, pressure is apparently time-independent, yet according to the kinetic theory of gases, pressure is determined in part by the velocity of molecules. Similarly, the internal motions of molecules are periodic and time-dependent, yet they are intimately related to thermodynamics through statistical mechanics. The idea of mechanism, which is central to this volume, seems at first sight to be time-independent, but if there is more information than is available from equilibrium information alone, it must pertain to which equilibria can be set up and which can be neglected—that is to say, which processes are fast and which are slow. The relation between rates and mechanism is indeed a very close one. Even spectroscopy can

be influenced by the rates of reaction, and, as we shall see in Part II, some rates can even be measured spectroscopically.

A further and still more arbitrary division between Parts I and II has been made on the basis of reaction rate. Part II will contain techniques, both experimental and theoretical, applicable to very fast reactions. Part I is devoted to methods suitable for measurements by conventional methods, implying the various extensions of methods such as taking a sample from time to time and doing an analysis. The distinction is quite arbitrary, and some overlap is inevitable. We call flow methods, spectral line broadening methods, and relaxation methods *fast*, and conventional sampling methods, pressure or optical absorbency methods with no special mixing methods *slow*. Stopped-flow methods, although of an intermediate range, are for our purposes classified as fast. It will be impossible to keep the separation complete.

Several omissions are deliberate. Among these is the omission of discussion of elementary theories of kinetics, as can be found in any physical chemistry text. The implicit use throughout of transition-state theory justifies a modern theoretical critique in Chapter II.

Reactions within the solid state are not discussed, mostly because the necessary extensive background in the solid state seemed inappropriate.

The kinetics and mechanisms of polymerization have also been omitted. After an early flowering of some aspects of polymerization kinetics, especially free-radical olefin polymerization [1], of great general interest, the subsequent work has been of a much more specialized nature of less general application.

There is no discussion of kinetics where the temperature is in part determined by the exothermicity of the reaction. This is of great concern in large-scale industrial practice and also in consideration of some explosions; this volume is primarily directed toward laboratory practice on a small scale, where isothermal conditions are readily achieved.

No consideration has been given to the techniques for following very slow reactions, in part because these measurements have not been used very much and in part because they are all based on the same principle: The reaction is allowed to proceed to a very small extent of completion; then an analysis for the very small amount of product in the presence of a great deal of reagent will give the reaction rate. The factors that limit the method and the description of a very general and sensitive isotopic-dilution analysis have been discussed [2]. Specialized earlier applications of the method have been used on reactions with half-lives of as much as  $10^5$  yr [3].

Another omission from the earlier edition is the technique of time measurement, on the grounds that a variety of excellent devices are available in any laboratory and the measurement of time is seldom a limiting factor in

accuracy. The experimenter should be warned that among the least accurate timepieces used in the laboratory are some stopwatches, but even here an accuracy of better than 1% (14 min/day) is to be expected.

## 2 REASONS FOR STUDYING RATES AND MECHANISMS

The study of rates and mechanisms can be undertaken for many reasons, some of which are now described.

Reaction rate is of great practical interest in both laboratory and industrial practice. No reaction that takes years to become sensibly complete is particularly useful in making its product, but reactions that are complete in fractions of a second include hazardous explosions. It is clearly necessary to understand the factors controlling the rate at least to some extent before a reaction becomes useful on almost any scale.

An understanding of reaction mechanism allows a more informed extension of the scope of the reaction to new, but mechanistically related, cases, and the understanding of mechanisms of related reactions is a useful way to classify the hosts of known reactions and to remember them.

Many structure determinations are based upon reactions, degradation to simpler molecules of known structure is a standard procedure, and the nature of the reactions themselves give structural clues—for example, about functional groups. Many of the most difficult problems of classical organic-structure determination were in systems in which carbon skeleton rearrangements abounded—for example, the terpenes. These problems have now become more straightforward, because organic chemists have an improved understanding of rearrangement mechanisms and know the circumstances under which they are likely to occur. Even the rate constant itself is sometimes of value in a structure proof if good models for the possible alternative structures are available.

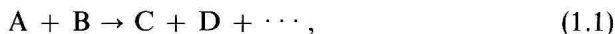
One important outcome of mechanistic studies has been the chemistry of unstable intermediates, of compounds that are normally not isolable. With carbon alone, the chemistry of carbonium ions, carbanions, carbenes, and free radicals constitutes a major part of all of organic chemistry. Of the numerous examples of unstable intermediates only a minute fraction have been isolated, observed, and characterized, and the isolation was usually made possible by the chemistry learned from mechanistic studies.

Finally, as an area of pure science in itself, the study of rates and mechanisms is one of rich variety, concerned with the chemistry of every element and full of experimental challenge. It is an area of chemistry where the practical application of theory lags far behind the realm of experiment, yet at several points theory has had notable successes. One example is in kinetic isotope effects, where the application of theory has been of inestimable use

in understanding the otherwise rather random experimental results. Another is the application of molecular orbital methods to the study of concerted reactions, giving an understanding of stereochemical course and a predictive power not previously available [4].

### 3 MEANING OF RATES AND MECHANISMS

It is necessary to define in usable terms what we mean by reaction rate. At a very early stage it is necessary to distinguish between closed (or batch) systems and open systems, of which flow systems are the most common example. A closed system, in which we wish to study a rate, is one such that all atoms present at the beginning in the system are also present at the end, and only those atoms are present at all times. We can, furthermore, specify that the system be kept at constant volume or at constant pressure, although most solution work is done with an assumption of constant volume even though experimentally it is done at constant pressure. We express the reaction rate as the number of moles (or mass) of a substance formed or destroyed per unit time. With all other factors constant, this rate turns out experimentally to be proportional to the volume of the system, so that the rate is usually measured as the concentration formed or destroyed per unit time. (We exclude here, as being related to other, nonconstant factors, cases of catalysis by the vessel surface and cases in which the reaction in a large volume occurs at a different temperature from that in a small volume because of heat-transfer problems. Heterogeneous systems obviously include special problems.) In solution work, the concentrations are usually expressed in moles per liter and time is preferably expressed in seconds; in the gas phase, concentrations are measured often as partial pressures or even as molecules per cubic centimeter. The definition of *rate* is clear in cases of simple stoichiometry for example,



because the rate can be measured by the rate of formation of C,  $d(C)/dt$  or of D,  $d(D)/dt$  or the disappearance of A or B, and the different ways of measuring the rate are simply related by

$$\frac{d(C)}{dt} = \frac{d(D)}{dt} = \frac{-d(A)}{dt} = \frac{-d(B)}{dt} \quad (1.2)$$

if the concentrations are expressed in moles per liter.

If the stoichiometry is more complicated, for example,





then the rates are related by

$$-\frac{d(A)}{a\,dt} = -\frac{d(B)}{b\,dt} = \frac{d(C)}{c\,dt} \quad (1.4)$$

However, there is no convention regarding what is meant by the *reaction rate* in this case, and it is *absolutely necessary* in quoting a rate or rate constant to define exactly which measure of rate—for example,  $d(C)/dt$  or  $d(D)/dt$ —is being used. The measure of rate needs to be defined even more carefully if there are side-reactions, so that reagent may disappear faster than product is formed, and no simple equation such as even (1.4) applies. All ambiguity is avoided when mentioning a rate or rate constant by writing explicitly the equation that it fits and giving the units. Thus, even if a reaction has the stoichiometry of reaction (1.3), and there are side-reactions, it is still possible that the disappearance of A might, for example, be given by

$$\frac{-d(A)}{dt} = k_5(A)(B) \quad (1.5)$$

with  $k_5 = 1.37 \times 10^{-5}$  liter/(mole)(sec). There is no uncertainty about what is meant, even though further statements of conditions, such as temperature, solvent, and such may be needed before it can be reproduced.

Flow systems are in general more complex to deal with than batch systems except in two limiting conditions known as *plug flow* and *stirred flow*. In *plug flow* we can deal with a volume element that passes through the system intact without mixing with neighboring volume elements; the treatment is effectively that of batch systems except that we use the distance along a tube, instead of time, as the measured variable but relate the distance to the time by the flow velocity. In *stirred-flow* systems the volume element cannot be identified; instead, the mixing is complete and concentrations throughout the system are uniform. When a steady state is achieved, the mathematics become very simple, in that the reaction rate itself is simply related to the measured extent of reaction; one does not have to measure the concentration as a function of time (or distance) as in batch or *plug-flow* systems. The equations are then algebraic equations rather than differential equations, and as a consequence, quite complex rate laws can be easily unraveled.

The definition of *mechanism* is more difficult, in part because it is an inherently more involved concept and in part because there is no universal meaning to the word. Before getting to our final definition it will be helpful to divide chemical reactions into two groups, simple and complex. *Simple reactions* are here defined as those consisting of a single step. There are no intermediates of any stability at all, there is only one path from reagent to product, and a simple stoichiometric equation describes the chemical