ZrB_2 cell until enough boron had been lost by volatilization to produce a PuB_4–PuB_6 mixture. No variation of the PuB_6 lattice parameter was observed during this process. This experiment, together with other experiments in which PuB_2 was converted into PuB_4 by evaporation of plutonium, imply that the tetraboride evaporates congruently.

It is possible to draw a parallel between the boride phases of the lanthanides and those of the actinides. The existence, or nonexistence, of lanthanide borides is correlated closely with the radii of the metal atoms involved. Thus dysprosium and holmium, which have radii close to that calculated for plutonium from the unit cell dimensions of PuB_4 and PuB_2, form MB_2, MB_4, MB_6, and MB_{12} phases. These four borides were found for plutonium in the present work. In addition, a hectoboride reported for some lanthanides[9] exists also in the plutonium system.

Uranium and erbium have similar effective radii (calculated from unit cell volumes) and both form MB_2, MB_4, and MB_{12} phases.[10] The MB_6 structure cannot be prepared with a cation radius comparable to that of erbium.[11]

The effective radius of thorium is large, comparable to that of lanthanum or cerium, both of which form only MB_4 and MB_6 phases. Thus only ThB_4 and ThB_6 are found.[12]

Borides with boron contents of MB_{12} or less appear to be fairly well understood. The situation as regards higher borides is not as well defined. Lundin[13] reports an yttrium boride of composition near YB_{70}, the X-ray pattern of which he has indexed tentatively with tet-

ragonal symmetry with $a_0 = 11.75 \pm 0.04$ Å., $c_0 = 12.62 \pm 0.04$ Å. Seybolt[14] reports that a micrographic examination of 1 to 2 atomic % yttrium–boron compositions heated in a BN crucible showed a boride estimated to be YB_{50}. Post[15] reports the preparation of cubic borides of holmium, terbium, and ytterbium of composition near MB_{70}, all with the same lattice parameter of 11.75 Å. as determined from powder patterns. Post states further, however, that examination of single crystals showed the true lattice parameter to be 23.50 Å. Smith and Gilles[9] report, for gadolinium and ytterbium, cubic MB_{100} phases with lattice parameters of 16.50 $\pm$ 0.02 Å.

The 99% B–1% Pu arc-melted specimen was found micrographically to contain two phases, one of which was PuB_{12}. When the PuB_{12} lines were subtracted from the X-ray powder pattern, the remaining lines could be indexed completely only on the basis of a simple cubic unit cell with $a_0 = 23.5$ Å. Either the 11.7 or 16.5 Å. (1.414×11.7) cubic cells accounted for part, but not all, of the lines. On this basis the plutonium "hectoboride" is assumed to be similar to that reported by Post and by Smith and Gilles. The plutonium analog of the tetragonal boride reported by Lundin was not found. Two extra, very weak lines appeared in the powder pattern of the 95:5 specimen. These lines, which did not correspond to the MB_{100} phase, were found in no other preparation and were too few and weak to attempt to fit to any structure.

(9) P. K. Smith and P. W. Gilles, to be published.

(10) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, New York, N. Y., 1957, p. 149; also, G. D. Sturgeon, Ph.D. Thesis, Michigan State University, 1964, p. 62.

(11) G. D. Sturgeon and H. A. Eick, *Inorg. Chem.*, **2**, 430 (1963).

(12) J. J. Katz and G. T. Seaborg, ref. 10, p. 39.

(13) C. E. Lundin, "Rare Earth Metal Phase Diagrams," Rare Earth Symposium, Annual Meeting, American Society for Metals, Chicago, Ill., 1959.

(14) A. U. Seybolt, *Trans. Am. Soc. Metals*, **52**, 971 (1960).

(15) B. Post, Document PIB-TR-6, Technical Report No. 6, NR 032-414, Office of Naval Research, 1962.

Correspondence

Assignment of 64.2-Mc. B^{11} Nuclear Magnetic Resonance Spectrum of Pentaborane-11

Sir:

The B^{11} n.m.r. spectrum of B_5H_{11} (containing ∼10% B_5H_9) at 12.8 Mc. was assigned as follows: A high-field doublet[1] representing the apex boron alone *with a single terminal hydrogen* and a superpositioned lower field doublet[2] and triplet[2] representing the base BH

groups and BH_2 groups, respectively; a small unobscured member of a doublet could be unambiguously assigned to the ∼10% B_5H_9 contaminant. Shortly after publication[2] J. R. Spielman and A. B. Burg furnished a sample of B_5H_{11} in which B_5H_9 was presumed to be absent. The B^{11} n.m.r. spectrum at 12.8 Mc. supported their conclusion and thus constituted the first B^{11} n.m.r. spectrum of pure (95+%) B_5H_{11}. Since the original assignment appeared to be unambiguous the spectrum of the pure material was not published. In the past few years B^{11} n.m.r. spectrometry has become more popular and at least two reviews[3,4]
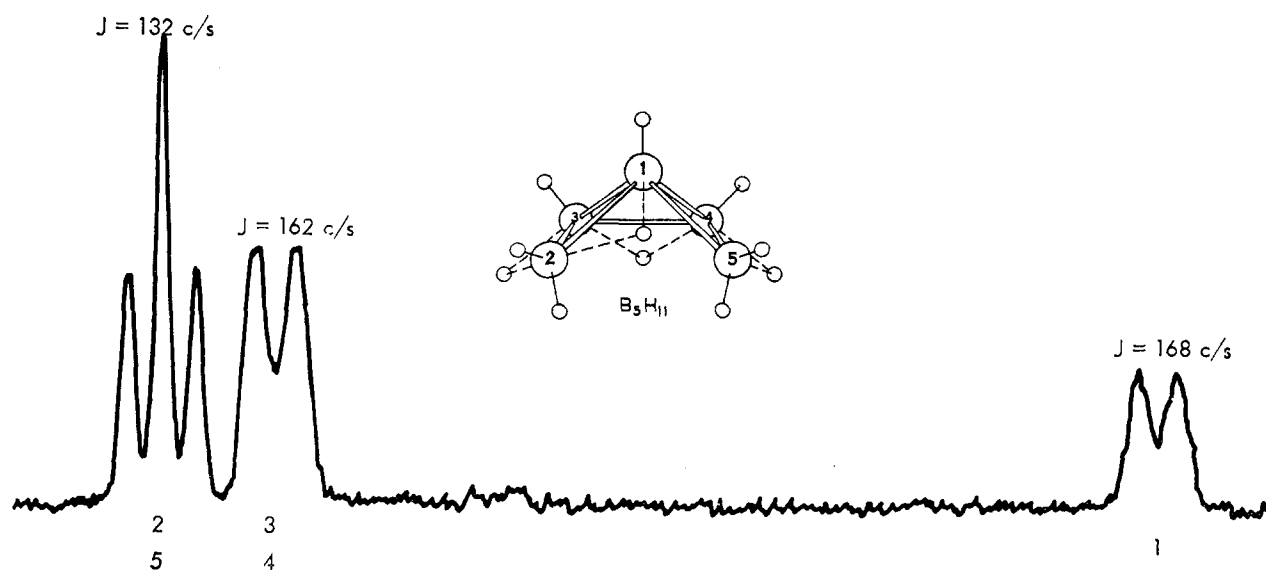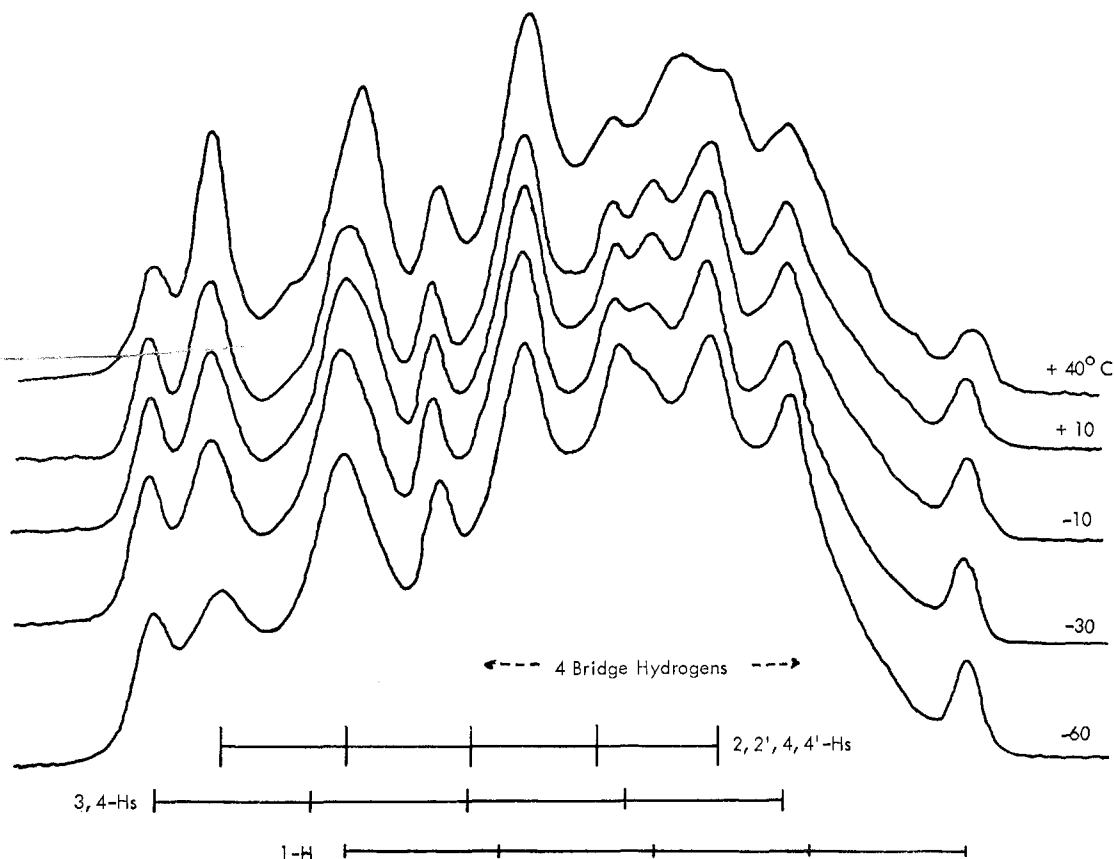
(1) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **79**, 4606 (1957).

(2) R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 320 (1959).

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York N. Y., 1963, p. 135.

(4) C. A. Lutz and D. M. Ritter, *Can. J. Chem.*, **41**, 1346 (1963).

Figure 1.—64.2-Mc. B^{11} n.m.r. spectrum of B_5H_{11}.

Figure 2.—60-Mc. H^1 n.m.r. spectra of B_5H_{11}.

reveal that a number of workers remain confused about the assignment[2,5] of B_5H_{11}. Since we had transient access to the Varian experimental (cryogenic magnet) nuclear magnetic resonance spectrometer[6] and had relatively large amounts of pure B_5H_{11} available, the B^{11} n.m.r. spectrum was obtained at 64.2 Mc. As may be seen in Figure 1, the low-field multiplet in

question[3,4] is completely resolved into a triplet and doublet and our previous assignment[2] is unambiguously confirmed. H^1 n.m.r. spectra (60 Mc.) were taken of the same pure sample of B_5H_{11} (99.5–100% B_5H_{11} by vapor phase chromatographic analysis) at several temperatures. These spectra, reproduced in Figure 2, show orderly changes with temperature especially in the bridge hydrogen region,[2] and in our estimation may be considered useful only in that they are compatible with the B^{11} n.m.r. spectra (they show three different

(5) Both ref. 3 and 4 strangely question the purity of the B_5H_{11} utilized in ref. 1 and 2, since we[2] had pointed out that B_5H_9 was present in both cases.

(6) F. A. Nelson and H. E. Weaver, *Science*, **146**, 223 (1964).

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 unique[10] bridge hydrogen in 1954[12] (see Figure 1) and the same hydrogen reassigned as a "second" apex terminal hydrogen in 1957.[13] It would seem that no unambiguous distinction[3] 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 $+40°$.

(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 $B_3H_8^-$, B_3H_7(Lewis base),[3] and $B_6H_{10}^{11}$ 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.

(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 engender 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