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W. G. Palmer

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VALENCY
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BY

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Fellow of St John's College, Cambridge

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P R E F A C E

It will be generally agreed that current opinions on the long-established conception of chemical valency, and on the ways in which it may be satisfied in chemical combination, originated in the attempts of Kossel, Lewis, and Langmuir (1916–1918) to derive a *modus operandi* from the contemporary ideas of atomic electronic structure. Since that time many manuals on the theory of valency have appeared, but they all expound principally, if not exclusively, the modern electronic views. To understand how a great and permanent theory first arose in the minds of its pioneers, how their successors contributed to its progress, or hindered it by misconceptions; to appraise justly how different the judgment of time and experimental application may be from the firm opinion of contemporaries, will always retain intense human, not less than scientific, interest. But in the subject of valency and chemical combination at least, there is the over-riding consideration that the rapid progress of modern theories would have been impossible, except upon the excellently laid foundations of pure chemistry. A volume attempting to exhibit the recent advances portrayed against the chemical background would therefore seem to be not inopportune at the present time, even though the modern theories are still far from complete, and many of the facts ascertained in classical chemistry await more than tentative explanations.

The subject of valency alone being as wide as the detailed chemistry of all the elements, not excluding carbon, it is essential to select for discussion in a work of limited size, and one intended for the use of students, only the main features and problems, and to confine the exemplifying compounds as far as possible to simple molecules. Although their quantitative powers cannot justly be ignored, I have made an effort to present electronic theories with the minimum of mathematical detail. At the same time some account of the spectroscopic basis of the present view of atomic structure has been regarded as necessary, in order to show how far the modern theory is independent of chemical reasoning. For I fear that two opposite kinds of false impression

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may be taken from some recent expositions; either that the idea of valency was coeval with the acceptance of the nuclear atom; or, on the other hand, that modern physical theories take all their cues from chemical facts, and are no more than an alternative mode of restating those facts. While it would be narrow-minded for physical theorists to be scrupulous to the point of ignoring chemical reasoning, I have made it one object of the later chapters of this book to demonstrate that they have indeed given solutions to problems, which, first brought to light in pure chemistry, by their very nature were insoluble by chemistry unaided.

After a short introductory chapter outlining the first tentative theories of chemical combination and the discovery of valency as an empirical conception, the second and the first part of the third chapter are concerned with the methods of determining chemical structure and valency; modern physical methods as well as the classical chemical methods are discussed and briefly explained. The second section of Chapter III illustrates the application of such methods to compounds of the commoner elements treated according to the arrangement in the periodic system. Up to this point all discussion follows classical lines, though aided and supported by the results of recently developed physical experimental methods. Only when the problems and anomalies arising insistently from such a treatment are thus clearly defined is the electronic theory introduced (in Chapter IV). This separation of the established chemical problem from the current electronic solution is deliberate, and, it is hoped, will not only set in a clear light the urgent need for a comprehensive theory of chemical combination and valency, but will permit the theory to display its power, without concealing its present defects. For the sake of simplicity only the 'light' elements (hydrogen to fluorine) and their important compounds are discussed in Chapter IV, and the basic ideas of the electronic theory are presented in a simplified form. The first four chapters thus present a compact but elementary account of classical and modern conceptions of valency, suitable for the more general reader, and not overstraining the capacity of candidates for University examinations of the standard of

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Part I of the Natural Sciences Tripos at Cambridge. The concluding chapters are more advanced in content and treatment. Chapter v shows how the electronic theory is applied to the heavier elements and their principal compounds, while the last chapter is devoted to current developments and theories still in their early stages.

Much of any merit the book may be found to possess is due to the generous help I have gratefully received from many colleagues at Cambridge; notably from Mr A. J. Berry, Dr F. G. Mann, Dr G. B. B. M. Sutherland and Dr M. L. Tomlinson, all of whom have been ready with most useful suggestions for improvements. I count myself fortunate also in having had encouragement and sage advice from my former teacher, Dr W. H. Mills, now President of the Chemical Society. I feel bound to add that any controversial opinions are advanced on my own responsibility, and must not be regarded as sponsored or condoned by any of these friends. All such friendly support from colleagues would hardly have sufficed to achieve publication, had I not also benefited from the long-suffering collaboration of the staff of the Cambridge University Press, to whose forbearance under the often excruciating difficulties of the times I shall ever be indebted.

I must plead guilty, not only to enlarging an already voluminous terminology, but to including in this expansion the objectionable word 'co-ionic' (Chapter iv). In mitigation I offer the excuse that great masters of chemistry were formerly content to use such terms as 'monovalent' and 'pentavalent'; in our own time acknowledged leaders have not despised 'electrovalent' and 'electronegativity', or even 'ionicness'. To avoid over-burdening the text with references to the literature, I have, when a recent communication supplies adequate bibliography, given as a rule only the recent reference. I hope to be pardoned, if, owing to the difficulties under which the book was prepared, I have failed to notice any important relevant work of the present day.

W. G. P.

April 1944

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PREFACE TO THE SECOND EDITION

During the decade preceding the War of 1939–45 the progress of chemistry had been vastly accelerated by the impetus gained on the one hand from the newly explored metrical methods of X-ray and electron diffraction, and on the other from the brilliant expansion of theoretical insight into what had remained for so long the mystery of chemical union. The first edition of this book in 1944 appeared after an inevitable period of slackening during the war years, and at a time when it was not easy to be sure that all the most recent advances had been noted.

The first task therefore in preparing a new edition has been to incorporate the more precise molecular measurements secured since the end of the war, not only by improvements in applying the older methods, but by new techniques, such as neutron-diffraction, micro-wave spectroscopy, and nuclear magnetic resonance. Re-validated thus, and by the correction of some surviving errors, the first four chapters remain ‘a compact but elementary account of classical and modern conceptions of valency, suitable for the general reader’. Chapter v also retains broadly its original form, but now includes a short account of ‘artificial’ and transuranic elements.

In Chapter vi substantial changes have proved imperative: the accounts of the metallic carbonyls, of acetylene, of the electro-affinity (electronegativity) of combined atoms, and of the energies of single links have all been entirely rewritten: the section on molecular orbits has been modernized, and amplified by new matter on electron deficient systems, such as the boron hydrides. A summary of the recent treatment of the *cyclo*alkanes has been introduced, and it is hoped that the now detailed knowledge of ‘hydrogen bonding’ is reflected in the greatly expanded section on this very wide-spread type of molecular interaction.

I must not fail to offer my thanks to certain of my colleagues, notably Dr A. G. Sharpe, Dr P. Maitland and Dr A. G. Maddock, who by reading and commenting upon drafts of new or amended sections have so greatly assisted in the attempt to ensure a correct and acceptable presentation.

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LIST OF ABBREVIATED TITLES

- Acta Cryst.* Acta Crystallographica.
Amer. Abstr. Abstracts of the American Chemical Society.
Angew. Chem. Angewandte Chemie.
Annalen. Liebig's Annalen der Chemie.
Ann. Chem. Annalen der Chemie und Pharmacie.
Ann. Physik. Annalen der Physik.
Ann. Reports. Annual Reports of the Chemical Society.
Atti Accad. Lincei. Atti della Accademia nazionale dei Lincei: Rendiconti della Classe di Scienze fisiche, matematiche e naturali.
Ber. Berichte der deutschen chemischen Gesellschaft.
Bur. Stand. J. Res. Bureau of Standards Journal of Research (to 1935).
Chem. Ind. Chemistry and Industry.
Chem. Rev. Chemical Reviews (American Chemical Society).
Compt. rend. Comptes rendus hebdomadaires des séances de l'Académie des Sciences.
I.C.T. International Critical Tables.
J. Amer. Chem. Soc. Journal of the American Chemical Society.
J. Chem. Physics. The Journal of Chemical Physics.
J. Chem. Soc. Journal of the Chemical Society.
J. Ind. Eng. Chem. Journal of Industrial and Engineering Chemistry.
J. Physical Chem. The Journal of Physical Chemistry.
J. Res. Nat. Bur. Stand. Journal of Research of the National Bureau of Standards (from 1935).
Naturwiss. Die Naturwissenschaften.
Phil. Mag. Philosophical Magazine.
Phil. Trans. Philosophical Transactions of the Royal Society of London.
Phys. Rev. Physical Review.
Pogg. Ann. Poggendorff's Annalen (Annalen der Physik).
Proc. Roy. Soc. Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. Proceedings of the Royal Society of Edinburgh.
Quart. Rev. Chemical Society Quarterly Reviews.
Rec. trav. chem. Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Mod. Phys. Reviews of Modern Physics.
Trans. Faraday Soc. Transactions of the Faraday Society.
Verh. dtsch. phys. Ges. Verhandlungen der deutschen physikalischen Gesellschaft.
Z. anorg. Chem. Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektroch. Zeitschrift für Elektrochemie.
Z. Krist. Zeitschrift für Kristallographie.
Z. Physik. Zeitschrift für Physik.
Z. physikal. Chem. Zeitschrift für physikalische Chemie, Stöchiometrie, und Verwandtschaftslehre.