CHEMICAL REACTIONS: THEIR THEORY AND MECHANISM

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BY

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PREFACE

The central idea of this book is the development of a general theory of reactions which will include both inorganic and organic reactions. The fundamental view upon which this theory is based is the "addition" theory according to which when two or more substances react a primary addition is the first step. This theory is not new. It has been used in more or less isolated cases for a number of reactions and may have been suggested as of general applicability. As far as the writer is aware, however, this is the first time that it is published in an extended form with modern conceptions of chemical structures, which themselves rest upon the development of valence views.

The modern interest in valence appears to have started in 1899 when Thiele published his paper on partial valence. Some years later, 1904, J. J. Thomson suggested the basic ideas of the electron conception of valence, but applied these to very few cases. From that time on, the electron conception of valence occupied the minds of a number of chemists who attempted its application as shown in sporadic publications. Professor Nelson and the writer believe that they were the first, dating from 1909 on, to publish extended applications of the electron conception of valence to organic as well as to inorganic compounds and reactions, and to develop certain lines of chemical theory from this point of view. In the development of these views, they travelled over a certain course of chemical thinking. Unquestionably, others have followed the same or similar lines of thought and reached similar conclusions. Among those who have published along these lines may be mentioned H. S. Fry, W. A. Noyes, J. Stieglitz, L. Jones, G. N. Lewis, R. F. Brunel, W. C. Bray and G. E. Branch, S. Dushman, J. Stark, H. Kauffmann, and a number of others. No attempt will be made to give a historical review of the problem or to determine who is responsible for any particular part of the theory. That it was possible for certain workers to publish before others does not negative the fact that such theoretical views may have been taught and used in planning experimental work by either group long before their publication.

For practical reasons, it was not possible for Professor Nelson and the writer to add to the experimental data from the newer point of view, but it seemed at the time as if sufficient facts were recorded in the literature to permit of a conclusive test of the theory.

The electron conception of valence has now apparently been widely accepted. At the same time, a number of chemists still speak of polar and non-polar valences. To the writer, no useful purpose is served by such a distinction.

As stated, chemical reactions form the keynote of this book. The first three chapters are preliminary in the sense that they treat of the underlying theoretical conceptions used in the later chapters. Certain parts of Werner's theoretical views are used. At present, these appear to offer the only explanation which is at all satisfactory for what have been termed at various times "molecular" compounds. In recent years, G. N. Lewis and I. Langmuir have developed certain conceptions of molecular structures from the point of view of electron distribution. These conceptions are of the utmost importance and indicate new methods of formulation. To apply them to the consideration of chemical reactions appears to be somewhat premature. At least, it appears to the writer that for him to attempt it would be so. Since their views are not used here and since this is in no way a historical treatise, they have not been given in detail. On the other hand, it is believed that enough of the general theoretical side has been given to permit any one interested to follow intelligently any further developments of structural chemical theory.

Questions of stereochemistry have not been included. It would appear that spatial chemistry is entering upon a new phase. The experimental and theoretical work on the arrangements of atoms in crystals as exemplified in the publications of the Braggs and of others, points to an entirely new conception of stereochemistry, while at the same time stereochemical explanations, such as steric hindrance, which have been accepted heretofore, are being superseded by explanations based upon different relationships.

A number of new points of view and explanations are advanced here. Many of these have been presented by Professor Nelson to his students at Columbia University during the past years. Whatever value this book may possess is due in a large measure to him, both in the development of the views and in the collection of material. Among others who have aided in various ways in the development of the views leading up to the preparation of this book and to whom thanks are due are Professors G. B. Pegram and H. T. Beans, of Columbia University, and Dr. Marston L. Hamlin.

New York, N. Y., June 15, 1920.