Moore
Pearson

# Kinetics and Mechanism

THIRD EDITION



WILEY-INTERSCIENCE

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# PREFACE TO THE THIRD EDITION

It is now 20 years since the second edition of *Kinetics and Mechanism* was written. Obviously, a revision was more than called for. There was also a strong possibility that an up-to-date version would differ so much from the original that a new title and a new literary identity should be created. Indeed the third edition appears quite different from the first and second. A full 80% of the material is new. Nevertheless, enough remains of the old to make its heritage obvious, and we felt that calling it *Kinetics and Mechanism*, the third, was in order.

There is also the spirit of the parent volumes, which we hope remains. That is, the attempt to emphasize the role of kinetics in unraveling reaction mechanisms. Of course in the last 20 years the subject of reaction mechanisms, in organic, inorganic, and biochemistry, has been very highly developed. Many excellent treatises have been written. As a result we did not feel it important to give as many examples of reactions whose mechanisms have been elucidated as in earlier editions.

Instead, we have concentrated more on recent developments in both the experimental and theoretical aspects of kinetics of which there have been many. The routine study of very rapid reactions and the use of computers to solve complex rate equations may be particularly mentioned on the experimental side. Plug and stirred flow, relaxation methods, molecular beam studies, laser applications, and other modern techniques for fast kinetics are described at appropriate points in the text when example reactions that have been studied by these methods are introduced. Chapters 2 and 3 have been expanded to include computerized analysis of experimental data, as well as exercises that require students to apply this technique. Theoretical advances are reflected in an expanded treatment of collision theory, an introduction to the calculation of potential energy surfaces and their use in trajectory studies, and considerable attention to the theory of unimolecular reactions. The concept of control of reaction rates by orbital topology is the major theoretical advance that applies most directly to an understanding of reaction mechanisms.

While reaction mechanism remains the primary goal of most kinetics research, considerable progress has been made in the ability to predict rates of reaction. In addition to *ab initio* theory we include empirical and semiempirical methods for estimating activation energies and reaction rates. We also describe how rate constants obtained from experiments, predicted by theory, or otherwise estimated can be combined in a computer simulation of a complex mechanism to obtain concentration-time behavior of all species involved.

The most important development in gas phase kinetics, and in the chemical physicist's view of kinetics, has been in the study of state-to-state transitions. At this time such research provides information that is too detailed to use in many studies of reaction mechanism. We nevertheless devote considerable attention to state-to-state chemistry, because it represents an important step toward our goal of a complete understanding of chemical reactions.

We hope this volume will make a small contribution towards such understanding.

We acknowledge the aid of a number of institutions and individuals. The libraries of Eastern Michigan University and of the University of Michigan, Ann Arbor, were essential to our efforts. The following persons supplied preprints or reprints that would otherwise have been unavailable: T. Bartfai, G.-M. Côme, David Edelson, V. Gold, Darrel G. Hopper, P. J. Kuntz, Bengt Mannervik, Michael L. Michelsen, William M. Moore, David T. Pratt, B. S. Rabinovitch, Warren L. Reynolds, Robert F. Sawyer, Henry F. Schaefer III, T. S. Sørensen, I. Ugi, and Jacques Weber. Dr. Kenneth W. Hicks read and constructively criticized significant portions of the manuscript. Much of JWM's contribution to this revision was accomplished during a sabbatical leave granted by Eastern Michigan University and supported by the National Science Foundation. Finally, and most importantly, we thank Elizabeth A. Moore. She typed the entire manuscript, did extensive literature searching and other bibliographic work, checked all references for accuracy, and did much of the work of indexing this volume. Without these indispensable efforts this revision would not have been possible.

RALPH G. PEARSON
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*Santa Barbara, California*
*Ypsilanti, Michigan*
*November 1980*

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# PREFACE TO THE SECOND EDITION

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

RALPH G. PEARSON

*Evanston, Illinois*
*January, 1961*

# 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 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.

ARTHUR A. FROST
RALPH G. PEARSON

*Evanston, Illinois*
*November, 1952*

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# ONE

# INTRODUCTION

Kinetics is part of the science of motion. In physics the science of motion is termed dynamics and is subdivided into kinematics, which treats 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 that influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism. In its most detailed form a reaction mechanism describes, as a function of time, the relative positions of all microscopic particles whose motion is necessary for the reaction to occur. Since it is concerned with both the motions and the forces among these particles, chemical kinetics might very well be called chemical dynamics.

Chemical kinetics with its emphasis on dynamics may be contrasted with the static viewpoint of chemical thermodynamics. Equilibrium thermodynamics† is interested only in the initial and final states of a system; the mechamism 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 equilibrium thermodynamics alone. Therefore chemical kinetics may be considered a more fundamental science than chemical 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 can tell with precision the extent of reaction, but only kinetics can tell (perhaps crudely) the rate of the reaction.

† Thermodynamics can be applied to nonequilibrium systems. See, for example, references 1 and 2 at the end of this chapter.

Theoretical methods for predicting reaction rates are based on a conclusion originally drawn by Arrhenius[3]: the most commonly observed relationship between rate of reaction and temperature implies an energy barrier to reaction. The kinetic-molecular theory can tell us the number of molecular collisions per unit volume per unit time as well as the fraction of those collisions whose energy exceeds some threshold energy. It does not, however, speak to the issue of how large the threshold energy must be, nor to the effectiveness of a collision as a function of relative molecular orientation. These issues can be addressed by using quantum mechanics[4] to evaluate the electronic and nuclear-repulsion energies of the collection of atoms involved in a reaction as a function of suitable bond distances and angles. Motion of the atomic nuclei, whether or not it results in the desired reaction, thus corresponds to movement on a multidimensional "potential" energy surface.[5,6] Holes or valleys (energy minima) on such a hypersurface correspond to stable molecular species—reactants, products, and intermediates. As a reaction occurs the coordinates of the collection of nuclei change in such a way that the energy rises and a mountain pass must be surmounted. The saddle point or col at the top of the pass corresponds to the *activated complex* or *transition state.* When allowance is made for the zero-point vibrational energies of reactant(s) and activated complex, the height of the col above the valley floor is the energy barrier to reaction.

A variety of paths or trajectories are available to a collection of nuclei passing over an energy barrier, and many of them may be used, depending on initial velocities and momenta of the nuclei. Large, high-speed digital computers have made possible accurate quantum-mechanical calculations of energy surfaces for reactions involving small numbers of nuclei and electrons. Once the energy surface is known, *molecular dynamics* calculations, in which the (usually classical) trajectories of collections of nuclei are followed over time, can be carried out. By starting with weighted random initial conditions, repeating the procedure a large number of times, and averaging the results, a computer can arrive at reaction rates and evaluate the parameters on which those rates depend.[7]

Such lengthy calculations can be avoided if we concentrate on the minimum-energy path from ground-state reactants to activated complex. This path is called the *reaction coordinate.* If it is assumed that reactants and activated complexes are in equilibrium, statistical mechanics may be used to calculate the concentration of activated complexes. This concentration can be combined with the speed at which activated complexes pass along the reaction coordinate toward products, enabling the reaction rate to be evaluated. This is the basis of the transition-state theory or theory of absolute reaction rates developed principally by Eyring.[8] In cases where statistical mechanics is difficult to apply from first principles, a "thermodynamic" approach may be taken. The increase in thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy on going from reactants to activated complex may be obtained from rate data and used to estimate properties of the activated complex.

## REACTION MECHANISMS

From the chemist's molecular viewpoint, the most interesting aspect of the study of reaction rates is the insight it provides into the mechanism of a reaction. *The*

*dependence of rate of reaction on concentrations of reactants, temperature, and other factors is the most general method for weeding out unsuitable reaction mechanisms.* Here the term mechanism is used in the classical sense (developed chiefly by physical chemists) to mean all the individual collisional or other elementary processes involving molecules (atoms, radicals, and ions included) that take place simultaneously or consecutively to produce the observed overall reaction. For example, the rate of the reaction

$$H_2(g) + Br_2(g) = 2\,HBr(g) \qquad 498\,K < T < 574\,K$$

was found by Bodenstein and Lind[9] to be proportional to the concentration of $H_2$ and to the square root of the concentration of $Br_2$. Furthermore, the rate was inhibited by the increasing concentration of HBr as the reaction proceeded. These observations are not consistent with a mechanism involving bimolecular collisions of a single molecule of each kind. The currently accepted mechanism is considerably more complicated, involving the dissociation of bromine molecules into atoms followed by reactions between atoms and molecules:

$$Br_2 \rightleftharpoons 2\,Br$$

$$Br + H_2 \rightarrow HBr + H \qquad \text{slow}$$

$$H + Br_2 \rightarrow HBr + Br \qquad \text{fast}$$

$$H + HBr \rightarrow H_2 + Br \qquad \text{fast}$$

It should be clear from this example that the mechanism cannot be predicted from the overall stoichiometry. This point is emphatically reiterated in the case of gas-phase formation of water from its elements:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

The reaction certainly does not involve simultaneous, trimolecular collisions of $2\,H_2$ with $O_2$. As many as 40 elementary steps have been suggested for the mechanism, and about 15 steps are needed to account for the slow reaction under simplified conditions.[10]

It cannot be overemphasized that a reaction mechanism is essentially a theory that has been devised to explain currently known experimental facts, such as the overall stoichiometry and the dependence of reaction rate on concentrations, temperature, or other variables. In general such experimental facts can be interpreted in several ways; that is, there are several mechanisms consistent with the data. Further experimentation may eliminate some of these, but even if only one mechanism remains that 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. A case in point is the reaction of $H_2(g)$ with $I_2(g)$. Because its rate is directly proportional to the concentrations of $H_2$ and $I_2$, this reaction was thought for over 60 years to occur in a single step involving bimolecular collisions of $H_2$ and $I_2$. However, a reinterpretation of the variation of reaction rate with temperature suggested that a mechanism involving atom–molecule collisions (like the mechanism of the $H_2 + Br_2$ reaction) could account for part of the reaction above 633 K.[11] Furthermore, the supposedly bimolecular $H_2 + I_2$ step has been shown more

recently[12] to probably involve individual I atoms rather than $I_2$ molecules. Thus one must be careful not to place absolute faith in any mechanism (or any other theory, for that matter).

As with other theories, new information can modify a reaction mechanism, rather than eliminate it completely. An example is provided by the nitration of benzene and other aromatic compounds (ArH):

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

Until recently this represented an example of a mechanism that was considered as firmly established as a mechanism could be.[13] The steps may be written as

$$H^+ + HNO_3 \overset{\text{fast}}{\rightleftharpoons} H_2ONO_2^+ \rightarrow H_2O + NO_2^+$$

$$NO_2^+ + ArH \rightarrow HArNO_2^+ \xrightarrow{\text{fast}} ArNO_2 + H^+$$

Depending on circumstances, the formation of $NO_2^+$ or the reaction of $NO_2^+$ with ArH may be the slowest, or rate-determining, step.

It now appears that the initial reaction of $NO_2^+$ with the aromatic molecule is an electron transfer to form a pair of free radicals, which then collapse to the intermediate $HArNO_2^+$.[14]

$$NO_2^+ + ArH \rightarrow NO_2\cdot + ArH^+\cdot \rightarrow HArNO_2^+$$

The evidence for the modified mechanism consists of two parts. The first is the experimental demonstration that energetically an electron transfer was favored, except for benzene itself, and perhaps toluene. The second is a review of old data on intramolecular selectivity (*ortho* versus *para* substitution) and the demonstration that it could be better explained by the radical pair intermediate.

Many students find it difficult to accept the fact that a theory is fundamentally different from an experimental fact, and that it can never be taken as completely established. Are there not some theories, such as the atomic theory, that are so in accord with countless observations that they can be considered as fact? The following discussion may be helpful.[15]

A theory is a mental model constructed to explain a set of observations on a subject. Like any model, it has some, but not all, of the properties of the real subject. Our view of the atom is like that of an astronomer on Jupiter who observes human beings on Earth with a superpowerful telescope. He sees us as black dots scurrying about engaged in various forms of activity. If our Jovian astronomer is as clever as we are, he will eventually develop a model of humans that has great detail. He may deduce that we are bipedal, that we communicate by sound waves, even that we have hands with an opposed thumb. Still it is clear that we, at least, would never mistake his model for a human being, if we met it face to face.

Despite these difficulties, there are theories that are so reasonable and so in accord with all experience, that we accept them as essentially true. The same

applies to reaction mechanisms. 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 reaction. That is, a theory is tested by the pragmatic criterion: Does it work? Does it make useful predictions about experiments as yet undone? When it no longer works, of course, we must abandon it.

In most cases, especially those involving molecules that contain numerous atoms and have more complicated structures, it is desirable to infer more than just the collection of elementary processes that constitutes the classical reaction mechanism mentioned above. Organic, and more recently, inorganic chemists have therefore broadened the concept of reaction mechanism to include a *detailed stereochemical picture* of each step in the overall reaction. This concept implies a knowledge not only of the composition of the activated complex in terms of the various atoms and molecules of reactants, but also of the geometry of the activated complex in terms of interatomic distances and angles. For example, it is generally accepted that the conversion of hypochlorite ion to chlorate ion occurs in two steps:

$$ClO^- + ClO^- \rightarrow ClO_2^- + Cl^- \qquad \text{slow}$$
$$ClO_2^- + ClO^- \rightarrow ClO_3^- + Cl^- \qquad \text{fast}$$

The formation of chlorite ion is the slower, rate-limiting step, and the formation of chlorate ion is rapid.[16] This can be deduced from the fact that the rate of formation of chlorate ion is proportional to the square of the hypochlorite concentration. Furthermore, separate experiments show that the reaction of chlorite ion with hypochlorite ion is fast. These facts would suffice to fix a probable mechanism according to the older definition. The new approach adds to the mechanism a picture such as (1.1) for the transfer of an oxygen atom between ions.

$$Cl{-}O^- + Cl{-}O^- \rightarrow \left[\begin{matrix} Cl \cdots O{-}Cl \\ | \\ O \end{matrix}\right]^{2-} \rightarrow \left[\begin{matrix} Cl{-}O \\ | \\ O \end{matrix}\right]^- + Cl^- \qquad (1.1)$$

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 the making and breaking of bonds between atoms and to attempt to understand the influence of minor alterations in molecular structure. In the case under discussion, for example, we might consider the effect of protonating the reactant ions by changing pH or 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.[17] The stereochemical picture also suggests the possibility that the mechanism may be more complex in that the oxygen atom that leaves one hypochlorite ion may not be the same as the oxygen that appears on the other. Thus the solvent might be involved in the oxygen transfer,[18] possibly as shown in (1.2). In this

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