14mm is eight, if the entropy increment associated with the 8% volume change is neglected.

The temperature of the α–β transformation was determined as 297.10 ± 0.04° after a drift toward equilibrium of several hours duration in runs 31 and 32 (Table IV). Attempts to establish the transition temperature by cooling curves were unsuccessful in that the sample usually supercooled as much as 5° before undergoing the $\beta \rightarrow \alpha$ transition and failed to reach the equilibrium temperature.

A thermal anomaly of unknown origin also was observed in the vicinity of 11°K. This appears to be a rather broad transformation with an entropy increment of about 0.01 cal. mole^{-1} deg.$^{-1}$.

Thermodynamic Properties of Gaseous Ammonia–Triborane.—Measurements on the sublimation pressure of ammonia–triborane have been made[8] over the range 304 to 327°K. by an effusion technique. These data may be represented by the equation

$$\log P_{(\mathrm{mm.})} = \frac{-3739}{T} + 9.200$$

This corresponds to a sublimation pressure of 5.46 $\times$ 10^{-4} mm. at 300°K. and a heat of sublimation of 17.1 ± 0.1 kcal. mole.$^{-1}$. Correction to the ideal gaseous state (at 1 atm. pressure) at 300°K. yields

$$(H^\circ - H_0^\circ)_{\mathrm{i.g.}} = 23.9 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$S^\circ_{\mathrm{i.g.}} = 68.8 \text{ cal. mole}^{-1}\text{ deg.}^{-1}$$

$$-\left(\frac{F^\circ - H_0^\circ}{T}\right)^{\prime}_{\mathrm{i.g.}} = -10.9 \text{ cal. mole}^{-}\text{ deg.}^{-1}$$

The significance of these three values is subject, of course, to the usual uncertainties inherent in the interpretation of the effusion method of vapor pressure determination.

Acknowledgments.—The authors acknowledge their indebtedness to Professor R. W. Parry and Dr. G. Kodama for their interest and advice regarding the handling of the compound, to Mr. J. C. Carter for the preparation and the analysis of the sample and to Mr. H. G. Carlson and Miss Elfreda Chang for their assistance with the heat capacity determinations. This work was supported by Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

ANN ARBOR, MICHIGAN

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[8] E. R. Alton, R. D. Brown, J. C. Carter and R. C. Taylor, THIS JOURNAL, **81**, 3550 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Trimethylamine–Triborane. The Heat Capacity, Heat of Transition and Thermodynamic Properties from 5 to 350°K.

BY NORMAN E. LEVITIN, EDGAR F. WESTRUM, JR., AND JAMES C. CARTER

RECEIVED DECEMBER 22, 1958

The heat capacity of pure trimethylamine–triborane ($(CH_3)_3NB_3H_7$) has been measured over the range from 5 to 350°K. with an adiabatic calorimeter. A sharp lambda-type transition was found at 209.6°K. It has a molal enthalpy of transformation of about 843.4 cal. mole^{-1} deg.$^{-1}$ and an entropy increment of 4.0 e.u. Values of the thermodynamic functions derived from the heat capacity data are given at rounded temperatures together with the smooth heat capacity data. At 298.15°, the heat capacity at constant pressure, entropy, enthalpy increment and free-energy functions are: 51.98 cal. mole^{-1} deg.$^{-1}$, 54.60 cal. mole^{-1} deg.$^{-1}$, 8732 cal. mole^{-1} and −25.31 cal. mole^{-1} deg.$^{-1}$, respectively. The preparation of this compound on the 20-g. scale is described.

Ammonia–triborane ($NH_3B_3H_7$) has been studied in this Laboratory by calorimetric[1] and X-ray diffraction techniques[2] and was found to undergo an interesting transition at 297.10°K. involving a disordering of the molecule in the crystalline lattice. The possible existence of a low temperature transformation in the trimethylamine–triborane ($(CH_3)_3NB_3H_7$) provided an inducement for the investigation of its low temperature thermodynamic properties, despite some difficulty and hazard in its laboratory scale preparation. A transition of magnitude quite similar to that found in the ammonia triborane was found at 209.6°K.

Preparation and Purity of Trimethylamine–Triborane.—The trimethylamine-triborane was prepared by a suitable modification of the combined procedures of Edwards, Hough and Ford[3] and of Kodama.[4] The reactions are

$$2B_4H_{10} + 2\underline{CH_2(CH_2)_4O} \longrightarrow 2\underline{CH_2(CH_2)_4O}:B_3H_7 + B_2H_6 \quad (1)$$

$$\underline{CH_2(CH_2)_4O}:B_3H_7 + (CH_3)_3N \longrightarrow (CH_3)_3N:B_3H_7 + \underline{CH_2(CH_2)_4O} \quad (2)$$

The contents of a 500-ml. Pyrex reaction vessel were stirred by a magnetically-driven paddle and connected to a vacuum line and manometer through a 195°K. reflux condenser. Toluene (100 ml. of reagent dried over CaH_2) as diluent and tetrahydropyran (100 ml., b.p. 81–82°, refluxed over CaH_2) were used in the reactor, and the system was cooled to 77°K. and evacuated. Tetraborane (50 ml. distilled *in vacuo* at 188°K., and freed of diborane at 147°K.) was distilled into the reactor and the temperature slowly increased until evolution of diborane was noted, whereupon the reaction was quenched by immersion of the reactor in liquid nitrogen and upon gradual warming the diborane was distilled off and the reaction allowed to proceed more moderately. After most of the diborane was removed, the reactor was cooled to 195°K. and allowed to stand 10 hr. Then the remainder of the diborane, the excess tetrahydropyran and the toluene were distilled off. Ethyl ether (200

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(1) E. F. Westrum, Jr., and N. E. Levitin, THIS JOURNAL, **81**, 3544 (1959).

(2) C. E. Nordman and C. R. Peters, Abstracts of Papers, 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958.

(3) L. J. Edwards, W. V. Hough and M. D. Ford, Transactions XVIth Congress, Int. Union Pure and Applied Chemistry, p. 475, Paris, July, 1957.

(4) G. Kodama, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1957.

ml., anhydrous, reagent) was added under streaming dry nitrogen and the reactor again cooled to 195°K. and evacuated. Upon warming to 0° the tetrahydropyran-triborane completely dissolved. Trimethylamine (37 cc. at 0°, anhydrous, dried over and distilled from $LiAlH_4$) was distilled slowly into the reactor at 195°K. to displace the tetrahydropyran. A stoichiometric amount of the amine was employed to avoid side reactions. The ethyl ether and liberated tetrahydropyran were distilled off at room temperature. The product was purified by recrystallization twice from anhydrous toluene at 178°K. and filtration through a fritted glass filter at 195°K. under a stream of dry nitrogen. The yield of pure product was 65 to 70% based on the tetraborane charged.

For analytical purposes the sample was hydrolyzed by heating with 10% hydrochloric acid for 100 hr. at 150° in a sealed tube. The evolved active hydrogen was measured in a calibrated gas buret after concentration with a Toepler pump. Boron was titrated as boric acid in the presence of mannitol. Trimethylamine was determined by the Kjeldahl procedure. Difficulty was experienced in obtaining complete reaction of the amine with the standard acid. The following results were obtained in duplicate (in millimoles per sample): active hydrogen, 7.28 (99.6% theoretical); boron, 0.546 (99.6% theor.); and trimethylamine, 0.181 (99.1% theor.). These results indicate an over-all composition corresponding to the ratios: $[(CH_3)_3N]_{0.995}$-$B_{3.00}H_{7.000}$ and when account is taken of the uncertainties of the several determinations, do not exclude the possibility of exact stoichiometry. The handling, loading and weighing of the sample into the calorimeter were all done in the anhydrous nitrogen atmosphere of a dry box.

Calorimetric Technique.—The measurements were made in the Mark I cryostat with platinum resistance thermometer A-3 calibrated by the National Bureau of Standards. Calorimeter of laboratory designation W-17 and an adiabatic technique of measurement were employed.[1]

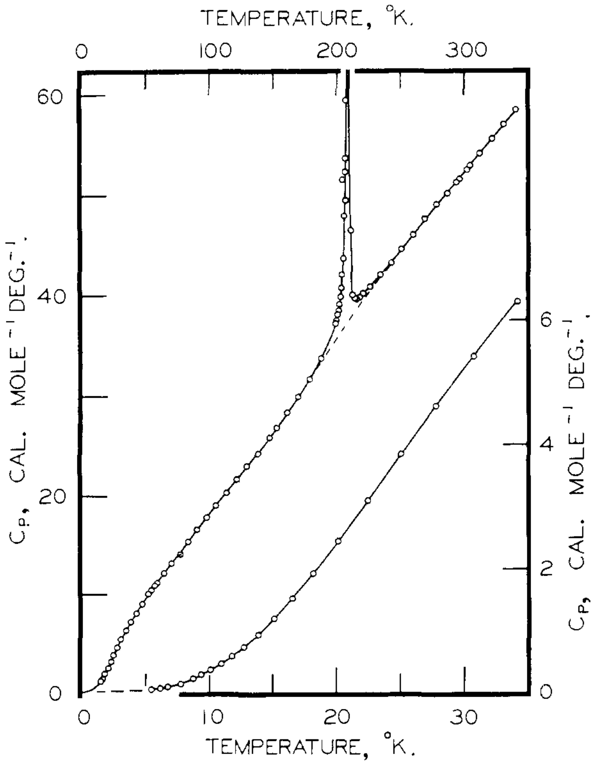

Fig. 1.—The heat capacity of trimethylamine-triborane showing the transition at 209.6°K. The dashed line represents the lattice contribution interpolated as described in the text.

Heat Capacity and Thermodynamic Properties.—The original experimental values of the molal heat capacity of the 19.473-g. (*in vacuo*) sample of trimethylamine–triborane are presented in Table I, together with the mean temperature for each determination in the sequence in which they were actually obtained. The temperature increments of these determinations usually can be inferred from the mean temperatures of the adjacent data. The results are expressed in terms of a defined thermochemical calorie equal to 4.1840 absolute joules, an ice point of 273.15°K., and a gram formula weight of trimethylamine triborane of 98.629 g. These data have been corrected to represent true heat capacities by the application of a curvature correction for the finite temperature increments actually used in the measurements.

The molal heat capacity and the thermodynamic functions derived from the heat capacity data are listed at rounded temperatures in Table II. These heat capacity values were read from a smooth curve through the experimental points after the application of the curvature correction and they are estimated to have a probable error of approximately 0.1% above 25°K., 1% at 14°K., increasing to about 5% at 5°K. The heat capacity was extrapolated below 5°K. with a Debye function. The effects of isotope mixing and of nuclear spin are not included in the entropy and free energy functions. The estimated probable error in the entropy, heat content and free-energy function is 0.1% above 100°K., but to make the table internally consistent and to permit accurate interpolation, some of the thermodynamic values are given to one more significant figure than is justified by the estimated probable error.

The Transition at 209.6°K.—As may be seen in Fig. 1, a very sharp lambda-type transition was observed with measured heat capacities at least as great as 515 cal. mole⁻¹ deg.⁻¹ in the transition region. The probable existence of a structural transformation had been anticipated from the interpretation[4] of disorder in the room temperature X-ray diffraction data[5] on trimethylamine–triborane and the subsequent observation of the change in structure.[6] The data indicate that the high temperature (β) form has trigonal symmetry.

It was not possible to determine heat capacity as a function of temperature with accuracy in the transition region because the slow rate of achievement of equilibrium made the drift correction very large and hence the small transitional temperature increments less certain. In order to evaluate the thermodynamic functions more exactly, therefore, a number of energy inputs were made which entirely bridged the transition region, enabling the direct evaluation of the enthalpy increments over this region. The results of these determinations and a series of regular determinations are shown in Table III. The form of the material stable below the 209.6°K. transition temperature has been designated as the α-form and that stable above this temperature as the β-form. It will be noted that these enthalpy increments are all in good accord. A curve was fitted to the heat capacity data in such a way that the total enthalpy obtained from its quadrature was the same as that obtained from the

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(5) C. E. Nordman, private communication.

(6) H. G. Norment, private communication.

TABLE I

HEAT CAPACITY OF TRIMETHYLAMINE–TRIBORANE, $(CH_3)_3N:B_3H_7$ IN CAL. MOLE^{-1} DEG.$^{-1}$

Mol. wt. = 98.629 g.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		Series II		205.76	47.92
54.18	10.380	5.45	0.042	206.34	52.33
58.53	11.145	6.18	.057	206.72	53.71
64.10	12.099	6.74	.080	207.06	49.46
70.33	13.092	7.74	.132	207.52	59.51
76.73	14.053	8.68	.225	207.96	91.45
83.20	15.29	9.39	.291	208.24	93.85
90.44	16.51	10.08	.366	208.53	152.42
97.95	17.72	10.91	.465	208.69	120.31
105.28	18.92	11.78	.581	208.78	154.50
113.07	20.21	12.72	.730		
121.33	21.58	13.79	.923	Series IV	
129.64	22.96	15.04	1.184		
138.03	24.34	16.48	1.511	209.10	271.04
146.60	25.78	18.12	1.920	209.27	380.49
152.27	26.78	20.09	2.448	209.43	341.37
160.95	28.35	22.43	3.102	209.52	535.24
169.83	29.91	25.01	3.845		
178.76	31.68	27.79	4.622	Series V	
187.69	33.75	30.78	5.423		
196.54	36.91	34.17	6.294	209.79	515.70
204.57	51.58	38.07	7.213	209.99	482.68
208.95	349.71	42.30	8.116	210.11	445.85
211.65	105.19	46.79	9.010	210.28	233.06
217.88	39.77	51.76	9.939	210.75	119.81
226.52	40.86	57.32	10.914	211.72	46.45
234.61	42.02			212.85	40.07
242.66	43.23	Series III		214.22	39.61
250.89	44.54			216.53	39.52
259.58	46.00	199.14	37.15	220.26	39.86
268.64	47.49	199.85	37.59		
277.67	48.92	200.56	38.08	Series VI	
286.92	50.14	201.27	38.47		
296.20	51.62	201.96	39.12	293.83	51.31
304.72	53.00	202.65	39.82	302.97	52.64
		203.33	40.70	312.11	54.16
		204.00	42.08	321.27	55.63
		204.65	43.65	330.73	57.18
		205.13	41.06	340.28	58.60

independent transitional enthalpy-increment determinations over the same temperature range. The heat capacities obtained from this curve were then integrated with respect to ln T to obtain the entropy increment.

Since there is some pre-transitional heat capacity rise, the resolution of the enthalpy and entropy increments of transition from the vibrational lattice contributions is somewhat arbitrary. To derive these, it is necessary to obtain a "normal" heat capacity curve over a rather broad range; *i.e.*, the heat capacity curve which would be observed if there were no transition present. To do this, values of Debye thetas (θ_D) were calculated from the heat capacity data from 160 to 250°K. and plotted as a function of temperature. A smooth curve then was interpolated readily which was tangent to the observed θ_D *vs.* T curve at 170° and again at 250°K. From values of θ_D read from this latter curve, the lattice heat capacity contributions were evaluated. The difference in the integral of the observed heat capacity curve and that of the interpolated lattice curve yields an enthalpy of transition of 843.4 cal. mole^{-1}. Similarly, a transitional entropy increment of 4.0 e.u. is indicated. About 90% of this has its origin in the 4° region between 207.0° and 211.0°K.

Inasmuch as a first-order transition is involved here, it would be more appropriate to extrapolate the heat capacity of both the high and low temperature phases to the transition temperature for obtaining the "normal" heat capacity curve. Unfortunately, this cannot be done with certainty

TABLE II

THERMODYNAMIC FUNCTIONS OF TRIMETHYLAMINE–TRIBORANE, $(CH_3)_3NB_3H_7$

Mol. wt. = 98.629 g.

T, °K.	C_p, cal./mole °K.	$S°$, cal./mole °K.	$H° - H_0°$, cal./mole	$\frac{-(F° - H_0°)}{T}$, cal./mole °K.
10	0.357	0.1012	0.7928	0.0219
15	1.174	.3814	4.394	.0885
20	2.422	.8831	13.27	.2198
25	3.842	1.575	28.89	.419
30	5.223	2.398	51.59	.678
35	6.496	3.301	80.94	.988
40	7.631	4.244	116.3	1.336
45	8.657	5.203	157.1	1.713
50	9.617	6.165	202.8	2.109
60	11.38	8.077	307.9	2.945
70	13.04	9.957	430.1	3.813
80	14.73	11.807	568.8	4.697
90	16.42	13.641	724.7	5.589
100	18.06	15.456	897.1	6.486
110	19.70	17.254	1085.9	7.383
120	21.36	19.039	1291.2	8.279
130	23.02	20.815	1513.1	9.176
140	24.67	22.581	1751.5	10.071
150	26.38	24.341	2006.7	10.963
160	28.17	26.100	2279.3	11.858
170	30.00	27.863	2570.2	12.744
180	31.92	29.631	2879.6	13.633
190	34.15	31.418	3210.4	14.521
200	37.66	33.246	3568.4	15.404
220	39.83	40.738	5144.4	17.354
230	41.29	42.540	5549.7	18.411
240	42.84	44.330	5970.4	19.454
250	44.40	46.110	6406.5	20.484
260	46.06	48.883	6858.8	22.503
270	47.71	49.653	7327.7	22.513
280	49.28	51.417	7812.8	23.514
290	50.79	53.173	8313.2	24.507
300	52.26	54.919	8828.5	25.491
350	60.12	63.570	11639	30.315
273.15	48.21	50.209	7478.8	22.829
298.15	51.98	54.596	8732.0	25.309

TABLE III

ENTHALPY INCREMENTS IN THE TRANSITION REGION

No. of energy increments	T_{final}, °K.	$T_{initial}$, °K.	$\Delta H°$,[a] cal. mole^{-1}
5	222.13	192.18	1575.7 ± 0.7
1	218.21	198.07	1574.8 ± 0.4
1	220.55	200.02	1577.7 ± 1.3
			1576.1 ± 0.6

[a] $\Delta H° = H°_{\beta,220°K.} - H°_{\alpha 200°K.}$.

from the low-temperature side, but the use of this method would tend to increase the transitional entropy increment by 0.1 to 0.3 e.u.

The transitional entropy increment of 4.0 e.u. is quite comparable with that in the ammonia–triborane (4.15), and the slow approach to equilibrium is also very suggestive of a similar process despite the fact that this transition occurs at a temperature 90° lower. Further elucidation of the mechanism of the presumed disordering in the molecular orientation awaits the availability of X-ray diffractional data on both forms.

Acknowledgment.—This work has been supported by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy. The preparation of the calorimetric sample was done under support of the Wright Air Development Center Contract No. AF 33(616)-3343. The authors appreciate the interest and coöperation of Professor R. W. Parry and the collaboration of Mr. H. G. Carlson with the heat capacity measurements.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Vapor Pressures of the Methylamine–Boranes and Ammonia–Triborane[1]

BY E. R. ALTON, R. D. BROWN, J. C. CARTER AND R. C. TAYLOR

RECEIVED JANUARY 26, 1959

Vapor pressures of the solid compounds, $CH_3NH_2BH_3$, $(CH_3)_2NHBH_3$, $(CH_3)_3NBH_3$ and $NH_3B_3H_7$, have been measured between 0° and their melting points by the Knudsen method. Vapor pressure equations and the heats of sublimation have been derived from a least squares analysis of the data. An upper limit has been set for the vapor pressure of NH_3BH_3 at 25°.

In connection with a program of study of the physical and chemical properties of boron hydride derivatives, the vapor pressures of ammonia-borane, mono-, di- and trimethylamine–borane and of ammonia–triborane have been measured in the neighborhood of room temperature by the Knudsen method. No vapor pressure data for these compounds have appeared previously in the literature with the exception of the trimethylamine compound.[2] In the latter case the data were determined manometrically from 23° to the melting point and cover a different range than the present measurements.

Experimental

Ammonia-borane,[3] trimethylamine–borane[2] and ammonia–triborane[4] were prepared by the methods described in the literature and purified by sublimation or, in the case of the triborane, recrystallization. Methylamine–borane and dimethylamine–borane were prepared by slightly modified procedures for ammonia–borane.[5] Contrary to reports in the literature,[6,7] these two methylamine–boranes are odorless, stable white solids with sharply defined melting points of 54 and 36°, respectively, and no tendency to evolve hydrogen when maintained *in vacuo*. In this respect they resemble many other boron hydride derivatives whose apparent properties and stability depend markedly upon the method of preparation and the resulting purity. Since the weight of material effusing was determined by the decrease in weight of the container, precautions were necessary to eliminate spurious weight loss. Where a solvent had been used in purification, the material was held *in vacuo* for several hours before measurement to ensure the absence of volatile impurities. Transfers were made in a dry box to prevent contamination by water with subsequent decomposition. Before weighing and again after the experiment and before reweighing, the vaporization chamber was filled with dry nitrogen. After each series of measurements, the sample was inspected and if an amine odor was detectable, the data were discarded. Tests carried out by sealing a sample in a small evacuated system with an attached manometer showed that decomposition with permanent gas (H_2) evolution under the conditions of the measurements was negligible.

The vaporization chamber consisted of a small monel cylinder with an i.d. of 15 mm. and a depth of 20 mm. It was fitted with an open cap at the top which compressed the platinum sheet containing the orifice between two thin copper gaskets to complete the closure. The orifices were carefully drilled, inspected under the microscope for imperfections and burrs and their diameters measured by a comparator. The two used had diameters of 0.0374 and 0.0776 cm. and ratios of thickness to radius of 0.163 and 0.314, respectively.

Effusion took place from the chamber into a vacuum of approximately 10^{-5} mm. of Hg, a surface maintained at liquid nitrogen temperature some 8 cm. above the orifice trapping most of the effused material. The vaporization chamber was recessed into a closely fitting 0.8 kg. block of copper to provide a large thermal reservoir and the latter was enclosed by a double walled section of the vacuum system through which constant temperature water was circulated. The temperature of the copper block immediately adjacent to the vaporization chamber was monitored by a copper–constantan thermocouple. In general, the loss in weight per run was of the order of 10–50 mg.

Experimental Results

Vapor pressures were calculated from the relationship[8]

$$P_{\text{mm}} = 17.14 \frac{W}{KAt} \left(\frac{T}{M}\right)^{1/2}$$

where W is the weight of the substance in grams effusing in time t seconds through an orifice of A cm.^{2} area. M is the molecular weight, assumed that of the simple 1:1 complex, T is the absolute temperature and K is the Clausing correction factor

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(1) This research was supported by the United States Air Force under Contracts No. AF 33(616)-3343 and AF 33(616)-5874 monitored by the Aeronautical Research Laboratory, Wright Air Development Center, Ohio.

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