

Heat Capacity of Potassium Borohydride (KBH_4) From 15 to 375 °K. Thermodynamic Properties From 0 to 700 °K

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The heat capacity of potassium borohydride (KBH_4) was determined from about 15 to 375 °K by means of an adiabatic calorimeter. A table of thermodynamic functions was calculated up to 700 °K using the data obtained along with those at high temperatures found in the literature. A solid-solid (order-disorder) transition was observed at 77.16 ± 0.02 °K and the entropy change associated with this transition was found to be 2.92 J/deg-mole. A broad transition from about 200 to 450 °K is attributed to a continuation of the order-disorder transition.

1. Introduction

The results of heat-capacity investigations on potassium borohydride (KBH_4) presented in this paper are a part of the program at the National Bureau of Standards to furnish thermodynamic data on various boron compounds.

Johnston and Hallett [1]¹ reported in their heat-capacity measurements on sodium borohydride (NaBH_4) a λ -type solid-phase transition at 189.9 °K with an entropy change of 1.22 cal/deg-mole. (Henceforth the unit of entropy in cal/deg-mole will be abbreviated to e.u.) Stockmayer and Stephenson [2] interpreted this transition as an order-disorder type involving changes in the orientation of the BH_4^- ion group and predicted, on the bases of the heat-capacity data in the neighborhood of the transition and on their previous investigations of ammonium halides (NH_4Cl , ND_4Cl , and NH_4I) [3,4], that the crystal structure of sodium borohydride below the λ point would be tetragonal. Abrahams and Kalnajs [5] found from x-ray diffraction measurements that sodium, potassium, rubidium, and cesium borohydrides have the face-centered cubic structure at room temperature and that sodium borohydride has the body-centered tetragonal structure below the λ point. The results of x-ray measurements of Ford and Powell [6] on sodium and potassium borohydrides at 90 and 293 °K are in agreement with those of Abrahams and Kalnajs [5]. Unfortunately, the measurements of Ford and Powell [6] were not made below the λ point (77.16 ± 0.02 °K, obtained in the work presented here) of potassium borohydride.

Stephenson et al. [3,4] obtained between 1.0 and 1.5 e.u. for the entropy of transition at the λ point for ammonium and deuterio-ammonium halides. They have interpreted these values, which are close to the theoretical value of $R \ln 2$, as arising from an order-disorder transition involving two possible orientations of the NH_4^+ tetrahedron in the ammonium halide lattice. Below the λ point all of the NH_4^+ tetrahedrons have one orientation and above the λ

point they have either of the two orientations. Infrared spectra [7] and neutron diffraction [8,9] measurements on the ammonium halides support the above interpretation.

Stephenson, Rice, and Stockmayer [10] found, from cooling and warming curve investigations, transitions in KBH_4 at 76 ± 1 °K, RbBH_4 at 44 ± 3 °K, and CsBH_4 at 27 ± 1 °K and interpreted these transitions to be the order-disorder type interpreted for the λ transitions in NaBH_4 and the ammonium halides. The alkali metal borohydrides have, in contrast with the ammonium halides, the face-centered cubic structure (NaCl) in the region above the λ transition [5]. (LiBH_4 has the orthorhombic structure [11].) The ammonium halides exist in the body-centered cubic form (CsCl) in the region above the λ transition and transform by first-order transition into the face-centered cubic form only at higher temperatures [3,9]. From heat-capacity measurements, Shigi [12] found the entropy associated with the transition in KBH_4 to be 0.771 e.u. which is considerably lower than the $R \ln 2$ or 1.38 e.u. for the order-disorder transition. Shigi [12] ascribed the observation to an order-disorder transition involving BH_4^- ions as interpreted by Stockmayer and Stephenson [2] for the λ transition in NaBH_4 .

In this paper, the results of new measurements on the heat capacity of KBH_4 from 16 to 376 °K are presented. A relatively low heat of λ transition, comparable to that observed by Shigi [12], was obtained. The low-temperature heat-capacity data were compared and analyzed with the relative enthalpy data (0 to 400 °C) reported by Douglas and Harman [13]. The "broad" transition extending from about 200 to 450 °K is interpreted as a continuation of the order-disorder transition still incomplete at 77.16 °K.

2. Apparatus and Method

The heat-capacity measurements were conducted in an adiabatic calorimeter similar in design to that described by Scott et al. [14]. The calorimeter vessel, which was filled externally and sealed by means

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¹Figures in brackets indicate the literature references at the end of this paper.

of a specially designed gold-gasket closure [15], was suspended within the adiabatic shield system by means of a linen cord instead of the filling tube shown in the above reference [14]. The design and operation of the calorimeter will be given in detail in a subsequent publication.

The platinum-resistance thermometer used in the measurements was calibrated on the International Practical Temperature Scale of 1948 [16]. The temperatures in degrees Kelvin ($^{\circ}\text{K}$) were obtained by adding 273.15 deg to the temperatures in degree Celsius ($^{\circ}\text{C}$). Below 90 $^{\circ}\text{K}$, the thermometer was calibrated on the NBS-1955 provisional scale which is numerically 0.01 deg lower than the NBS-1939 provisional scale [17]. The resistance measurements were made to the nearest 0.00001 ohm by means of a Mueller bridge and a galvanometer of high sensitivity.

The electrical power introduced into the calorimeter heater (100 ohms of constantan wire) was measured by means of a Wenner potentiometer in conjunction with a volt box, standard resistor, and saturated standard cells. The duration of each heating interval was measured by means of an interval timer of high precision operated on the 60-cycle frequency standard provided at the National Bureau of Standards. The 60-cycle frequency standard is derived from a 100 kc/s quartz oscillator which is stable to 0.5 ppm. The operation of the interval timer was checked periodically with seconds signals also derived from the same 100 kc/s oscillator. The variations were not more than 0.02 sec for any time interval. The heating periods were never less than 2 min.

The observed gross (calorimeter vessel plus sample) heat-capacity values were corrected for curvature wherever significant by a method previously described [18]. The values of net heat capacity (heat capacity of sample only) were obtained by subtracting the values of tare heat capacity (heat capacity of empty calorimeter vessel) from those of the gross heat capacity at the corresponding temperatures. The values of the tare heat capacity at the various temperatures were obtained by four-point Lagrangian interpolation in a table of tare heat-capacity values previously obtained. Corrections were applied for the heat capacity of helium gas and for the small difference in the mass of the calorimeter vessel between the gross and tare measurements. The values of net heat capacity were corrected for the KBO_2 impurity and converted to molal basis using the atomic weights based on C-12 [19]. These converted values will be referred to as observed molal heat capacity. Whenever a reference to the energy unit calorie is made, the defined calorie (4.1840 absolute joules) is intended.

3. Sample

The potassium borohydride sample used in the investigation was purchased from Metal Hydrides, Inc. The analyses furnished by the supplier showed the sample to contain 99.5 percent of the theoretical

hydrogen by a gasometric method and 100.5 and 100.7 percent of the alkali and boron, respectively, by acid-base titration. The supplier believed the sample to have a purity no less than 99.5 percent. The analyses furnished with the sample are summarized in table 1. A portion of the above sample was used for the low-temperature measurements and another portion of the same sample was used by Douglas and Harman [13] in the high-temperature measurements previously reported. After the completion of the measurements, a separate set of chemical analysis was obtained, however, on the portion that was actually used in the low-temperature measurements because of the relatively low stability of the substance.

The sample was received, sealed with paraffin, in a screw-cap jar. The jar was opened approximately two weeks after receipt in an inert atmosphere box containing dry argon and a portion of the sample was transferred without further treatment into a calorimeter vessel. The sample was pumped in the vessel for two days, purged with helium gas several times, and finally sealed with a small quantity of helium gas. The helium gas serves to increase the rate of temperature equilibrium in the sample during the heat-capacity measurements.

TABLE 1. Analyses of the potassium borohydride sample

Gram formula weight=53.94488 g

Elements	Percentage by weight ^a	
	Analysis	Theoretical
Potassium.....	71.2 (flame photometry).....	72.49
	72.8 (titration).....	
Boron.....	20.2 (titration).....	20.04
Hydrogen.....	7.44 (gasometry).....	7.474
Chloride.....	0.10 (titration).....	
Methods	Percentage in weight of KBH_4 ^b	
	Specimen A	Specimen B
Hydrogen (by evolution).....	98.69	99.12
	98.73	99.12
Boric acid titration.....	99.56	99.91
	99.70	100.00

^a These values were supplied by the Metal Hydrides, Inc.; the percentages of potassium borohydride, based on potassium (titration), boron, and hydrogen, are 100.4, 100.8, and 99.5, respectively.

^b These analyses were obtained by R. A. Paulson of the Applied Analytical Research Section of the National Bureau of Standards. Specimen A was sampled from the top and specimen B from the bottom of the storage jar.

After completion of the heat-capacity measurements the purity of the sample was redetermined by hydrogen-evolution analysis and by titration of the boric acid. The analyses were performed by R. A. Paulson of the Applied Analytical Research Section of the Bureau. In the hydrogen analysis, the hydrogen was liberated by hydrolysis with 6*N* hydrochloric acid. The liberated hydrogen gas was swept by nitrogen through an absorber containing Ascarite and Anhydrone to remove any acid and

water. The dried hydrogen gas was then oxidized on copper oxide at 700 °C to water which was absorbed on Anhydron and weighed. For the boric acid analysis, the sample was first titrated with standard hydrochloric acid to the methyl red end point, and after the addition of several grams of mannitol, was titrated with standard sodium hydroxide to the phenolphthalein end point.

The analyses were not done immediately after the completion of the heat measurements; the composition of the sample investigated is therefore somewhat uncertain. The sample upon removal from the calorimeter vessel was stored in a screw-cap jar in a desiccator containing Drierite and the analyses were performed approximately one year later. Two samples taken from the top of the jar analyzed 98.69 and 98.73 percent by hydrogen analysis and 99.56 and 99.70 percent by titration of the boric acid. Another pair of samples from the bottom of the jar both analyzed 99.12 percent by hydrogen analysis and 99.91 and 100.00 percent by titration of the boric acid. These analyses suggest that the heat-capacity measurements were made on a sample that was at least 99.1 percent KBH₄, probably 99.5 percent.

Most literature information indicates that KBH₄ is stable, but a test sample exposed continuously for 48 days to the laboratory atmosphere changed in KBH₄ content from 98.4 to 96.7 percent according to hydrogen analysis. Considering the analyses given for the sample by the supplier and those obtained approximately one year later, the composition of the sample investigated was taken to be 99.5 percent KBH₄ and 0.5 percent KBO₂ possibly formed according to the reactions:



and



Corrections were made to the observed values of heat capacity on the basis that the heat capacities of KBH₄ and KBO₂ were additive. Because of the lack of heat-capacity data on KBO₂, the corrections were calculated on the basis that the ratio of the heat capacity of KBO₂ to KBH₄ is the same as that of NaBO₂ [20] to NaBH₄ [1].

4. Experimental Results

4.1. Heat Capacity

The observed values of molal heat capacity from about 15 to 375 °K are summarized in table 2 and plotted in figure 1. The heat-capacity curve indicates a broad transition starting from about 200 °K and begins to flatten from about 300 °K. A part of the same transition was observed by Douglas and Harman [13] in their measurements of the enthalpy relative to 273 °K up to 673 °K. Figure 2 shows how the smoothed low-temperature values of heat

TABLE 2. Observed heat capacity of potassium borohydride

Gram formula wt = 53.94488 g, $T \text{ deg K} = t \text{ deg C} + 273.15$

Run No.	T^a	C_p^c	ΔT^b
	Deg K	Deg ⁻¹ Mole ⁻¹	Deg K
1-----	81.9262	36.333	6.5263
	91.4848	40.047	12.5910
	103.4338	44.529	11.3070
	114.3040	48.453	10.4333
	124.4201	51.861	9.7990
	134.6828	55.131	10.7265
	145.9480	58.489	12.3533
	158.0094	61.922	11.7695
	169.5360	65.097	11.2836
	181.4994	68.352	12.6433
	193.9026	71.710	12.1629
	205.8546	74.943	11.7411
	218.2744	78.379	13.0987
	231.0480	81.848	12.4483
	243.6110	85.117	12.6777
	256.1038	88.200	12.3081
	268.2558	90.902	11.9958
	280.5140	93.250	12.5205
	292.9078	95.188	12.2673
	2-----	80.2196	35.680
85.2256		37.625	6.7209
91.7576		40.170	6.3431
100.7470		43.526	11.6358
110.1627		46.980	7.1956
118.8492		50.003	10.1775
129.4421		53.488	11.0082
141.2379		57.108	12.5834
153.6396		60.683	12.2201
165.6021		64.029	11.7048
177.0837		67.147	11.2584
187.8338		70.068	12.6470
200.2511		73.443	12.1876
212.2289		76.733	11.7680
223.8089		79.890	11.3920
235.8074		83.109	12.6051
248.2734		86.315	12.3267
260.5716		89.274	12.2698
272.8466		91.918	12.2802
285.2636		94.144	12.5537
297.7020	96.045	12.3231	
311.2642	97.892	14.8014	
325.9442	98.979	14.5585	
340.4102	99.754	14.3736	
354.7243	100.05	14.2546	
368.9214	100.26	14.1395	
3-----	16.0784	1.150	1.1323
	17.3290	1.474	1.3689
	18.9010	1.920	1.7752
	20.8022	2.617	2.0273
	23.4736	3.672	3.3154
	26.3709	4.981	2.4792
	29.0787	6.293	2.9364
	31.5788	7.543	2.0639
	33.9314	8.797	2.6411
	36.7419	10.296	2.9800
	39.5210	11.806	2.5781
	42.6738	13.527	3.7277
	46.5295	15.694	3.9836
	51.3304	18.471	5.6182
	56.3556	21.450	4.4322
	60.5536	24.097	3.9637
65.1810	27.221	5.2913	
70.9554	31.678	6.2573	
75.6252	90.625	3.0824	
79.6041	44.427	4.8754	

See footnotes at end of table.

TABLE 2. Observed heat capacity of potassium borohydride—
Continued

Gram formula wt = 53.94488 g, T deg K = t deg C + 273.15

Run No.	T^a	C_p^c	ΔT^b
	Deg K	Deg ⁻¹ Mole ⁻¹	Deg K
4-----	71. 8152	32. 545	3. 2608
	74. 5014	35. 330	2. 1115
	76. 3579	55. 138	1. 6016
	77. 1587	Infinity	0
	77. 8554	67. 049	1. 3934
5-----	68. 2424	29. 397	5. 2497
	71. 6737	32. 179	1. 6130
	73. 9988	34. 714	3. 0372
	76. 3361	58. 618	1. 6374
	77. 1626	9381. 1	. 0155
	78. 0424	52. 498	1. 7443
	80. 3469	35. 729	2. 8646
	83. 1655	36. 789	2. 7726
6-----	317. 3758	98. 210	14. 8361
	332. 1227	99. 143	14. 6578
	346. 7124	99. 653	14. 5216
	361. 4790	99. 884	15. 0116
	376. 1383	99. 993	14. 3070
7-----	73. 0428	33. 675	3. 2367
	75. 7802	37. 675	2. 2383
	77. 2337	347. 46	. 6686
	79. 0754	35. 393	3. 0149

^a T is the mean temperature of the heating interval.

^b ΔT is the temperature interval of heating.

^c C_p is the observed mean heat capacity over the interval ΔT .

^d The temperatures given are believed to be accurate to ± 0.01 deg K. The figures beyond the second decimal are significant only insofar as small temperature differences are concerned.

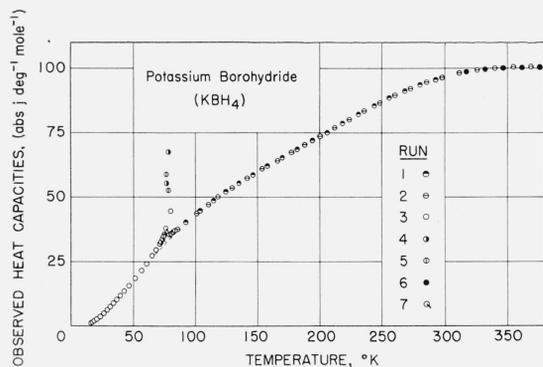


FIGURE 1. Observed heat capacity of potassium borohydride.

capacity join with those calculated from the heat-capacity equation:

$$C_p = 0.9999422 \times 4.1840(80.810 - 0.130681T) + 1.0217 \times 10^{-4}T^2 - 8.303/T \text{ J/deg-mole, (3)}$$

given by Douglas and Harman [13] for the range 273 to 700 °K. (The equation actually given by Douglas and Harman [13] is in cal/deg-mole. The factor 4.1840 for conversion to J/deg-mole was applied to obtain eq (3). The factor 0.9999422 is the ratio of new to old molecular weight of KBH₄.) The inflection point is around 460 °K and above this temperature the heat capacity increases "normally."

The values of heat capacity obtained were at helium-gas pressures varying from 50 torr at room temperature to about one-twentieth of this pressure at the lowest temperature and to about 60 torr at the highest temperature. In the case of KBH₄ the conversion of its heat capacity from any of the above pressures to 1 atm pressure would make a negligible change. Therefore, all computations and analyses have been carried out as if the measurements were made at constant 1 atm pressure.

4.2. Heat of Transition

A solid-phase transition was observed and the transition temperature was estimated from the observed values of the heat capacity to be 77.16 ± 0.02 °K. (In this paper, the figure associated with the symbol \pm indicates the uncertainty estimated by examining the precision of the measurements and possible sources of systematic errors. The figure has a 50 percent confidence limit.) The apparent heat capacities in this temperature region are given in table 2 and in figure 1. The heat associated with the transition was evaluated by subtracting the enthalpy change calculated from the "normal" heat-capacity curve, shown as a broken line in figure 1, between 65 and 80 °K from the total change obtained for the temperature interval. The total change in enthalpy between 65 and 80 °K was determined by summing the various experimental increments of energy introduced to determine the heat capacity over this range. Adjustments were made to the even 65 to 80 °K temperature interval using the observed values of the heat capacity. These results are summarized in table 3 on a molal basis, obtained after subtracting the contribution of the calorimeter vessel to the observed enthalpy increment.

The heat of transition obtained is 225 J/mole (53.8 cal/mole) and the entropy of transition is 2.92 J/deg-mole (0.70 e.u.). These values are in close agreement with 58.4 cal/mole and 0.771 e.u. for the heat and entropy of transition, respectively, reported by Shigi [12] and with the unpublished values 52.8 cal/mole and 0.69 e.u., respectively, obtained by Stull et al. [21].

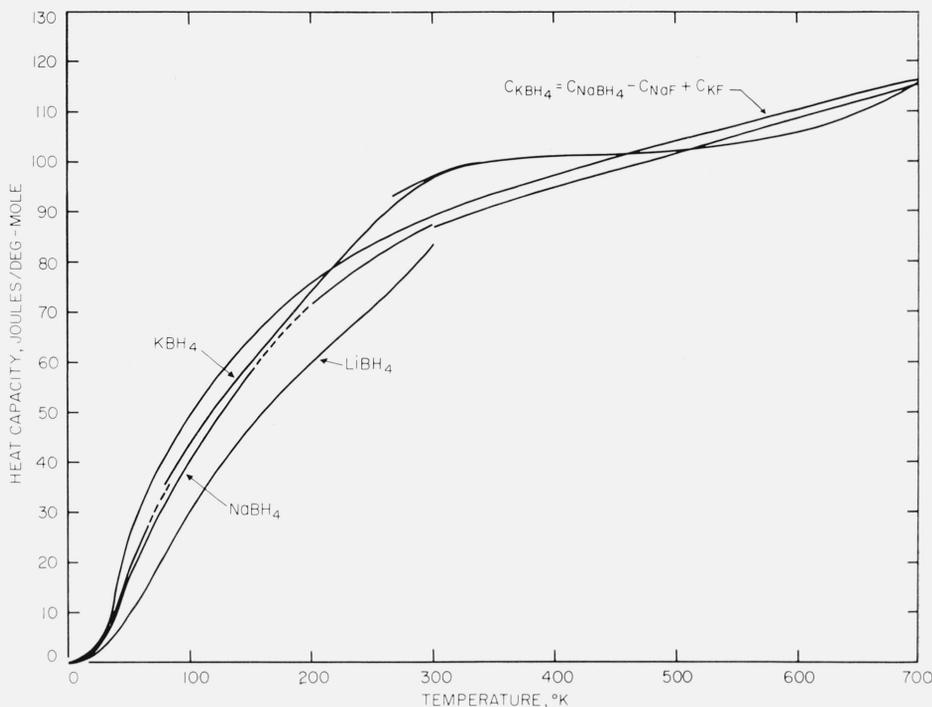


FIGURE 2. Comparison of heat capacities.

KBH₄, 15° to 375°K, this work.
 KBH₄, 273° to 673°K, Douglas and Harman [13].
 NaBH₄, 15° to 300°K, Johnston and Hallett [1].
 NaBH₄, 273° to 673°K, Douglas and Harman [13].
 $C_{KBH_4} = C_{NaBH_4} - C_{NaF} + C_{KF}$, KBH₄ (calculated),
 LiBH₄, 15° to 300°K, Hallett and Johnston [26].

TABLE 3. Molal enthalpy change of potassium borohydride between 65° and 80°K. The enthalpy and entropy of transition.

Gram formula weight = 53.94488 g, °K = t°C + 273.15°
 Transition temperature = 77.16 ± 0.02 °K

Temperature interval °K	Energy input J/mole	Heat capacity correction J/mole	ΔH 65° to 80°K J/mole
62.5354 to 82.0418	838.94	-138.39	700.55
70.1848 to 78.5521	499.81	+201.75	701.56
65.6175 to 81.7792	747.64	-47.20	700.44
71.4244 to 80.5829	532.82	+168.26	701.08
Mean			700.91
Standard deviation of the mean ^a			±0.26
Enthalpy change along normal heat capacity curve			475.94
Enthalpy of transition			224.97
Entropy of transition = 2.92 J/deg-mole (0.70 cal/deg-mole)			

^a Standard deviation of the mean as used above is defined as $[\sum d^2/n(n-1)]^{1/2}$; where d is the difference between a single observation and the mean, and n is the number of observations.

4.3. Derived Thermodynamic Properties

The values of the observed molal heat capacity were smoothed and combined with the results of the relative enthalpy measurements between 0 and 400 °C reported by Douglas and Harman [13] (see eq (3)) to calculate the thermodynamic functions from 0 to 700 °K. The smoothing method used with the

observed low-temperature values of heat capacity involved a combination of analytical and graphical procedures. Several overlapping empirical equations were fitted to the observed values of heat capacity over the range of measurements and the deviations from the empirical equations plotted. Smooth curves were drawn through the deviation points and the values of heat capacity at equally and closely spaced integral temperatures were obtained by combining the values from the empirical equations and the deviation curves. In the regions where the equations overlapped, the values that joined most smoothly were selected. The tabular values were finally checked for smoothness by examining the differences and wherever necessary they were smoothed further by numerical methods [22].

The smoothed low-temperature values of heat capacity were compared with those obtained from the heat-capacity equation (eq (3)) given by Douglas and Harman [13]. The values from the two sets of measurements were found to join best at about 370 °K (see fig. 2) and were smoothed together by a numerical method (a nine-point cubic smoothing procedure) [22]. The enthalpy change between 0 and 100 °C given in the final table of thermodynamic functions (table 5) is 9779 J/mole and the experimental values reported for this temperature interval by Douglas and Harman [13] are 9818 and 9790

J/mole for samples 1 and 2, respectively. The enthalpy increment based on the low-temperature measurements was calculated to be 9776 J/mole.

TABLE 4. Comparison of thermodynamic functions for potassium borohydride (KBH₄) with those reported by Douglas and Harman [13].

Gram formula weight = 53.94488 g, T deg K = t deg C + 273.15
1 defined calorie = 4.1840 joules

T	This work			Douglas and Harman ^a		
	C	S	(H _T -H ₀)/T	C	S	(H _T -H ₀)/T
^o K	cal/deg-mole	cal/deg-mole	cal/mole	cal/deg-mole	cal/deg-mole	cal/mole
298.15	22.958	25.404	13.204	23.08	25.48	13.244
400	24.125	32.385	15.896	24.13	32.46	15.925
500	24.402	37.794	17.566	24.41	37.87	17.590
600	25.339	42.311	18.769	25.34	42.39	18.789
700	27.531	46.362	19.847	27.54	46.44	19.765

^a Gram formula weight used by Douglas and Harman [13] was 53.952 g. Their values were not converted to the new gram molecular weight 53.94488 g. The new molecular weight will lower the values of Douglas and Harman by 0.013 percent, making the variations in the two sets of values smaller.

These values indicate that the low-temperature measurements are on the average in this range about 0.3 percent lower than the average of the two high-temperature measurements. Above about 370 °K, the thermodynamic functions given in table 5 are derived from eq (3) obtained by Douglas and Harman [13]. A few of the values from table 5 are given in table 4 for comparison with those reported by Douglas and Harman. The differences in the values arise primarily from the revised entropy and enthalpy at 298.15 °K given in the present paper. The earlier preliminary entropy and enthalpy values that were furnished Douglas and Harman [13] had not been corrected for the impurities.

The values of heat capacity below the lower limit of measurements (16 °K) were obtained by extrapolation using a Debye heat-capacity function fitted to the experimental values between 16 and 30 °K. The equation used was

$$C = 58.3 D\left(\frac{250}{T}\right) \text{ J/deg-mole.} \quad (4)$$

TABLE 5. Molal thermodynamic functions for potassium borohydride (KBH₄)

Gram formula wt = 53.94488 g, T deg K = t deg C + 273.15

T	C _p	(H _T -H ₀)	(H _T -H ₀)/T	(S _T -S ₀)	-(G _T -H ₀)	-(G _T -H ₀)/T
Solid phase						
deg K	deg ⁻¹	J	J deg ⁻¹	J deg ⁻¹	J	J deg ⁻¹
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	.036	.045	.009	.012	.015	.003
10.00	.290	.725	.072	.097	.242	.024
15.00	.978	3.670	.245	.326	1.223	.082
20.00	2.312	11.531	.577	.769	3.853	.193
25.00	4.327	27.928	1.117	1.493	9.388	.376
30.00	6.733	55.468	1.849	2.490	19.238	.641
35.00	9.356	95.617	2.732	3.723	34.680	.991
40.00	12.059	149.14	3.728	5.148	56.787	1.420
45.00	14.820	216.02	4.801	6.721	86.411	1.920
50.00	17.690	297.26	5.945	8.430	124.24	2.485
55.00	20.625	393.02	7.146	10.253	170.90	3.107
60.00	23.735	503.83	8.397	12.179	226.94	3.782
65.00	27.092	630.79	9.704	14.210	292.87	4.506
70.00	30.5*	774.89	11.070	16.344	369.22	5.25
75.00	33.3*	934.45	12.459	18.545	456.42	6.086
77.16	34.3*	1007.5	13.057	19.505	497.52	6.448
77.16	34.3*	1232.4	15.972	22.420	497.52	6.448
80.00	35.583	1331.7	16.647	23.684	562.99	7.037
85.00	37.544	1514.6	17.818	25.900	686.95	8.082
90.00	39.476	1707.1	18.968	28.101	821.96	9.133
95.00	41.384	1909.3	20.098	30.287	967.94	10.189
100.00	43.261	2120.9	21.209	32.457	1124.8	11.248
105.00	45.108	2341.8	22.303	34.613	1292.5	12.309
110.00	46.922	2571.9	23.381	36.753	1470.9	13.372
115.00	48.686	2811.0	24.443	38.878	1660.0	14.435
120.00	50.392	3058.7	25.489	40.986	1859.7	15.497
125.00	52.048	3314.8	26.519	43.077	2069.8	16.559
130.00	53.661	3579.1	27.532	45.150	2290.4	17.618
135.00	55.224	3851.3	28.528	47.205	2521.3	18.676
140.00	56.733	4131.3	29.509	49.240	2762.4	19.732
145.00	58.205	4418.6	30.473	51.257	3013.7	20.784

TABLE 5. Molal thermodynamic functions for potassium borohydride (KBH₄)—Continued

T	C_p	(H_T-H_0)	$(H_T-H_0)/T$	(S_T-S_0)	$-(G_T-H_0)$	$-(G_T-H_0)/T$
Solid phase						
<i>deg K</i>	<i>deg⁻¹</i>	<i>J</i>	<i>J deg⁻¹</i>	<i>J deg⁻¹</i>	<i>J</i>	<i>J deg⁻¹</i>
150.00	59.643	4713.2	31.422	53.255	3275.0	21.833
155.00	61.066	5015.0	32.355	55.234	3546.2	22.879
160.00	62.476	5323.9	33.274	57.195	3827.3	23.920
165.00	63.858	5639.7	34.180	59.138	4118.1	24.958
170.00	65.213	5962.4	35.073	61.065	4418.6	25.992
175.00	66.574	6291.9	35.954	62.975	4728.7	27.021
180.00	67.941	6628.2	36.823	64.869	5048.3	28.046
185.00	69.304	6971.3	37.683	66.750	5377.4	29.067
190.00	70.656	7321.2	38.533	68.616	5715.8	30.083
195.00	72.001	7677.8	39.373	70.468	6063.5	31.095
200.00	73.355	8041.2	40.206	72.308	6420.5	32.102
205.00	74.722	8411.4	41.031	74.137	6786.6	33.105
210.00	76.108	8788.5	41.850	75.954	7161.8	34.104
215.00	77.489	9172.5	42.663	77.761	7546.1	35.098
220.00	78.849	9563.3	43.470	79.558	7939.4	36.088
225.00	80.229	9961.0	44.271	81.345	8341.7	37.074
230.00	81.575	10366	45.068	83.123	8752.8	38.056
235.00	82.883	10777	45.858	84.892	9172.9	39.034
240.00	84.186	11194	46.643	86.650	9601.7	40.007
245.00	85.470	11619	47.423	88.400	10039	40.977
250.00	86.717	12049	48.196	90.139	10486	41.943
255.00	87.922	12486	48.963	91.868	10941	42.905
260.00	89.085	12928	49.724	93.587	11404	43.863
265.00	90.201	13376	50.477	95.294	11877	44.817
270.00	91.257	13830	51.222	96.990	12357	45.768
273.15	91.892	14119	51.688	98.052	12665	46.365
275.00	92.253	14289	51.960	98.674	12846	46.714
280.00	93.187	14752	52.687	100.34	13344	47.657
285.00	94.060	15221	53.406	102.00	13850	48.596
290.00	94.870	15693	54.114	103.64	14364	49.531
295.00	95.617	16169	54.811	105.27	14886	50.462
298.15	96.055	16471	55.244	106.29	15220	51.047
300.00	96.300	16649	55.497	106.89	15418	51.393
310.00	97.466	17618	56.832	110.07	16503	53.235
320.00	98.402	18598	58.117	113.18	17619	55.060
330.00	99.134	19585	59.350	116.22	18766	56.867
340.00	99.653	20580	60.528	119.18	19943	58.657
350.00	99.966	21578	61.651	122.08	21150	60.427
360.00	100.19	22579	62.718	124.90	22385	62.179
370.00	100.42	23582	63.734	127.65	23647	63.912
373.15	100.49	23898	64.044	128.50	24051	64.453
380.00	100.63	24587	64.702	130.33	24937	65.624
390.00	100.80	25594	65.626	132.94	26254	67.317
400.00	100.94	26603	66.507	135.50	27596	68.990
425.00	101.19	29130	68.540	141.62	31061	73.084
450.00	101.41	31662	70.360	147.41	34674	77.054
475.00	101.70	34201	72.002	152.90	38429	80.903
500.00	102.10	36748	73.496	158.13	42317	84.635
550.00	103.52	41885	76.154	167.92	50472	91.767
600.00	106.02	47118	78.530	177.03	59098	98.497
650.00	109.86	52509	80.784	185.66	68167	104.87
700.00	115.19	58129	83.041	193.98	77658	110.94

*Integration over the temperature interval 65 to 80 deg K is based upon the estimated base line heat capacity. While the distribution of energy in this temperature interval is less accurate, the value of the enthalpy at 80 deg accurately represents the experimentally observed increment over the temperature interval.

H_0° and S_0° are the reference states at absolute zero of temperature.

The thermodynamic functions were calculated from the values of heat capacity according to the following thermodynamic relations:

$$H_T - H_0^c = \int_0^T C dT + \Delta H_{tr} \quad (5)$$

$$S_T - S_0^c = \int_0^T C(dT/T) + \Delta H/T_{tr} \quad (6)$$

$$\begin{aligned} (G_T - H_0^c) &= - \int_0^T (S_T - S_0^c) dT - TS_0^c \\ &= (H_T - H_0^c) - T(S_T - S_0^c) - TS_0^c. \end{aligned} \quad (7)$$

The functions $(H_T - H_0^c)/T$ and $(G_T - H_0^c)/T$ were obtained by dividing the respective quantities given in eqs (5) and (7) by the corresponding temperatures. The Gibbs energy was calculated using the two equivalent relations given in eq (7) to check the internal consistency of the calculations. The equations were evaluated by step-wise numerical integration and subtubulated using four-point Lagrangian integration coefficients [23] on the IBM 7094 computer at the Bureau.

Between 65 and 80 °K where the solid-phase transition was observed, the thermodynamic functions were calculated on the basis of the "normal" heat-capacity curve shown as a broken line in figure 1. At 77.16 °K the heat and entropy of transition were added in accordance with eqs (5) and (6) and the evaluation continued to the higher temperatures.

4.4. Reliability of the Results

The uncertainty in the final smoothed values of heat capacity obtained from the results of the measurements was estimated to be ± 0.3 percent. At temperatures below about 50 °K the uncertainty increases because of the decrease in sensitivity of the thermometric method used. At the lowest temperature (16 °K) of the measurements, the uncertainty was estimated to be as much as ± 1 percent. A precision of 0.02 percent or better can generally be achieved, however, with the calorimetric system in which the measurements were made. With a stable substance of high chemical and phase purity, and considering possible systematic errors, the accuracy of 0.1 percent or better is expected, except at the lowest temperatures for reasons mentioned above. In the present investigations the uncertainty in the chemical composition of the sample contributed more to the uncertainty of the final values than the uncertainty in the measurements.

The thermodynamic functions derived from the heat capacity are as reliable as the heat capacity. The calculations were performed with an accuracy greater than the precision of the measurements. Some discrepancies may be present in the tabulated thermodynamic functions because of the rounding.

5. Discussion of the Results

The λ -type solid-phase transition (transition temperature = 189.9 °K, $\Delta S = 1.22$ e.u.), observed in NaBH_4 by Johnston and Hallett [1], was interpreted by Stockmayer and Stephenson [2] as an order-disorder transition involving two orientations of the tetrahedral BH_4^- ions. Stephenson et al. [10] similarly interpreted the transition found in KBH_4 at 76 ± 1 °K from cooling and warming curve investigations. The heat capacity investigations on KBH_4 presented in this paper show an entropy of transition of 0.70 e.u. at 77.16 °K, which is about one-half of the expected 1.38 e.u. ($R \ln 2$) for completely random arrangement of the BH_4^- tetrahedra between the two orientations. This suggests that the tetrahedra in KBH_4 may still remain essentially paired with local ordering just above the transition temperature. From the consideration of the larger lattice parameters of KBH_4 relative to those of NaBH_4 [5, 6], the interactions between the BH_4^- ions in KBH_4 would be expected to be weaker and the rearrangement less hindered. The low entropy increment for the transition in KBH_4 indicates, however, that the interactions between the BH_4^- ions are somewhat more complex and involve more than simple interpretations based on lattice parameters.

The heat capacity of KBH_4 shown in figure 2 suggests that another "transition" occurs from about 200 °K to as high as 450 °K. This transition is interpreted as the continuation of the order-disorder orientations of the tetrahedral BH_4^- ions. The x-ray diffraction investigations by Ford and Powell [6] show, however, that the crystal structure of KBH_4 is the same at 90 and 293 °K. The lower temperature limit of this broad transition is higher than the transition temperature (189.9 °K) found for NaBH_4 by Johnston and Hallett [1], which indicates further that the BH_4^- ions in KBH_4 interact more than in NaBH_4 .

The transition at the higher temperatures was expected to contain the remaining 0.7 e.u. The estimation of the entropy contribution of the transition, based on the subtraction from the observed heat capacities the contributions of $C_p - C_v$, lattice vibrations, and internal vibrations and torsional oscillations of the BH_4^- ion, was not satisfactory. For the $C_p - C_v$ and lattice vibration contributions, the heat capacity of KF [24] was taken. For the contributions from internal vibrations in BH_4^- , the frequency values given by Altshuller [25] for NaBH_4 were used. For the torsional oscillations the value 350 cm^{-1} estimated for BH_4^- in NaBH_4 by Stockmayer and Stephenson [2] was used. The sum of the various contributions was found to be considerably lower than the expected heat capacity. The heat capacity of KBH_4 is expected to be slightly above that of NaBH_4 (see figure 2). For example, at 300 °K the difference between the expected heat capacity and the sum of the heat capacity of KF and the contributions from the internal vibrations in BH_4^- is larger than the classical limit for an oscillator (three degrees of freedom). The results at 400 °K are the same. This

indicates that the frequencies used for the internal vibrations in BH_4^- are too high or that the observed resultant heat capacities are considerably more complex than the simple summation of the contributions given earlier.

The heat capacities obtained from the following relation were found to be fairly satisfactory:

$$C_{\text{KBH}_4} = C_{\text{NaBH}_4} - C_{\text{NaF}} + C_{\text{KF}}, \quad (8)$$

where the symbol C represents the heat capacity corresponding to the substance indicated by the subscript [1, 26, 24]. The results are plotted in figure 2 (solid line). The entropy difference in the interval 200 to 500 °K between the observed values for KBH_4 and that calculated according to eq (8) is 1.11 e.u. This value is somewhat larger than the expected value (0.7 e.u.). The calculations based on eq (8) probably yielded heat capacities that are too low. The two values are sufficiently close to suggest that the higher-temperature transition contains the remaining order-disorder transition.

For comparison, heat-capacity measurements should be interesting on the other alkali-metal (Rb and Cs) borohydrides, which have the face-centered cubic crystal structure similar to KBH_4 and NaBH_4 [5]. Stephenson et al. [10] observed transitions in RbBH_4 and CsBH_4 in cooling and warming curve investigations. Neither the entropy of these transitions nor the higher-temperature broad transitions have been investigated. Lithium borohydride, LiBH_4 , which is orthorhombic [11], does not exhibit any transition between 16 and 303 °K [27] similar to those found in NaBH_4 or KBH_4 . (See fig. 2.) A close examination of the LiBH_4 data at the upper limit of measurements [27] does, however, show a slight indication of an on-set of a possible transition. The indication may be just a scatter in experimental data. Further measurements on LiBH_4 above 300 °K would also be interesting.

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6. References

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