

limited time available there is a reasonable coverage of material. The author of this book has solved this problem nicely (the book is based on courses of lectures given over a number of years) in that he has combined a fairly wide coverage with an essential unity of approach.

L. S. GODDARD

### Hyperconjugation

By Prof. Michael Dewar. Pp. vi+184. (New York: The Ronald Press Company, 1962.) 6.00 dollars.

**H**YPERCONJUGATION is the name given to a series of chemical effects. These begin with the observations by Baker and Nathan that an alkyl group can influence the rate of a chemical reaction, and then go on to the further effects of such a group (for example, methyl) on bond-lengths, ultra-violet spectra, heat of formation and other measurable properties of a molecule. It is as if the alkyl group could conjugate with a double or triple bond to which it was attached. But it has recently become very difficult to sort out how much of all this is truly a 'resonance' situation, how much an 'inductive' one, and how much is simply the result of changes of hybridization on one or more of the carbon atoms. Neither theory nor experiment is sufficiently clear-cut, and much confusion surrounds the whole topic.

Prof. Dewar has done a most useful job in setting out the evidence, from as many different points of view as possible. Each chapter of this book is concerned with one aspect of hyperconjugation. First, he examines the arguments in favour of hyperconjugation, and then he shows how inconclusive most of them are. One is left with the feeling that except perhaps for free radicals and certain carbonium ions, the concept has been rather over-emphasized during the thirty years of its existence.

The writing and general style of this book bear the unmistakable imprint of the author's wide knowledge and tremendous enthusiasm. Despite occasional evidence of over-hasty preparation, this is easily the best available account of a very puzzling chemical phenomenon.

C. A. COULSON

### Microdiffusion Analysis and Volumetric Error

By Prof. Edward J. Conway. Fifth revised edition. Pp. xviii+467. (London: Crosby Lockwood and Son, Ltd., 1962.) 42s. net.

**M**ICRO-DIFFUSION analysis and Prof. E. J. Conway are almost synonymous, and it is fortunate that he and the publishers are prepared to bring this book up to date at fairly regular intervals. The method is extremely elegant, eminently suited to the determination of micro-amounts, provided that the substance sought can participate in a reaction in which a gas or vapour is quantitatively liberated. For some tastes, the time required for a single determination is rather long, but with serial determinations this is reduced to a few minutes. For this and other reasons, the most important applications are in clinical and biochemical analysis. Most of the new material incorporated in this fifth edition consists of methods and applications in this field.

The second part of the book, that dealing with the errors of volumetric analysis, remains unaltered. Recently, there has been a renewal of activity in this subject, witness the work of Bishop and of Dean, and the alteration in 1961 of the British Standards method for emptying pipettes. Much of this work no doubt stems from Prof. Conway's exposition, which is a classic and should be read by all analysts.

The publishers have maintained the high standard of production of previous editions of this unique book.

J. F. HERRINGSHAW

### Basic Principles of the Tracer Method

Introduction to Mathematical Tracer Kinetics. By Prof. C. W. Sheppard. Pp. xviii+282. (New York and London: John Wiley and Sons, Inc., 1962.) 60s.

**I**T should be clearly understood that this book does not attempt to provide information about the techniques available for the use of radioactive and non-radioactive substances as tracers. It is assumed that the reader is already familiar with the basic principles involved, and the book is devoted to an account of the ways in which experimental results can be treated in given systems. The book is thus largely mathematical in its description and handling of various experimental situations.

A treatment is given for one, two, three and multi-component systems of both closed and open types and also for continuous flow systems and membrane processes. These mathematical analyses are clearly and logically developed and are illustrated by figures and diagrams. One chapter is devoted to a description of analogues (electrical and non-electrical) for the various systems and to a discussion of the use of analogue computer techniques.

The mathematical models arise, of course, from real systems which are referred to in the text, and the examples chosen come from the field of physiology and deal largely with the transport of body fluids.

This volume can be recommended to those interested in, and concerned with, the use of tracers in biological systems and should form a useful reference book. It is clearly written, well produced and good value.

J. C. ROBB

### The Third Law of Thermodynamics

By J. Wilks. (Oxford Library of the Physical Sciences.) Pp. viii+142. (London: Oxford University Press, 1961.) 15s. net.

**T**HIS monograph contains chapters dealing with the statistical aspects of entropy and others in which various chemical and low-temperature phenomena are discussed in terms of statistical entropy. I had managed, with no great resolve, to do without the Third Law, and therefore welcomed the opportunity of reading Dr. Wilks's book, if only to find out why feelings about the Third Law seem to run so deeply. I now know that the Law provides a test of whether a system will do anything interesting if cooled to lower temperatures. For example, a magnetic material which obeys Curie's law to the lowest temperatures explored must begin to deviate from this at lower temperatures because the Third Law requires that magnetic susceptibility should be independent of temperature at absolute zero. When Dr. Wilks goes beyond this kind of conclusion, as he generally does by the introduction of statistical mechanical ideas, the relevance of the Third Law becomes confused. He points out that the statistical basis of the Third Law is simply the contention that the ground-state of a system is non-degenerate, or at least only somewhat degenerate.

In a situation where one can turn to statistical descriptions this seems to me a more explicit assumption than the Third Law itself. The Third Law (like the other two) should be useful mainly when microscopic knowledge is unavailable or finally irrelevant, and in overlaying most of the topics in the book with