

experiments the Andrews and Keefer treatment appeared to be giving results of precision—excellent linear plots with all experimental points apparently on the line.

This apparent precision was in part, at least, a delusion, for a more searching and penetrating analysis would reveal a considerable area of uncertainty in the values obtained. Since 1957 progress in this field has been explosive, and the basis for a more rigorous treatment of experimental data is available. In this connection it is, perhaps, pertinent to cite the following references:

- (1) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).
- (2) E. Grunwald and W. C. Coburn, Jr., *ibid.*, **80**, 1322 (1958).
- (3) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).
- (4) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).
- (5) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).
- (6) N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, **86**, 3217 (1964).
- (7) W. B. Person, *ibid.*, **87**, 167 (1965).

Of the foregoing references, ref. 1 and 4 are cited in the text, "Molecular Complexes in Organic Chemistry," by Professors Andrews and Keefer, ref. 7 appeared after publication of the book, and ref. 5 and 6 were probably published after it was written. If I find myself somewhat dissatisfied with this text, it is not, however, because of the authors' failure to include a particular reference or references. It is rather that the authors' treatment of experimental methods in this field is unduly optimistic, and their discussion of the results obtained is consequently devoid of healthy scepticism. This reaction was particularly prevalent during my reading of Chapter IV which discusses the experimental methods for determining association constants and the stabilities of the complexes in solution. Here it would have been of real service to organic chemists to stress the many difficulties in these measurements and more clearly mark the numerous pitfalls that await the inexperienced investigator. The neophyte in this field will surely profit from a reading of this book, but I would strongly urge the seven references cited as supplementary reading.

Of the remaining five chapters in the book, Chapter II, which describes the spectra of complexes, Chapter III, which details the complex geometry, and Chapter VI, which discusses the relationship of complexes to reaction mechanism, will prove of most interest to organic chemists. The coverage in all three chapters is detailed and comprehensive. Where divergent views exist, they are given with little or no editorial comment. My own preference would be for a more critical even if less objective discussion.

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Thermodynamics of Irreversible Processes. By PIERRE VAN RYSELBERGHE, Stanford University. Blaisdell Publishing Co., 501 Madison Ave., New York, N. Y. 1964. 165 pp. 17 × 23.5 cm. \$7.50.

Since there have been a number of books published recently on irreversible thermodynamics, the first question which comes to mind is what features, if any, of the present book set it apart from previously published books on the subject. The material which is presented in the major books on irreversible thermodynamics falls into three major categories: (1) equilibrium thermodynamics and the calculation of entropy production rate, (2) the theoretical basis for and derivation of Onsager's reciprocal relations, and (3) applications of the theory. Both the present book and Prigogine's book of the same title include material in category 1, but Van Rysselberghe includes little material of category 2. On the other hand, he discusses many more applications of the theory than Prigogine. DeGroot's books jump almost immediately into a discussion of the theoretical basis without including a section on equilibrium thermodynamics. The present book is written on a somewhat more introductory level than the other books mentioned. Thus the book should find its place as an introductory text for those who are more interested in applications than in the development of the theory.

Van Rysselberghe's book is taken from his lecture notes for a course which he has given. The general outline of the book is similar to Prigogine's book, but the treatment is different. In terms of the number of words, Van Rysselberghe's book is approximately three times larger. Roughly the first third of the book is devoted to a discussion of those parts of equilibrium thermodynamics which are required for the remainder of the book. Thus the first and

second laws of thermodynamics and terms such as entropy, enthalpy, affinity, activity, uncompensated heat, and the chemical potentials are defined and discussed. Entropy production rates are calculated for a number of different types of systems.

Onsager's reciprocal relation is introduced as a postulate with very little mention of its theoretical basis. There is little explicit discussion of the restrictions on the fluxes and forces which are required to make the Onsager relations apply. The remaining two-thirds of the book is devoted to a discussion of various applications of the theory. These include electrochemical reactions at the electrodes in galvanic cells; transport processes between two homogeneous phases, including a discussion of the Knudsen effect and thermosmosis; fluid motion; diffusion in isothermal systems, in systems having temperature gradients (Soret and Dufour effects), and in systems having mobile charge carriers (relations between electrical mobility and diffusion coefficient); thermoelectricity and thermo-electrochemistry; chemical reactions at constant affinity and states of minimum entropy production; and viscous fluid flow. The book concludes with a short discussion of thermodynamic time.

The author's style is rather terse with a high ratio of mathematical expressions to text. There is no index; however, the Table of Contents is quite detailed.

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Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field. By NORMAN S. BHACCA, Varian Associates, Palo Alto, Calif., and DUDLEY H. WILLIAMS, Churchill College, Cambridge. Holden-Day, Inc., 728 Montgomery St., San Francisco, Calif. 1964. ix + 198 pp. 19 × 26 cm. \$7.95.

All persons interested in the use of n.m.r. spectroscopy for obtaining structural information of organic molecules should own this book.

In such a rapidly developing field as n.m.r. spectroscopy, the major books written on this subject 2 to 6 years ago are now seriously outdated. This timely book by Bhacca and Williams is a welcomed sight, and it is hoped that others covering different aspects of the subject will be forthcoming.

The book emphasizes proton magnetic resonance spectral correlations with the structures of steroids. Much of the material presented should be extended readily to conformationally more mobile molecules. A large part of the presentation follows closely the style of a review article. As such, the discussion in parts tend to be lacking in depth; however, this unattractive feature is offset partly by the fairly thorough and up-to-date (through mid-1964) literature references provided.

The authors' approach is to present and tabulate well-documented empirical correlations of n.m.r. parameters with structure along with a minimum of theoretical discussion. This is followed generally by carefully selected illustrations of the applications of these correlations to evaluate various structural features of steroids. The authors emphasize the numerous variables that cumulatively affect proton chemical shifts and coupling constants and they stress, often with illustrations, the potential dangers of extracting proton coupling constants from apparent first-order spectra. Examples are given that illustrate the various techniques (e.g., double and triple resonance, "tickling" experiments, selective deuterium labeling, and effects of solvents) that are useful for obtaining the maximum information from complex spectra.

Particularly noteworthy are (1) the authors' review in Chapter 5 of long-range H,H and H,F spin-spin couplings, and (2) their discussions in Chapter 7 of the "reaction field" solvent effects and of the effects of benzene solvent on proton chemical shifts. Most of Chapter 7 derives from the authors' unpublished work.

The book is organized well, the spectral reproductions and drawings are clear, and only a few typographical errors are apparent (4.5 cos² φ should read 4.5 cos 2φ in eq. (3-6) on p. 49). It should serve as an excellent reference source. Because of its somewhat limited general coverage and its deficiency in presenting the fundamental aspects of the topics discussed, this book alone would not be suitable as a text for an introductory course in n.m.r. spectroscopy for the organic chemist.

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