

## A TREATISE ON ANALYTICAL CHEMISTRY

### Comprehensive Analytical Chemistry

Edited by Prof. Cecil L. Wilson and David W. Wilson. Vol. 1B: Classical Analysis. Pp. xxii + 878. (Amsterdam; Elsevier Publishing Company; London: D. Van Nostrand Company, Ltd., 1960.) 155s.

**T**HIS book, Vol. 1B, comprises the second part of the first volume of this series on "Comprehensive Analytical Chemistry" which is being produced under the direction of an advisory board of acknowledged world experts in the various fields of analysis. This monumental scientific work is edited by Prof. C. L. Wilson and his brother, D. W. Wilson, both of whom are particularly eminent as microchemists and as teachers of the analytical method.

The first volume, 1A, has already received much well-merited eulogistic comment from readers and reviewers, and this second volume, dealing with classical methods of inorganic titrimetric and organic quantitative analysis, is also an extensive and scientifically detailed publication of the highest standard. The text is lucidly annotated where necessary and the reference bibliographies to each section are both helpful and comprehensive. The construction of laboratory apparatus is illustrated with great diagrammatic clarity, and the numerical tables and graphical representations form a most useful supplement to the text.

The theoretical and thermodynamical principles governing the analytical procedures are presented in much detail, and the academic student will welcome those extensive sections dealing with complexans, redox potentials, ionic equilibria, etc.

Much practical laboratory detail is also included in those descriptive parts relating to reagents, apparatus, methods, etc.; this makes the book singularly attractive to the young chemical analyst, who will find a wealth of experience and sound advice presented in a most assimilable manner. For the more mature analyst, there are descriptions of the recent modern techniques, of reagent standards, chelate compounds, a very extensive section on complexan reactions and titrimetry, potentiometric and amperometric methods, etc. The inorganic sections covers every titrimetric reagent normally used in the most up-to-date laboratory, and ends with an interesting note on the application of a miscellany of the more unusual reagents.

The section of the book dealing with organic quantitative analyses is equally comprehensive and detailed, both macro- and micro-techniques being described for the determination of the main elements, specific groups, etc. Various alternative methods are presented; for example, the determination of carbon gravimetrically as carbon dioxide, by acid titration after absorption in baryta, or by determining the change in conductivity of the baryta solution. All the usual non-metallic and metallic elements are covered, as are also the distinctive groups, nitroso, azo, thiocarbonyl, methoxy, alkyl, etc.

The volume ends with an excellent section covering titrations in non-aqueous solvents, a subject which is still one of the most attractive fields for those

interested in pure research. The theoretical approach is again clear; aprotic, protogenic, protophyllic and amphiprotic solvents are discussed in relation to the Brönsted-Lowry-Lewis theories. Visual fluorescent, photometric, conductimetric and potentiometric indicator systems are described for various non-aqueous titrimetric determinations, and typical reaction phenomena are given graphical representation.

There is no doubt whatsoever that an authoritative, detailed and scientifically pre-pollent work of this nature will find its way on to the bookshelves of all institutions dealing with either the practice or teaching of analytical chemistry and will retain its status as a unique analytical vade-mecum for many years to come.

D. T. LEWIS

## FREE RADICALS IN AROMATIC SUBSTITUTION

### Homolytic Aromatic Substitution

By G. H. Williams. (International Series of Monographs on Organic Chemistry, Vol. 4.) Pp. vii + 133. (London and New York: Pergamon Press, 1960.) 45s. net.

**I**NTEREST in homolytic, as distinct from heterolytic, reactions dates from the recognition by Prof. D. H. Hey in 1934 that the nuclear phenylation reaction, discovered some ten years earlier by Gomberg and Bachmann, did not conform with current ideas of aromatic substitution in terms of reactions by electrophilic and nucleophilic reagents. He postulated that this reaction represented a new type of aromatic substitution, involving electrically neutral free radicals. Further reactions displaying the same characteristics were soon discovered and were intensively studied. Homolytic substitution has since become a subject of considerable theoretical and practical interest.

In recent years, thanks to new and refined physical techniques, organic chemists have been able to accumulate reliable quantitative data on aromatic substitution processes of all types and this new knowledge has often necessitated a revision of theoretical concepts. The appearance of this monograph by Dr. Williams, a collaborator of Prof. Hey for many years, is timely, and it represents a valuable contribution towards a more comprehensive understanding of aromatic substitution generally.

The author subjects to critical scrutiny the various theoretical treatments, based on wave mechanics, which have been applied in attempts to rationalize the observed phenomena of aromatic substitution. Particular emphasis is placed on those aspects germane to the problems of orientation and reactivity in homolytic substitution. The limitations and deficiencies of these theoretical treatments are exposed. Thus, some unwarranted assumptions are made; for example, the failure to take cognizance of the intrinsic reactivity and polar characteristics of free radicals. Evidence, based on partial rate factors, is adduced to show that all homolytic substitution reactions exhibit some partial ionic character.

The reactions surveyed include homolytic arylation, both inter- and intra-molecular, alkylation, hydroxylation, acetoxylation, benzyloxylation, amination