

The objections common to the 23 kK. region being d-like or charge-transfer bands could be overcome, in part, by supposing the electron to move into an orbital that is roughly xy . Such a transition would involve minimum changes in the vanadyl vibrations.

Finally, the origin of the splitting of the 23 kK. band into two components must be considered. The 0.35 kK. splitting seems too great to be accounted for by spin-orbit coupling. Therefore, it is likely that the two components represent two distinct orbital states and that the spin-orbit splitting is much smaller and might be resolved only at very low temperatures. An attractive explanation is that the 0.35 kK. represents splitting of an orbital which would be E in C_{4v} into two

orbitals, namely B_1 and B_2 , in C_{2v} . Another possibility is a splitting caused by neighboring molecule interactions in the crystal.

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Book Reviews

Valency and Molecular Structure. Edited by E. CARTMELL and G. W. A. FOWLES. Butterworths, Inc., 7235 Wisconsin Ave., Washington 14, D. C. 1961. xii + 294 pp. 14 × 22 cm. Price, \$7.00.

The first edition of this book was published in 1956 and was thus one of the earliest of the many books of its type which are now available. The new edition retains the basic structure of the first edition, being divided into three parts, "Quantum Theory and Atomic Structure," "Quantum Theory of Valency," and "The Application of the Principles of Chemical Bonding."

As the authors say in their preface, the first part is almost unchanged, the second part now places a greater emphasis upon molecular orbital theory, and the third part is almost entirely rewritten because of the advent of crystal field and ligand field theories and their impact upon structural aspects of modern inorganic chemistry.

It is pleasing to note that many of the inaccuracies of the first edition have been removed, *e.g.*, the identification of the real d-orbitals d_{xy} , d_{xz} , etc., with particular m_l values (see Fig. 19). On the whole, the changes in accent in part II are for the better and no new errors seem to have been introduced along with these changes. The addition of small sections on the hydrogen bond and metallic bonds is also welcomed, as brief as they are.

The reviewer's main criticisms stem from part III, where the principles are applied to structural and reaction chemistry. This part contains many errors, some printing, others of fact and/or of logic. In the first place, it seems a waste to have increased the accent on molecular orbital theory in part II when the main descriptive method of part III remains the valence bond theory.

The extensive use of the concept of hybridization has led to many passages which are either irrelevant or factually incorrect. One particularly annoying aspect is the repeated use of such phrases as "... the beryllium atom uses sp hybrid orbitals ..." etc. (p. 184, my italics), "... and arsenic uses sp^3 orbitals to form simple tetrahedral structures ..." (p. 171), and so on, as though such hybrids were physically measurable and their nature exactly ascertainable. The same sort of approach leads to statements such as (p. 212), "The valence-bond method predicts two possible configurations: tetrahedral and square-coplanar. In the tetrahedral arrangement, the atom uses *either* the sp^3 combinations . . . or sd^3 hybrid orbitals . . ." (my italics). The *either/or* exclusion apart, there are, in addition, the tetragonal pyramid and the various asymmetric tetrahedral structures which can also be described by hybrids.

The following paragraph on p. 212 is also inconsistent with the second last paragraph on p. 209. In the latter paragraph the authors discuss sd hybridization as the "reason" for the existence of such compounds as $HgCl_2$, whereas, in the former, they claim that sp^3 hybrids must be used for tetrahedral mercury compounds because "there are no d-electrons of suitable energy available." These logical nonsequiturs are quite common in the whole of part III. As a final illustration, consider the general discussion of crystal field stabilization energy (CFSE) as a criterion for structure determination, *e.g.*, on p. 216, for d^0 , d^5 , and d^{10} complexes. "In each case the ligands will take up the tetrahedral position . . . Tetrahedral arrangements are *thus* found in $TiCl_4$, $[FeCl_4]^-$ and $[ZnX_4]^{2-}$." The authors carefully avoid $[AuCl_4]^-$, for example, and there is also XeF_4 , etc., if a further example is required. Surely it is now possible to realize, and to state, that while certain approximations are useful, nonetheless there are still more factors at work than any single one of the theories is usually capable of taking into account.

In somewhat the same vein as the above, is the matter of "bonds being shorter than normal." In organic chemistry there are enough data available to even allow a statistical analysis to have been performed on bond lengths, but in inorganic chemistry, knowledge of what constitutes "normal" or "single bond" lengths is, at most, rudimentary. It is, therefore, misleading to base theoretical explanations of such shortenings on insufficient data, particularly in the matter of bonding and back donation "phenomena" (see, *e.g.*, p. 241).

Finally, the authors have included a very brief section on the "Experimental Determination of Configuration" which, one feels, could be amplified at the expense of some of the more "theoretical" ideas. This would give room for a mention of what type of information, other than vibration frequencies, comes from a study of spectroscopy. This kind of information, and a discussion of the order of accuracy to be expected, is surely something which could reasonably be expected in a book of this type.

There is much of value in this book and the authors have, indeed, succeeded in their efforts to maintain an essentially non-mathematical approach, while at the same time, they have been able to produce a relatively concise summary of the modern approach to the subject. It is a pity, therefore, that very many of the errors of the type described above have been allowed to slip past their scrutiny and to slightly mar what could otherwise have been an excellent introduction to valency and modern inorganic chemistry.

In summing up his opinion, the reviewer realizes that much of what he has criticized could be claimed by the authors to be in conformity with present theoretical-cum-practical inorganic fashions, but surely it is their duty to be critical in their approach toward compartmentalized thinking and uncritical reproduction, since such a book will be read by the beginners in the subject. It is on such a basis that the criticism has been made.

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Annual Review of Physical Chemistry. Volume 14. Edited by H. EYRING. Annual Reviews, Inc., Palo Alto, Calif., 1963. 433 pp. 15 × 22 cm. Price, \$8.50 (U. S. A., \$9.00 elsewhere).

The latest edition in the Annual Review of Physical Chemistry series displays particularly well a balance between new directions and traditional domains of physical chemistry. The sixteen scientific chapters range from the physical organic chemistry of nucleophilic reactivity through electrolytic and nonelectrolytic solutions, heterogeneous catalysis, and polymers to infrared and n.m.r. spectroscopy, to low-temperature solution thermodynamics (really quantum liquids), to four chapters dealing with different aspects of solids (kinetics, superconductivity, lattice dynamics, and electronic spectra), and to fast reactions in solution, statistical mechanics, radiation chemistry, and molecular beams.

I was especially glad to see the chapter on molecular beams. The induction period for this field of research is clearly past, the basic hardware is developed and operating in several laboratories, and important results are appearing at an increasing rate. A review of a subject at this stage of its development serves the dual function of summarizing the work and exhibiting the subject itself to the attention of a new and broad audience. Fite and Datz have done a great service in fulfilling both these functions admirably.

The chapters on lattice dynamics and superconductivity also reflect new areas in which physical and inorganic chemistry is done. The former chapter contains a short and clear section on the Mössbauer effect, with a useful bibliography.

The chapter on nuclear magnetic resonance by S. Meiboom was one I particularly enjoyed reading, for the way each piece of work was put into a context and, frequently, discussed critically.

The editors have continued the policy of including one introductory chapter in the nature of a memoir. I, for one, applaud the policy. This year it is "Fifty Years of Physical Chemistry in Berkeley" by Joel H. Hildebrand. Hildebrand certainly gives a hard sell for Berkeley, and, as he does, he passes on some delightful stories and conveys a clear feeling for the atmosphere in which the department and its members developed. Written in as forthright and engaging style as this one, these introductory chapters could well be longer than the four pages allotted this year.

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Metallic Solid Solutions. By J. FRIEDEL and A. GUINIER. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. xi + 660 pp. 16 × 24 cm. Price, \$19.75.

This book is a compilation of a series of papers dealing with the electronic and atomic structure of metal solutions. The papers were presented at an international symposium held by the University of Paris at Orsay in July, 1962.

The volume is made up of 52 papers of varying length; some are very short and cryptic, 2 or 3 pages, while others run to as many as 38 pages. They have been printed in the order of their presentation and it is obvious that little if any editing has been at-

tempted in order to make a coherent presentation. The structure of the book follows roughly the aim of the conference. Approximately three-fifths of the articles deal with electronic structure and related phenomena while the balance are concerned with short- and long-range order and Guinier-Preston zones.

This is not a book for practicing metallurgists but seems to be aimed at the knowledgeable theoretical metal physicist. A few articles are based on experimental data, others are essentially literature reviews, while others are speculation or calculations based on new approximations for the solution of the many-bodied problem. Throughout the many papers the casual reader will encounter the annoying tendency to substitute names of workers in the field for phenomena or theories. The Kohn anomaly, the Ruderman-Kittel exchange, Fletcher's band structure, the Kuhlman-Wilsdorf reaction are just a few of what could be an extensive list. Perhaps to workers in these fields these names sufficiently describe various concepts; it must since it is so endemic to the field, but if one hopes to reach a wide audience or a receptive audience this has the opposite effect.

One wonders why such a book is ever published since the articles, if really significant, would probably appear in the literature after having been subjected to a critical review. When published in book form without this review the reader, unless he himself is expert, is hard put to separate the significant from the inconsequential.

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Handbook of Laboratory Distillation. By ERICH KRELL. Edited by E. C. Lumb. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1963. x + 561 pp. 36 × 54 cm. Price, \$18.00.

There is not a word about the distillation of inorganic substances in this book, except for a ten-page treatment of isotope separation. But where would one look for a treatment of the distillation of inorganics? The same two sentences can be written with "metallo-organics" substituted for "inorganics." For specific information on such materials an investigator must go to the original or specialized literature, which, except for an occasional mention in one of the annual reviews on distillation, has not been adequately indexed since the last volume of "Distillation Literature, Index and Abstracts for 1953-54."

As compared with other books currently available on laboratory distillation, Krell is intermediate in length and detail of treatment. In the basic areas the treatment is good, though not outstanding, and in general tends to be lengthy and detailed, which is of some advantage for the uninitiated. For those who are versed in the art, the tendency toward wordiness may increase hop and skip reading so much as to cause missing the unique and useful ideas that are present. In general, the symbols and terminology are conventional and will cause no difficulty to a United States reader. There is a good glossary and a satisfactory index.

The unique feature of the book is that it tells how the Germans and other Europeans approach and perform distillation. There is much of interest in the way of laboratory-built and commercially obtainable equipment and accessories that are available abroad. The initial portion of the book has an excellent historical summary. Cleopatra is mentioned. There is a nice collection of figures, which include comparisons of ancient and modern apparatus. As mentioned earlier, the treatment of isotope separation is relatively extensive, but still can serve only as an introduction to this specialized type of distillation. There is more detailed treatment of laboratory continuous distillation than in other available literature.

Of special interest to this reviewer were the number of instances when a non-English reference could be found and cited as an alternate to the customary United States or English refer-