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Heat Content of Sodium Borohydride and of Potassium Borohydride from 0° to 400° C

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The heat content of sodium borohydride, $NaBH_4$, and of potassium borohydride, KBH_4, was measured, relative to that at 0° C, at 50-degree intervals from 0° to 400° C. The so-called "drop" method was used with a precision Bunsen ice calorimeter and a silver-core furnace. Preliminary tests showed that spontaneous decomposition of these compounds is very slow at temperatures up to 400° C. Measurements were made on two samples of each compound, those of sodium borohydride having been obtained from different sources. Smoothed values of the heat-content function, heat capacity, entropy, and the Gibbs free-energy function were derived from the data. These values were increased by 0.5 percent to correct for the presence of an estimated 1 percent of the corresponding *meta*borate in each sample. The heat capacity of sodium borohydride increases monotonically with temperature in the range investigated; that of potassium borohydride passes through a point of inflection, which suggests that there may be a broad second-order transition in the neighborhood of room temperature.

1. Introduction

There has been a wide interest for many years in the unusual properties and possible uses of compounds between boron and hydrogen, and a great many of them have been prepared and studied. More recently, chemical methods have been devised for preparing metallic borohydrides, which contain the monovalent group BH_4^-. The borohydrides of the alkali metals are much more stable than the known hydrides of boron, dissolving in water at room temperature with but slow decomposition, and resisting spontaneous decomposition in the dry state up to temperatures of several hundred degrees C. Since X-ray patterns indicate a crystal lattice of metallic and borohydride ions, it appears that the relative stability of these compounds can be attributed directly to the high coulomb energy characterizing such typical ionic salts.

In recent years a number of investigators have measured some of the fundamental thermodynamic properties of the borohydrides of the alkali metals.[1] The work reported in this paper contributes to this general program. The heat content of the borohydrides of sodium and potassium was measured from 0° C up to temperatures where decomposition begins, and from these values other important thermodynamic properties were derived.

2. Samples

The heat-content measurements were on two samples of $NaBH_4$ and two of KBH_4. Each sample was in the form of fine white crystals, and was used as received without further purification, except for preliminary heating and evacuation as described later. It appears that purification of these compounds, to a high degree (e. g., to a purity of 99.9 weight percent), is difficult with present techniques. This fact may be due to slight solvolysis of the salts when in solution, with subsequent decomposition of the free acid, for it has been reported that increasing the *p*H of the solution increases the stability of the salt.

One of the samples of $NaBH_4$, hereafter designated as No. 1, was obtained from Metal Hydrides Inc., Beverly, Mass., who reported it to have a purity in excess of 99 percent. This sample was received in a glass-stoppered bottle, and was so kept until used. The other sample, designated as No. 2, was obtained from another source. Its suppliers had recrystallized it twice from liquid ammonia. Their subsequent analyses indicated the following percentages of the theoretical: Potassium, 99.9 percent; boron, 99.9 percent; and hydrogen, 99.4 percent. (The hydrogen reported was that obtained by hydrolysis.) However, considering the limitations of reliability of the analytical methods used, they believed that the purity of this sample (No. 2) could not be more precisely stated than as "safely above 99 percent". The sample was received in a sealed glass ampule, which was not opened until very shortly before the sample was used.

Both "samples" of the KBH_4, distinguished subsequently as No. 1 and No. 2, were really specimens of the same sample, but specimens on which heat-content measurements were made 2 months apart. This "stock" sample was obtained from Metal Hydrides Inc., who had found it to contain 0.1 percent by weight of chlorine and 99.6 percent of the theoretical hydrogen (the latter figure resulting from gasometric analysis). On this basis they believed the sample to have a purity of approximately 99.5 percent. The sample was kept in a vacuum desiccator until very shortly before the heat-content measurements were begun.

Assuming that at some stage during their purification these borohydrides were nearly 100-percent pure, contamination by the atmosphere very likely occurred by conversion of some of the borohydride to borates. It appears that whatever borate is thus

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[1] References to such work are given later in this paper.

formed would maintain the 1:1 atomic ratio of alkali metal and boron characterizing the parent borohydride. Such a borate might be a *meta*borate or, before an opportunity for dehydration, more likely an *ortho*borate (such as $KH_2BO_3 \cdot H_2O$). All such borates other than the *meta*borate are known to dehydrate to form the corresponding *meta*borate at the higher temperatures of the present work, and at lower temperatures they would be expected to possess heat capacities which are approximately additive combinations of the heat capacities of the constituent *meta*borate and chemically bound water. For these reasons it seems simpler to interpret the analyses of the samples as though the somewhat impure sample consisted wholly of borohydride, *meta*borate, and water. Letting M represent either Na or K, decomposition by water or oxygen could then be formulated by the following reactions:

$$MBH_4+2H_2O=MBO_2+4H_2, \quad (1)$$

$$MBH_4+2O_2=MBO_2+2H_2O. \quad (2)$$

(In time, the water formed according to eq (2) might react with additional borohydride according to eq (1).)

Several months after the completion of the thermal measurements reported in this paper, specimens of the unused portions of the stock samples were analyzed in the Chemistry Division of the Bureau. The analytical procedures were as follows.

Hydrogen Evolved. A sample of 0.5 to 1.0 g was transferred to a gas-evolution flask and dissolved in 50 ml of water. Twenty milliliters of 1:1 hydrochloric acid was then slowly added dropwise. The hydrogen gas generated was swept by nitrogen through a condenser and an absorber containing Ascarite (sodium hydroxide on asbestos) and anhydrous magnesium perchlorate. The dry hydrogen was then burned in a combustion tube packed with copper oxide heated to 700° C, the water formed being absorbed in a weighed absorption tube containing anhydrone. Each such determination required about 4 hr. The accuracy of the method was tested by using standard melting-point aluminum (NBS standard sample 44d). The hydrogen evolved in four such analyses of aluminum corresponded to 99.80, 99.62, 99.69, and 99.66 percent of aluminum respectively. Spectrographic analysis had shown the aluminum to contain 0.1 percent of impurities, but the content of oxygen, carbon, and nitrogen was not known.

Boron. Either an aliquot portion of the solution of borohydride used in the preceding procedure or a new sample of 0.25 g was used. After the solution had been adjusted in pH to the methyl-red endpoint, it was treated with mannitol and then titrated with $0.1N$ NaOH to the phenolphthalein endpoint. The titration was continued until further addition of mannitol no longer destroyed the pink color.

Alkali Metal, Volumetrically. A 0.25-g sample was dissolved in water, treated with a few drops of methyl-red indicator, and titrated with $0.1N$ HCl.

Alkali Metal, Gravimetrically. After decomposition of the borohydride with strong acid, the solution was evaporated with sulfuric acid. After evaporation of the boric acid and ignition of the residue, the alkali metal was weighed as sulfate.

The foregoing procedures were tested on potassium borohydride using an extra sample on which no heat-content measurements were made. The results are given in table 1. Each value in the third column was calculated with the assumption that the particular element determined was present only in the form of KBH_4. Of these values, the last three, resulting from the analyses for boron and potassium, agree closely among themselves but are all appreciably higher than the first value, which resulted from the amount of hydrogen evolved. Averaging the last three values and assuming that the sample contained only KBH_4, KBO_2, and H_2O, it is calculated that the weight percentages of these components were respectively 98.8, 0.8, and 0.4.

TABLE 1. *Test of analytical methods on an extra sample of potassium borohydride*

Element determined	No. of determinations	Mean result as weight % KBH_4	Average deviation from mean
Hydrogen (evolution)	3	98.79	0.10
Boron (by titration)	6	99.28	.07
Potassium (by titration)	3	99.36	.09
Potassium (gravimetrically)	4	99.30	.09

The methods for determining hydrogen evolved and boron present were extended to unused portions of the samples on which heat-content measurements had been made, duplicate determinations being made in each case. The mean results, calculated as percentages of borohydride, *meta*borate, and water, are given in table 2. The KBH_4 stock sample analyzed was the source of both heat-content samples No. 1 and No. 2 of this substance, and it will be noted that three sets of results are given for this material. The first set was obtained on a specimen protected from the atmosphere, and the second and third sets were obtained on two specimens which had deliberately been exposed to the laboratory atmosphere for 5 and 20 days respectively, just preceding analysis.

It will immediately be evident from table 2 that these analyses, which were carried out after the heat-content measurements, indicate decidedly less borohydride content than the analyses that preceded the

TABLE 2. *Analyses of borohydride samples after the heat-content measurements*

Stock samples	Borohydride	Metaborate	Water
	Weight %	*Weight %*	*Weight %*
$NaBH_4$, sample No. 1	92.6	5.3	2.1
$NaBH_4$, sample No. 2	98.60	1.18	0.22
KBH_4, unexposed	98.36	1.58	.06
KBH_4, exposed 5 days	98.02	2.17	−.19
KBH_4, exposed 20 days	97.78	----------	----------

heat-content measurements and which were referred to at the beginning of this section. The slow decomposition of potassium borohydride in contact with moist air also is evident. An attempt is made later (section 4) to estimate the chemical composition of the samples at the times when the heat-content measurements were made, so that appropriate corrections to the observed heat-content values may be applied.

3. Preliminary Tests of Chemical Stability at High Temperatures

It was desirable to extend the heat-content measurements to temperatures as high as possible without incurring sufficient chemical decomposition to invalidate the thermal values. In such cases it is obviously important to know not only the initial purity of the samples but also any significant change in the degree of purity resulting from decomposition during the measurements through exposure of the samples to high temperatures.

Some qualitative information about the borohydrides of sodium and potassium is available in the literature. It has been reported [1],[2] for example, that when potassium borohydride of 98.8-percent purity was heated in a fused silica tube in vacuum, decomposition commenced at about 500° C with the evolution of hydrogen and the simultaneous distillation of potassium. Others have reported that sodium borohydride decomposed only very slowly below its melting point (about 500° C), with formation of free boron and free sodium, but that at the melting point the liquid evolved hydrogen rapidly.

The present authors tested small specimens (each weighing approximately 1 g) of their samples of these two compounds in open containers in a furnace constantly being swept out with pure helium, controlling temperature and time of exposure and observing changes in weight and appearance after each test. Sometimes there were small gains in weight, amounting to a few hundredths of 1 percent, which naturally would mask any small losses in weight that might have occurred simultaneously. The gains in weight that occurred during heating at the higher temperatures were probably due to absorption of traces of oxygen or water vapor from the furnace atmosphere. Sometimes a loss in weight that occurred only on heating to a temperature of several hundred degrees C was followed by a comparable gain in weight (up to 0.1%) during standing overnight in a desiccator. This may be explained if owing to hydrolysis the dried specimens actually contained small amounts of the corresponding metal hydroxides, which are hygroscopic.

The weight changes mentioned above will next be described quantitatively in the case of first, sodium borohydride, then potassium borohydride. Immediately following the discussion of the behavior of each substance in the tests of a small specimen, will be given a description of the preliminary conditioning of the heat-content specimens of that substance, with the weight changes then observed.

The test specimen of sodium borohydride, sample No. 1, lost 0.5 percent of its weight in 35 min at 350° C; in a subsequent 35 min at 400° C the same specimen showed no further significant change in weight, but became somewhat gray. In view of this behavior, the specimens whose heat contents were to be measured were first subjected to preliminary heating to establish approximately constant weight. Sample No. 1 lost 0.1 percent in weight during several hours of drying in vacuum at 80° C, no more during several hours while being similarly treated at 130° C, and an additional 0.2 percent during 30 min of drying at 200° and 50 min at 350° C. Sample No. 2, when first heated for 30 min at 300° C, lost 0.3 percent in weight, but a repetition of this heating produced no further sensible weight change.

The preliminary tests on a small specimen of the stock sample of potassium borohydride, with intermediate cooling and weighing, showed the following consecutive results: The only sensible weight change was a 0.2-percent loss during the initial heating, which was for 40 min at 300° C; there was still no change in appearance of the specimen after 35 min at 350° C; after 50 min at 400° C, some sintering was noted; then 50 min at 450° C led to a dirty-gray appearance; and a subsequent heating for 10 min at 500° C produced somewhat further darkening. The only preliminary treatment of the specimens whose heat contents were to be measured was the heating of each in vacuum at 85° C for several hours, with a weight loss of less than 0.05 percent. During the subsequent heat-content measurements, each specimen gradually underwent further losses in weight totaling about 0.1 percent.

It may be pointed out that these specimens of the two borohydrides initially underwent appreciable weight losses, but no comparable losses in subsequent heatings even at higher temperatures. Barring conceivable catalytic behavior of volatile contaminants initially removed, it would thus seem that the initial loss was not through any sensible, *spontaneous* decomposition of the nominal compound, or else comparable or even more rapid weight losses would have continued to occur. The losses found are assumed to have occurred through the removal of water. Whether this loss of water was more likely by simple evaporation or by chemical reaction with borohydride is discussed in section 4.

4. Correction for Impurity

The immediate aim of the present work is to obtain the best values of the relative heat content of the pure borohydrides of sodium and potassium over the temperature range covered by the thermal measurements. As the precision of these measurements was several times the errors that would be caused by neglecting the presence of impurities in the samples measured, these errors will be estimated and corrected for.

It is convenient to calculate first, the changes in heat content per unit mass of sample as given by the

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[2] Figures in brackets indicate the literature references at the end of this paper.

thermal data, and then to estimate the corrections corresponding to replacement of the impurities by an equal mass of the nominal substance. This correction for each impurity is obviously proportional to the weight percentage of the impurity and, approximately, to the difference between the average specific heat (heat capacity per unit mass), of the impurity and that of the nominal substance. The results of the chemical analyses given in section 2, and the interpretation of the mass changes summarized in section 3, necessitate some arbitrariness in deducing the compositions of the samples at the times when their heat contents were measured. Fortunately, however, fairly adequate values are available for the specific heats of the minor components (assumed to be water and $NaBO_2$ or KBO_2, as discussed in section 2).

The specific heats of the crystalline *meta*borates were calculated from equations given by Kelley [2]. These equations,[3] giving the heat capacity C_p in cal mole^{-1} deg K^{-1} at T°K, are:

$$NaBO_2{:}C_p=12.9+0.0122\,T\,(289°\text{–}1239°\text{K}), \quad (3)$$

$$KBO_2{:}C_p=12.6+0.0126\,T\,(288°\text{–}1220°\text{K}). \quad (4)$$

Also using the results on the borohydride samples reported in this paper, it can readily be shown that the heat content of the sample would be increased by very nearly 0.5 percent for each 1 percent of *meta*borate, in the sample, that is replaced by the same mass of the corresponding borohydride. This is true for any temperature in the present range 0° to 400° C, and in the case of either the sodium or the potassium compound.

A value for the effective specific heat of chemically-bound water near room temperature was obtained from the calculated losses in heat capacity when a number of salts are dehydrated [2], the mean value found being 10 cal mole^{-1} deg C^{-1}.[4] This value corresponds to a specific heat for such water not far from that of either sodium borohydride or potassium borohydride. Only the potassium compound contained an appreciable amount of water during any of the heat-content measurements, and the amounts present are believed to have been so small (not more than 0.1%) as to make the corrections in heat content for water negligible.

As described in section 3, the samples on which heat-content measurements were made were first heated to dry them. Each of the samples of sodium borohydride thereby decreased in weight by 0.3 percent, and the samples of potassium borohydride by less than 0.05 percent (but by an additional 0.1% when they reached about 200° C during the heat-content measurements). If these losses in weight represent escape of water only, the effects on the heat content of the drying are small and can be easily allowed for. It is conceivable, however, that heating caused the reaction of eq (1) to occur and that the mass loss was due largely to escape of hydrogen, in which case the proper corrections to the heat-content values would be many times as great. However, the second alternative explanation, while it cannot be proved to be entirely false, does not fit the observed facts. It would require that the sample contain, before being heated, about five times as much water as the decrease in mass on heating; also, the large amount of borate formed would lower the specific heat of the sample by 1 percent or more. Excepting the final analyses of sodium borohydride sample No. 1, discussed below, the water contents, roughly deduced from the chemical analyses, approximate these mass losses on heating. Furthermore, as the data in the next section will show, a repetition of heat-content measurements on potassium borohydride sample No. 1 was carried out at 150° and 200° C; these later values were lower than before the loss of 0.1 percent in weight (at 200° to 300° C) by 0.05 to 0.2 percent, amounts which correspond approximately to a simple escape of water vapor.

The analyses of the samples after the heat-content measurements all show less borohydride than the analyses before (section 2), and interpolations may be attempted to give estimates of the compositions of the samples when their heat contents were measured. In this way it may be reasonably assumed that sodium borohydride sample No. 2 and each of the samples of potassium borohydride should be considered as consisting of 99 weight percent of the nominal substance and 1 percent of the corresponding *meta*borate.

A similar interpolation of the analyses on sodium borohydride sample No. 1 would indicate several times as much water as the total weight loss on heating and enough $NaBO_2$ to give heat-content values some 2-percent lower than those of sample No. 2. Actually, sample No. 2 gave the lower heat-content values, but by only 0.25 percent at 100° and 0.15 percent at 200° and 300° C (section 5). It is believed that inferior preservation of sample No. 1 is responsible for the finding of so much impurity in its final analysis, and that it too must have been about 99-percent pure when its heat content was measured.

In accordance with the foregoing conclusions, each heat content of a borohydride sample plus container observed in this work was increased by an amount equal to 0.5 percent of the contribution due to the sample. Any decrease of mass during a measurement was assumed to represent a loss of water, and was treated as though the mass of the specimen had decreased by that amount. But when a mass *increase* occurred, it was assumed to have occurred entirely through conversion, by a trace of water vapor or oxygen gas, of borohydride into *meta*borate by the reaction of eq (1) or eq (2), or both. An additional correction to the measured heat was applied accordingly.

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[3] Although these equations are based on old data, at least the equation for $NaBO_2$ gives values in the range 0° to 400° C in approximate agreement with the values additively predicted from more accurate results on other sodium oxysalts and other borates.

[4] Insufficient data were found to justify assigning values at higher temperatures, where the amounts of water left in the borohydride samples were usually negligible anyhow.

5. Measurement of Heat Content

The calorimetric apparatus and "drop" method used have been described in detail in numerous reports and papers from the Bureau, most recently in a paper on the thermal properties of aluminum oxide [3]. Briefly, the method is as follows. The specimen in a suitable container is suspended in a furnace for a sufficient length of time to ensure its reaching the known furnace temperature. It is then dropped into a Bunsen ice calorimeter, which, by absorbing a volume of mercury equivalent to the change in volume due to melting of ice, measures the heat evolved by the sample and container in cooling to 0° C. A similar measurement on the empty container at the same furnace temperature provides correction for the contribution of the container and for the heat lost during the fall into the calorimeter, and enables a computation of the net change in heat content of the specimen alone. Repetition at a sufficient number of furnace temperatures establishes the heat content as a function of temperature.

The temperature of the furnace, adjusted to some desired even value, was measured by an accurately calibrated strain-free platinum-resistance thermometer and was kept constant to ±0.01 deg C. A silver pipe, 10 in. long and of 1/2-in. wall thickness, together with end silver "guards," reduced the temperature gradients to negligible amounts, thereby permitting the sample to assume the same temperature as that measured. That the time of the sample in the furnace was adequate was established by determining the relaxation time in a special drop run after a time in the furnace deliberately too short to give thermal equilibrium. The adequacy of the times used was tested also by varying the times in the furnace in each set of duplicate measurements so as to detect any systematic time-dependence, which did not appear. The furnace core, calorimeter, and specimen container were filled with pure helium, which flowed through during the measurements to minimize not only the times required for reaching thermal equilibrium but also the oxidation of specimen and container. A cylindrical vessel constructed of the alloy 80 Ni–20 Cr, closed approximately but not gas-tight by a screw lid of nickel, served to contain the specimen.[5] The inside surface of the container had been thoroughly cleaned of oxide to prevent oxidation of the borohydride specimens. The container was evacuated and filled with helium just before each introduction into the furnace, but with air after each run in order to place the weight on a known and reproducible buoyancy basis.[6]

The corrected individual measurements of the heat content of the empty container are recorded in absolute joules in table 3. In terms of absolute amount of heat, the agreement of the duplicate results at each furnace temperature is typical of that usually obtainable with this apparatus in the absence of a material undergoing chemical or physical change with time. According to table 3, the deviation from the mean of two duplicates averaged 0.4 j, with a maximum of 1.0 j. It may be noted that these variations seem to be independent of furnace temperature.

TABLE 3. *Individual heat-content measurements on the empty container*

Furnace temperature	Measured heat	Furnace temperature	Measured heat	Furnace temperature	Measured heat
° C	*abs j*	*° C*	*abs j*	*° C*	*abs j*
50	252.0	250	1,331.3	450	2,491.5
	253.6		1,330.5		2,489.5
100	514.3	300	1,614.0	500	2,789.4
	513.8		1,614.3		2,789.0
150	780.7	350	1,902.2		
	780.7		1,902.4		
200	1,053.4	400	2,192.6		
	1,054.5		2,193.4		

TABLE 4. *Individual heat-content measurements on sodium borohydride+container*

Furnace temperature, t	Time in furnace	Mass in excess of original	Corrected measured heat, sample +container	Relative heat content of $NaBH_4$, $H_t-H_{0°C}$		
				Individual run	Mean observed for set	Observed minus calculated, eq (5)
Sample No. 1 (2.5715 g)[a]						
°C	*min*	*mg*	*abs j*	*abs j g⁻¹*	*abs j g⁻¹*	*abs j g⁻¹*
350	35	−0.8	4,229.2	904.9	904.4	−0.4
	45	−.7	4,226.5	903.8		
50	40	+.5	546.2	114.1	113.9	−.3
	35	+.6	545.1	113.7		
100	30	+.7	1,115.1	233.7	233.8	.0
	40	+.9	1,115.8	234.0		
150	45	+1.3	1,704.7	359.3	359.4	+.8
	30	+1.4	1,705.0	359.5		
200	30	+1.8	2,311.6	489.0	488.7	+.4
	40	+2.0	2,309.6	488.3		
250	30	+3.0	2,933.9	623.4	623.2	+.6
	40	+3.5	2,933.1	623.1		
300	30	+3.7	3,573.2	761.8	761.6	+.1
	40	+4.0	3,572.0	761.4		
400	30	+6.1	4,903.9	1,054.2	1,053.0	+.5
	40	+7.5	4,896.1	1,051.2		
	30	+12.0	4,902.5	1,053.6		
Sample No. 2 (3.4104 g)[b]						
300	30	+0.4	4,207.6	760.4	760.4	−1.0
	40	+.8	4,207.6	760.4		
100	30	+.8	1,309.5	233.2	233.3	−0.6
	40	+1.0	1,309.8	233.3		
200	30	+1.3	2,718.1	488.0	488.0	−.2
	40	+1.6	2,718.5	488.1		

[a] Sample No. 1 was obtained from Metal Hydrides, Inc.
[b] Sample No. 2 was obtained from an independent source.

The results of the individual measurements on container with sample are given, in chronological order for each of the four samples, in table 4 for sodium borohydride and in table 5 for potassium borohydride. The third column of each table indicates the change in the mass of specimen plus container as compared with the mass before the heat-content measurements were begun. These changes were due almost entirely to changes in the mass of the specimen itself, as discussed in section 4. The values in the

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[5] There was no reason other than convenience for choosing this particular container; preliminary tests had shown that it was not attacked by the specimens.

[6] All weights were corrected to vacuum.

TABLE 5. *Individual heat-content measurements on potassium borohydride+container*

Furnace temperature, t	Time in furnace	Mass in excess of original	Corrected measured heat, sample +container	Relative heat content of KBH_4, $H_t-H_{0°C}$		
				Individual run	Mean observed for set	Observed minus calculated, eq (6)
Sample No. 1 (3.4892 g) [a]						
°C	*min*	*mg*	*abs j*	*abs j g⁻¹*	*abs j g⁻¹*	*abs j g⁻¹*
50	35	+0.1	564.3	89.3	89.1	−0.2
	35	+.1	563.0	88.9		
100	30	.0	1,149.4	182.1	182.0	+.2
	40	−.1	1,148.6	181.9		
150	30	−.1	1,743.3	275.9	275.8	+.6
	40	−.6	1,742.9	275.8		
200	30	−1.6	2,342.0	369.1	369.0	−.2
	40	−2.4	2,340.8	368.8		
250	30	−2.7	2,948.9	463.7	463.8	.0
	35	−2.8	2,949.7	463.9		
300	30	−1.3	3,577.4	(562.6) [b]	559.9	+.2
	40	+0.3	3,568.4	560.1		
	35	+.1	3,567.0	559.7		
150	30	+.1	1,741.7	275.4	275.3	.0
	40	+.4	1,740.5	275.1		
200	30	+.7	2,340.7	368.8	368.8	−.4
	40	+.7	2,340.5	368.7		
350	30	+.5	4,198.5	658.1	658.0	+.1
	40	+.1	4,197.9	657.9		
400	30	+.2	4,845.1	760.1	760.0	+.3
	35	.0	4,844.4	759.9		
Sample No. 2 (3.3794 g) [a]						
100	40	+0.2	1,127.5	181.5	181.5	−0.2
	30	.0	1,127.3	181.4		
400	40	−4.2	4,759.4	759.4	759.3	−.4
	45	−3.7	4,758.4	759.1		
100	30	−2.8	1,127.4	181.5	181.4	−.3
	40	−2.2	1,127.0	181.4		

[a] Samples 1 and 2 were actually specimens of the same sample, obtained from Metal Hydrides, Inc.
[b] Discarded because of poor precision.

fourth column have been corrected to the basis of the fixed mass of pure compound given in the heading. Each value in the fifth column was obtained by subtracting from the corresponding "gross" value in the fourth column the mean value for the empty container (table 3) and then dividing by the mass of sample. The "calculated" values of heat content referred to in the last column of tables 4 and 5 are the final smoothed values derived as described in section 6.

For some temperatures, two mean values of net heat content are listed in the sixth column of table 5. If both these values were exactly correct, they would naturally be the same. Their small disagreement was discussed in section 4. Potassium borohydride sample No. 2, though really a specimen of the same stock sample as sample No. 1 but measured 2 months later, gave mean values of heat content lower than those of sample No. 1 by 0.3 percent at 100° and 0.1 percent at 400° C. The consistent decrease with time of values for potassium borohydride indicates that, to at least the extent of these rather small discrepancies, the corrections for changing degree of purity (incorporated in the values of table 5) are not completely adequate.

6. Thermodynamic Functions, 298.15° to 700° K

The observed values of heat content for each compound were smoothed by using them to derive the coefficients of an empirical equation giving the relative heat content as a function of temperature. For each substance equal weight was given to the average of the mean values for each furnace temperature given in the sixth column of table 4 or 5.[7] For each substance, a form of equation was so chosen that the deviations between calculated and mean observed values (shown in the last column of table 4 or 5) are comparable in magnitude to the differences between the individual values from duplicate runs at the same temperature.[8] With the heat content at t° C in excess of that at 0° C expressed in absolute joules per gram, the equations obtained for the crystalline salts from 0° to 400° C are as follows.

$NaBH_4$:

$$H_t-H_{0°C}=2.4384t+8.083(10^{-4})t^2 -133.0\log_{10}[(t+273.15)/273.15]. \qquad (5)$$

KBH_4:

$$H_t-H_{0°C}=4.0898t-2.9030(10^{-3})t^2 +2.641(10^{-6})t^3-1{,}482.7\log_{10}[(t+273.15)/273.15]. \qquad (6)$$

Equations (5) and (6) were then converted to the form most commonly used in chemical thermodynamics by expressing the heat content relative to that at 0° K, in calories per mole, with the temperature in deg K.[9] From the resulting equations the common thermodynamic functions (at the standard thermodynamic pressure of 1 atm) were derived using the following relations.

$$(H^\circ-H_0^\circ)/T=(H^\circ+H_{298.15}^\circ)/T+(\mathrm{H}_{298.15}^\circ-\mathrm{H}_0^\circ)/T, \qquad (7)$$

$$C_p^\circ=d(H^\circ-H_0^\circ)/dT, \qquad (8)$$

$$S^\circ=S_{298.15}^\circ+\int_{298.15}^{T}(C_p^\circ/T)dT, \qquad (9)$$

$$-(F^\circ-H_0^\circ)/T=S^\circ-(H^\circ-H_0^\circ)/T, \qquad (10)$$

where C_p is heat capacity at constant pressure, S is entropy, F is Gibbs free energy, and the subscript "0" refers to 0° K. Equation (10) permits the cal-

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[7] Except that the two mean values given in table 5 for sample No. 2 at 100° C were each given half weight.

[8] The logarithmic terms and those in t and t^2 were introduced because they have been found to account closely for the relative heat content at these temperatures of a number of crystalline solids devoid of apparent transitions [3]. In the case of potassium borohydride, an equation containing also a term in t^4 was first derived. However, the resulting equation gave values almost identical with those of eq (6).

[9] Taking one defined calorie=4.1840 abs j, 0° C=273.15° K, and the molecular weights of $NaBH_4$ and KBH_4 as 37.843 and 53.952, respectively [4].

culation of the free energy of formation of the compound at various temperatures when its heat of formation and its absolute entropy at some one temperature are both known, provided that the corresponding thermodynamic functions of the free elements also have been evaluated. The heat of formation of sodium borohydride has been measured [5], but no corresponding value for the potassium compound was found in the literature.

Values for the constants in eq (7) and (9) were selected from the work of other investigators. Although the low-temperature heat capacity of sodium borohydride had been measured earlier [6], the work of Johnston and Hallett [7] appears to be more comprehensive and more accurate, leading to the values of $(H^\circ_{298\cdot15}-H^\circ_0)$ and $S^\circ_{298\cdot15}$ adopted here, 3,889.5 and 24.26 respectively.[10] In the case of potassium borohydride, the values adopted for the same constants, 3,948.8 and 25.48 respectively, were obtained in preliminary measurements at the Bureau [8].

The thermodynamic functions derived in the foregoing manner are as follows (in cal mole^{-1} deg K^{-1} at T°K and for the temperature range 298° to 700°K).[11]

$NaBH_4$:

$$(H^\circ-H^\circ_0)/T=18.0607+7.3108(10^{-3})T-1{,}202.94(1/T)\log_{10}T+831.4/T, \qquad (11)$$

$$C^\circ_p=18.061+0.014622T-522/\mathrm{T}, \qquad (12)$$

$$S^\circ=41.586\log_{10}T+0.014622T+522/T-84.754, \qquad (13)$$

$$-(F^\circ-H^\circ_0)/T=41.586\log_{10}T+1{,}202.9(1/T)\log_{10}T+7.311(10^{-3})T-309/\mathrm{T}-102.815. \qquad (14)$$

KBH_4:

$$(H^\circ-H^\circ_0)/T=80.8100-0.0653403T+3.4055(10^{-5})T^2-19{,}119.18(1/T)\log_{10}T+32{,}070.2/\mathrm{T}, \qquad (15)$$

$$C^\circ_p=80.810-0.130681T+1.0217(10^{-4})T^2-8{,}303/T, \qquad (16)$$

$$S^\circ=186.072\log_{10}T-0.130681T+5.108(10^{-5})T^2+8{,}303/T-428.371, \qquad (17)$$

$$-(F^\circ-H^\circ_0)/T=186.072\log_{10}T+19{,}119.2(1/T)\log_{10}T-0.065340T+1.703(10^{-5})T^2-23{,}767/T-509.181. \qquad (18)$$

Values of the thermodynamic functions calculated for even temperatures from eq (11) to (18) are given in tables 6 and 7.

TABLE 6. *Thermodynamic functions of sodium borohydride* [a]

Temperature	$\frac{H^\circ-H^\circ_0}{T}$	C°_p	S°	$-\left(\frac{F^\circ-H^\circ_0}{T}\right)$
°K	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*
298.15	13.045[b]	20.67	24.26[b]	11.21
300	13.093	20.71	24.39	11.29
320	13.581	21.11	25.74	12.15
340	14.035	21.50	27.03	12.99
360	14.460	21.87	28.27	13.81
380	14.860	22.24	29.46	14.60
400	15.238	22.60	30.61	15.37
420	15.597	22.96	31.72	16.12
440	15.940	23.31	32.80	16.86
460	16.268	23.65	33.84	17.57
480	16.582	23.99	34.85	18.27
500	16.885	24.33	35.84	18.95
520	17.178	24.66	36.80	19.62
540	17.461	24.99	37.74	20.28
560	17.736	25.32	38.65	20.92
580	18.003	25.64	39.55	21.54
600	18.263	25.96	40.42	22.16
620	18.516	26.28	41.28	22.76
640	18.764	26.60	42.12	23.35
660	19.007	26.92	42.94	23.93
680	19.244	27.24	43.75	24.51
700	19.477	27.55	44.54	25.07

[a] Molecular weight=37.843.
[b] Taken from reference [7].

TABLE 7. *Thermodynamic functions of potassium borohydride* [a]

Temperature	$\frac{H^\circ-H^\circ_0}{T}$	C°_p	S°	$-\left(\frac{F^\circ-H^\circ_0}{T}\right)$
°K	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*	*cal deg^{-1} mole^{-1}*
298.15	13.244[b]	23.08	25.48[b]	12.23
300	13.305	23.12	25.62	12.32
320	13.931	23.51	27.13	13.20
340	14.503	23.77	28.56	14.06
360	15.023	23.94	29.92	14.90
380	15.495	24.05	31.22	15.73
400	15.925	24.13	32.46	16.53
420	16.317	24.18	33.64	17.32
440	16.675	24.22	34.76	18.09
460	17.004	24.27	35.84	18.84
480	17.308	24.33	36.87	19.57
500	17.590	24.41	37.87	20.28
520	17.854	24.52	38.83	20.97
540	18.103	24.66	39.75	21.65
560	18.340	24.84	40.66	22.32
580	18.568	25.07	41.53	22.96
600	18.789	25.34	42.39	23.60
620	19.006	25.67	43.22	24.22
640	19.220	26.05	44.04	24.82
660	19.433	26.49	44.85	25.42
680	19.648	26.98	45.65	26.00
700	19.865	27.54	46.44	26.57

[a] Molecular weight=53.952.
[b] Taken from reference [8].

7. Discussion of Results

Although the thermal measurements reported in this paper are of relative heat content, it is more informative to examine the resulting values of heat capacity. These are shown for the two compounds in figure 1. The curves represent the smooth values calculated from eq (12) and (16). The points may be considered the unsmoothed values, as each one represents the difference between the mean values of heat content for two adjacent furnace temperatures as given in the sixth column of table 4 or 5.[12]

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[10] These values are based on a molecular weight of 37.843.

[11] Though the heat content was actually measured relative to 273°K, its temperature derivative has increased uncertainty near the end of the range of measurement and it therefore seems better to limit the derived thermodynamic functions to temperatures of 298°K and above.

[12] The points so computed were corrected for the curvature of the smooth curves, but the largest such correction amounted to only 0.2 percent of the heat capacity.

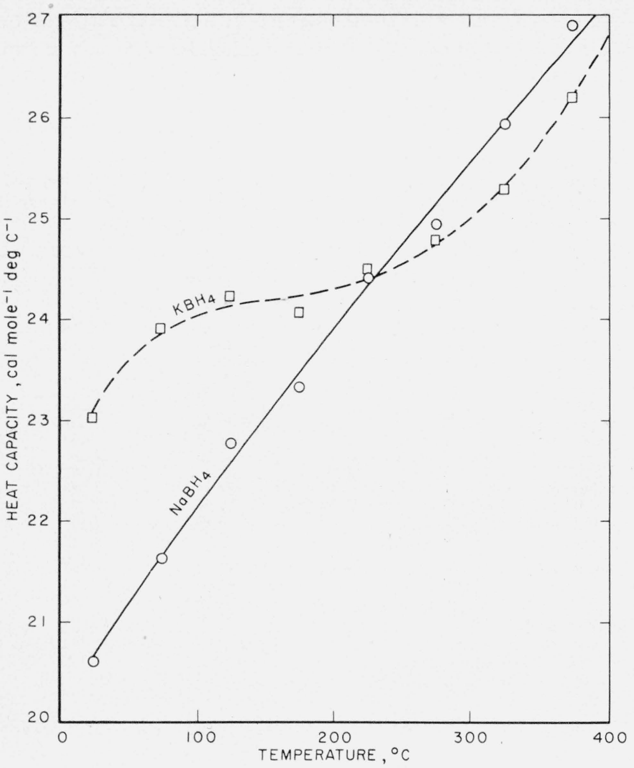

FIGURE 1. *Heat capacity of sodium borohydride and potassium borohydride, as determined by the drop method.*

○, $NaBH_4$, mean observed; □, KBH_4, mean observed;—, $NaBH_4$, smoothed; — —, KBH_4, smoothed.

It will be noted that in the temperature range investigated, the heat capacity of sodium borohydride increases with temperature in the usual manner observed for many crystalline solids. On the other hand, the heat-capacity-temperature curve of potassium borohydride shows a distinct point of inflection, which suggests the existence of a broad second-order transition of some sort in the neighborhood of room temperature.

The authors' smoothed values of heat capacity may be compared with the results of other investigators. The present measurements on sodium borohydride overlap those of Johnston and Hallett [7] from 277° to 301° K. The agreement in mean heat capacity over this temperature range is almost perfect, but their value at 298° K is about 0.25-percent higher. The less precise values for sodium borohydride of Boodman, Stegeman, and Mason [6] are somewhat lower in this temperature range than those of Johnston and Hallett. Davis, Mason, and Stegeman [5] obtained a value of 0.55 ±0.01 cal g^{-1} deg C^{-1} for the mean heat capacity between 273° and 298° K; this is 2-percent higher than the authors' corresponding value. In the case of potassium borohydride, Furukawa et al. [8], who use an adiabatic calorimeter to make the preliminary measurements from low temperatures to 370° K referred to in section 6, obtained somewhat higher values of heat capacity than the authors. In the range from 298° to 370° K the discrepancy averaged 0.3 percent and reached a maximum of 0.5 percent.[13]

The authors believe that their corrected and smoothed values of the heat capacity of these two compounds are reliable to within 1 percent. The thermal measurements were made using a method and apparatus that appears to give consistently much greater accuracy than this when the substance measured is pure, stable, and physically reproducible. It is therefore likely that in the present case the uncertainty in the exact chemical compositions of the samples contributed the major uncertainty in the heat capacity, and, as indicated in section 4, by approximately the same percentage for each of the two compounds over the whole range from 0° to 400° C. If this is true, approximately the same percentage error for each compound resulted in the parts of the entropy and heat-content function which are in excess of the respective values at 298° K.

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8. References

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[13] As can be seen from figure 1, the authors could have chosen a smooth heat-capacity function for KBH_4 which passes through the observed points below 200° C. Such a function would have corresponded to a slightly sharper transition peak in this temperature region and at the same time would have agreed substantially better with the preliminary adiabatic-calorimeter values referred to. However, unless the latter values are explicitly given considerable weight, the observations reported in this paper are really not sufficiently precise nor at enough different temperatures to justify this more detailed formulation.