PHYSICAL CHEMISTRY

AN ADVANCED TREATISE

Edited by
HENRY EYRING
DOUGLAS HENDERSON
WILHELM JOST

VOLUME VIA

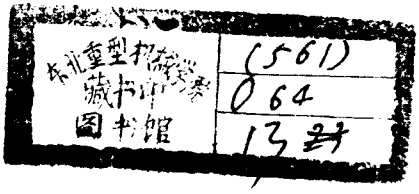
PHYSICAL CHEMISTRY

An Advanced Treatise

Volume VIA / Kinetics of Gas Reactions

Edited by

WILHELM JOST
Institut für Physikalische Chemie der Universität Göttingen
Göttingen, Germany



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List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

C. F. Curtiss, Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin (77)

H. Eyring, Department of Chemistry and Metallurgy, University of Utah, Salt Lake City, Utah (121)

W. Jost, Institut für Physikalische Chemie der Universität Göttingen, Göttingen, Germany (1)

S. H. Lin, Department of Chemistry, Arizona State University, Tempe, Arizona (121)

E. E. Nikitin, Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow (187)

J. C. Polanyi, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada (383)

J. L. Schreiber, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada (383)

J. Peter Toennies, Max-Planck-Institut für Strömungsforschung, Göttingen, Germany (227)

Foreword

In recent years there has been a tremendous expansion in the development of the techniques and principles of physical chemistry. As a result most physical chemists find it difficult to maintain an understanding of the entire field.

The purpose of this treatise is to present a comprehensive treatment of physical chemistry for advanced students and investigators in a reasonably small number of volumes. We have attempted to include all important topics in physical chemistry together with borderline subjects which are of particular interest and importance. The treatment is at an advanced level. However, elementary theory and facts have not been excluded but are presented in a concise form with emphasis on laws which have general importance. No attempt has been made to be encyclopedic. However, the reader should be able to find helpful references to uncommon facts or theories in the index and bibliographies.

Since no single physical chemist could write authoritatively in all the areas of physical chemistry, distinguished investigators have been invited to contribute chapters in the field of their special competence.

If these volumes are even partially successful in meeting these goals we will feel rewarded for our efforts.

We would like to thank the authors for their contributions and to thank the staff of Academic Press for their assistance.

HENRY EYRING
DOUGLAS HENDERSON
WILHELM JOST

Preface

Reaction Kinetics began with the formal treatment of overall reactions (Wilhelmy, 1850; Guldberg and Waage, 1864), followed by attempts to understand the reaction mechanism (van't Hoff, Arrhenius, Boltzmann). The present aim in theory and practice is to gain a detailed understanding single reaction steps, i.e. of transformations of atoms and molecules in specified velocities, impact parameters, and inner states into products of specified states. This line developed roughly within the last 50 years, with outstanding experimental success during the last decade. Formal kinetics, at the beginning of this century, dealt with comparatively trivial problems. At that time, however, it was discovered that periodic reactions are feasible, unless a restriction holds, corresponding to what we now call the principle of microscopic reversibility. Explicit application of classical thermodynamics and of thermodynamics of irreversible processes led to more insights, allowed of certain statements on the formal behavior of reaction systems, especially near equilibrium and near stationary states, e.g. in open systems. In the first chapter an attempt has been made to cover the domain between the almost trivial and the not-at-all trivial in formal kinetics, where there are rapid new developments.

The second chapter, by C. F. Curtiss, gives a modern survey of kinetic theory, as one of the bases of reaction kinetics. H. Eyring and S. H. Lin, in a critical review, deal with potential energy surfaces of reacting systems, while Chapter 4 by E. E. Nikitin is devoted to the theory of energy transfer in molecular collisions, considering the several possible types of energy exchange (translational–rotational, translational–vibrational, rotational–vibrational, etc.).

Molecular beam technique has contributed much to our knowledge of elementary scattering processes, elastic, inelastic, and reactive. In Chapter 5 J. P. Toennies covers this field giving sufficient details of experimental methods, as necessary for an understanding of the results.

Chapter 6 by J. C. Polanyi deals with the dynamics of bimolecular reactions. Reaction dynamics is defined as the details of a reaction event at the molecular level. One of the aims of this chapter is to establish the connection between bulk properties and microscopic details, while in further sections detailed models and simple models are treated, which essentially contribute to understanding.

WILHELM JOST

July, 1974

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