

kinds of terminal hydrogens) and seem to be superior at lower temperatures.^{7,8}

The structure of B_5H_{11} remains in a state of flux, the X-ray data indicating a molecule with a unique¹⁰ bridge hydrogen in 1954¹² (see Figure 1) and the same hydrogen reassigned as a "second" apex terminal hydrogen in 1957.¹³ It would seem that no unambiguous distinction³ can be made with present X-ray technique.

The B^{11} n.m.r. data clearly support a molecule with a single hydrogen on the apex boron atom. We assume that a microwave study will one day observe the controversial bridge hydrogen off center or at least determine its position most accurately.

The 64.2-Mc. spectrum is quite revealing. The small half-width of the low-field triplet is in keeping with little bonding to other boron nuclei. Would not one expect to observe coupling to bridge hydrogens when such narrow lines are present? BH_2 groups show bridge hydrogen coupling in both B_2H_6 and B_4H_{10} . The probable answer is that the two bridge hydrogens would be expected to couple to the BH_2 boron with

(7) An implausible assignment of the H^1 n.m.r. spectrum (wherein spin-coupling relationship is not conserved) has been published.⁴

(8) The B^{11} n.m.r. spectrum of 99+% B_5H_{11} at 64.16 Mc. revealed no spin-coupling changes from the spectrum at 12.8 Mc.⁹ The 60-Mc. H^1 spectra were superior in area measurement at -60° but showed more detail at $+40^\circ$.

(9) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Soc.*, 333 (1959).

(10) We do not support the position that the bridge hydrogen is "unique"; it behaves like other bridge hydrogens which have neighboring unoccupied and equivalent positions. In $B_2H_5^-$, $B_2H_7^-$ (Lewis base),⁵ and B_4H_{10} ¹¹ neighboring vacancies exist and hydrogens tautomerize.

(11) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(12) L. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954).

(13) E. B. More, L. L. Lohr, and W. N. Lipscomb, *ibid.*, **27**, 209 (1957).

different spin-coupling values, in contrast to B_2H_6 and B_4H_{10} ; thus instead of a triplet, due to bridge hydrogen coupling, four less resolved peaks would be expected. Were the BH_2 groups associated with only one bridge hydrogen, each member of the low-field triplet (Figure 1) would be expected to be resolved into a doublet. The values (J_{B-H}) of both terminal hydrogens to boron in the BH_2 groups in Figure 1 seem identical; a few cycles difference would, however, tend to lessen the probability of observing bridge hydrogen coupling. One would expect J_{B-H} (for both terminal B-H bonds) to be identical in B_2H_6 ,^{14,15} somewhat different in B_4H_{10} ¹⁶ (unless rapid intermolecular inversion averages the two terminal B-H bonds), and even more different in B_5H_{11} , where, if boron-boron bonds exist, the terminal hydrogens in the BH_2 groups would be quite different. A structure with the BH_2 groups tied to the other nuclei by bridge hydrogens might well engage in rapid intermolecular exchange, which would allow the terminal hydrogens in the BH_2 groups to exchange.

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(14) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

(15) R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960).

(16) R. Williams, S. G. Gibbins, and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6164 (1959).

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Book Review

Chemical Transport Reactions. By HARALD SCHÄFER, Inorganic Chemistry Institute of the University, Münster, Westphalia, Germany. Translated by Hans Frankfort, Chapel Hill, N. C. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. xi + 161 pp. 15.5 × 23.5 cm. \$6.55.

This book was first published in the German language under the title "Chemische Transportreaktionen" and copyrighted in 1962 by Verlag Chemie GmbH, Weinheim/Bergstrasse, Germany. However, as the author indicates in the Preface, some more recent developments in areas involving the use of chemical transport reactions have been considered, and numerous references to the literature covering the period 1962 to 1963 have been included in the English edition.

The author of this book has contributed heavily to the understanding and application of chemical transport reactions through his many publications since about 1950. The book underlines the great versatility of transport reactions, both for use in preparative chemistry and as a tool for estimating thermodynamic data. Some definite benefits will be derived from the appearance of the English edition. A large volume of information, some of it previously unpublished, is made more readily accessible to the reader, and because so many proven and potential applications are discussed in one source, the book should en-

gender a greater appreciation of the power of this method in preparative inorganic chemistry.

The book consists of six well-organized chapters. In the first chapter a chemical transport reaction is defined as one in which a solid or liquid substance A reacts with a gas to form exclusively vapor phase reaction products, which, in turn, undergo the reverse reaction at a different place in the system, resulting in the re-formation of A. In by far the most common case discussed, the sites of the forward and reverse reactions are maintained at different temperatures (temperature gradient technique).

The remaining five chapters deal with experimental and theoretical principles, examples of transportable solid substances and applications, reaction processes in the gas phase, transport processes as an aid in preparative chemistry, and the use of transport experiments in the determination of thermodynamic values. Many of the examples and applications cited are of interest not only to chemists, but also to metallurgists, physicists, and geologists. In this respect the use of the method for purification and growth of single crystals is especially noteworthy.

A bonus feature of the book is the generally complete referencing to the literature. The bibliography of some 263 references included at the end of the book will be very useful to those desiring more detailed information on specific systems. On the negative side, however, is the frequent reference to data or information

not accessible to the reader. Whereas occasional references of this kind may not be avoided if pertinent information is to be considered, too frequent reference to unpublished results is undesirable. The reader must accept or reject these results without the benefit of resort to a paper where a more detailed account of experimental data or discussion of the validity of the results is given.

On the whole this book is worth careful study by experimental chemists interested in preparative methods, purification processes, or heterogeneous equilibria at elevated temperatures. The book is moderately priced and should make a valuable addition to the personal library.

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BOOKS RECEIVED

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- HANS B. JONASSEN and ARNOLD WEISSBERGER, Editors. "Technique of Inorganic Chemistry." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1965. ix + 401 pp. \$15.00.
- MYRON ROSENBLUM. "Chemistry of the Iron Group Metalloenes: Ferrocene, Ruthenocene, Osmocene." Interscience Publishers, a Division of John Wiley and Sons, 605 Third Ave., New York 16, N. Y. 1965. vii + 241 pp. \$12.50.
- G. SCHWARZENBACH and H. FLASCHKA. "Die komplexometrische Titration." Ferdinand Enke Verlag, Stuttgart, Germany. 1965. vii + 339 pp. 48 DM.