

to polynomials of various orders were tried. To obtain a good fit without using polynomials of very high order, it was necessary to express concentrations as mole per cent, X , rather than weight per cent. Doing this, the data for $\log P$ could be fit by a cubic polynomial for each of the four temperatures. At any given concentration, $\log P$ was a linear function of $1/T$. Therefore, a least squares fit to all the data was obtained for the following expression

$$\log P = A_0 + A_1X + A_2X^2 + A_3X^3 + (A_4 + A_5X + A_6X^2 + A_7X^3)T^{-1} \quad (7)$$

The values for the coefficients in Equation 7 are listed in Table V, along with heats of vaporization and boiling points, which may be calculated from it. Equation 7 reproduces the experimental data to within $\pm 0.4\%$ in $\log P$ (or about 2% in P).

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RECEIVED for review December 11, 1968. Accepted April 24, 1969. This work was supported by the U. S. Army Engineering Research and Development Laboratories under Contract No. DA44-009-ENG-4909.

Heat Capacities and Thermodynamic Properties of α -Beryllium Nitride from 25° to 310° K.

BRUCE H. JUSTICE¹

Thermal Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640

The low-temperature heat capacity of α -Be₃N₂ was measured from 25° to 310° K. by adiabatic calorimetry. No thermal anomalies were observed. Corrections were applied for the impurities, 2.7% BeO, 0.2% Be, 0.1% C, and 0.3% Fe. Smoothed thermodynamic functions at even temperatures are tabulated. The values of C_p° , S_p° , $(H_p^\circ - H_f^\circ)/T$, and $-(G_p^\circ - H_f^\circ)/T$ at 298.15° K. are 15.39, 8.170, 5.682, and 2.488 cal. per mole ° K.

THE LOW-TEMPERATURE heat capacity of α -Be₃N₂ has been measured in connection with a program to measure and tabulate the thermodynamic properties of rocket exhaust products. Heretofore, the entropy of α -Be₃N₂ has been determined from high-temperature equilibrium studies (7, 15) with relatively low precision. Recently, Furukawa and Reilly (5) reported the heat capacity of α -Be₃N₂. The high-temperature enthalpy has been reported (1, 13) in two investigations.

¹ Present address: Semi-Conductor Components Laboratory, Texas Instrument Co., Dallas, Tex. 75222

EXPERIMENTAL

Sample. The sample was supplied by Brush Beryllium Co. Before measurements were made, the sample was checked for purity and crystal structure. The x-ray powder pattern revealed only cubic or α -Be₃N₂ (2). The various analyses showed the following composition: α -Be₃N₂, 96.7% (hydrolysis of nitride to ammonia and titration); BeO, 2.7% (neutron activation analysis for oxygen); Be, 0.2% (quantitative hydrogen gas evolution in acid); C, 0.1% (combustion to CO₂); Fe, 0.3% (neutron activation and spectrographic analyses).

Table I. Heat Capacities of α -Beryllium Nitride^a

T	C _p	T	C _p
Series I			
156.18	5.00	244.51	11.85
165.39	5.71	254.66	12.57
174.92	6.46	264.50	13.23
183.97	7.24	274.06	13.83
192.63	7.86	283.38	14.46
201.61	8.59	292.49	15.07
211.54	9.37	301.40	15.58
221.72	10.16	310.11	16.09
241.49	11.62		
251.75	12.31	Series III	
261.69	13.02		
271.36	13.63	26.69	0.012
280.76	14.27	29.16	0.016
289.94	14.85	32.02	0.022
298.92	15.43	35.44	0.058
307.70	15.89	39.12	0.076
		42.88	0.109
		47.12	0.130
Series II			
25.29	0.006	52.20	0.179
28.11	0.017	57.71	0.235
30.90	0.020	63.57	0.336
33.91	0.043	70.08	0.443
37.26	0.050	77.21	0.602
40.97	0.064	85.22	0.886
44.97	0.129	93.97	1.21
49.43	0.156	103.22	1.61
54.25	0.203	112.63	2.11
59.52	0.255	121.57	2.63
65.32	0.359	129.87	3.18
71.87	0.481	138.26	3.75
79.12	0.667	146.78	4.37
87.27	0.954	154.82	4.95
95.77	1.28	162.48	5.54
104.73	1.67	169.79	6.10
114.10	2.18	176.82	6.62
122.88	2.71	183.59	7.21
131.04	3.24	190.14	7.73
139.90	3.86	198.21	8.34
149.43	4.52	208.36	9.18
158.38	5.21	218.73	9.97
166.87	5.85	238.28	11.45
174.96	6.47	248.15	12.11
182.71	7.10	258.29	12.83
190.17	7.72	268.13	13.49
197.37	8.25	277.70	14.10
204.77	8.85	287.04	14.68
213.75	9.57	296.17	15.29
223.80	10.34	305.10	15.78

^a Units: cal., mole, ° K.

Calorimetric Apparatus. The adiabatic calorimeter used in this investigation is described elsewhere (11). The measuring circuits have been recently recalibrated. The heat capacity of benzoic acid was measured after this as a check on the system. The entropy of benzoic acid was 40.01 cal. per mole °K., as compared to 40.055 cal. per mole °K. reported by Furukawa *et al.* (3) and 40.11 cal. per mole °K. reported by Oetting and McDonald (11).

The calorimeter used (laboratory designation CU-3) is a gold-plated copper container of about 70-cc. internal volume. The sample was weighed into the container in an inert nitrogen atmosphere (dry box), not only to prevent hydrolysis, but as a safety precaution, due to the toxicity of beryllium compounds. The heat capacity of the empty container was measured separately. Measurements were carried out with the container, either empty or loaded, charged with 1 atm. of helium to hasten thermal equilibrium. Corrections were applied for slight differences in solder and helium on the loaded and empty calorimeter. The sample heat capacity varied from 1% of the total

Table II. Thermodynamic Functions of α -Beryllium Nitride^a

T	C _p	S°	H° - H ₃	-(G° - H ₃)/T
25	(0.009)	(0.003)	(0.056)	0.001
30	0.020	0.005	0.118	0.001
35	0.043	0.010	0.269	0.002
40	0.078	0.018	0.567	0.003
45	0.116	0.029	1.059	0.006
50	0.154	0.043	1.722	0.009
60	0.267	0.080	3.781	0.017
70	0.444	0.134	7.274	0.030
80	0.699	0.209	12.919	0.047
90	1.039	0.310	21.539	0.071
100	1.463	0.441	33.981	0.101
110	1.966	0.603	51.06	0.139
120	2.540	0.798	73.54	0.186
130	3.175	1.026	102.07	0.241
140	3.861	1.287	137.22	0.306
150	4.587	1.577	179.43	0.381
160	5.342	1.897	229.05	0.466
170	6.119	2.245	286.34	0.560
180	6.907	2.617	351.47	0.664
190	7.700	3.011	424.50	0.777
200	8.492	3.426	505.5	0.899
210	9.278	3.860	594.3	1.030
220	10.051	4.309	691.0	1.168
230	10.809	4.773	795.3	1.315
240	11.548	5.249	907.1	1.469
250	12.265	5.735	1026.2	1.630
260	12.958	6.229	1152.3	1.797
270	13.626	6.731	1285.2	1.971
273.15	13.832	6.890	1328.5	2.026
280	14.271	7.238	1424.8	2.150
290	14.895	7.750	1570.6	2.334
298.15	15.39	8.170	1694.0	2.488
300	15.50	8.265	1722.6	2.523
310	16.11	8.783	1880.7	2.717

^a Units: cal., mole, ° K.

at 25° K. to 51% at 310° K. The sample weighed (in vacuo) 61.698 grams, and the molecular weight of α -Be₃N₂ was taken as 55.0500 (1961 atomic weights). The density used for buoyancy corrections was 2.709 grams per cc.

The ice point was taken as 273.15° K., and one defined calorie as 4.1840 joules. The measurements of mass, time, electromotive force, and temperature can all be traced to standards maintained by the U. S. National Bureau of Standards.

RESULTS AND DISCUSSION

Heat Capacities and Thermodynamic Functions. The measured values of heat capacity of α -Be₃N₂ are presented in chronological order in Table I. Temperature increments employed were approximately the smaller of the two quantities, 10% of the absolute temperature, or 10° K. These increments can generally be inferred from differences in adjacent mean temperatures. The heat capacity of the sample was obtained by subtracting the smoothed heat capacity of the empty calorimeter from the gross heat capacity after correcting for curvature (12). Corrections to the individual points were made for the heat capacities of the impurities, BeO (6, 10), Be (8), C (14), and Fe (8). Approximating polynomials for each impurity were used in conjunction with a computer program to derive the corrected points of Table I. The corrections to the points were 3.5 ± 0.5% of the uncorrected sample heat capacity. Measurements were made below 25° K., but were smaller than the errors associated with the apparatus in this temperature range. Thus, these values are not tabulated.

The smoothed heat capacities and thermodynamic functions at selected temperatures were obtained by integrating a polynomial approximation of the data on a digital com-

puter (9). The entropy and enthalpy at 25° K. were derived from a Debye T^3 extrapolation. The smoothed data are presented in Table II. The data generally carry an extra digit for internal consistency and interpolation. The experimental heat capacities were generally within 0.5% of the smooth curve above 100° K. Below this temperature, the scatter increased gradually to 20% of the heat capacity at 25° K., due to the relative smallness of the heat capacity of α -Be₃N₂ with respect to the total and the decreasing sensitivity of the thermometer and thermocouples. Although the precision of the measurements is within 0.5% above 100° K., the thermodynamic functions are not accurate to better than 1% because of the uncertainty in impurity corrections. The entropy at 298.15° K. was 8.17 ± 0.10 cal. per mole °K., in good agreement with the value 8.23 ± 0.08 cal. per mole °K. of Furukawa and Reilly (5). The earlier estimated value of $S_{298.15}^{\circ}$ by Furukawa *et al.* (4) was consistent with high-temperature equilibrium data (7, 15). However, a recent analysis (14) of these data (7, 15) shows they were not precise enough to define the entropy to better than 4 cal. per mole °K.

Gibbs Energy of Formation. The enthalpy of formation (ΔH_f°) is tabulated as -140.6 ± 0.3 kcal. per mole (14). The entropy of formation (ΔS_f°) is calculated from the same tabulation and the measured entropy ($S_{298.15}^{\circ}$) of α -Be₃N₂ as -44.4 ± 0.1 cal. per mole °K. This leads to a value of ΔG_f° of -127.4 ± 0.3 kcal. per mole.

ACKNOWLEDGMENT

The encouragement and technical support of D.R. Stull, G.C. Sinke, Harold Prophet, C.E. Van Hall, O.U. Anders, and H.W. Rinn are acknowledged.

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RECEIVED for review January 10, 1969. Accepted April 21, 1969. The partial support of this investigation by the U.S. Air Force Rocket Propulsion Laboratory under Contract FO4611-67-C-0009 is gratefully acknowledged.