from a ground state molecule which is formed by internal conversion, it is not known whether such a reaction can occur thermally. The stereoisomerization reaction (7) is known as a thermal process but its pressure dependence does not show the expected trend. The reaction is known even in solution,[10] which suggests that it may not be subject to collisional quenching at all. But it should also be borne in mind that the large spectral shifts displayed by dienes and trienes in going from the vapor phase to even a hydrocarbon solution make a correlation between the photochemistry in the two phases rather obscure.

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[10] N. I. Shuikin and V. A. Tulupov, *Vestnik Moskow Univ.* **9**, No. 8, Ser Fiz-Mat.; *Estesven Nauk*, No. 5, 91 (1954); *C. A.*, **49**, 3776 (1955); R. Srinivasan, *J. Am. Chem. Soc.*, in press.

BOOK REVIEWS

The Wave Mechanics of Electrons in Metals. BY STANLEY RAIMES, Reader in Mathematics, Imperial College, University of London. Interscience Division, John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. xi + 367 pp. 15.5 × 23.5 cm. Price, $13.00.

This is an unusual book among the many recent volumes on solid state physics. Some 350 pages are devoted to discussion of what most solid state physics books take for granted or else discuss briefly in perhaps one third to one tenth the space. The author makes his purpose completely clear in his preface, and the potential reader is advised not to ignore it.

This is *not* the place to seek a complete picture of band structures of solids, nor a description of transport phenomena. What this book does present is a fairly detailed mathematical treatment of elementary aspects of the behavior of electrons in a periodic potential.

The level is such that a well-trained physics major in his senior year should have no difficulty in reading it from cover to cover. The required quantum mechanical aspects are covered in early chapters and where needed. I found the writing clear and self-contained.

The point of view is distinctly theoretical, and much pertinent experimental material is not mentioned. This is quite consistent with the avowed purpose of the text.

A reviewer's criticism of specific sections seems irrelevant. When a book is unique it will be used (or not) because of its uniqueness, and not because it is (or is not) the best possible treatment of the material included. A more relevant question to be discussed here would seem to be the potential uses of this book in contemporary American education. Certainly this will not be widely selected as a text book for a first course in solid state physics; there is insufficient coverage of experimental aspects, and no pretense of covering perhaps ninety per cent. of solid state material. The elementary nature of the treatment will also prevent it from being chosen as a text book for an advanced course in theory of solids. Where it may well find popular usage is as a supplementary text in elementary courses at points where a simple but rigorous treatment is wanted for some aspect of electrons in solids, either in courses on solids or in modern physics.

Particularly worthy of note is the chapter on plasma oscillations. I know of no other text which contains such a lucid, modern, and complete treatment of this topic. The footnote on p. 197 will also be welcomed as containing the essence of a decent proof of Bloch's theorem.

A clear and fairly complete treatment of the Wigner-Seitz "cellular" method is presented in Chap. 9. The author gives enough detail so that anyone should be able to understand it on his first encounter, and indeed one wishes that he had chosen also to discuss some of the newer techniques such as the OPW and APW methods.

The strongest impression that this reviewer received from the book is that every topic included is discussed right from the beginning, with no steps omitted. As a result some fairly sophisticated material is reached without the reader becoming aware that he is learning anything "hard." I think it is an excellent book to learn from, and students who use it will be grateful to the writer for his great care to make it comprehensible in every respect.

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Acids, Bases, and the Chemistry of the Covalent Bond. By CALVIN A. VANDERWERF, Professor of Chemistry and Chairman of the Department, University of Kansas. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1961. ix + 117 pp. 12.5 × 18.5 cm. Price, $1.95.

This book is one of the first two titles to appear in the publisher's series "Selected Topics in Modern Chemistry." The stated main purpose of both this volume and the series as a whole is to serve as supplementary material for the first-year college chemistry course.

The present volume is devoted to the chemistry of ionic reactions at the covalent bond. The treatment begins with Brønsted-Lowry acid-base theory, continues with Lewis theory, and concludes with base displacement and acid displacement and addition reactions. These are developed successively in a logical fashion, each as an extension of the previous concept.

The book consists of six chapters, the first of which is introductory. Chapter 2 is concerned with the Brønsted-Lowry concept of acids and bases. This is the one part of the book in which the treatment is not above the level of that in the usual modern first-year college chemistry textbook. Although acidity constants are mentioned, there are essentially no examples of calculations involving them. The over-all pattern of the book does not really suffer from the lack of such calculations, but in their place is presented, without any qualifications, the idea that equilibrium in the reaction of any acid with the conjugate base of a weaker acid will lie at least 50% to the right. This concept comes to grief in even the elementary example of a very dilute aqueous solution of an acid such as acetic acid, and is likely to cause future difficulties if taken too seriously by the student. The presentation of the Brønsted-Lowry concept is done in a fashion which permits its use as a foundation for the remaining material in the book.

Chapter 3 deals with the effect of structure on relative acid and base strengths. The roles of relative electronegativity, of ion sizes and of resonance are presented in an effective manner. As seems customary in elementary treatments, the relative electronegativity concept is stretched a bit beyond its original meaning, but the author makes allowance for this. Another custom, and one which now is perhaps less justified, is the attributing of the dipole moments of molecules such as water to bond polarity, thus ignoring the important role of the lone pair electrons.

In Chapter 4 the author introduces the Lewis concept of acids and bases. Most of the chapter consists of a well-organized discussion of the kinds of chemical species which behave as Lewis acids.

The last two chapters are devoted to base and acid displacement and addition reactions. A wide range of topics is treated, with the main concern being the nucleophilic and electrophilic substitution and addition reactions, and the acid- and base-catalyzed elimination reactions, of organic chemistry. A thorough and up-to-date introduction to these topics is presented. Relative rates of electrophilic substitution in aromatic systems are, for example, quite properly considered from the standpoint of the stability of the transition state, and only then is the older "electron availability" approach mentioned as yielding "largely equivalent" predictions.

The book is written in a quite readable style. It should be of particular interest to students who plan to take courses in organic chemistry. The book should also serve as a good starting point for those chemists whose academic training occurred in earlier years, and who wish to learn something about the more recent theoretical principles of ionic reactions at the covalent bond.

The concept of a series of supplementary monographs such as this one is a relatively new approach to the first-year college chemistry course, and one which is being adopted by more than one publisher. Offsetting the increased cost to the student of a textbook plus several monographs is the obvious advantage of having each topic discussed by an authority in the particular field. This approach will undoubtedly make available some fresh and timely new text material.

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Contributions to the Thermodynamics of Surfaces. By J. J. BIKERMAN. Published by the Author, 20-c-223, Massachusetts Institute of Technology, Cambridge 39, Massachusetts, 1961. 76 pp. 13.5 × 21.5 cm.

Professor Bikerman here presents a collection of our papers which, as he states in his preface, he "did not succeed to place. . . in suitable scientific journals." They are entitled "Two Notes on the Thermodynamics of Capillarity. I. The Surface Free Energy, II. The Adsorption Equation," "The Nature of Surface Pressure," "Theory of Young's Equation of Wetting" and "Experiments on Young's Equation of Wetting."

In this reviewer's opinion each article in this collection contains errors or garblings of concepts serious enough to make their publication difficulties with reputable scientific journals understandable. The book may serve a purpose in causing readers to re-examine critically some of the classical concepts in surface thermodynamics, but if the re-examination is careful the classical concepts will survive it.

For example, the first paper attributes to Gibbsian thermodynamics the hypothesis that if the interfacial layer "say 100 angstroms thick" were separated from the bulk phases and then "homogenized" no free energy change would result. This is absurd, and is not implied by Gibbsian thermodynamics; Eq. 5 preceding it is allegedly based on Gibbsian thermodynamics, but is incorrect in omitting a surface tension term (so is Eq. 13), and is not to be found in Gibbs[1] work (it apparently resulted from an incorrect integration of an equation for dE (Gibbs Eq. 477), applicable (and so stated by Gibbs) to a system with fixed boundaries.

The paper on surface pressure asserts that the ideal spreading pressure equation $\pi = nkT$ is incorrect and that the derivation based on Henry's law limiting adsorption equations is fallacious since with finite solubilities no equilibrium spreading pressure could exist. This latter statement is strictly true, but in the same sense one could claim that application of equilibrium thermodynamics to gases in cylinders is invalid, since no cylinder material can be found for which the gas diffusion constant is zero. (A statistical derivation of the equation $\pi = nkT$ for "insoluble" mobile monolayers is given by Fowler and Guggenheim[2]). According to Bikerman, the correct equation is $\pi = NS(\gamma_0 - \gamma_2 - \gamma_{12})$, where S is the area occupied by one molecule. An equation such as this might be justified for condensed monolayers ($NS \approx 1$); to demonstrate its validity, Bikerman presents experimental data for siloxanes on various host liquids, but at monolayer concentrations 10^{-7} g./cc. (*i.e.*, approximately a condensed film 10 Å. thick). The experiments, in short, were not relevant to the ideal monolayer model.

A recent paper by Johnson[3] gives a clear discussion of Young's equation; this equation depends on a tension balance (or virtual work argument) applied to *the drop periphery*, and Bikerman's examples suggest that this point is not clear to him. For a deformable solid (such solids were used by Bikerman in the fourth paper to illustrate his ideas experimentally) arguments similar to those used in obtaining Neuman's triangle are applicable; the validity of this treatment has been demonstrated, for the case in which the solid is replaced by mercury and all tensions are subject to direct measurement, in a recent paper by Smolders.[4]

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(1) J. W. Gibbs, "Collected Works," Yale University Press, New Haven, Conn., 1948, Vol. 1, pp. 219ff.

(2) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, England, 1956, p. 424, Eq. 1003, 4.

(3) R. E. Johnson, Jr., *J. Phys. Chem.*, **63**, 1655 (1959).

(4) C. A. Smolders, *Rec. trav. chim.*, **80**, 699 (1961).