PHYSICAL CHEMISTRY

An Advanced Treatise

Volume IV / Molecular Properties

Edited by

DOUGLAS HENDERSON

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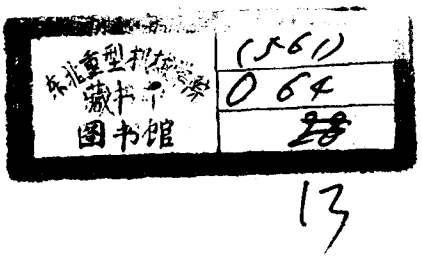

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Foreword

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

The understanding and classification of atomic and molecular structure is one of the principal aims of physical chemistry. This volume is the second of three volumes in this treatise devoted to this topic.

The electronic structure of atoms and molecules was treated in Volume III. The present volume is devoted to those aspects of the properties of single molecules not treated in Volume III and to the physical methods available for their determination. This volume is intended for those students of physical chemistry who are not expert in this field. It is our aim that, in so far as is possible, this volume be understandable by graduate students in chemistry and physics without supplementary reading, and that, together with Volumes III and V, a student can obtain an understanding of atomic and molecular structure sufficient to enable him to read and contribute to the current literature.

The editor would like to thank the authors for their contributions. Thanks are also due to Dr. G. W. King and Dr. N. S. Ham for many valuable suggestions relating to the organization of this volume.

DOUGLAS HENDERSON

April, 1970

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Chapter 1

The Variety of Structures Which Interest Chemists

S. H. BAUER

I. Introduction

In the following "baker's dozen" of chapters on molecular properties attention is focused on those observations of the properties of matter which have been interpreted in terms of features ascribed to individual molecules. In these discussions the effects of neighboring molecules are treated by assuming that the latter produce relatively small, but not necessarily negligible, perturbations. The unifying concept is that the properties of molecules are determined by their individual structures. For over a century it has been recognized by chemists that to fully characterize a molecule, specification of its static structure was as essential as the statement of its molecular formula. Initially, the term was reserved for a description of the connectivity between the atoms. The significance of spatial relations was recognized by Pasteur in 1860, but his comments were overlooked by chemists for over a decade, until the need for a three-dimensional structure was reemphasized by Wislicemus (1873), LeBell (1874), and van't Hoff (1875). Their proposals were bitterly, but unsuccessfully attacked by Kolbe (1877). From this qualitative beginning the concept of molecular structure evolved during the past half century into a quantitative description based on a dynamic model, so that at present, average interatomic distances and root-mean-square amplitudes of vibration can be quoted in some cases to a precision of 0.002 Å. The