

the equilibrium between inner sphere and outer sphere complex ions will find their counterpart in labile systems of the same charge type, as for example $\text{Fe}^{+++}\text{-SO}_4^-$ and $\text{Ce}^{+++}\text{-SO}_4^-$. In general the equilibrium behavior of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ in association reactions with anions is very nearly the same as for other tripositive ions forming 1:1 complexes. Thus, the equilibrium constant for association with Cl^- at 25° and $\mu = 0.05$ is 4.1⁹ and the association reaction is slightly endothermic. This behavior is in striking similarity to that of $\text{Fe}^{+++}\text{-Cl}^-$.¹⁰ Furthermore, for $\text{Co}(\text{NH}_3)_5^{+++}$ the affinities decrease in order from Cl^- to I^- , as they do for Fe^{+++} . The association constant observed¹¹ for La^{+++} and SO_4^- at $\mu = 1.00$ and 25° is 25 and for Ce^{+++} and SO_4^- under the same conditions is

(9) F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937).

(10) E. Rabinowitch and W. H. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

(11) K. L. Mattern, Thesis, University of California, Berkeley, 1951.

17.5.¹² In the present system in the same salt environment (but at 31.1°) the constant for association involving outer sphere complexes is only 16, and if the inner sphere complexes are included, the constant would be roughly doubled. These similarities strengthen the view that for the labile systems consisting of SO_4^- and tripositive ion, the ratio of concentrations of inner and outer sphere forms will also be of the order of magnitude of unity.

Acknowledgments.—One of the authors (H. T.) wishes to acknowledge the contributions of Dr. Estelle R. Katzenellenbogen and Dr. W. K. Wilmarth in directing his attention early in the investigation to the importance of outer sphere ion association. We are also grateful to the Office of Naval Research for support of this investigation under contract N6-Ori-02026.

(12) T. W. Newton, private communication.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XIV. Heat Capacity of Sodium Borohydride from 15–300°K.¹

BY HERRICK L. JOHNSTON AND NATHAN C. HALLETT

RECEIVED MAY 24, 1952

The heat capacity of sodium borohydride has been measured from 15 to 300°K. and the thermodynamic functions have been calculated. A second-order transition, with an entropy of 1.22 e.u. occurs at 189.9°K. The entropy at 298.16 is 24.26 e.u.

Introduction

The first low-temperature heat capacity data for sodium borohydride were obtained by Boodman, Stegeman and Mason² for the temperature range 55–298°K.

During the present investigation, the heat capacities and thermodynamic functions have been measured in the range 15–300°K., in order to extend the earlier measurements.

Apparatus

The heat capacity measurements were made in calorimeter No. 7, one of a group of seven calorimeters for the measurement of the heat capacity of solid materials. This calorimeter is identical in all respects to calorimeter No. 1 which has been described in an earlier paper.³

The sample of sodium borohydride was obtained through the courtesy of the General Electric Research Laboratory at a reported purity of approximately 87%. The sample was purified and analyzed by the method of Davis, Mason and Stegeman⁴ resulting in a purity of 99.60%. All handling of the sample, including filling, sealing and emptying the calorimeter was done under anhydrous conditions in a dry-box. The calorimeter contained 26.0530 g. (0.68835 mole) of sodium borohydride.

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) D. Boodman, G. Stegeman and L. Mason, Thermal Properties of some Hydrides, Univ. of Pitts., ONR Contract Number N6 ori 43, T.O.I, Technical Report, Oct. 10, 1949.

(3) H. L. Johnston and E. C. Kerr, *THIS JOURNAL*, **72**, 4733 (1950).

(4) W. D. Davis, L. S. Mason and G. Stegeman, *ibid.*, **71**, 2775 (1949).

Experimental Results

The heat capacity data, as shown in Table I and in Fig. 1, follow a normal curve from 15°K. to about 169°K. at which point a second-order type transition occurs and the apparent heat capacity rises from about 16 calories/mole/degree to over 100 calories/mole/degree. From 193.5°K. to room temperature the heat capacity again follows a normal curve.

Below 30°K. the heat capacities followed the T^3 law so that it was possible to evaluate the region below 15°K. using the equation

$$C_v = 4.90 \times 10^{-5} T^3$$

Three determinations were made to obtain an accurate value for the heat of transition. The average value obtained (see Table II) is 635.3 calories per mole for the total enthalpy change from 169–193.5°K., which corresponds to an entropy change of 3.35 e.u. By subtracting the area between 169–193.5°K. under the extrapolated portion of the normal capacity curve (Fig. 1) a value of 232.6 calories/mole was obtained for the heat of transition and a corresponding value of 1.22 e.u. for the transition entropy increase. This value is 0.22 e.u. higher than the value of 0.99 e.u. given by Boodman, Stegeman and Mason.² This is understandable, however, since their heat of transition was evaluated by a method used by Giauque and Wiebe.⁵ The boundaries of transition were arbitrarily set as those points where the heat capacity became 0.500 calorie/gram/degree (18.924 calories/mole/degree). Since there is an apparent "pre-heat of transition" below the 0.500 calorie/gram/degree, their results would be lower than those of this research.

The values for the entropy and enthalpy (Table III) were obtained from large scale graphs of C_p/T versus T and C_p versus T , respectively, with the aid of Simpson's rule.

(5) W. F. Giauque and R. Wiebe, *ibid.*, **50**, 2193 (1928).

TABLE I
HEAT CAPACITY OF SODIUM BOROHYDRIDE (NaBH₄)
Mol. wt. = 37.8482; 0.68835 mole

Mean T, °K.	15.76	18.84	21.11	23.51	25.83	28.62	31.64	35.66
C _p , cal./mole/degree	0.180	0.321	0.428	0.663	0.894	1.111	1.508	2.018
Mean T, °K.	40.11	44.24	48.65	53.37	58.58	64.29	69.69	75.18
C _p , cal./mole/degree	2.571	3.111	3.705	4.439	5.116	5.778	6.347	7.100
Mean T, °K.	81.57	89.49	98.34	103.75	112.81	122.98	133.66	144.15
C _p , cal./mole/degree	7.760	8.576	9.438	9.957	10.80	11.66	12.51	13.35
Mean T, °K.	154.12	164.63	175.18	181.95	182.87	185.09	186.75	187.21
C _p , cal./mole/degree	14.26	15.14	16.26	17.08	17.54	19.03	29.39	32.69
Mean T, °K.	188.24	188.61	188.91	189.42	190.88	191.81	192.59	193.45
C _p , cal./mole/degree	82.90	101.65	117.29	120.59	26.94	25.96	23.72	16.88
Mean T, °K.	195.83	198.89	207.13	215.74	225.22	234.00	240.85	249.01
C _p , cal./mole/degree	16.93	17.03	17.39	17.78	18.16	18.52	18.79	19.09
Mean T, °K.	256.14	266.43	276.92	286.61	296.42	301.26		
C _p , cal./mole/degree	19.33	19.76	20.14	20.44	20.70	20.76		

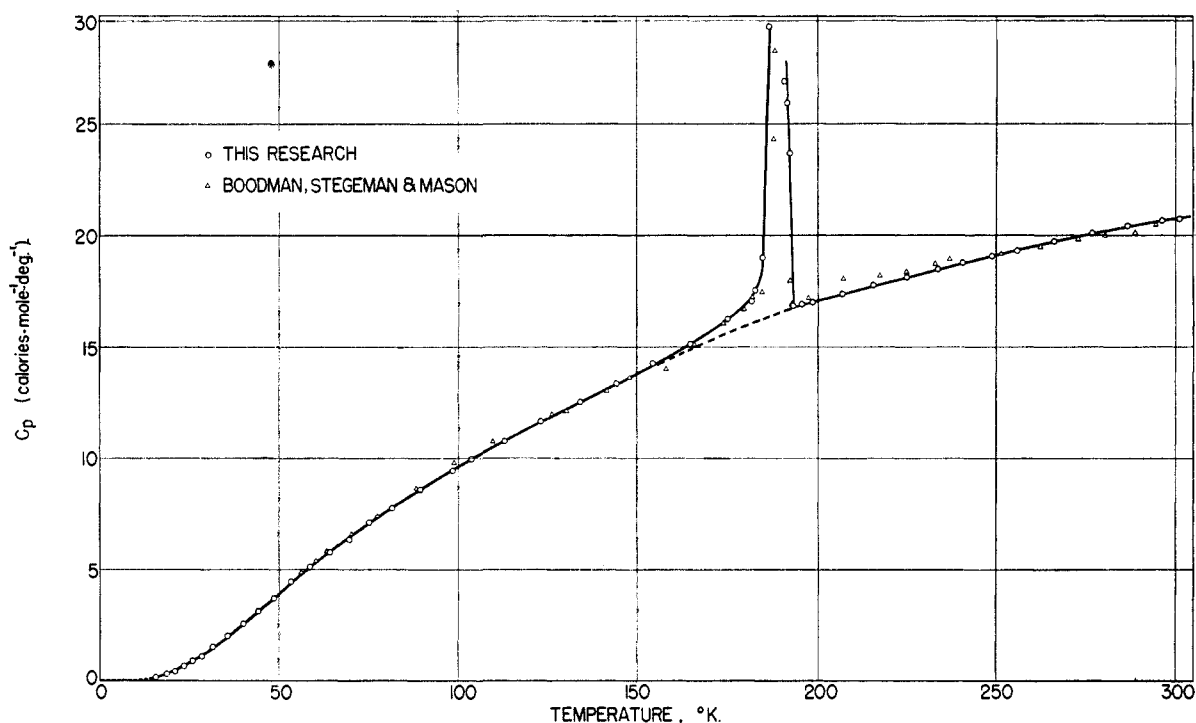


Fig. 1.—Heat capacity of sodium borohydride from 15–300°K.

TABLE II

HEAT OF TRANSITION OF SODIUM BOROHYDRIDE (NaBH₄)
TEMPERATURE OF TRANSITION—189.9°K.

Interval, °K.	ΔH (169–193.5°K.) ^a	ΔH (transition) ^b
184.1–193.1	633.9	231.2
171.0–195.5	634.3	231.6
170.2–194.9	637.6	234.9
Av. ΔH (cal./mole)	635.3	232.6
Av. ΔS (e.u.)	3.35	1.22

^a Net molar enthalpy to heat NaBH₄ from 169–193.5°K.

^b Net molar enthalpy in excess of that due to an extrapolation of the normal heat capacity curve.

The entropy of 24.26 e.u. at 298.16°K. is 0.76 e.u. lower than that obtained by Boodman, Stegeman and Mason²; of

TABLE III

ENTROPY AND ENTHALPY OF SODIUM BOROHYDRIDE (NaBH₄)

Interval, °K.	Enthalpy ΔH cal./mole	Entropy ΔS e.u.
0–15	0.56 ^a	0.05 ^a
15–169	1277.7	12.76
Transition 169–193.5	635.3	3.35
193.5–298.16	1976.5	8.10
193.5–300	2014.8	8.23
298.16	$(H - H_0) = 3890.1$	$(S - S_0) = 24.26$

^a Extrapolated, $C_v = 4.90 \times 10^{-5} T^3$.

which, 0.47 e.u. is due to their extrapolation from 0–60°K.
COLUMBUS, OHIO