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PHYSICAL CHEMISTRY

AN INTRODUCTION

by

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PREFACE

For fifteen years I have been teaching physical chemistry; my students, no less than I, have felt the need for a treatise, in English, to cover the ground from an introduction to the subject up to the Natural Science Tripos at this University or to the corresponding Honours elsewhere. There have, of course, always been available a number of disconnected monographs—most of them useful and many of them authoritative—but the student lacks a work which reveals the fundamental principles of the new physical chemistry and at the same time enables him to view in correct perspective the multifarious specialist theses. I have given what is, I submit, a clear account of the basic principles of modern physical chemistry and have applied them to a number of simple problems so arranged as to form a logical introduction to the specific treatment of the most relevant of current physicochemical themes. To embrace all these themes within a single book is impossible.

Facts come first. This book derives from the laboratory and expresses the views of one who regards himself as primarily an experimental physical chemist. Facts suggest hypotheses; hypotheses cohere into theories; theories require mathematical presentation; and finally, each theory must be subject to critical examination in the light of the facts it was intended to explain, and, where possible, in the light of new experiments directed by theoretical implications. Throughout this work, this order of development, which alone has scientific sanction, is not only followed but is particularly stressed.

In some mathematical approaches to the field of physical chemistry there is a tendency to put the cart before the horse. It is not unusual to find the conclusions of pure experimental research on some difficult problems presented as natural consequences of mathematical theory. Prudence, no less than scientific duty, compels one to discredit any theory that pronounces with alleged authority after experiments have been performed but which retains a discreet silence before experience has solved the problem. In the teaching of physical chemistry, at any rate, relevance comes before elegance.

The essential emphasis upon the factual side of the subject sufficiently explains the numerous tables of data which appear on about every fourth page. The structure of physical chemistry must be securely founded upon the sure work of experimentalists. The tables are, with few exceptions, new compilations from carefully selected sources. Many of them are summaries of the present full extent of physicochemical attainment in the fields which they cover, and they will, it is hoped, be of direct use to chemists who are not approaching the subject for the first time.

In the first half of the book, experimental and theoretical paths are trodden in turn. The physical chemist must be familiar with both routes. His hand must be trained as well as his mind. He must learn to appreciate the apparatus used by Rutherford to demonstrate the relation between the α -particle and the helium atom, as well as the argument used by Boltzmann to demonstrate the relation between entropy and probability. The complete physical chemist blows his own apparatus and solves his own equations.

This book is complete in itself; it does not expect of the student that he shall have at his elbow a number of other books. All theorems are derived; no proof is taken for granted. I have not hesitated, for example, to remind the reader of the content of the binomial theorem, for I assume him to possess no greater knowledge of mathematics than the student of mathematics has of chemistry. Not only in the older text-books are many of even the simpler proofs omitted but they are often wanting in modern monographs which deal at great length with experimental data in the light of unproved theories. The inclusion of the derivations of theorems in this work should be of assistance to those already familiar with the descriptive aspects of modern physical chemistry.

The quantum theory naturally takes a prominent place in modern physical chemistry. I have sought to introduce it harmoniously with its classical predecessor, and to show clearly the relation of both theories to the facts.

The first three Chapters of the second part of this work are designed as a systematic presentation of the application of the accepted principles of modern physical chemistry to specific systems. Had I not deemed it advisable to limit the scope of this work, it would have been of advantage to follow these by a consideration of tetratomic molecules and the Raman effect, of pentatomic molecules and optical activity, and of polyatomic molecules and electron diffraction. However, it is of greater moment to arouse interest than to be exhaustive. I have, therefore, contented myself thereafter with the treatment of equilibria, kinetics and crystals.

The subtitle is a humiliating reminder of the vast and important fields of physical chemistry which are not so much as mentioned in the present work. The most important of these topics is solutions, a subject to which the major part of my research activities has been directed. The treatment of solutions has not, in my view, been sufficiently elucidated to justify its inclusion in the present book.

E. A. M-H.