PHYSICAL CHEMISTRY

An Advanced Treatise

Volume V / Valency

Edited by
HENRY EYRING

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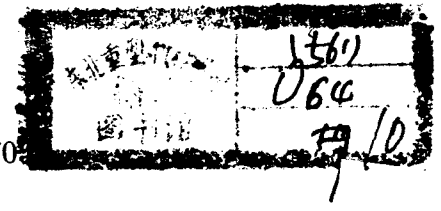

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Foreword

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
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Preface

Valence theory has come a long way since G. N. Lewis developed his ideas of the electron pair bond and Kossell and Langmuir emphasized polar bonds and the stability of molecules with valency shells isoelectric with the rare gases. Until wave mechanics gave us a way of treating kinetic energy on a par with potential energy, no quantitative theory of bonding was possible, and although we now may think we know valency theory in principle the quantitative development of the theory still involves many knotty problems. Pauling's work* has illuminated many dark corners.

In this volume some of the ablest specialists of valence theory have given us their best thinking on those problems which have elicited their attention. The reader will be repaid if he gets this material in proper perspective.

It is our pleasure to thank the staff of Academic Press as well as our other friends who have helped to bring this book to completion.

HENRY EYRING

January, 1970

* L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry," 3rd. ed. Cornell Univ. Press, Ithica, New York, 1960.

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Chapter 1

General Remarks on Electronic Structure

E. TELLER
and
H. L. SAHLIN

I. Introduction

The quantum theory has made possible the explanation from first principles, of the chemical, electromagnetic, and spectroscopic properties of molecules. The nature of this explanation is, of course, somewhat involved, because the number of particles that must be considered is neither large nor small, and in addition, we must deal with a mixture of particles (electrons and nuclei) that have very different physical properties. As we shall see, this latter complication can be turned into an advantage.

Problems involving only a few particles may either be solved exactly, in the simplest cases, or, for the more complex cases, be calculated to an accuracy equal to that of the best experiments with modern high-speed computers. On the other hand, for systems of a very large number of identical particles, much of the detailed behavior of the system is not relevant to the properties of interest, and one may employ the methods of statistical mechanics. The majority of the problems of molecular and atomic physics occupy a middle ground between exact solubility and the

use of simplifications obtainable through the technique of statistical mechanics. Careful attention to many details is required, and solutions of unlimited accuracy are not feasible.

The spectral structure of atoms and molecules provides a detailed and accurate experimental mechanism for exploring the intricate behavior of these systems. The recent development of the laser and the maser, which themselves depend on this structure, provides a powerful and delicate probe that opens new possibilities for both exploring and utilizing the level structure of atoms and molecules. For example, it is possible to selectively populate a single level, and this ability might in some cases permit significant alterations to be made in the chemical reaction rates for the excited species.

Despite the complexity of molecular systems, helpful simplifications may be introduced which facilitate understanding and in some cases even lead to accurate computation. Three factors contribute significantly to making the study of these complicated systems tractable. One is the fact that nuclei are much more massive than electrons. This leads to a picture of fixed, or, more precisely, of slowly oscillating nuclei imbedded in a gas-like envelope representing the average charge density of the rapidly moving electrons. The mathematical development of this picture will be discussed in Section II, where the Born–Oppenheimer approximation is introduced. This approximation permits a particularly accurate decoupling of the electronic and nuclear motions.

The second simplifying feature is the fact that atomic structures are held together by electromagnetic forces. Electrostatic forces are dominant, and the $(1/r^2)$ dependence of these forces permits the virial theorem to take on a particularly useful form relating the average kinetic and potential energies of the system to the work done against constraining forces when the nuclear separation distances are changed. The virial theorem is developed in Section III.

The third and most general factor is the influence of symmetry and the states of individual electrons on molecules. An exhaustive discussion of this topic would require an extensive presentation and involve a considerable amount of mathematics. We shall limit our discussion to the classification of electronic states of diatomic molecules; this is presented in Section V. This, combined with the classification of electron spin states, provides a useful nomenclature without which discussion of diatomic energy levels would become exceedingly clumsy.

The fact that electromagnetic forces are relatively weak is also of considerable significance. An effective mathematical attack on a complicated system usually involves the assumption that the system may be considered to a first approximation as more or less weakly interacting