Entropies

The evaluation of the entropy at 298.16°K. is obtained by graphical integration of a plot of C_p against log T. This necessitates the extrapolation of the specific heat curve from the temperature of the lowest measurement down to the absolute zero of temperature. It was found that the following function sums adequately represent the measured specific heats in the temperature ranges indicated.

$$\text{TiO:}\quad D\left(\frac{437}{T}\right) + E\left(\frac{653}{T}\right) \quad (1\%,\ 50\text{–}298\,^\circ\text{K.})$$

$$\text{Ti}_2\text{O}_3\text{:}\quad 2D\left(\frac{441}{T}\right) + 3E\left(\frac{663}{T}\right) \quad (1\%,\ 50\text{–}225\,^\circ\text{K.})$$

$$\text{Ti}_3\text{O}_5\text{:}\quad 3D\left(\frac{399}{T}\right) + 5E\left(\frac{654}{T}\right) \quad (2\%,\ 50\text{–}298\,^\circ\text{K.})$$

$$\text{TiN:}\quad {}^1/_2E\left(\frac{273}{T}\right) + D\left(\frac{927}{T}\right) + {}^1/_2E\left(\frac{580}{T}\right) \quad (2\%,\ 50\text{–}298\,^\circ\text{K.})$$

The symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the specific heat curves to 0°K.

The total heat absorption in the region of the "hump" in titanium sesquioxide at 242°K. was obtained by summing the energies of three successive specific heat determinations in the manner described by Shomate.[8] The excess energy in the "hump," above that calculated from a smooth "normal" curve drawn through this region, is only 3.6 cal./mole, and the excess entropy 0.015 e.u./mole.

Table II summarizes the entropy calculations for the four substances.

TABLE II

ENTROPIES AT 298.16°K. (E. U./MOLE)

	TiO	Ti_2O_3	Ti_3O_5	TiN
0–52.00° K.	0.25	0.50	0.97	0.13
52.00–298.16° K.	8.06	18.33	29.95	7.07
	8.31 ± 0.04	18.83 ± 0.06	30.92 ± 0.10	7.20 ± 0.04

Summary

Specific heats of the monoxide, sesquioxide, tritapentoxide and mononitride of titanium were measured in the temperature range 52 to 298°K. Titanium sesquioxide has a small "hump" in its specific heat curve, the maximum being at 242°K. There is only 0.015 e.u./mole of excess entropy in the "hump," above the "normal" curve.

The following molal entropies at 298.16°K. were computed: titanium monoxide, 8.31 ± 0.04; titanium sesquioxide, 18.83 ± 0.06; titanium tritapentoxide, 30.92 ± 0.10 and titanium mononitride, 7.20 ± 0.04.

BERKELEY, CALIF. RECEIVED OCTOBER 26, 1945

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[8] Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of the Hydrides of Boron. VII. Beryllium Borohydride, BeB_2H_8

BY G. SILBIGER AND S. H. BAUER

Of the three metallo borohydrides prepared by H. I. Schlesinger[1] and his co-workers, an electron diffraction study of aluminum borohydride has already been carried through.[2] In this paper, the results of a similar investigation of the beryllium compound and further work on aluminum borohydride are reported. A probable configuration for the beryllium compound has been deduced and the interatomic distances in that molecule have been estimated. The $Be(BH_4)_2$ was furnished by Dr. H. C. Brown, to whom we wish to express our sincere appreciation.

The sample was transferred, by sublimation, to a metal, high temperature nozzle and electron diffraction pictures of varying densities were obtained with the material between 40 and 50° (reported vapor pressure at 45° is 37.1 mm.).[1b] The visually estimated diameters and intensities are listed in Table I. We were unable to measure accurately the diameter of the shoulder to the left of the third peak and hence the position indicated for the maximum on the observed intensity curve is approximate. A radial distribution curve (Fig. 1, R. D.) was computed following the method of Walter and Beach.[3] It shows principal peaks at 1.73, 2.71 and 3.41 Å. Since these

TABLE I

Max.	Min.	s_0	Inten.	$s_c(D_2)$	s_c/s_0
1		1.57	8	1.37	(0.873)
	2	3.52	−5	3.20	(.909)
2		4.47	8	4.37	.978
	3	5.35		5.20	.972
3		6.05		6.00	.992
	4	6.60	−2	6.50	.985
4		7.56	3	7.45	.985
	5	9.54	−1	9.35	.980
5		11.97	1	11.43	.955
				Av.	.978
				Av. dev.	.008

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(1) (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940), (c) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(2) J. Y. Beach and S. H. Bauer, THIS JOURNAL, **62**, 3440 (1940).

(3) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).

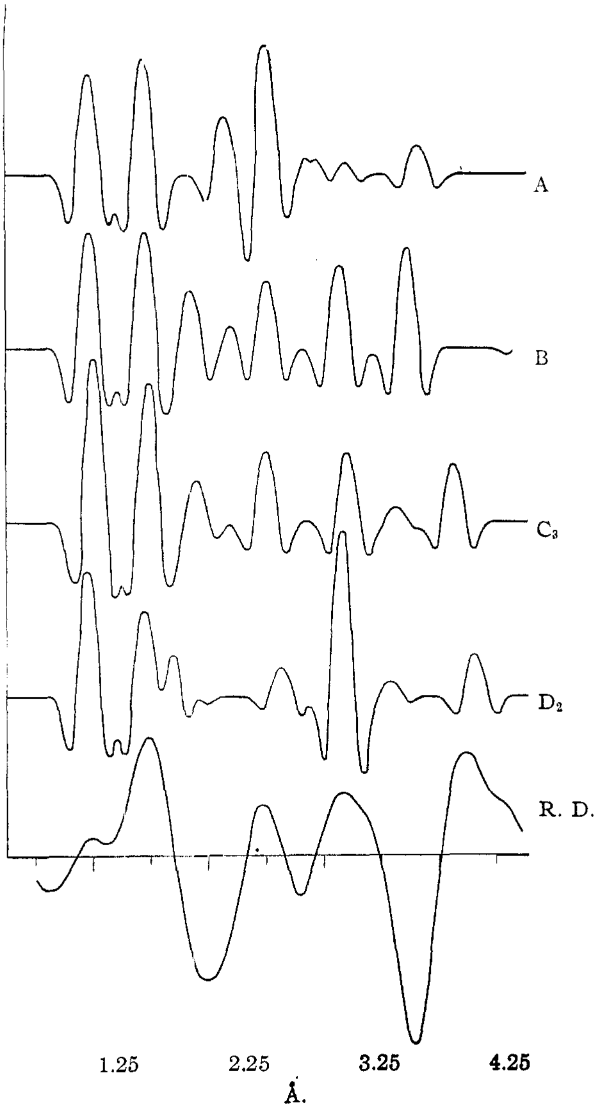


Fig. 1.—Radial distribution curves for BeB_2H_8. R.D. was computed from the diffraction data; A, B, C_3 and D_2 are "synthetic."

peaks are due to the B–Be, Be–B–H and B–Be–B distances, one may assign them according to two alternative general configurations. In one model we supposed the boron and beryllium atoms are colinear, so that the first principal peak corresponds to the B–Be distance, the second to a Be–B–H distance and the third to the B–Be–B separation. In the other structure we placed the beryllium atom in B–Be–B at the apex of a tetrahedral angle. In this case, the first principal peak is due to the B–Be bond, while the second and third are attributed to B–Be–B and B–Be–H distances, respectively. Since chemical properties[1b] eliminate a structure of the type Be–B–B, we did not consider such models in our computations.

Synthetic radial distribution curves are shown in Fig. 1 for the following models

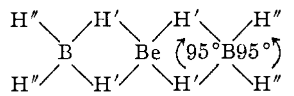
A: $H_3B-BeH_2-BH_3$

all angles tetrahedral
B-Be, 1.70 Å.
B-H, 1.22
Be-H, 1.22

B: $H_3B-BeH_2-BH_3$

Tetrahedral valence angles for the boron atoms
Square bonds for beryllium
Same distances as above

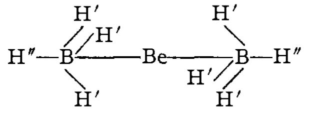
C_3:[4]



Bond angles of B and Be are distorted tetrahedral

B-Be, 1.73 Å.
B-H′, 1.28
B-H″, 1.22
Be-H′, 1.28

D_2:



B-Be, 1.70 Å.
B-H″, 1.18
B-H′, 1.22
∠Be-B-H′, 80
∠B-Be-B, 180

The values given above for the distances and angles are those which permitted the best over-all fit between the observed and synthetic radial distribution curves. On the basis of these curves,

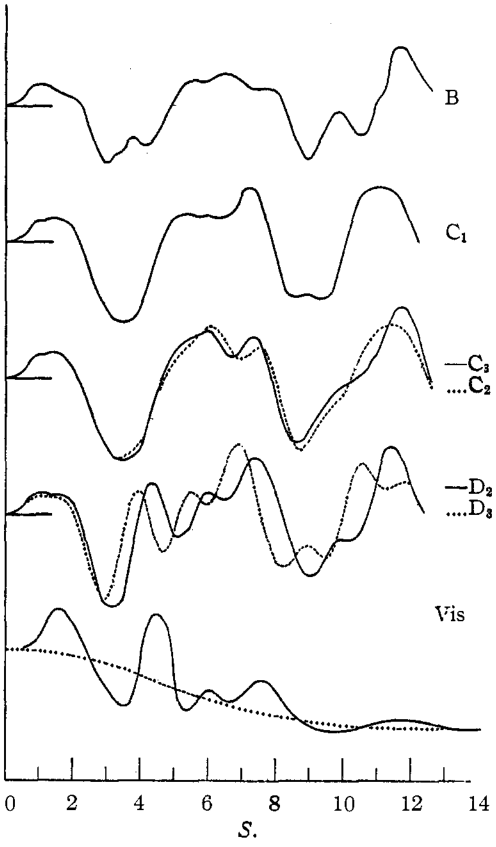


Fig. 2.—Intensity curves for BeB_2H_8.

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[4] H. E. Lonquet-Higgins and P. P. Bell, *J. Chem. Soc.*, 250 (1943); K. S. Pitzer, THIS JOURNAL, 67, 1126 (1945).

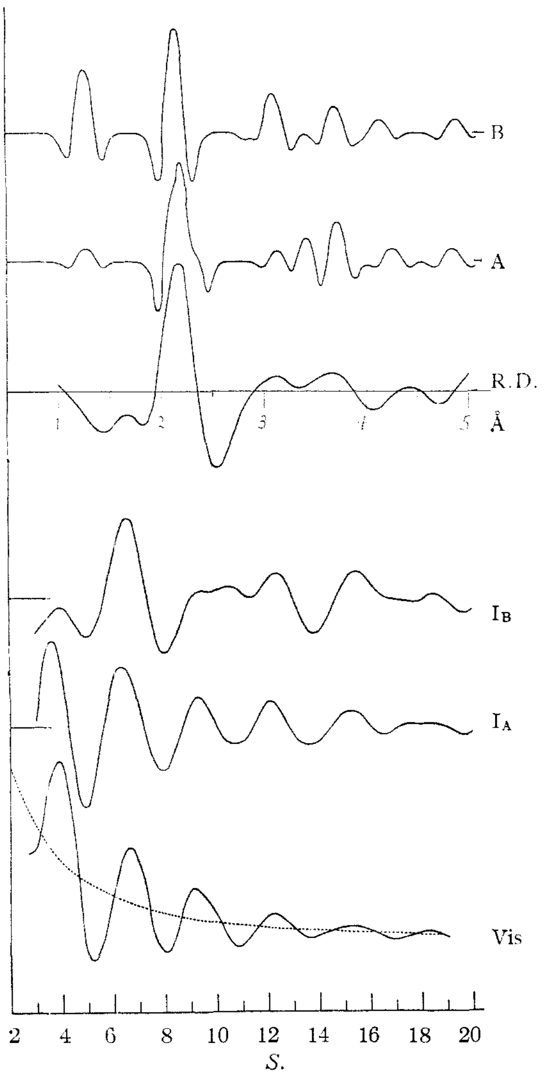

Fig. 3.—Curves for AlB_3H_{12}. R.D. computed radial distribution curve; A, B "synthetic." I_A and I_B are computed intensity curves, to be compared with the sketch of the pattern apparent to the eye.

models A and B are definitely eliminated. The intensity curve calculated for model B confirms its inadequacy (Fig. 2, B). With respect to the positions of the maxima, models C_3 and D_2 are acceptable and agree as well as might be expected with the observed radial distribution curve. C_3, however, does have an extra peak at 2.15 Å. while in D_2, this peak is shifted so that it almost coincides with the broad maximum at 1.70 Å. With respect to the relative weights of the peaks, D_2 agrees with the observed curve better than does C_3.

To differentiate between models C_3 and D_2, intensity curves were computed using the formula

$$(\text{relative})\ I = \sum_{i=1}^{n}\sum_{j=1}^{n}(Z - F)_i(Z - F)_j\frac{\sin r_{ij}s}{r_{ij}s}$$

The use of atomic form factors in this calculation was necessary because the background of our photographs was cleared to such an extent that we were able to observe a maximum at a value of s smaller than has ever been observed before. This was made possible by the introduction of an electron stop near the point of diffraction. A discussion of this stop will appear in a forthcoming publication.

The first peak at $s = 1.4$ (Fig. 2) is not significant since it is not determined by the molecular structure of the diffracting sample. It arises from a shift of the peak which would appear at zero, due to the introduction of atomic form factors. Model B has been eliminated (see above). Models C_1, C_2 and D_1 differ in distance ratios and angles from C_3 and D_2 described for Fig. 1

C_1:	B–Be, 1.85 Å. B–H′, 1.31 Be–H′, 1.31 B–H″, 1.18	∠H′BH′, 90° ∠H″BH″, 120
C_2:	B–Be, 1.73 Å. B–H′, 1.28 Be–H′, 1.28 B–H″, 1.22	∠H′BH′, 95° ∠H″BH″, 115
D_1:	B–Be, 185 Å. B–H, 1.27 ∠BeBH′, 85°	

Comparison of the calculated intensity curves with the visually observed pattern definitely eliminates the bridge model. This model fails to show the intense peak observed at $s = 4$, and predicts an incorrect form for the curve for s values between 4 and 7. D agrees with the observed curve over the entire range of observation. Hence we believe that D is the structure in best agreement with the electron diffraction data and the observed chemical properties. To summarize, the best model has the configuration given for D_2, with the following distances and angles

B–Be, 1.66 ± 0.04 Å.	∠Be–B–H′, 85 ± 5°
B–H′, 1.19 ± 0.05	∠Be–B–H″, 180° (assumed)
B–H″, 1.15 ± 0.05	

Before attempting to interpret the above conclusions regarding $Be(BH_4)_2$, we reconsidered the aluminum analog, since the bridge model was not eliminated in the original discussion. For this we assumed a bridge structure, with an aluminum atom at the center of an equilateral triangle determined by the three boron atoms. The bridge hydrogens were placed in planes perpendicular to the plane of the three boron atoms and of the terminal hydrogen atoms. As with the beryllium compound, the synthetic radial distribution curves for both the bridge and previously reported models (Fig. 3, B and A, respectively) compare well with the observed curve (R. D.). Intensity calculations, however, again eliminate the bridge structure. Curve I_B exhibits a peak at $s = 4.0$ which is too low in comparison with the second peak. In addition, the structure in the region of the third and fourth peaks differs from that sketched in the visual curve. The previously reported configuration (curve I_A, Fig. 3) agrees much better with the observed curve.

Discussion

The deduction of structures from visually estimated electron diffraction data can rightfully be subjected to a certain amount of criticism since such interpretations are based on subjective impressions. The identification of what the eye sees with the peaks and valleys found in the computed curve requires both care and practice. In this Laboratory, we have been able to compare patterns, traced by a microphotometer, of electron diffraction photographs taken with a sector, with visually estimated patterns taken in the usual manner. We found, as has been observed previously, that the eye accentuates various features, making shoulders sometime appear as prominent as peaks and introducing minima where inflections in the shoulders appear. However, the eye *does not* introduce new features in the pattern. Hence for an experienced investigator it is possible to state with a considerable amount of assurance when an assumed model has been eliminated. The use of a radial distribution curve, based upon visual data, can serve only to help find the best combination of distances and angles for a given model. Since the relative weights of the radial distribution peaks cannot be considered quantitatively, it is not legitimate, as yet, to base the entire analysis upon this argument. In the selection of the model and the distances finally reported above, both the intensity curves and radial distribution curves were considered.

The B–Be distance deduced is quite short when compared with the sum of the covalent radii for beryllium and boron ([5]1.06 + 0.85 − 0.05 = 1.86 Å.). This, however, can be explained as follows. If we consider diborane, aluminum, beryllium and lithium borohydride, the ionic character of the compounds increases[1c] in the order listed. The B–Be bond, therefore, probably is highly polar. Usually, increasing the ionic character of a bond has little influence on its length, since the radius of the electropositive atom decreases by about the same amount as the radius of the electronegative atom increases. In this case, however, the BH_4 group is electron deficient, so that the effective radius of boron toward beryllium will not be altered, although the beryllium radius will be shortened with increasing amounts of ionic character. This results in a B–H distance which is shorter than expected for one with considerable one-electron bond character, and a B–Be distance which is shorter than the sum of the covalent radii. Because of the increase in ionic properties, and the corresponding change in bond distances from aluminum to beryllium to lithium borohydride, we predict that the Li–B bond distance will be found to be considerably less than the sum of the covalent radii, and the B–H distance to be smaller than that observed in the beryllium compound.

Summary

From an electron diffraction study of beryllium borohydride vapor a configuration for the molecule was deduced which is analogous to that previously reported for aluminum borohydride. In beryllium borohydride, H″–B–Be–B–H″ are linearly arranged, with three hydrogen atoms (H′) uniformly spaced in the girdle of each boron atom. B–Be = 1.66 ± 0.04 Å.; B–H″ = 1.15 ± 0.05 Å.; B–H′ = 1.19 ± 0.05 Å.; ∠BeBH′ = 85 ± 5°. Proton bridge structures were considered for both the beryllium and aluminum borohydrides; these were definitely eliminated.

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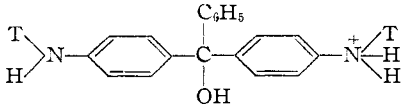
[5] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

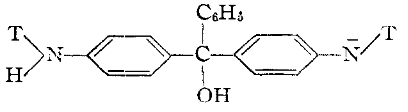
The Absorption Spectra of the Negative Ions of Two Diaminotriphenylmethane Dyes

BY BERT M. TOLBERT AND GERALD E. K. BRANCH

If a carbinol of a diaminotriphenylmethane dye having hydrogen atom on each nitrogen atom is treated with dilute acid a positive ion may be formed (I), or if treated with a strong alkali a negative ion (II) may be formed



(I)



(II)

where T represents a terminal group. The equilibrium constants for such reactions are approximately equal to those for the formation of the positive ion or the negative ion, respectively, from the base of which the dye is a derivative. The positive ion is therefore formed in dilute acid solution, but the negative ion is obtainable only in very strongly basic solutions.

Each of these ions is in equilibrium with a quinoidal ion, (III) or (IV), obtained by the loss of one molecule of water.

An estimate of the relative stability of the quinoidal ion with respect to the benzenoidal ion may be obtained by a comparison of the reso-