

## Trimethylamineborane and triethylamineborane: low-temperature thermodynamic properties†

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(Received 23 August 1969)

The low-temperature thermal properties of trimethylamineborane and triethylamineborane were determined by adiabatic calorimetry over the range 12 to 390 K and 12 to 310 K, respectively. The quantities measured include the heat capacity of the condensed phases, enthalpies of transition, transition temperatures, enthalpies of fusion, and triple-point temperatures. The results were used to calculate the following thermodynamic functions at selected temperatures for the solid and liquid phases:  $(G_s - H_0^0)/T$ ,  $(H_s - H_0^0)/T$ ,  $H_s - H_0^0$ ,  $S_s$ , and  $C_s$ . Third law entropies and Gibbs energies of formation in the ideal gas state at 298.15 K for both compounds were computed from the results together with vapor pressures and enthalpies of formation from the literature.

### 1. Introduction

As part of a continuing program of study of the thermochemical and thermophysical properties of organic derivatives of the lighter elements important in the development of high energy fuels, low-temperature thermal studies on trimethylamineborane  $(\text{CH}_3)_3\text{N}:\text{BH}_3$  and triethylamineborane  $(\text{C}_2\text{H}_5)_3\text{N}:\text{BH}_3$  were made. With the derived results, the thermodynamic properties of the condensed phases were calculated from 10 to 400 K for trimethylamineborane and from 10 to 310 K for triethylamineborane. Third law entropies and Gibbs energies of formation of the two compounds in the ideal gas state at 298.15 K were calculated from the measured results plus enthalpies of vaporization, vapor pressures, and enthalpies of formation from the literature.

### 2. Experimental

#### MATERIALS

The samples of trimethylamineborane and triethylamineborane were provided by the Ethyl Corp. through the courtesy of Mr. W. E. Foster. The trimethylamineborane, purified by recrystallization from diethyl ether at  $-70^\circ\text{C}$  under nitrogen by Ethyl

† Work conducted in part under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, Contract No. OAR-ISSA-65-7, Project 9713, Program Element 681308, and the Bureau of Mines, U.S. Department of the Interior; Annual Technical Summary Report for the period March 1 1965 to March 1 1966.

Corp., was dried by passing the vapor through molecular sieves. The triethylamineborane, purified by zone melting at the Laramie (Wyo.) Petroleum Research Center of the Bureau of Mines, was dry and was used as received. The purity of each sample is estimated in a later section.

#### APPARATUS AND METHOD

The measurements were carried out in an adiabatic cryostat very similar in principle and design to that previously described.<sup>(1, 2)</sup> The temperatures of the three sections of the adiabatic shield and the tempering ring of wires were controlled to within about 1 mK with separate electronic controls. These controls operated automatically with individual channels of recording circuitry provided with proportional, rate, and reset control. The sample (about 0.50 mol trimethylamineborane or 0.26 mol triethylamineborane) was sealed in a platinum calorimeter equipped with horizontal, perforated, heat-distributing disks of gold. A small pressure of helium (about 40 Torr) was left in the calorimeter to promote thermal equilibration at low temperatures. The 1961 International Atomic Weights<sup>(3)</sup> and the 1963 values of the fundamental constants<sup>(4)</sup> were used. The electrical power supplied to the calorimeter heater and the resistance of the platinum resistance thermometer were measured with a White double potentiometer. Measurements of potential were in terms of a bank of six saturated cadmium cells calibrated at the National Bureau of Standards. The duration of each heating interval was determined by an electrical stopclock driven by a constant-frequency ( $50 \pm 0.001$  Hz) a.c. power source; the estimated uncertainty in time measurements was less than 0.01 per cent. Temperatures were measured with platinum resistance thermometers calibrated from 90 to 400 K in terms of the International Practical Scale of 1948, text revision of 1960,<sup>(5)</sup> and from 11 to 90 K in terms of the provisional scale of the National Bureau of Standards.<sup>(6)</sup> Celsius temperatures were converted to thermodynamic temperatures by adding 273.15 K.<sup>(7)</sup> Throughout this paper 1 cal = 4.184 J.

### 3. Results

#### HEAT CAPACITY

The observed values of heat capacity at saturation pressure  $C_s$  of solid and liquid trimethylamineborane and triethylamineborane are listed in table 1. The differences between  $C_s$  and  $C_p$  calculated from the thermodynamic relation<sup>(8)</sup>  $C_p - C_s = T(\partial V/\partial T)_p(\partial P/\partial T)_s$ , were much smaller than the precision uncertainties at all experimental temperatures, the maximum difference being less than 0.01 per cent at the highest temperature for the most volatile material. The temperature increments used in the experiments were small enough so that correction for nonlinear variation of  $C_s$  with  $T$  was unnecessary. With the exception of temperature regions near phase changes, the increments employed were approximately 10 per cent of the thermodynamic temperature below 50 K, 5 to 8 K from 50 to 150 K, and 8 to 10 K above 150 K. The precision of the heat capacity measurement was usually better than 0.1 per cent (above 30 K the accuracy uncertainty of the values of  $C_s$  should not exceed 0.2 per cent). The values of heat capacity determined in the premelting range were of lower precision and accuracy because of rapid changes in  $C_s$  with  $T$ , slow

TABLE 1. Experimental molar heat capacity of trimethylamineborane and triethylamineborane

$T^a$ K	$C_p^b$ cal K <sup>-1</sup> mol <sup>-1</sup>	$T^a$ K	$C_p^b$ cal K <sup>-1</sup> mol <sup>-1</sup>	$T^a$ K	$C_p^b$ cal K <sup>-1</sup> mol <sup>-1</sup>
TRIMETHYLAMINEBORANE					
Crystals III					
11.67	0.511	66.20	10.555	198.71	26.446
11.69	0.505	67.77	10.731	201.74	26.938
12.81	0.676	68.16	10.786	201.92	26.982
13.19	0.745	73.99	11.465	206.37	27.489
14.12	0.925	74.22	11.499	209.38	27.923
14.62	1.021	80.14	12.245	210.08	28.011
15.40	1.177	80.94	12.347	213.80	28.463
16.14	1.338	86.79	13.109	216.88	28.844
16.69	1.465	87.80	13.226	218.17	29.047
17.91	1.747	94.26	14.009	221.02	29.400
18.35	1.854	100.99	14.839	224.79	29.912
19.84	2.218	107.99	15.709	228.92	30.468
20.66	2.420	114.68	16.539	237.45	31.675
21.86	2.720	116.29	16.667	245.48	32.756
23.15	3.055	121.09	17.351	253.51	34.026
24.18	3.306	122.61	17.469	261.30	35.206
25.58	3.663	127.26	18.079	265.87	35.914
26.80	3.956	128.69	18.227	269.60	36.532
28.56	4.376	135.04	19.016	275.21	37.466
29.71	4.646	141.65	19.808	284.22	38.989
31.91	5.161	148.50	20.639	292.94	40.574
35.37	5.904	155.58	21.475	301.38	42.127
39.16	6.624	162.43	22.291	317.21	45.284
43.45	7.362	169.78	23.133	325.11	47.071 <sup>c</sup>
48.11	8.111	178.21	24.132	329.01	47.982 <sup>c</sup>
50.12	8.412	185.68	24.810	332.43	48.793 <sup>c</sup>
52.72	8.803	186.36	25.105	336.04	49.682 <sup>c</sup>
55.35	9.189	191.81	25.439	339.20	50.511 <sup>c</sup>
57.63	9.525	193.61	25.894	345.76	52.344 <sup>c</sup>
60.69	9.914	194.25	26.043		
62.23	10.092				
Crystals II					
352.03	45.319 <sup>c</sup>	356.48	46.638 <sup>c</sup>	357.47	46.903 <sup>c</sup>
354.69	46.028 <sup>c</sup>				
Crystals I					
362.14	44.536 <sup>c</sup>	364.10	44.861 <sup>c</sup>	364.69	44.973 <sup>c</sup>
362.20	44.586 <sup>c</sup>				
Liquid					
373.01	48.236	378.66	48.552	380.08	48.586
375.19	48.289				
TRIETHYLAMINEBORANE					
Stable crystals					
13.27	1.237	45.17	10.295	131.93	27.494
13.28	1.245	49.46	11.329	139.68	28.784
13.40	1.278	52.17	11.956	147.57	30.144
14.93	1.669	54.20	12.419	155.58	31.458
14.99	1.685	57.14	13.117	163.67	32.826

TABLE 1—*continued*

$T^a$ K	$C_s^b$ cal K <sup>-1</sup> mol <sup>-1</sup>	$T^a$ K	$C_s^b$ cal K <sup>-1</sup> mol <sup>-1</sup>	$T^a$ K	$C_s^b$ cal K <sup>-1</sup> mol <sup>-1</sup>
TRIETHYLAMINEBORANE (Stable crystals)— <i>continued</i>					
16.43	2.069	61.74	14.131	171.83	34.176
17.11	2.262	63.28	14.473	180.20	35.616
18.33	2.628	67.46	15.353	184.64	36.410
18.40	2.661	70.28	15.924	193.05	37.960
18.69	2.728	73.81	16.642	201.60	39.616
20.42	3.276	77.35	17.345	210.17	41.232 <sup>d</sup>
20.63	3.330	79.69	17.842	218.59	43.140 <sup>d</sup>
20.69	3.354	83.02	18.507	226.60	43.923 <sup>d</sup>
22.89	4.052	86.01	19.135	235.38	45.353 <sup>d</sup>
22.92	4.044	88.64	19.647	238.07	45.833 <sup>d</sup>
25.11	4.749	93.34	20.524	238.30	45.884 <sup>d</sup>
25.28	4.789	94.24	20.693	243.77	46.992 <sup>d</sup>
27.60	5.513	99.84	21.741	246.13	47.603 <sup>d</sup>
27.94	5.604	100.54	21.845	252.39	49.185 <sup>d</sup>
30.83	6.463	108.11	23.239	253.86	49.326 <sup>d</sup>
33.99	7.379	115.83	24.673	260.93	51.170 <sup>d</sup>
37.50	8.346	123.82	26.058	262.89	52.053 <sup>d</sup>
41.23	9.316				
Metastable crystals					
97.45	21.432	144.19	29.604	191.97	37.369
105.20	22.852	151.97	30.867	200.29	38.777
113.11	24.302	159.90	32.174	208.66	40.234
120.83	25.618	167.92	33.443	217.37	41.809
128.64	26.995	176.02	34.739	225.80	43.393
136.58	28.338	183.87	36.029	230.22	44.163
Liquid					
268.49	58.120	286.92	60.163	296.37	61.252
277.29	59.075	290.82	60.608	305.25	62.272

<sup>a</sup>  $T$  is the mean temperature of each heat capacity measurement.

<sup>b</sup>  $C_s$  is the heat capacity of the condensed phase at saturation pressure. Values of  $C_s$  are not corrected for the effects of premelting caused by impurities.

<sup>c, d</sup> The temperature increments of these measurements are in order of increasing  $T/K$ : <sup>c</sup> 7.774, 7.136, 6.865, 6.922, 6.665, 6.463, 2.497, 2.817, 2.567, 2.767, 1.988, 2.158, 1.976, 2.853; <sup>d</sup> 8.596, 8.298, 8.926, 8.698, 9.284, 7.957, 8.441, 7.727, 8.872, 8.761, 8.586, 9.332.

equilibration, and uncertainties caused by the presence of impurities. The results reported in table 1 are uncorrected for any effect of premelting caused by impurities, but to permit this calculation, pertinent  $\Delta T$  values are included as a footnote. Table 4 lists values at selected temperatures determined from smooth curves drawn through all the results from table 1 after corrections for premelting had been made.

#### SOLID-STATE PHASE TRANSFORMATIONS

Polymorphic crystalline states were observed for both substances. Trimethylamineborane exists in three enantiotropic crystalline modifications. Both solid-solid transitions occurred regularly and without difficulty, as would be expected for iso-

thermal or first order transitions (Type 1, classification of McCullough<sup>(9)</sup>). Crystalline triethylamineborane exhibited a second order or  $\lambda$  type transition (Type H<sup>(9)</sup>) which was quite diffuse with a "smeared-out peak" at about 219 K. Because the high-temperature stable crystals could be supercooled readily, it was necessary to maintain the metastable crystalline modification in the temperature region near 70 K for several days until transformation to the stable crystals was completed. In addition to the heat capacity studies of the equilibrium crystals of triethylamineborane, several series of heat capacity observations were made for the metastable crystals and are listed in table 1. The molar heat capacity curves for the two materials studied are illustrated in figure 1.

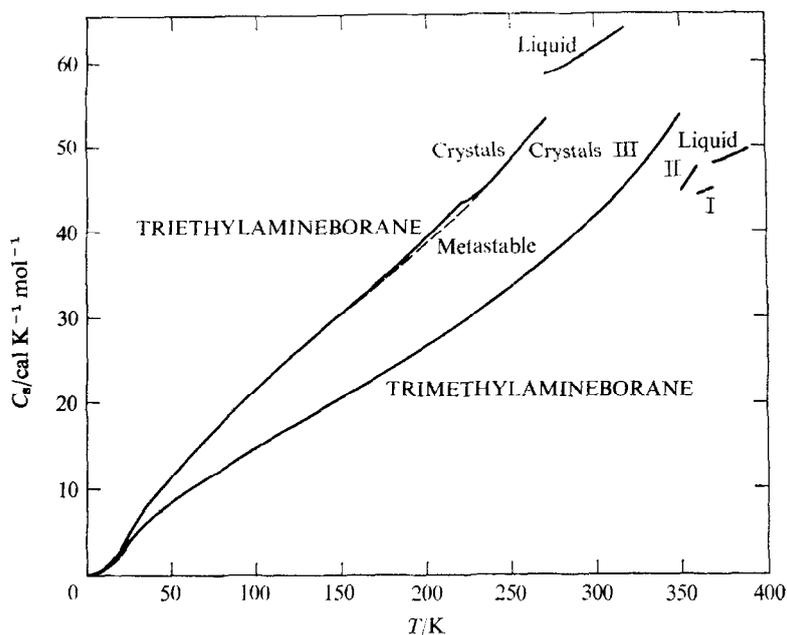


FIGURE 1. Heat capacity curves for trimethylamineborane and triethylamineborane.

#### ENTHALPY OF FUSION, TRIPLE POINT TEMPERATURE, CRYOSCOPIC CONSTANTS, AND SAMPLE PURITY

The enthalpy of fusion  $\Delta H_m$  was determined from the total enthalpy between an equilibrium temperature below the melting point and one above. The isothermal increment was calculated by subtracting the sum of the enthalpies required to raise the temperature of the crystals from the initial temperature to the melting point and the liquid from the melting point to the final temperature. Appropriate corrections for the effect of premelting<sup>(10)</sup> caused by impurities were applied to each measurement of the enthalpy of fusion. Two or more measurements for each compound were averaged to obtain the results in table 2; the uncertainties are maximum deviations from the mean. Because of the lack of knowledge of the nature of the impurities and the exact amount of heterophase premelting, the accuracy uncertainty in the enthalpies of fusion may be considerably greater than the precision uncertainty listed in table 2.

TABLE 2. Molar enthalpies of transition and fusion

$T/K$	$\Delta H/\text{cal mol}^{-1}$	$T/K$	$\Delta H/\text{cal mol}^{-1}$
Trimethylamineborane		Triethylamineborane	
350.1	$605.9 \pm 1.1$ (Transition)	269.48	$3562.7 \pm 0.9$ (Fusion)
360.4	$1419.5 \pm 1.5$ (Transition)		
368.70	$1182.4 \pm 0.8$ (Fusion)		

This uncertainty should have an effect of less than  $0.01 \text{ cal K}^{-1} \text{ mol}^{-1}$  on the thermodynamic properties calculated from all the results.

Equilibrium melting temperatures  $T_F$  as a function of fraction  $F$  of total sample melted are given in table 3. Also listed are values derived<sup>(10)</sup> for the triple point temperature  $T_{ip}$ , the mole fraction  $x_2^*$  of impurity in the sample, and the cryoscopic constants,  $A = \Delta H_m/RT_{ip}^2$  and  $B = 1/T_{ip} - \Delta C_m/2\Delta H_m$ , calculated from the observed values of  $T_{ip}$ ,  $\Delta H_m$ , and  $\Delta C_m$  (heat capacity difference in solid and liquid state at  $T_{ip}$ ).

TABLE 3. Melting point summaries

$F$	$1/F$	$T_F/K$	$T(\text{calc})/K$
Trimethylamineborane			
$A = 0.00438 \text{ K}^{-1}$ , $B = 0.00141 \text{ K}^{-1}$ , $x_2^* = 0.06 \text{ mol per cent}$			
0.2444	4.092	368.3643	368.1438
0.4690	2.132	368.4208	368.4123
0.6904	1.448	368.4932	368.5060
0.9139	1.094	368.5678	368.5545
1.0000	1.000		368.5674
Pure	0		368.7044
Triethylamineborane			
$A = 0.02469 \text{ K}^{-1}$ , $B = 0.00296 \text{ K}^{-1}$ , $x_2^* = 0.005 \text{ mol per cent}$			
0.1164	8.591	269.4598	269.4595
0.2600	3.846	269.4686	269.4686
0.4741	2.109	269.4723	269.4720
0.6893	1.451	269.4732	269.4732
0.8803	1.136	269.4738	269.4738
1.0000	1.000		269.4741
Pure	0		269.4760

#### THE TRANSITION TEMPERATURES AND ENTHALPIES OF TRANSITION

The solid-solid phase transformations of trimethylamineborane were nearly isothermal, each taking place over about a 0.1 K temperature interval. From studies of equilibrium temperatures as a function of fraction transformed, values of 350.1 K and 360.4 K were chosen for the temperatures of the two solid-solid transitions. Duplicate measurements of the enthalpies of transition were made and calculated in a manner similar to that described for the enthalpies of fusion, and the results are summarized in table 2.

#### THERMODYNAMIC PROPERTIES IN THE SOLID AND LIQUID STATES

The low-temperature results were used in calculating values of the Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity for the materials

in the solid and liquid states at selected temperatures from 10 to 400 K for trimethylamineborane and from 10 to 310 K for triethylamineborane, which tends to decompose when warmed to higher temperatures. The thermodynamic properties at 10 K were calculated from a Debye function, the parameters of which were evaluated from the heat capacities between 11 and 20 K. The number of degrees of freedom used and the characteristic Debye temperatures are, respectively, trimethylamineborane, 5.8 and 139.0 K; and triethylamineborane, 5.5 and 115.15 K. Thermodynamic properties above 10 K were calculated from values of enthalpy and temperature of phase changes, and from appropriate integration of smoothed values of the heat capacity at regular intervals. The results are given in table 4; corrections for effects of premelting were applied as necessary in computing the "smoothed" results.

TABLE 4. Molar thermodynamic functions of trimethylamineborane and triethylamineborane<sup>a</sup>

$T$ K	$-(G_s - H_0^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$(H_s - H_0^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$H_s - H_0^0$ cal mol <sup>-1</sup>	$S_s$ cal K <sup>-1</sup> mol <sup>-1</sup>	$C_s$ cal K <sup>-1</sup> mol <sup>-1</sup>
TRIMETHYLAMINEBORANE					
Crystals III					
10	0.028	0.084	0.836	0.111	0.334
12	0.048	0.144	1.729	0.192	0.572
14	0.076	0.227	3.174	0.303	0.897
16	0.113	0.336	5.370	0.449	1.308
18	0.160	0.469	8.444	0.629	1.770
20	0.218	0.623	12.468	0.841	2.257
25	0.404	1.076	26.901	1.480	3.514
30	0.644	1.583	47.50	2.228	4.715
35	0.928	2.112	73.93	3.040	5.829
40	1.245	2.638	105.50	3.882	6.775
45	1.585	3.145	141.51	4.729	7.615
50	1.941	3.631	181.55	5.572	8.396
60	2.685	4.547	272.83	7.233	9.823
70	3.450	5.386	377.0	8.836	10.994
80	4.221	6.162	493.0	10.383	12.227
90	4.990	6.907	621.7	11.897	13.494
100	5.755	7.627	762.7	13.382	14.716
110	6.515	8.328	916.0	14.843	15.957
120	7.269	9.016	1081.9	16.285	17.213
130	8.018	9.692	1260.0	17.710	18.409
140	8.760	10.358	1450.1	19.118	19.610
150	9.497	11.015	1652.2	20.512	20.816
160	10.229	11.665	1866.3	21.894	22.003
170	10.956	12.307	2092.2	23.263	23.161
180	11.677	12.943	2329.7	24.620	24.345
190	12.394	13.574	2579.1	25.968	25.536
200	13.106	14.202	2840.4	27.308	26.744
210	13.814	14.829	3114.0	28.643	27.983
220	14.518	15.456	3400.3	29.974	29.265
230	15.22	16.08	3700	31.30	30.62
240	15.92	16.72	4013	32.64	32.04
250	16.61	17.36	4341	33.97	33.50
260	17.31	18.01	4683	35.32	35.00

TABLE 4—*continued*

$T$ K	$-(G_s - H_0^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$(H_s - H_0^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$H_s - H_0^0$ cal mol <sup>-1</sup>	$S_s$ cal K <sup>-1</sup> mol <sup>-1</sup>	$C_s$ cal K <sup>-1</sup> mol <sup>-1</sup>
TRIMETHYLAMINEBORANE (Crystals III)— <i>continued</i>					
270	18.00	18.67	5041	36.67	36.60
273.15	18.21	18.88	5157	37.09	37.12
280	18.69	19.34	5415	38.03	38.27
290	19.38	20.02	5807	39.40	40.03
298.15	19.94	20.59	6139	40.53	41.53
300	20.07	20.72	6216	40.79	41.87
310	20.76	21.43	6644	42.19	43.79
320	21.45	22.16	7093	43.61	45.90
330	22.15	22.92	7563	45.07	48.21
340	22.84	23.70	8057	46.54	50.72
350	23.54	24.51	8578	48.05	53.58
350.10	23.55	24.52	8584	48.07	53.61
Crystals II					
350.10	23.55	26.25	9190	49.80	44.68
355	23.92	26.51	9412	50.43	46.11
360	24.29	26.79	9646	51.08	47.48
360.40	24.32	26.82	9665	51.14	47.56
Crystals I					
360.40	24.32	30.76	11085	55.08	44.30
365	24.71	30.93	11289	55.64	44.61
368.70	25.02	31.07	11455	56.09	44.86
Liquid					
368.70	25.02	34.27	12637	59.29	47.95
370	25.14	34.32	12699	59.46	48.02
380	26.06	34.69	13183	60.75	48.60
390	26.97	35.05	13672	62.02	49.18
400	27.86	35.42	14166	63.28	49.76
TRIETHYLAMINEBORANE					
Crystals					
10	0.046	0.139	1.390	0.185	0.552
12	0.080	0.238	2.854	0.318	0.930
14	0.126	0.370	5.180	0.496	1.415
16	0.186	0.534	8.548	0.720	1.953
18	0.260	0.724	13.029	0.983	2.538
20	0.347	0.936	18.713	1.282	3.145
25	0.618	1.532	38.30	2.150	4.710
30	0.955	2.189	65.65	3.143	6.219
35	1.343	2.869	100.40	4.212	7.663
40	1.771	3.553	142.11	5.324	9.003
45	2.228	4.229	190.28	6.457	10.255
50	2.708	4.892	244.57	7.600	11.451
60	3.715	6.178	370.7	9.893	13.756
70	4.760	7.414	519.0	12.174	15.869
80	5.828	8.597	687.7	14.425	17.887
90	6.907	9.743	876.8	16.650	19.906
100	7.991	10.851	1085.1	18.843	21.747
110	9.076	11.926	1311.8	21.002	23.595
120	10.159	12.974	1556.9	23.133	25.400
130	11.238	13.997	1819.6	25.236	27.152

TABLE 4—continued

$T$ K	$-(G_s - H_s^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$(H_s - H_s^0)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>	$H_s - H_s^0$ cal mol <sup>-1</sup>	$S_s$ cal K <sup>-1</sup> mol <sup>-1</sup>	$C_s$ cal K <sup>-1</sup> mol <sup>-1</sup>
TRIETHYLAMINEBORANE (Crystals)—continued					
140	12.312	14.998	2099.7	27.310	28.845
150	13.38	15.98	2396.7	29.36	30.54
160	14.44	16.94	2710.4	31.38	32.20
170	15.50	17.89	3041	33.39	33.87
180	16.55	18.82	3388	35.37	35.58
190	17.59	19.75	3753	37.34	37.39
200	18.63	20.68	4136	39.31	39.30
210	19.66	21.61	4538	41.27	41.19
220	20.68	22.55	4961	43.23	43.37
230	21.71	23.47	5399	45.18	44.41
240	22.72	24.38	5852	47.10	46.21
250	23.74	25.30	6325	49.04	48.54
260	24.75	26.24	6822	50.99	50.84
269.48	25.71	27.14	7313	52.85	52.89
Liquid					
269.48	25.71	40.36	10876	66.07	58.23
270	25.78	40.40	10907	66.18	58.28
273.15	26.25	40.60	11090	66.85	58.62
280	27.27	41.05	11495	68.32	59.38
290	28.72	41.70	12094	70.42	60.52
298.15	29.88	42.23	12591	72.11	61.45
300	30.14	42.35	12705	72.49	61.66
310	31.54	42.99	13327	74.53	62.88

<sup>a</sup> The values tabulated are at saturation pressure.

### ENTROPY OF THE VAPOR

To calculate the entropies of the two compounds in the ideal gas state at 298.15 K, values of the enthalpies of vaporization and vapor pressure were required. For trimethylamineborane the enthalpy of sublimation given by Alton *et al.*<sup>(11)</sup> was used together with a value of 0.911 Torr for the vapor pressure as calculated from their vapor pressure equation. For triethylamineborane the enthalpy of vaporization was calculated from the Clapeyron equation with values of  $dP/dT$  and  $P$  obtained from the Antoine equation of Smith and Laran:<sup>(12)</sup>

$$\log_{10}(P/\text{Torr}) = 7.17398 - 1808.4/(t/^\circ\text{C} + 200), \quad (90 \text{ to } 150^\circ\text{C}).$$

TABLE 5. Conversion of molar entropy values to the ideal gas state at 298.15 K

Compound	$S$ cal K <sup>-1</sup> mol <sup>-1</sup>	$\Delta H_{\text{vap}}$ kcal mol <sup>-1</sup>	$\Delta S_{\text{vap}}$ cal K <sup>-1</sup> mol <sup>-1</sup>	$R \ln(P/760 \text{ Torr})$ cal K <sup>-1</sup> mol <sup>-1</sup>	$S^\circ$ cal K <sup>-1</sup> mol <sup>-1</sup>
Trimethylamineborane	40.53 ± 0.08 <sup>a</sup>	13.6 ± 0.2 <sup>a</sup>	45.6 ± 0.7 <sup>a</sup>	-13.4 ± 0.1 <sup>a</sup>	72.7 ± 0.9 <sup>c</sup>
Triethylamineborane	72.11 ± 0.14 <sup>a</sup>	14.5 ± 0.5 <sup>b</sup>	48.6 ± 1.7 <sup>b</sup>	-17.1 ± 0.1 <sup>b</sup>	103.6 ± 2.0 <sup>c</sup>

<sup>a</sup> Authors' own estimate of the overall uncertainty in their results.

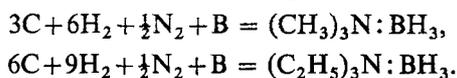
<sup>b</sup> Estimated to be the uncertainty resulting from the long extrapolation of the vapour pressure equation.

<sup>c</sup> Maximum overall uncertainty.

The results of these calculations and the entropies  $S^\circ(298.15 \text{ K})$  in the ideal gas state are summarized in table 5. For both compounds corrections to the entropy for gas imperfection were negligible in terms of the probable accuracy compared with the uncertainties in the values for the enthalpy of vaporization and gas compression.

#### GIBBS ENERGY OF FORMATION

The experimental values at 298.15 K of the entropy in the ideal gas state were used, together with values of the enthalpy of formation<sup>(13,14)</sup> and of the entropy of the elements,<sup>(15)</sup> C (c, graphite), H<sub>2</sub> (g), N<sub>2</sub> (g), and B (c), to determine the Gibbs energy of formation in the ideal gas state of trimethylamineborane and triethylamineborane to be +22.2 and +29.6 kcal mol<sup>-1</sup>, respectively, for the reactions:



From the thermodynamic relation,  $\Delta G_f^\circ = -RT \ln K_f$ , the common logarithms of the equilibrium constant of formation for the above reactions are -16.3 and -21.7.

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