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Final Report

DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF CERTAIN SUBSTANCES

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ABSTRACT

This report summarizes the heat-capacity measurements on vitreous and crystalline sodium tetraborate, on sodium metaborate, on sodium methoxide, on sodium hydride, and on ammonia triborane. Most of these measurements were made over the range of from 5 to 350°C by the adiabatic technique in a high-precision low-temperature calorimeter. The thermodynamic functions and thermal properties of these materials have been summarized in tabular and graphical presentation and the interpretation of the data has been made. Most of these details have been submitted from time to time in the technical reports under the above contract.

OBJECTIVE

The objective of this project was to obtain chemical thermodynamic data and thermal measurements on certain compounds over the low-temperature range.

INTRODUCTION

Because the several compounds which were studied have no immediate scientific relation to each other and were of interest to the sponsor primarily for technical reasons, this report is essentially a summation of the data on the individual substances presented in the separate sections of this report. These compounds are also of considerable scientific interest. The comparison of the thermal properties of the vitreous and crystalline forms of the sodium tetraborate shows an unusual effect. Data on the heat capacity of sodium hydride (and deuteride) have long been proposed to test the relative merits of heat-capacity theories. The study of the changes in the thermodynamic functions at the transformation in ammonia borane is of considerable interest in its own right. But apart from the scientific interest, the evaluation of the thermodynamic functions provide data useful in the design of production apparatus and in evaluating the potentialities of the material for applications.

THE CRYOSTAT AND CALORIMETER

The Mark I cryostat and electrical circuits employed for the heat capacity measurements are very similar to the equipment described by Westrum, Hatcher, and Osborne. Figure 1 is a cross-sectional view of the cryostat with the calorimeter in place.

The adiabatic determinations of heat capacity were made by measuring the temperature rise produced by a measured input of electrical energy. Current and potential measurements were made on the electrical heater during the energy input and on the capsule-type platinum resistance thermometer during drift periods. These measurements were made with an autocalibrated White double potentiometer used in conjunction with a galvanometer having a rated sensitivity of 0.04 μv/mm at 1-m distance.

The platinum resistance thermometer (laboratory designation A-3) was calibrated at the National Bureau of Standards by measuring its resistance at the boiling point of oxygen, the ice point, the steam point, and the boiling point of sulfur. The constant in the Callendar-Van Dusen equation, which relates resistance to temperature, were evaluated from these measurements made at the fixed points on the International Temperature Scale. In the region from 10 to 90°K, the resistance was measured at 19 different temperatures given by the Bureau's standard thermometer. Between 4 and 10°K we established a provisional temperature scale[2] from the value of dR/dT at 10°K, the resistance of the thermometer at 10°K, and the resistance at the boiling point of helium, by evaluating the constants in the equation $R = A+BT^2+CT^5$. It is believed that the temperature scale agrees with the thermodynamic scale within 0.1° from 4 to 14°K, within 0.02° from 14 to 90°K, and within 0.04° from 90 to 373°K.

Essentially adiabatic conditions were achieved by surrounding the calorimeter

Fig. 1. Cross-sectional schematic view of cryostat.

Legend:

1. Helium exit connector
2. Helium transfer tube
3. Nitrogen inlet and outlet connector
4. Sleeve fitting to helium transport Dewar
5. Nitrogen filling tube

6. Helium transfer-tube extender and cap
7. Screw fitting at inlet of helium transfer tube
8. Brass vacuum can
9. Outer "floating" radiation shield
10. Nitrogen tank

11. Helium exit tube
12. "Economizer" (effluent helium vapor heat exchanger)
13. Nitrogen radiation shield
14. Helium tank
15. Bundle of lead wires

16. Adiabatic shield
17. Helium radiation shield
18. Ring for block and tackle
19. Windlass
20. Vacuum seal and terminal plate for leads

21. Head plate
22. O-ring gasket
23. Coil spring
24. Supporting string
25. "Floating" ring

26. Calorimeter

with a shield that was maintained at the same temperature as the calorimeter. Energy input and drift periods were timed with clocks driven by an electrical timing circuit. Solid nitrogen, at reduced pressure, was used as a refrigerant for temperatures as low as 50°K and liquid helium for temperatures down to about 5°K.

The calorimeter (laboratory designation W-9) used on most of the compounds herein, with 0.0001-in. gold plating on the exterior surfaces, is similar in design and dimensions to W-6, which is shown in Fig. 2 with the two exceptions that the inside was gold-plated (0.001-in.) to protect the calorimeter from possible corrosion by the sample, and the number of vertical conduction vanes was reduced from eight to four. Reducing the number of vanes permitted easier loading and unloading of the sample, had no adverse effects on the attainment of temperature equilibrium in the calorimeter, and facilitated the gold-plating procedure. The top of the calorimeter made a snug fit in the monel neck and the poor thermal conductivity of monel permitted the top to be soldered in place easily and without appreciably heating the calorimeter and contents, thereby avoiding possible thermal decomposition of certain samples. The calorimeter had a measured interior volume of about 92 ml and a calculated exterior volume of about 102 ml. The weight of the calorimeter, helium, and solder (as run) was approximately 90 g.

The calorimeter (laboratory designation W-17), constructed especially for ammonia triborane and trimethylamine triborane, has very thin gold plating on the exterior and interior surfaces. It, too, is similar in design to calorimeter W-6, except that the inside was gold plated to protect the calorimeter from possible corrosion by the sample and that the number of vertical conduction vanes was reduced from eight to four. This calorimeter also had a monel neck, which permitted the top to be soldered in place easily and without appreciably heating the calorimeter and contents. This avoided possible thermal decomposition of the sample which takes place at temperatures above 320°K at an appreciable rate. The calorimeter had an interior volume of about 60 ml and weighed (including helium and solder) approximately 33 g.

After the calorimeter was filled, weighed, and its top sealed in place with Cerroseal-35 solder,* it was quickly transferred from the dry box to a vacuum line and evacuated for several hours through a pinhole in the helium seal-off tube. Following evacuation, 1- to 2-cm pressure of very pure helium gas was admitted through the pinhole which was then sealed with Cerroseal solder. A glass apparatus contained a small electric soldering iron fitted to the vacuum chamber through a ground-glass ball and socket joint so that the pinhole could be sealed off under reduced helium pressure.

The amount of solder was carefully adjusted so that the weight of the empty calorimeter was maintained the same in all heat-capacity determinations. Since the heat-capacity measurements were made up to 350°C, the conduction grease used in the thermometer well and thermocouple sleeve was Apiezon T stopcock grease. Grease corrections were made negligible by reproducing, to within a few tenths of a milligram, the weight of the grease on the calorimeter for each heat-capacity determination.

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*Low-melting solder (m.p. 117°C) 50% Sn + 50% In by weight.

Fig. 2. Cross-sectional schematic view of calorimeter W-6.

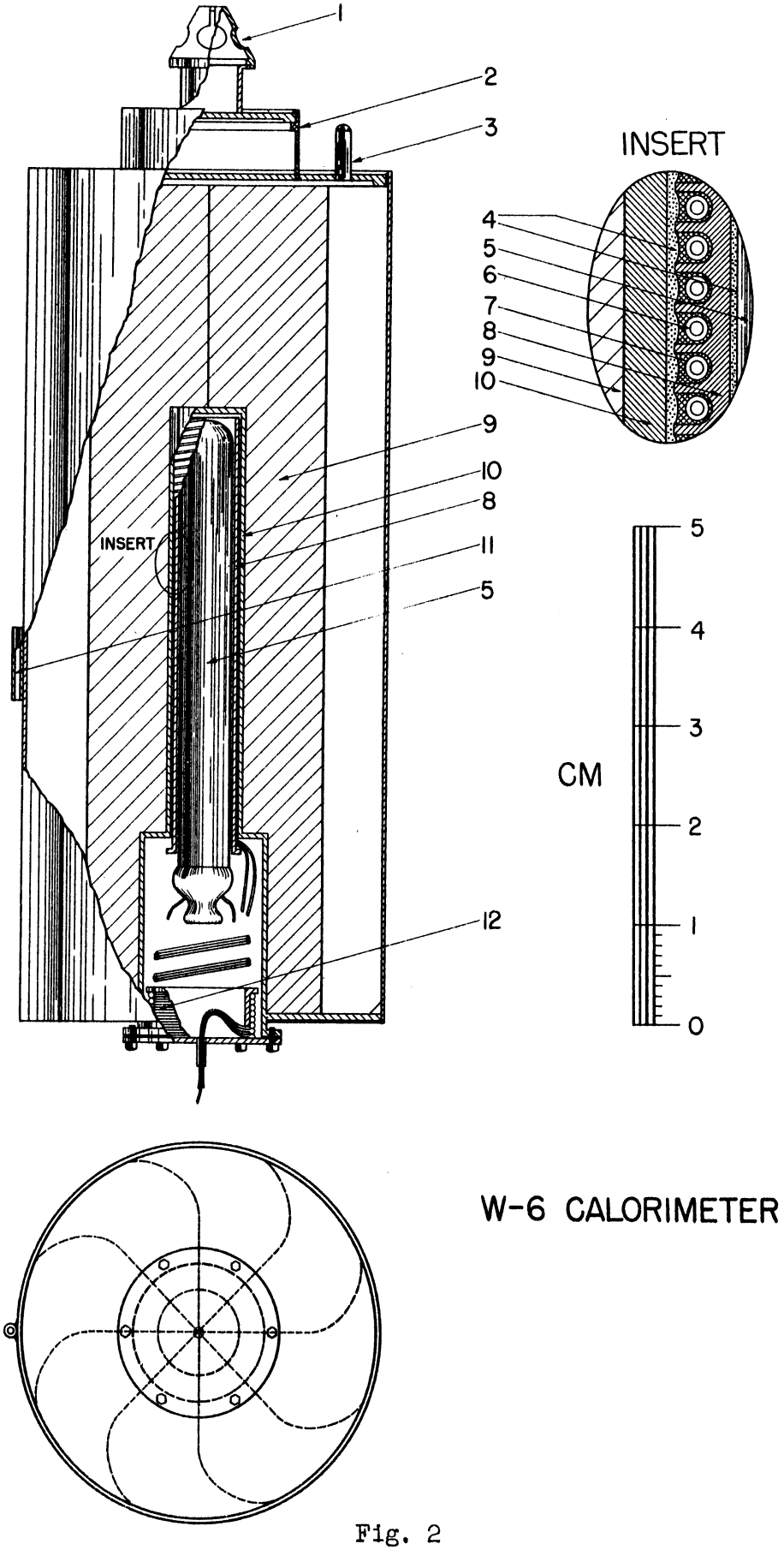
Legend:

1. Thermal-conductivity cone
2. Monel neck
3. Monel helium seal-off tube
4. Apiezon T stopcock grease
5. Leeds and Northrup platinum resistance thermometer

6. Glass-fiber-insulated No. 40 advance (constantan) wire
7. Formvar varnish
8. Gold-plated copper heater sleeve
9. Gold-plated copper vane
10. Gold-plated copper heater well

11. Differential thermocouple sleeve
12. Spool to bring leads into thermal equilibrium with calorimeter

M-970 D-56-5 JEM 2-27-63



W-6 CALORIMETER

Fig. 2

THE HEAT CAPACITY OF A STANDARD SAMPLE OF BENZOIC ACID

To verify the overall accuracy of our technique, measurements were made on the heat capacity of pure benzoic acid made available by the National Bureau of Standards in conjunction with the program of the Calorimetry Conference.[3] The heat capacities measured in our apparatus agree excellently with the values reported by the National Bureau of Standards.[4]

DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY OF ANHYDROUS SODIUM METABORATE*

PREPARATION OF ANHYDROUS SODIUM METABORATE

Anhydrous sodium metaborate ($NaBO_2$) is a hygroscopic crystalline solid and melts at about 966°C to a viscous liquid which does not yield a vitreous (glassy) phase.

Data from the chemical literature on the physical properties of anhydrous sodium metaborate pertain almost exclusively to melting points,[5-7] sublimation pressures,[8] phase equilibria on the Na_2O-B_2O_3 system,[5] optical properties,[5-7] and structural studies and densities based on fragmentary X-ray diffraction data.[6,7,9,10]

A very pure sodium metaborate tetrahydrate was used as the starting material. This substance is sold commercially (Eastman Kodak Co.) under the trade name of "Kodalk." On the advice that the compound might contain a trace of calcium, a purification of the material was accomplished by recrystallization from distilled water. Most of the water of hydration was removed by pumping on the sample in a vacuum dessicator with a hyvac pump for three days. Then the sample was heated to 100°C and evacuation was continued with a high-speed diffusion pump to remove the balance of the water. This method effectively removed the water contained in the sample. It is essential that almost all the water be removed before the substance is placed in the furnace because the evolution of water vapor causes a large increase in volume of the sample.

Since most of the water had been removed as previously described, the sample was placed in a platinum dish and was heated gradually in a furnace 966°C, the melting point of anhydrous sodium metaborate. The material was allowed to cool gradually to 200°C; then it was transferred from the furnace to a dessicator containing P_2O_5. White crystals of acicular habit were formed during the slow cooling. The best crystals from the various batches were removed in a dry box, combined, fused again, and recrystallized slowly to insure purity, homo-

*By George Grenier and Edgar F. Westrum, Jr.

geneity, and good crystal development of the calorimetric samples.*

Determination of water was made by loss in weight on fusion.[11,12] The usual Karl Fischer reagent is unsatisfactory because complicating reactions are involved with borates. No water was detected within ± 0.01%.

The Na_2O content of the sample was determined by carefully evaporating the sample to dryness in hydrochloric acid and titrating the residual chloride with standardized silver nitrate solution using dichlorofluorescein as an indicator.[11-15]

The B_2O_3 content of the sample was obtained by first neutralizing a sample of the metaborate with hydrochloric acid, then adding mannitol and titrating the boric acid potentiometrically.[16-19]

The percent by weight of sodium as Na_2O was 47.11, 46.91, 47.30; average, 47.11 ± 0.20%, in accord with the claimed ± 0.2% reliability of the method. (Theoretical Na_2O: 47.10%.)

The percent by weight of boron reported as B_2O_3 was 52.77, 52.84, 53.12; average, 52.91 ± 0.13%. (Theoretical B_2O_3: 52.90%.)

The material, therefore, is stoichimometrically anhydrous sodium metaborate.

HYGROSCOPICITY OF SODIUM METABORATE

Although the anhydrous material used in this investigation was handled in an anhydrous chamber, it was desirable to know the rate of adsorption of water from the ambient air at 40% relative humidity and 25°C. For this purpose a 2.0-g sample was fused, crystallized, and cooled in a dessicator in a platinum crucible and weighed at various times at room temperature in the ambient laboratory atmosphere. At 30 min after exposure, the increase in apparent sample weight was 0.24%, at 100 min, 0.77%, and after 11 hr, 3.2%. The necessity of handling this material in an anhydrous atmosphere is readily apparent.

RESULTS OF HEAT-CAPACITY MEASUREMENTS ON ANHYDROUS CRYSTALLINE SODIUM METABORATE

The original experimental values of the molal heat capacity of sodium metaborate at the mean temperature of the runs are given in Table I and Fig. 3. A column also gives the temperature increments, ΔT, of the individual determinations. Small corrections have been made for these finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules.

*The analyses of product material were performed by Lynn J. Kirby of this laboratory.

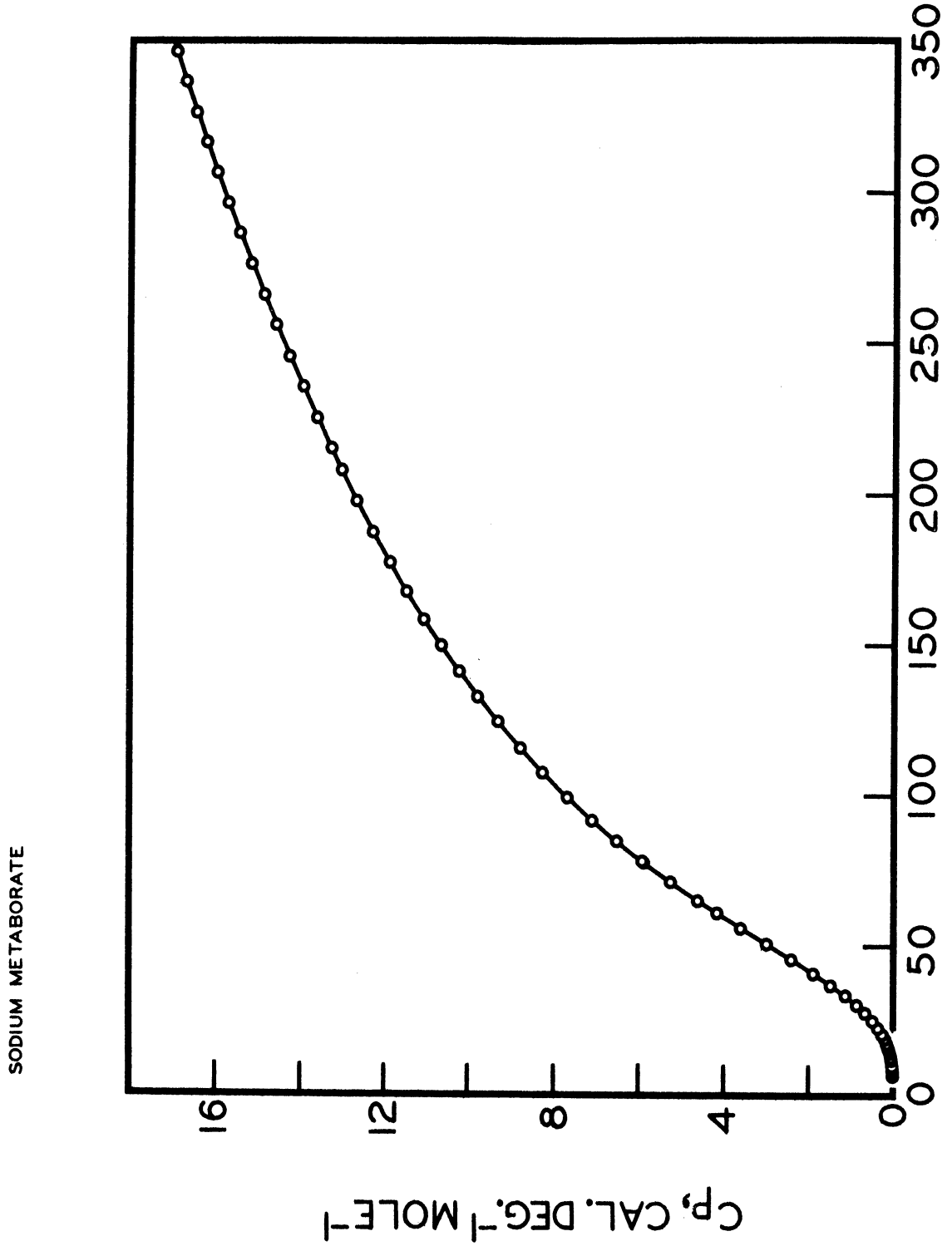


Fig. 3. Molal heat capacity of sodium metaborate as a function of absolute temperature (6-350°K).

TABLE I

THE MOLAL HEAT CAPACITY OF SODIUM METABORATE

T, °K	ΔT, °K	C_p, cal deg^{-1}	T, °K	ΔT, °K	C_p, cal deg^{-1}
5.48	1.252	0.003	107.29	8.402	8.257
6.68	1.213	0.005	115.59	8.207	8.796
7.83	1.255	0.010	123.94	8.489	9.310
9.08	1.337	0.017	132.48	8.594	9.797
10.38	1.349	0.027	140.98	8.402	10.25
11.72	1.382	0.040	149.44	8.426	10.66
13.06	1.360	0.057	158.07	8.824	11.06
14.40	1.342	0.078	167.33	9.704	11.48
15.74	1.363	0.105	177.16	9.954	11.88
17.14	1.443	0.139	187.21	10.142	12.28
18.69	1.674	0.185	197.36	10.177	12.66
20.53	2.003	0.253	207.75	10.172	13.02
22.74	2.423	0.354	215.06	10.112	13.28
25.15	2.404	0.487	225.14	10.059	13.62
27.64	2.578	0.652	235.23	10.113	13.94
30.36	2.858	0.859	245.47	10.380	14.27
33.41	3.243	1.125	255.80	10.287	14.58
36.89	3.717	1.464	265.98	10.078	14.88
40.89	4.282	1.883	276.10	10.158	15.16
45.57	5.082	2.405	286.16	9.970	15.45
50.72	5.218	2.997	296.22	10.141	15.71
55.96	5.268	3.598	306.34	10.102	15.99
60.88	4.564	4.152	316.45	10.128	16.24
64.98	6.425	4.604	326.55	10.092	16.48
71.20	6.015	5.244	336.56	9.944	16.73
77.18	5.945	5.839	346.49	9.924	16.96
77.94	6.447	5.908			
84.46	6.594	6.515			
91.34	7.153	7.099			
99.00	8.166	7.674			

The ice point was taken to be 273.16°K, and the gram molecular weight of sodium metaborate ($NaBO_2$) was taken as 65.811 g. A calorimetric sample of 133-6378 g (2.03061 moles) was employed for these determinations.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table II. These heat-capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K, 1.0% at 14°K, and 5.0% at 5°K. The heat capacity was extrapolated below 10°K with a Debye function. The effect of nuclear spin is not included in the entropy and free-energy function. The estimated probable error in the entrophy, heat content, and free-energy function is 0.1% above 100°K, but to make the table internally consistent and to permit accurate interpolation, some of the values are given to one more figure than is justified by the estimated probable error. Small corrections have been made for the finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.16°K.

The molal heat capacity and thermodynamic functions (in calories per degree) may be extrapolated to higher temperatures by the following three formulas predicated on the method described by Shomate.[20]

$$C_p = 10.23 + 0.0212\ T - 7.02 \times 10^4\ T^{-2}$$

$$(H^\circ_0 - H^\circ_0)/T = 10.23 + 0.0106\ T + 7.02 \times 10^4\ T^{-2} - 1447.9\ T^{-1}$$

$$S^\circ = 23.58 \log T + 0.0212\ T + 3.51 \times 10^4\ T^{-2} - 47.44$$

These formulas should be used with caution as they are an approximation justified only by the absence of experimental determinations. However, no thermal transformations or anomalies were detected by Morey and Merwin[5] by thermal analysis between 350°K and the melting point.

DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY OF ANHYDROUS CRYSTALLINE SODIUM TETRABORATE*

Despite the use of borax and related materials in ceramic technology for many centuries and their widespread utilization in current chemical technology, reliable thermodynamic data on alkali borates are relatively rare. Data in the

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TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF SODIUM METABORATE

T, °K	C_p, cal deg^{-1}	S°, cal deg^{-1}	$H^\circ - H_0^\circ$, cal	$-(F^\circ - H_0^\circ)/T$, cal deg^{-1}
5	0.002	0.0006	0.002	0.0001
10	0.024	0.008	0.059	0.002
15	0.090	0.028	0.32	0.007
20	0.232	0.071	1.09	0.017
25	0.479	0.147	2.82	0.034
30	0.830	0.264	6.05	0.062
35	1.276	0.425	11.28	0.103
40	1.788	0.628	18.92	0.155
45	2.341	0.870	29.23	0.220
50	2.913	1.146	42.36	0.299
60	4.054	1.779	77.22	0.492
70	5.122	2.485	123.20	0.725
80	6.102	3.234	179.38	0.992
90	6.982	4.005	244.91	1.284
100	7.751	4.781	318.65	1.595
110	8.438	5.553	399.63	1.920
120	9.066	6.314	487.17	2.254
130	9.646	7.063	580.8	2.596
140	10.19	7.798	680.0	2.941
150	10.70	8.519	784.5	3.289
160	11.16	9.224	893.7	3.638
170	11.59	9.914	1007.5	3.988
180	12.00	10.588	1125.4	4.336
190	12.38	11.246	1247.3	4.681
200	12.74	11.891	1373.0	5.026
210	13.10	12.521	1502.2	5.368
220	13.44	13.139	1634.9	5.707
230	13.77	13.743	1771.0	6.043
240	14.10	14.337	1910.4	6.377
250	14.40	14.918	2052.9	6.707
260	14.70	15.489	2198.4	7.034
270	14.99	16.049	2346.9	7.357
280	15.27	16.600	2498.2	7.678
290	15.55	17.140	2652.3	7.994
300	15.81	17.672	2809.1	8.308
350	17.04	20.203	3631.0	9.829
273.15	15.08	16.224	2394.4	7.459
298.15	15.76	17.574	2780.0	8.250

chemical literature on the physical properties of anhydrous vitreous and crystalline sodium tetraborate are concerned primarily with melting point and phase equilibrium studies[5] on the Na_2O-B_2O_3 systems. We use the designation sodium tetraborate to refer to the chemical composition $Na_2B_4O_7$, although a contrary usage is occasionally found.[5] Although two or possibly three distinct crystallographic phases of this material exist,[5] the material prepared for this work is the α-form and is ordinarily obtainable and commercially available. No evidence for an enantiotropic inversion between the various forms has been found,[5] despite a careful search from below 500° to the melting point. The rate of conversion of β to α is very slow and the reverse transformation has not been observed.

PREPARATION AND ANALYSIS OF CRYSTALLINE SODIUM TETRABORATE

The crystalline sodium tetraborate sample was prepared by crystallizing a dehydrated sample of analytical-reagent grade sodium tetraborate decahydrate from the molten state in a platinum dish under carefully controlled conditions. Since rapid cooling or prolonged periods of heating at temperatures appreciably higher than the melting point of 742.5°C[5] result in glass formation, it is essential for crystal growth that the temperature does not exceed 760°C nor remain at this temperature for a period of more than about 10 min, and that a controlled rate of cooling be maintained. This was achieved by gradually decreasing the temperature in the electric muffle to about 300°C in 10-hr time. The covered platinum dish was then transferred to a dessicator over phosphorus pentoxide to cool to room temperature without adsorption of water. The resulting white crystals were shown to be free of glass particles by a careful examination of the sample under a polarizing microscope.*

Determination of water was made by loss in weight on fusion.[11,12] The usual method involving Karl Fischer reagent is unsatisfactory because complicating reactions are involved with borates. Although it is reported by Morey and Merwin[5] that the crystalline material at 300°C and the molten tetraborate itself will take up water in humid weather, this is lost upon crystallization of the compound under anhydrous conditions, so the method as employed here is efficacious. Determination of water by this technique indicated 0.01 ± 0.01% water.

The N_2O_3 content of the sample was determined by carefully evaporating the sample to dryness in hydrochloric acid and titrating the residual chloride with standardized silver nitrate solution using dichlorofluorescein as an indicator.[11-15]

The B_2O_3 content of the sample was obtained by first neutralizing a sample of the metaborate with hydrochloric acid, then adding mannitol and titrating the

*The analyses of the final calorimetric samples were performed by Lynn J. Kirby of this laboratory.

boric acid potentiometrically.[15-17]

The percent by weight of sodium as Na_2O was 30.80, 30.78, 30.79; average, 30.79 ± 0.01%. (Theoretical Na_2O: 30.80%.)

The percent by weight of boron reported as B_2O_3 was 69.26, 69.20, 69.07; average, 69.18 ± 0.04%. (Theoretical B_2O_3: 69.20%.)

The material is, therefore, stoichimometrically anhydrous sodium tetraborate, $Na_2B_4O_7$.

The mass of the crystalline sample used in the calorimeter was 79.6707 g (in vacuo).

RESULTS OF HEAT-CAPACITY MEASUREMENTS ON ANHYDROUS CRYSTALLINE SODIUM TETRABORATE

The experimental values of the heat capacity of crystalline sodium tetraborate are presented in Table III and Fig. 4. Small corrections have been made for the finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.15°K.

The molal heat capacity and the thermodynamic functions derived from the heat capacity of these substances are listed at rounded temperatures in Table IV. These heat-capacity values were read from a smooth curve through the experimental points, and are estimated to have a probable error of 0.1% above 25°K, 1% at 14°K, increasing to 5% at 5°K. The heat capacity was extrapolated below 10°K with a Debye function. The effect of nuclear spin is not included in the entropy and free-energy function. The estimated probable error in the entropy, heat content, and free-energy function is 0.1% above 100°K, but to make the table internally consistent and to permit accurate interpolation, some of the values are given to one more figure than is justified by the estimated probable error.

Formulas for the extrapolation of the molal thermodynamic functions to temperatures above 350°K are derived by the method described by Shomate[20] using 300°K as the base temperature. The equations for crystalline sodium tetraborate (in cal deg^{-1} $mole^{-1}$)are

$$C_p = 21.83 + 0.0850T - 2.250 \times 10^5 T^{-2},$$

$$(H^\circ - H_0^\circ)/T = 21.83 + 0.0425T + 2.250 \times 10^5 T^{-2} - 3779.8 T^{-1}$$

and

$$S^\circ = 50.27 \log T + 0.0850T + 1.125 \times 10^5 T^{-2} - 105.70.$$

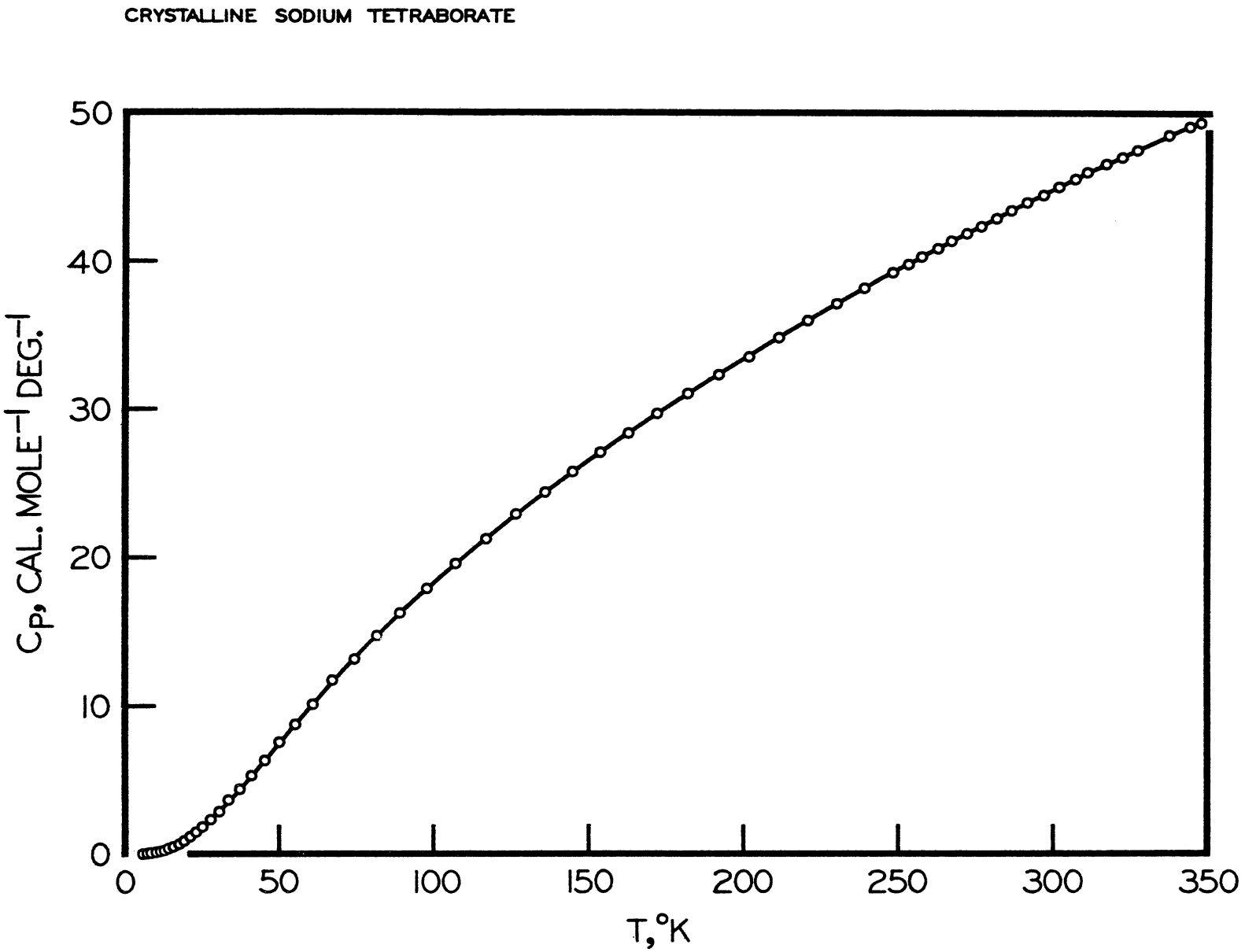

Fig. 4. Molal heat capacity of crystalline anhydrous sodium tetraborate. (The centers of the open circles represent the direct experimental determinations. The diameter of the circles does not represent an estimate of precision.)

TABLE III

THE MOLAL HEAT CAPACITY OF CRYSTALLINE SODIUM TETRABORATE
(Calories per degree)

T, °K	ΔT, °K	C_p
	SERIES I	
5.82	0.575	0.015
6.60	2.104	0.019
7.81	1.538	0.030
9.07	1.246	0.055
10.21	1.235	0.089
11.50	1.490	0.144
12.92	1.423	0.226
14.37	1.558	0.328
15.92	1.571	0.460
17.52	1.631	0.623
19.21	1.753	0.843
21.03	1.893	1.097
23.02	2.097	1.430
25.23	2.322	1.824
27.73	2.664	2.289
30.61	3.095	2.882
33.80	3.276	3.591
37.25	3.621	4.380
41.09	4.067	5.296
45.45	4.636	6.346
50.18	4.832	7.506
55.32	5.433	8.746
61.01	5.939	10.11
67.36	6.750	11.59
74.48	7.484	13.15
81.61	6.920	14.70
89.18	8.218	16.27
97.84	9.098	17.89
107.29	9.798	19.60
117.03	9.673	21.28
126.62	9.517	22.91
135.89	9.015	24.38
144.71	8.611	25.73
153.70	8.826	27.08
162.66	9.081	28.38
172.08	9.738	29.70
181.88	9.869	31.03
191.80	9.958	32.34
201.60	9.648	33.60
211.13	9.397	34.83
220.53	9.400	35.99
229.84	9.168	37.12
238.94	9.020	38.17
248.07	9.242	39.22
257.40	9.428	40.32
266.90	9.558	41.36
276.50	9.622	42.36
286.39	10.171	43.41
296.65	10.336	44.47
306.88	10.131	45.52
317.02	10.175	46.54
327.09	9.990	47.51
337.30	10.443	48.48
347.69	10.348	49.33
	SERIES II	
253.26	9.136	39.78
262.55	9.456	40.81
271.91	9.273	41.88
281.41	9.731	42.89
291.36	10.152	43.92
301.61	10.355	44.99
311.91	10.253	46.02
322.22	10.386	47.00
333.05	11.260	48.02
343.97	10.411	49.06

TABLE IV

MOLAL THERMODYNAMIC PROPERTIES OF CRYSTALLINE SODIUM TETRABORATE

T, °K	C_p, cal/deg	S^o, cal/deg	$H^o - H^o_0$, cal	$-(F^o - H^o_0)/T$, cal/deg
5	0.012	0.004	0.014	0.001
10	0.081	0.027	0.202	0.007
15	0.379	0.108	1.255	0.024
20	0.949	0.288	4.449	0.066
25	1.781	0.585	11.19	0.138
30	2.751	0.993	22.46	0.244
35	3.861	1.499	38.96	0.386
40	5.036	2.091	61.17	0.562
45	6.238	2.753	89.34	0.768
50	7.462	3.474	123.57	1.003
60	9.870	5.047	210.22	1.543
70	12.18	6.744	320.60	2.164
80	14.35	8.512	453.26	2.846
90	16.38	10.322	607.1	3.576
100	18.29	12.149	780.6	4.343
110	20.08	13.976	972.5	5.135
120	21.79	15.797	1181.9	5.948
130	23.43	17.607	1408.1	6.776
140	25.00	19.401	1650.3	7.613
150	26.53	21.178	1908.0	8.458
160	27.99	22.938	2180.6	9.309
170	29.41	24.678	2467.6	10.163
180	30.77	26.399	2768.6	11.018
190	32.10	28.097	3083.0	11.871
200	33.40	29.777	3410.5	12.725
210	34.68	31.438	3750.9	13.576
220	35.93	33.080	4105.0	14.425
230	37.12	34.705	4469.4	15.273
240	38.29	36.310	4846.5	16.117
250	39.43	37.896	5235.1	16.956
260	40.57	39.463	5635.1	17.789
270	41.67	41.016	6046.3	18.622
280	42.75	42.552	6468.4	19.451
290	43.79	44.070	6901.1	20.273
300	44.83	45.572	7344.2	21.091
350	49.65	52.850	9708.1	25.112
273.15	42.01	41.504	6178.6	18.885
298.15	44.64	45.296	7261.9	20.940

These equations should be used with caution above 350°K as they represent an approximation justified only by the absence of experimental determinations. However, no evidence for thermal transformations or anomalies was detected by Morey and Merwin[5] by thermal analysis between 350°K and the melting point.

DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY OF VITREOUS SODIUM TETRABORATE*

PREPARATION AND PURITY OF VITREOUS SODIUM TETRABORATE

The vitreous sodium tetraborate was prepared from the same material as the crystalline sample. The dehydrated sample was heated to 820°C for 30 min to insure glass formation. The glass was annealed for 15 min at 420°C and cooled in an anhydrous atmosphere.

Analytical data by identical methods on the vitreous material indicated: water, 0.0% ± 0.1%; Na_2O, 30.75%, 30.79% (theoretical, 30.80%); B_2O_3, 69.16%, 69.27% (theoretical, 69.20%), in good accord with theory.

The mass of the vitreous sample consisting of fragments of 2-5 mesh, was 112.6441 g (in vacuo).

RESULTS OF HEAT-CAPACITY MEASUREMENTS ON VITREOUS SODIUM TETRABORATE

The experimental values of the heat capacity of this material are listed in Table V using the same conventions as previously noted. The molal thermodynamic functions are reported in Table VI; however since the third law of thermodynamics may not be assumed for the vitreous phase, the entropy increment is tabulated, and the free-energy function cannot be specified at present.

Formulas for the extrapolation of the molal thermodynamic functions to temperatures above 350°K for vitreous sodium tetraborate (in cal $mole^{-1}$ deg^{-1}) are:

$$C_p = 27.83 + 0.0270T - 4.320 \times 10^5 T^{-2},$$

$$(H^\circ - H_0^\circ)/T = 27.83 + 0.0360T + 4.320 \times 10^5 T^{-2} - 5819.5 T^{-1}$$

and

$$S^\circ - S_0^\circ = 64.09 \log T + 0.0720T + 2.160 \times 10^5 T^{-2} - 137.96.$$

*By Edgar F. Westrum, Jr., and George Grenier.

TABLE V

THE MOLAL HEAT CAPACITY OF VITREOUS SODIUM TETRABORATE
(Calories per degree)

T, °K	ΔT, °K	C_p	T, °K	ΔT, °K	C_p
5.31	1.337	0.015	121.62	10.250	21.33
6.68	1.800	0.027	131.54	9.594	22.94
8.09	1.252	0.057	140.88	9.093	24.42
9.22	1.110	0.099	149.95	9.036	25.79
10.32	1.140	0.150	159.04	9.141	27.14
11.54	1.322	0.217	168.25	9.280	28.48
12.82	1.265	0.305	177.49	9.206	29.77
14.13	1.373	0.411	186.79	9.392	31.05
15.59	1.563	0.549	196.08	9.183	32.30
17.21	1.674	0.724	205.13	8.907	33.49
19.01	1.935	0.947	214.14	9.113	34.66
21.08	2.206	1.231	223.13	8.863	35.80
23.41	2.460	1.598	232.21	9.298	36.92
25.95	2.623	2.030	241.51	9.286	38.06
28.71	2.890	2.543	250.99	9.685	39.18
31.69	3.070	3.137	360.78	9.895	40.36
34.85	3.253	3.794	270.61	9.745	41.42
38.23	3.508	4.540	280.35	9.726	42.49
41.92	3.873	5.361	290.09	9.763	43.56
46.13	4.546	6.326	300.00	10.059	44.60
51.00	5.176	7.445	310.30	10.571	45.68
56.39	5.605	8.694	320.84	10.511	46.77
62.26	6.116	10.00	331.13	10.102	47.74
68.55	6.468	11.38	343.63	14.917	48.92
75.01	6.455	12.72			
81.43	6.370	14.08			
88.06	6.885	15.41			
95.20	7.395	16.73			
103.03	8.270	18.14			
111.83	9.324	19.67			

TABLE VI

MOLAL THERMODYNAMIC PROPERTIES OF VITREOUS SODIUM TETRABORATE

T, °K	C_p, cal deg^{-1}	$S^\circ - S^\circ_0$, cal deg^{-1}	$H^\circ - H^\circ_0$, cal
5	0.013	0.004	0.016
10	0.134	0.044	0.334
15	0.490	0.158	1.795
20	1.078	0.375	5.635
25	1.866	0.697	12.92
30	2.795	1.117	24.51
35	3.838	1.625	41.04
40	4.933	2.207	62.93
45	6.063	2.853	90.40
50	7.220	3.552	123.61
60	9.499	5.072	207.30
70	11.69	6.702	313.32
80	13.78	8.400	440.64
90	15.77	10.138	588.5
100	17.60	11.895	755.4
110	19.36	13.655	940.1
120	21.06	15.413	1142.2
130	22.70	17.163	1361.1
140	24.28	18.903	1596.0
150	25.80	20.631	1846.4
160	27.29	22.343	2111.8
170	28.70	24.041	2391.8
180	30.11	25.721	2686.0
190	31.48	27.387	2993.9
200	32.82	29.036	3315.4
210	34.12	30.668	3650.1
220	35.40	32.285	3997.7
230	36.65	33.887	4357.9
240	37.87	35.471	4730.5
250	39.07	37.042	5115.2
260	40.23	38.597	5511.7
270	41.36	40.136	5916.6
280	42.46	41.660	6338.7
290	43.54	43.169	6768.7
300	44.61	44.663	7209.5
350	49.50	51.918	9565.2
273.15	41.71	40.620	6050.9
298.15	44.42	44.391	7127.6

DISCUSSION

A comparison of heat capacities of crystalline and vitreous sodium tetraborate is depicted in Fig. 5. It is striking that the heat capacity of the vitreous material is lower than that of the crystals above 35°K, as may be seen even more clearly in the deviation plot, Fig. 6. This contrasts with data on other crystalline-vitreous pairs. For example, the heat capacity of quartz rises above that of vitreous silica only at about 210°K.[21] Moreover, the heat capacity of crystalline boron trioxide[21] exceeds the heat capacity of vitreous boron trioxide only at temperatures above 300°K.

From the heats of solution in nitric acid of Na_2O, B_2O_3 and two forms of $Na_2B_4O_7$[22] and the heats of formation of Na_2O and B_2O_3,[23] the heats of formation of crystalline and vitreous $Na_2B_4O_7$ are calculated as -786.5 ± 3 and -781.5 ± 3 kcal mole^{-1}, respectively, at 25°. The present measurements, together with entropy data on the elements, [23,24] permit the evaluation of the free energy of formation of crystalline $Na_2B_4O_7$ as -739.7 ± 3 kcal mole^{-1} at 25°. It is not possible to evaluate the zero-point entropy of the vitreous material; however, for the devitrification reaction, $H^{\circ}_{0°K}$ = -4.99 kcal mole^{-1}.

THE LOW-TEMPERATURE HEAT CAPACITY OF SODIUM METHOXIDE*

Sodium methoxide has long been used as a laboratory reagent in the preparation of important organic intermediates. Since 1944 it has been commercially available and currently is widely used on a large scale in the manufacture of certain pharmaceuticals, dyestuffs and other important organics. There is, therefore, considerable technological interest in accurate thermal properties of this material. No previous measurements of the heat capacity of sodium methoxide have been reported in the literature.

PREPARATION AND PURITY OF SODIUM METHOXIDE

The reaction of sodium metal with methyl alcohol to yield sodium methoxide and hydrogen was performed in a closed Pyrex vacuum system in a nitrogen atmosphere purified by passage over hot copper to remove oxygen, over potassium hydroxide pellets to remove acid, and through two phosphorus pentoxide columns to remove the remaining traces of water. Analytical reagent grade methyl alcohol (ketone, aldehyde and organic acid content to pass ACS test) was purified by refluxing for 24 hr over magnesium methoxide[25] followed by subsequent fractional distillation in the nitrogen atmosphere directly into a storage bulb connected to the reaction vessel. About 60 g of sodium metal (99.95% purity) was cut under xylene into one-cm cubes with fresh metallic surfaces and quickly transferred

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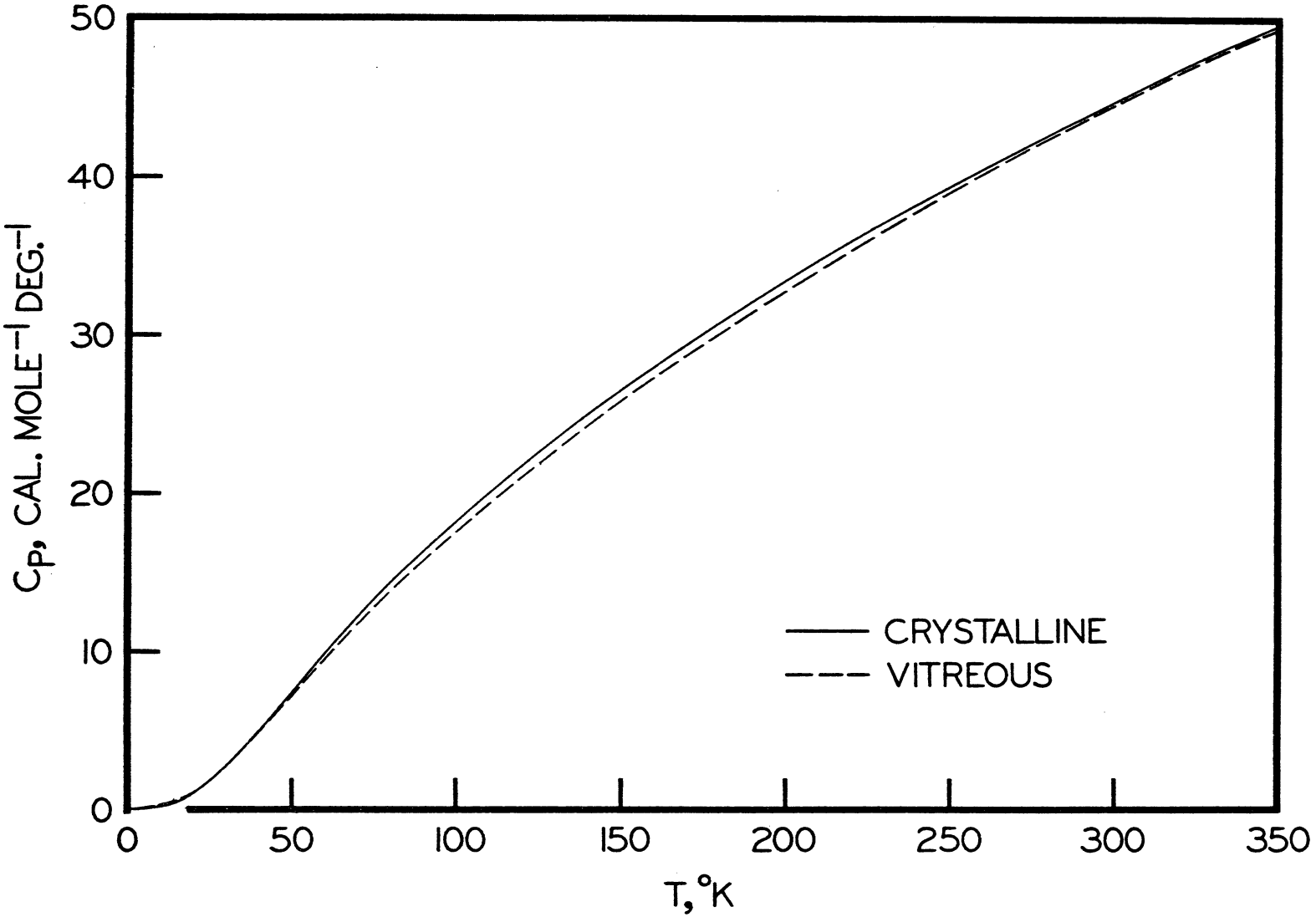

Fig. 5. Comparison of the heat capacities of anhydrous crystalline vitreous sodium tetraborate.

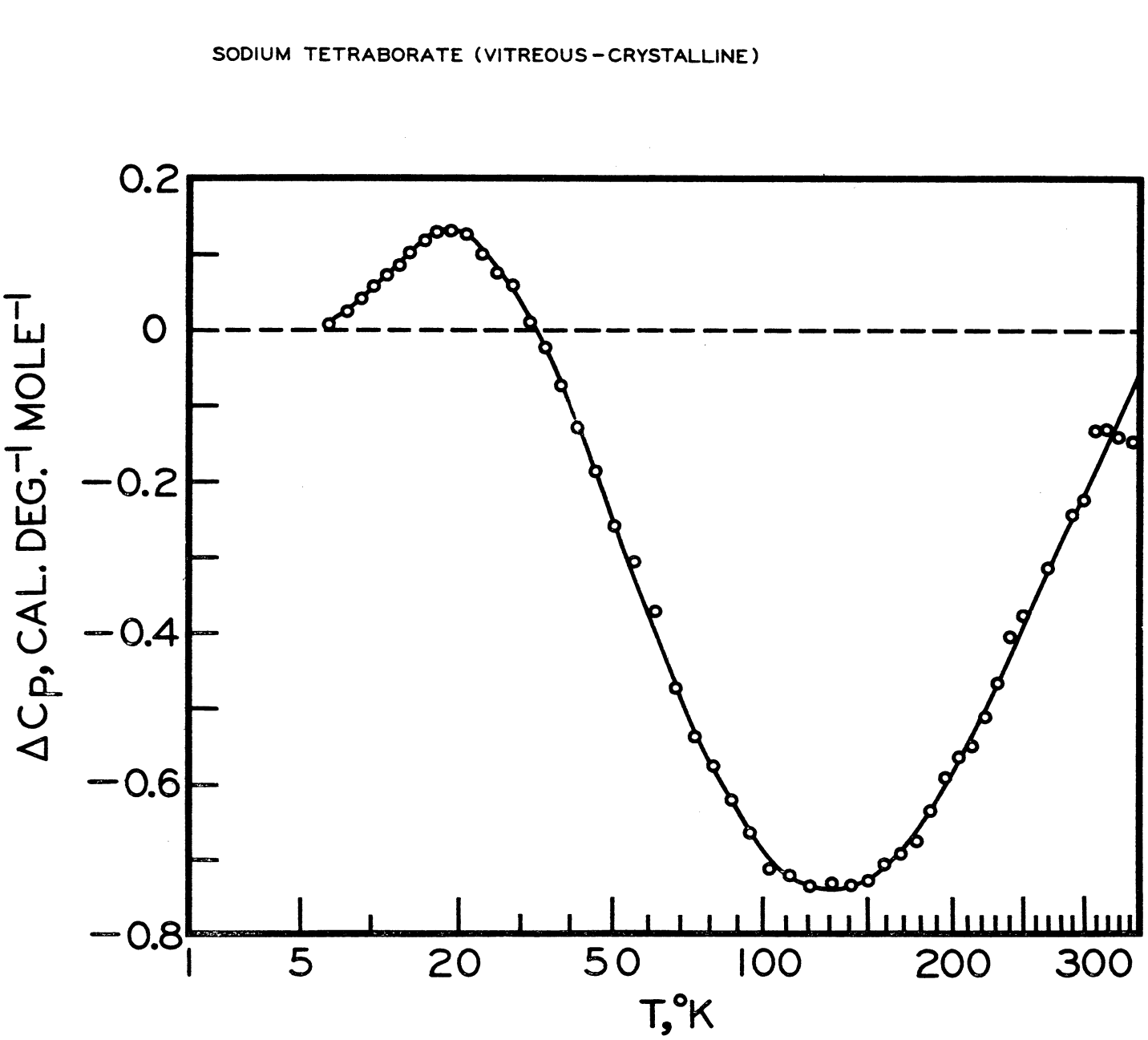

Fig. 6. Deviation plot for the heat capacities of sodium tetraborate forms. C_p = C_p, vitreous - C_p, crystalline.

into a cylindrical receiver 4-cm diam by 25 cm in length. This receiver communicated with the spherical one-liter reaction vessel below it through a coaxial Pyrex capillary tube of 0.9-mm ID and 4-cm length. After evacuation of the sodium for 20 hr (while the alcohol was refluxing), the sodium was fused to permit possible slag to float to the surface.

Five hundred milliliters of methanol were added to the reaction vessel, and molten sodium was then injected under a slight nitrogen pressure. The sodium flow into the reactor was regulated by partially withdrawing a close-fitting steel twist drill from the capillary connecting the sodium cylinder to the reactor. The position of the drill was manipulated with a coaxial steel shaft which extended from the shank of of the drill up through the sodium and out of the vacuum/nitrogen space through a vacuum-tight Teflon standard taper o-ring gland. The use of a drill made possible the penetration of a tip of solid sodium methoxide which occassionally formed on the reactor side of the capillary. The rate of addition of the sodium was limited by the capability of the exit tube reflux condenser to dissipate the heat of the reaction. The hydrogen left the exit tube via a mercury-seal-bubbler.

The excess methanol was removed by continuous evacuation over several days as the temperature was gradually increased to 100° to decompose any dialcoholate ($NaOCH_32CH_3OH$) present. The product was subsequently exposed only to the anhydrous nitrogen atmosphere of the dry box for as short a time as possible.

Total alkali plus carbonate was determined by titration of weighed samples with standard acid to the methyl orange end-point yielding 99.87 ± 0.02% (as sodium methoxide). Total alkali was determined on additional weighed samples to the phenolphthalein end-point as 99.72 ± 0.01% (as sodium methoxide). The difference of the two titrations indicates the carbonate content to approximate 0.15%. No water or hydroxide was detected by high-sensitivity Karl Fischer reagent. Perhaps the best indication of the absence of traces of water or of methanol is the freedom of the heat-capacity curves of anomalous behavior near the fusion temperatures of these substances. Spectrochemical analysis confirmed the presence of less than 0.02% metallic contaminants.

Attempts to obtain macroscopic crystals were unsuccessful. The $NaOCH_3$ consisted of a fine, white powder. To increase the amount of material in the calorimeter and to improve the thermal conductivity, the material was pelleted into rods with rounded ends about 5 mm in diameter and 10 mm in length. The measurements were made on 39.8571 g (in vacuo) of sodium methoxide, the molecular weight of which was taken to be 54.026.

RESULTS OF HEAT-CAPACITY MEASUREMENTS ON SODIUM METHOXIDE

The heat-capacity determinations were made with the Mark I adiabatic cryostat in calorimeter W-9. The calorimeter was loaded in a dry box, evacuated under high vacuum and 2.8 cm of helium gas were added at 27° to aid in the establishment of thermal equilibrium. The original experimental values of the

molal heat capacity of sodium methoxide at the mean temperature of the runs are given in Table VII. Since the determinations are presented in chronological sequence, the approximate temperature increments can be readily inferred. Small corrections have been made for the finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.15°K.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table VIII. These heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K, 1% at 10°K, and 4% at 5°K. The heat capacity was extrapolated below 6°K with a T^3 function. The effect of nuclear spin is not included in the entropy and free-energy function. The estimated probable error in the entropy, heat content and free-energy function is 0.2% above 100°K, but to make the table internally consistent, some of the values are given to one more figure than is justified by the estimated probable error.

The measured heat capacities from 5 to 70° are plotted in Fig. 7 together with an estimate of the "excess" heat capacity near 34° obtained by interpolating the temperature dependence of the Debye theta over the anomalous range. The molal enthalpy and entropy increments associated with this anomaly of unknown origin are 11.5 cal $mole^{-1}$ and 0.43 cal $mole^{-1}$ deg^{-1}, respectively.

DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF AMMONIA TRIBORANE*

The desirability of data on the thermal and thermodynamic properties of a material with as many technological possibilities and fundamentally interesting physical properties as ammonia triborane needs no argument.

The preparation of ammonia triborane was reported by Parry and Kodama[26] in 1957. It is, unfortunately, rather difficult to prepare in high purity on a fairly large scale at the present time and is sufficiently unstable to require some care in its handling.

Very little information is presently available concerning the physical properties of this interesting compound. Nordman, Reimann, and Peters[27] have made a single crystal x-ray diffraction study to elucidate its structural and crystallographic properties. They find that the $NH_3B_3H_7$ molecule contains a triangle of boron atoms with one side only slightly shorter than the other two.

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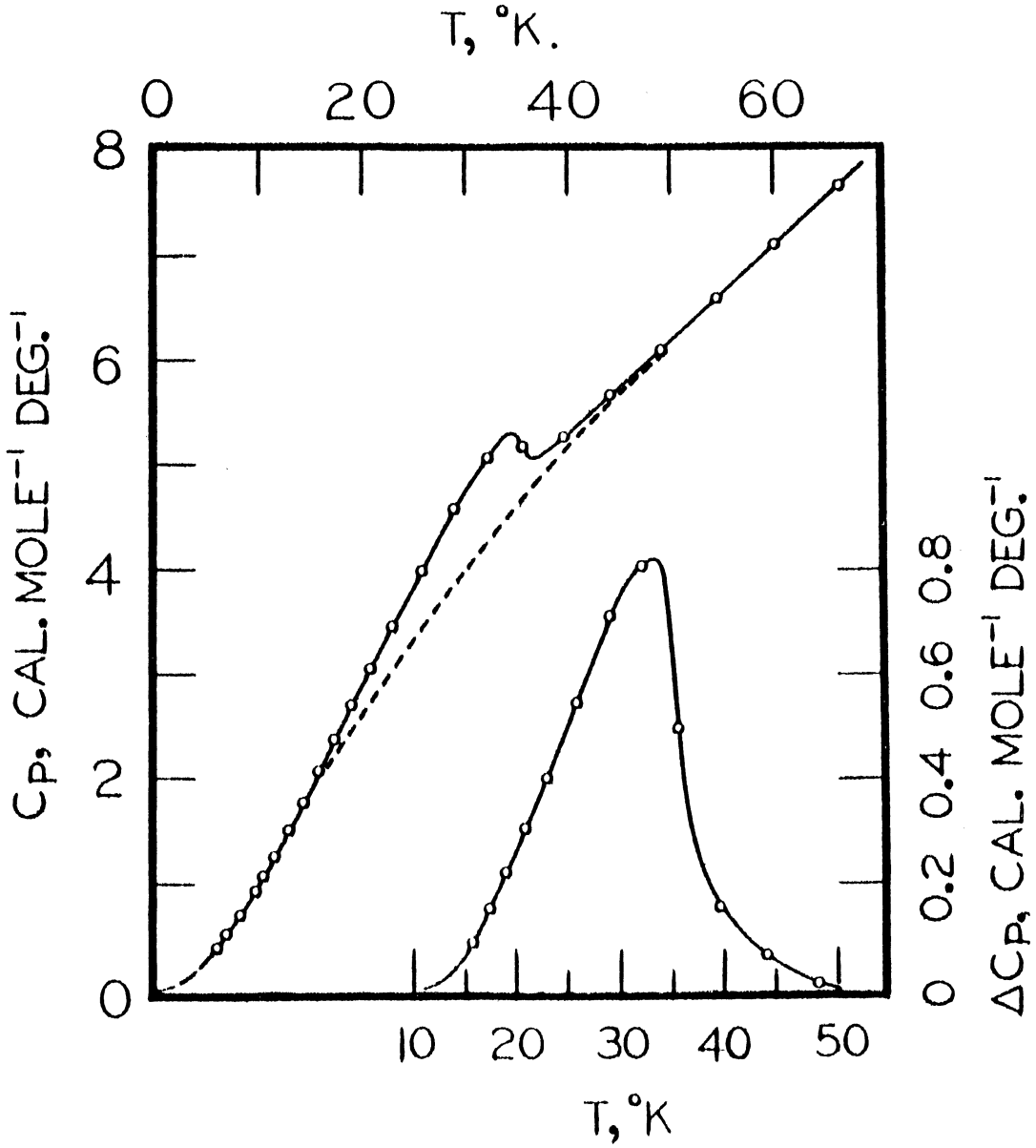

Fig. 7. Molal heat capacity of sodium methoxide. Experimental heat capacities are plotted and resolved into the lattice contribution (dashed curve) and the anomalous portion (inset).

TABLE VII

MOLAL HEAT CAPACITY OF SODIUM METHOXIDE (IN CAL/DEGREE)

T, °K	C_p	T, °K	C_p	T, °K	C_p
5.84	0.41	39.69	5.266	177.95	13.76
6.74	0.53	44.20	5.659	187.57	14.03
8.14	0.71	49.22	6.105	197.05	14.27
9.65	0.96	54.53	6.590	206.37	14.49
7.92	0.76	60.23	7.114	215.62	14.72
8.92	0.81	66.45	7.682	218.71	14.79
10.16	1.05	72.62	8.203	228.60	15.03
11.50	1.260	79.33	8.773	238.62	15.25
12.94	1.517	86.88	9.390	248.52	15.48
14.27	1.777	94.52	9.937	258.24	15.71
15.85	2.079	101.56	10.38	268.09	15.89
17.41	2.387	108.92	10.86	278.11	16.13
19.02	2.707	117.64	11.36	288.23	16.38
20.83	3.063	127.63	11.88	298.40	16.55
22.99	3.464	138.03	12.35	308.44	16.86
25.86	3.994	148.20	12.77	318.46	17.10
28.93	4.570	158.20	13.14	328.73	17.23
32.15	5.062	168.15	13.41	339.41	17.48
35.66	5.173				

TABLE VIII

MOLAL THERMODYNAMIC FUNCTIONS OF SODIUM METHOXIDE

T, °K	C_p cal/deg	S° cal/deg	$(H^\circ - H_0^\circ)$, cal	$-(F^\circ - H_0^\circ)/T$, cal/deg
5	(0.318)	(0.106)	(0.40)	(0.026)
10	1.002	0.500	3.50	0.150
15	1.915	1.074	10.73	0.359
20	2.895	1.759	22.75	0.621
25	3.837	2.507	39.60	0.923
30	4.799	3.289	61.13	1.251
35	5.160	4.067	86.38	1.599
40	5.282	4.762	112.40	1.952
45	5.728	5.408	139.87	2.300
50	6.177	6.035	169.63	2.642
60	7.091	7.242	235.96	3.309
70	7.977	8.402	311.32	3.954
80	8.831	9.523	395.39	4.581
90	9.615	10.609	487.7	5.190
100	10.305	11.659	587.4	5.785
110	10.925	12.671	693.5	6.366
120	11.489	13.646	805.6	6.932
130	11.990	14.585	923.1	7.484
140	12.438	15.490	1045.2	8.024
150	12.840	16.362	1171.7	8.551
160	13.197	17.203	1301.9	9.066
170	13.520	18.013	1435.5	9.569
180	13.821	18.795	1572.2	10.060
190	14.098	19.549	1711.8	10.539
200	14.353	20.279	1854.1	11.009
210	14.593	20.985	1998.8	11.467
220	14.828	21.669	2145.9	11.915
230	15.058	22.333	2295.4	12.353
240	15.285	22.979	2447.1	12.783
250	15.511	23.608	2601.1	13.204
260	15.736	24.220	2757.3	13.615
270	15.960	24.818	2915.8	14.019
280	16.189	25.403	3076.5	14.415
290	16.417	25.975	3239.5	14.804
300	16.645	26.536	3404.9	15.186
350	17.722	29.185	4264.5	17.001
273.16	16.031	25.004	2966.3	14.145
298.16	16.604	26.433	3374.3	15.116

The NH_3 group is attached to the boron atom opposite the shortest boron-boron bond and is pointed at about a 65° angle out of the plane of the boron atoms. They also found evidence of a structural transformation taking place below room temperature, but were not able to establish the temperature of the transition. We find that the transition takes place at 297.10°K and that it is an unusually entropic one.

PREPARATION OF AMMONIA TRIBORANE

The ammonia triborane was prepared by the method of G. Kodama.[26] Tetraborane and tetrahydropyran were reacted at a temperature of about -120°C to moderate the reaction:

$$2\ B_4H_{10} + 2\ \underline{CH_2(CH_2)_4O} \rightarrow 2\ \underline{CH_2(CH_2)_4O}{:}B_3H_7 + B_2H_6.$$

After excess tetrahydropyran was removed, the tetrahydropyran triborane was then reacted in ethyl ether with ammonia at -78°C.

$$\underline{CH_2(CH_2)_4O}{:}B_3H_7 + NH_3 \rightarrow NH_3B_3H_7 + \underline{CH_2(CH_2)_4O}.$$

The excess ammonia, ethyl ether, and displaced tetrahydropyran were removed at room temperature. The product was dissolved in benzene and removed from the reactor. It was subsequently precipitated by addition of methylcyclohexane to the solution and was filtered under a nitrogen atmosphere. Further purification of the product was achieved by dissolving it in benzene, filtering the solution, and precipitating the ammonia triborane with a large excess of methylcyclohexane. The product was then dissolved in toluene and recrystallized at -95°C. The product was filtered again in an anhydrous nitrogen atmosphere, and the adsorbed toluene was removed by evacuating for two hours under high vacuum. The sample was stored under vacuum at -196°C until it was used. The yield of crude ammonia triborane was between 70 and 80% of the theoretical based on the tetraborane used. The yield of the finally purified product was approximately 50% of theoretical.

Chemical analyses for nitrogen, boron, and active hydrogen were made with the following results: N_2, 24.8% (theoretical, 24.9%); B, 57.4% (theoretical, 57.2%); and active H_2, 12.47% (theoretical, 12.46%). There is every indication then that the product was 99.8% pure. The absence of the toluene used as a recrystallizing solvent is established by the absence of a hump in the heat capacity curve at or near the melting point of toluene.

The preparation was made by J. Carter and analyzed by him. The details of the large scale preparation will be presented elsewhere.[28]

THE RESULTS OF THE HEAT-CAPACITY MEASUREMENTS ON AMMONIA TRIBORANE

The original experimental values of the molal heat capacity of the sample of ammonia triborane weighing 15.085 grams (vacuo) are presented in chronological sequence together with the mean temperature of the individual runs in Table IX 2nd in Fig. 8. These data have been corrected to represent true heat capacities by applying a curvature correction for the finite temperature increments actually used in the measurements. The size of these temperature increments can be inferred in general from the mean temperatures of the adjacent data points. The results are expressed in terms of a defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.15°K and the gram formula weight of ammonia triborane was taken to be 56.548 g.

The molal heat capacity and the thermodynamic functions derived from the heat capacity data are listed at rounded temperatures in Table X. These heat-capacity values were read from a smooth curve through the experimental points and they are estimated to have a probable error of approximately 0.1% above 25°, 1% at 14°K increasing to about 5% at 5°K. The heat capacity was extrapolated below 5°K using a Debye function. The effect of nuclear spin and of mixing of isotopes is not included in the entropy and free-energy function. The estimated probable error in the entropy, heat content, and free-energy function is 0.1% above 100°K, but to make the table internally consistent and to permit accurate interpolation, some of the thermodynamic values are given to one more figure than is justified by the estimated probable error.

In addition to the numerical quadrature of points read from the smooth curve, the data of Table IX were fed into a program on the IBM 650 calculator which independently evaluated the heat capacity at rounded temperatures, and which performed the integration leading to the thermodynamic functions. In this manner a completely independent check has been obtained on the numerical values, within the precision indices indicated in the above paragraph.

Because of the slow rate of achievement of temperature equilibrium in the transition region, it was not possible to delineate heat capacity as a function of temperature with great exactitude. To evaluate more precisely the thermodynamic functions, therefore, a number of energy inputs of varying magnitude were made in the transition region to obtain the enthalpy and entropy increments. We have designated the form of the material stable below the 297.10°K transition temperature as the α-form and that stable above this temperature as the β-form.

It will be noted in Table IX that the heat capacity near the transition temperature approximates 3×10^3 cal $mole^{-1}$ deg^{-1} suggesting very strongly that the transition is indeed a first-order one. However, there is a considerable pre-transitional rise in heat capacity. This fact makes rather difficult the evaluation of the entropy and enthalpy increments on transition. To obtain these values it is necessary to obtain a "normal" heat-capacity curve for the substance in the absence of the aforesaid transition over a rather broad range. As a zeroth approximation to this "background" heat capacity, we have simply

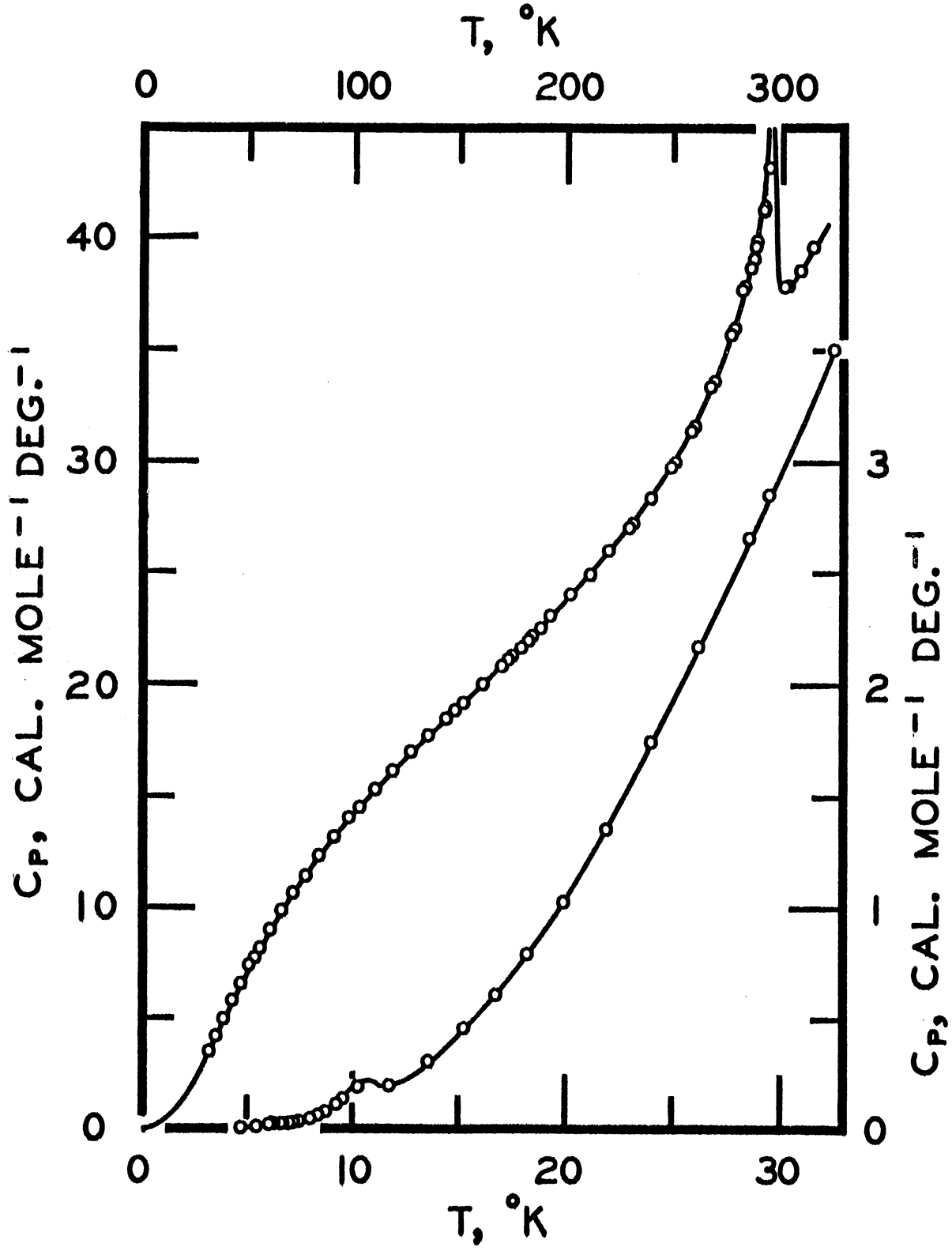

Fig. 8. Low-temperature heat capacity of ammonia triborane.

TABLE IX

MOLAL HEAT CAPACITY OF AMMONIA TRIBORANE

T,°K	C_p
Series I	
147.26	18.81
172.38	21.09
181.38	21.96
174.40	21.27
183.09	22.15
192.18	23.03
201.77	23.97
211.04	24.94
219.92	25.96
229.26	27.06
230.71	27.20
239.61	28.36
249.06	29.76
258.44	31.36
267.76	33.35
276.85	35.63
286.03	38.62
293.84	(84.)
297.03	(2130)
Series II	
282.75	37.70
288.93	39.86
294.46	(69.)
298.23	(400)
303.26	37.86
308.78	38.54
314.95	39.58
Series III	
283.79	37.78
288.27	39.62
291.79	41.27
295.20	43.17
297.00	(2660)
297.20	(2660)
298.87	(72.)
302.36	37.81
Series IV	
53.57	7.743
56.07	8.185
60.63	8.962
66.06	9.831
71.45	10.595
77.20	11.388
83.50	12.291
90.49	13.162
97.71	13.969
102.34	14.465
109.99	15.266
118.11	16.09
126.66	16.92
134.87	17.68
143.03	18.42
151.59	19.20
160.51	20.01
169.54	20.82
178.63	21.66
187.68	22.57
Series V	
5.49	0.012
6.80	0.026
7.35	0.033
6.38	0.018
7.16	0.028
8.03	0.048
8.76	0.082
9.57	0.140
6.13	0.019
4.79	0.008
5.47	0.011
6.06	0.017
6.72	0.021
7.52	0.035
8.40	0.066
9.25	0.116
10.21	0.195
11.72	0.199
13.54	0.306
15.20	0.453
16.71	0.609
18.16	0.790
19.82	1.024
21.84	1.351
23.95	1.741
26.14	2.170
28.52	2.656
29.44	2.847
32.49	3.500
35.74	4.185
39.34	4.974
43.19	5.771
47.19	6.569
51.49	7.385
56.09	8.180
86.56	(12)
153.87	(19)
241.15	(26)
297.31	(107)
Series VI	
250.73	30.02
260.05	31.59
269.49	33.59
278.69	35.98
287.35	39.13
292.57	41.51
298.74	(148)
296.38	(213)
297.09	(2270)
297.20	(3150)

TABLE X

MOLAL THERMODYNAMIC FUNCTIONS OF AMMONIA TRIBORANE

T, °K	C_p cal / deg mole	S° cal / deg mole	$H^\circ - H_0^\circ$ cal / deg mole	$\frac{H^\circ - H_0^\circ}{T}$ cal / deg mole	$-\frac{(F^\circ - H_0^\circ)}{T}$ cal / deg mole
5	(0.009)	(0.003)	(0.01)	(0.002)	(0.001)
10	0.176	0.036	0.29	0.029	0.007
15	0.435	0.140	1.60	0.107	0.033
20	1.052	0.342	5.19	0.260	0.082
25	1.946	0.668	12.59	0.504	0.164
30	2.967	1.112	24.83	0.828	0.284
35	4.027	1.649	42.33	1.210	0.439
40	5.109	2.258	65.18	1.629	0.629
45	6.135	2.919	93.31	2.074	0.845
50	7.102	3.616	126.43	2.529	1.087
60	8.857	5.070	206.41	3.440	1.630
70	10.412	6.551	302.9	4.327	2.224
80	11.820	8.035	414.2	5.177	2.858
90	13.080	9.502	538.8	5.986	3.516
100	14.215	10.940	675.3	6.753	4.187
110	15.27	12.344	822.8	7.480	4.864
120	16.27	13.716	980.5	8.171	5.545
130	17.23	15.056	1148.0	8.831	6.225
140	18.15	16.367	1324.9	9.464	6.903
150	19.06	17.650	1510.9	10.073	7.577
160	19.96	18.909	1706.0	10.662	8.247
170	20.86	20.146	1910.1	11.236	8.910
180	21.82	21.365	2123.4	11.797	9.568
190	22.82	22.571	2346.6	12.351	10.220
200	23.80	23.767	2579.7	12.898	10.869
210	24.83	24.953	2822.8	13.442	11.511
220	25.95	26.133	3076.7	13.985	12.148
230	27.12	27.313	3342.0	14.530	12.783
240	28.41	28.494	3619.6	15.082	13.412
250	29.90	29.683	3911.0	15.644	14.039
260	31.57	30.888	4218.3	16.224	14.664
270	33.76	32.120	4544.6	16.832	15.288
280	36.52	33.396	4895.5	17.484	15.912
290	40.24	34.740	5278.4	18.202	16.538
295	43.01	35.451	5486.6	18.598	16.853
300	38.22	39.895	6807.8	22.693	17.202
273.15	34.55	32.516	4652.2	17.032	15.484
298.15	(50)	(39.627)	(6727)	(22.562)	(17.065)

interpolated a smooth curve which is tangent to the observed heat capacities at 250°K and again at 310°K. The difference in the integral of the enthalpy along the observed curve minus that along the interpolated curve from 250 to 310°K indicates an enthalpy increment of transition of 1233 cal $mole^{-1}$ and the corresponding transitional entropy increment is 4.15 cal $mole^{-1}$ deg^{-1}. It is interesting to note that the transitional entropy increment approximates rather closely the value R ln 8 = 4.13 cal $mole^{-1}$ deg^{-1}. This increment is consistent with a tentative interpretation of the possible configurations of the ammonia triborane molecule in the β-form.

The temperature of the α-β transformation was determined as 297.10 ± 0.04° after a drift toward equilibrium of several hours duration. Attempts to establish the transition temperature by cooling curves were unsuccessful; the sample usually supercooled as much as 5° before undergoing the β → α transition and failed to reach the equilibrium temperature.

A thermal anomaly of unknown origin was also observed in the vicinity of 11°K. This appears to be a rather broad transformation with an entropy increment of about 0.01 cal $mole^{-1}$ deg^{-1} and is thus quite insignificant.

DETERMINATION OF HEAT CAPACITY OF SODIUM HYDRIDE

PREPARATION AND PURITY OF SODIUM HYDRIDE

Although for the study of the thermodynamic properties of sodium hydride, as with any other substance, it would be desirable to have macroscopic crystals, we were unsuccessful in preparing macroscopic crystals in sufficient yield to make heat-capacity measurements possible on them. Several attempts to prepare sodium hydride by direct combination between hot sodium at 400 to 550°C were unsuccessful. And after considerable study and analysis, it was decided to take advantage of commercial preparations of the highest quality available and to purify these further. Although approximately seven samples of sodium hydride from several suppliers were tried, the sample actually used in the calorimeter was obtained from a sodium hydride dispersion of claimed 99.9+% purity obtained from Metal Hydrides, Inc., at Beverly, Massachusetts. This material was obtained in the form of a 25% dispersion in a mineral oil designated at Bayol 85. To refine the sodium hydride and separate it from the oil in which it was dispersed, extraction with rather volatile solvents such as hexane and normal pentane was used repeatedly. Research-grade, carefully dried Phillips Petroleum Co. hydrocarbons were used in a special, enclosed, fitted glass-funnel— drying-chamber similar to one shown by Sayre and Beaver.[29] The sodium hydride dispersion was placed in the funnel within the nitrogen atmosphere of the dry box, and all possible filtrate was drawn off by mechanical evacuation through the fitted glass plate. The funnel with its standard taper connections was then connected to a high-vacuum line;

the anhydrous solvents were added, and the stopcocks were closed, isolating the funnel-drying chamber which was then removed and shaken. The glass balls in the drying chamber effectively broke up any packed hydride allowing effective washing of the hydride. The hexane was then removed on the vacuum line by flushing with a slight pressure of anhydrous nitrogen. Repeated washings, shakings, and reattachment of the funnel-drying chamber were made until no further mineral oil was obtained in the washings. The last traces of hexane and pentane were removed by evacuation under high vacuum. Following analysis, the sample was transferred in the anhydrous nitrogen atmosphere of the dry box to the calorimeter with as much dispatch as possible and the small calorimeter cover sealed into place. The calorimeter was then transferred to the usual loading-high-vacuum line, the requisite amount of helium added after evacuation, and the calorimeter sealed as previously described.

We determined the purity of the resultant sodium hydride by chemical analysis. The sodium-to-hydrogen ratio was determined by decomposing a sample in water within a hydrogen atmosphere. The amount of hydrogen liberated was compared to the basicity of the resulting solution. Sodium metal was used in checking the effectiveness of this procedure. Inert contaminants were proved to be absent by decomposing the sample in water and titrating the resulting alkalinity. Determination of free sodium was made by method of Eddy, Messner, and Weber[30] and carbonate was determined by a modification of the method of Frazer and Schoenfelder.[31] Neither sodium nor carbonate were present to the extent of more than a few hundredths of one percent. The absence of any mineral oil in the resultant product was established by dissolving large quantities of the hydride and examining the resultant solution for the oily layer. A further proof of the absence of hydrocarbon contaminants, both mineral oil and hexane, may be argued from the absence of anomalies at the melting temperatures of these substances in the final heat capacity measurements.

RESULTS OF LOW-TEMPERATURE HEAT-CAPACITY DETERMINATION ON SODIUM HYDRIDE

The results of the low-temperature heat-capacity determinations are presented in Table XI and shown also in Fig. 9. The same conventions and conditions apply to these data as have been used generally throughout this report. It is interesting to note that there is no evidence of any thermal anomaly over the entire temperature range of the measurements, nor are there small humps indicating contamination of the sample by hydrocarbon solvents.

It is interesting to compare these results of considerably higher precision with those of Sayre and Beaver over the rather limited temperature range from 60 to 90°K which they measured. We find that our heat capacities differ from theirs on the average by approximately 3%, but the trend at the upper end of their range is somewhat different. The trend of our curve is indeed more consistent with their theoretical calculation but both sets of data are approximately 20% lower than their theoretical curve. This suggests the desirability of re-examining the bases of their theoretical calculations and also of extending the work on sodium deuterides over a much larger temperature range than

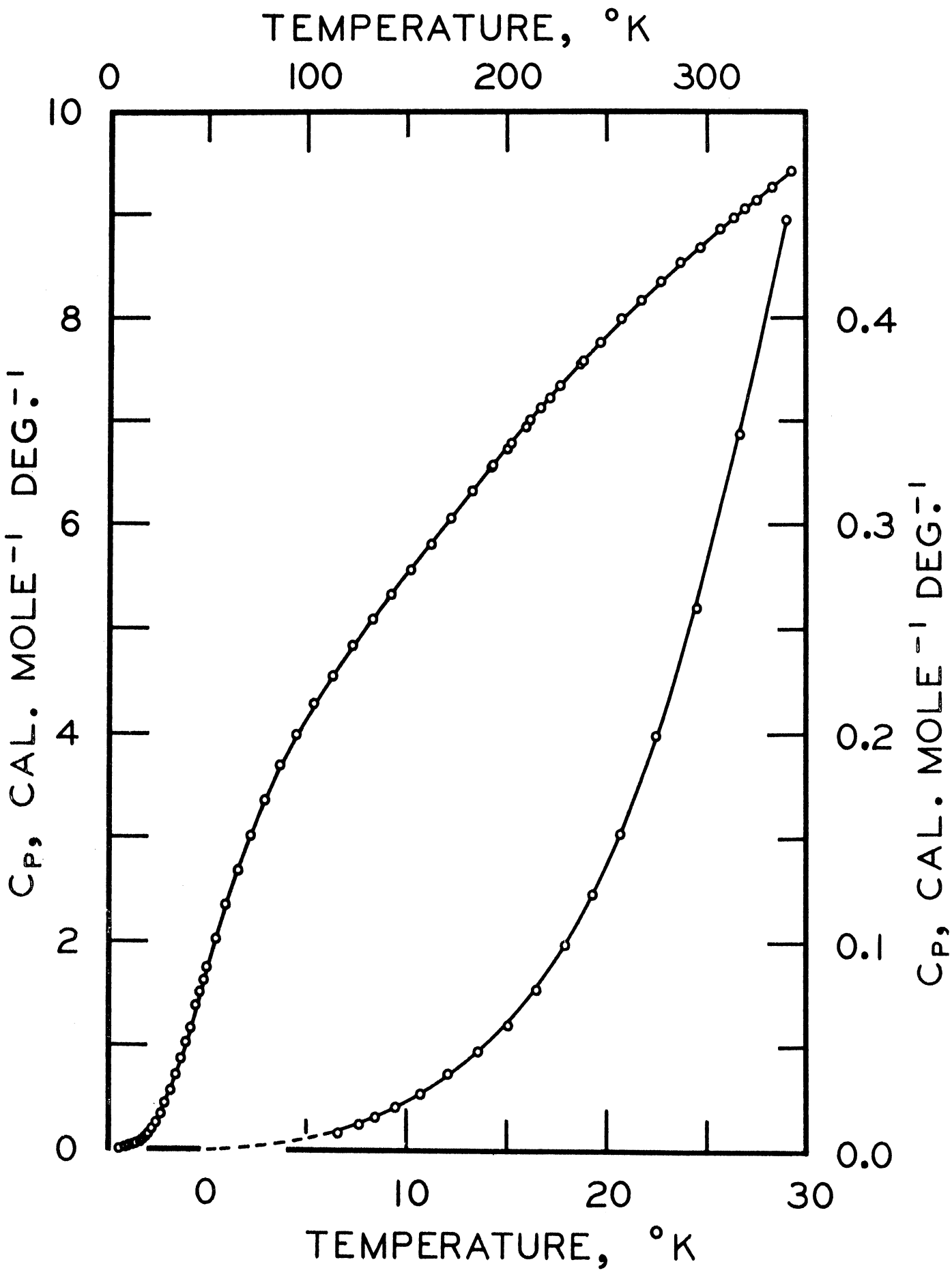

Fig. 9. Molal heat capacity of sodium hydride.

TABLE XI

MOLAL HEAT CAPACITY OF SODIUM HYDRIDE
(in cal mole^{-1} deg^{-1})

T, °K	Cp	T, °K	Cp	T, °K	Cp
Series I		13.52	0.048	78.57	3.361
		15.02	0.061	86.13	3.691
216.35	7.130	16.45	0.077	94.04	3.985
226.05	7.346	17.89	0.099	103.10	4.280
236.45	7.556	19.22	0.123	112.22	4.552
246.68	7.759	20.61	0.152	122.69	4.841
256.75	7.967	22.40	0.199	132.57	5.100
266.68	8.143	24.45	0.264	142.11	5.337
276.44	8.328	26.59	0.344	151.83	5.572
286.29	8.492	28.92	0.447	161.81	5.809
296.25	8.668	31.40	0.570	171.82	6.066
306.21	8.848	34.08	0.722	181.88	6.333
326.01	9.182	36.67	0.874	191.87	6.557
335.81	9.326	39.04	1.026	201.69	6.789
345.62	9.528	41.55	1.186	211.52	7.014
		44.60	1.389	200.00	6.737
Series II		48.26	1.634	209.42	6.953
		46.29	1.502	221.22	7.232
6.54	0.009	49.93	1.745	238.01	7.583
7.62	0.012	54.30	2.028	313.09	8.960
8.31	0.015	59.41	2.346	318.70	9.042
9.36	0.020	65.06	2.679	324.27	9.133
10.61	0.028	71.48	3.025	331.94	9.254
12.01	0.036			341.68	9.412

they did. (A comparison of our results with theirs is shown in Fig. 10.)

The thermodynamic functions of sodium hydride have been computed by a numerical quadrature of the heat-capacity data as previously described in this report and tabulated in Table XII.

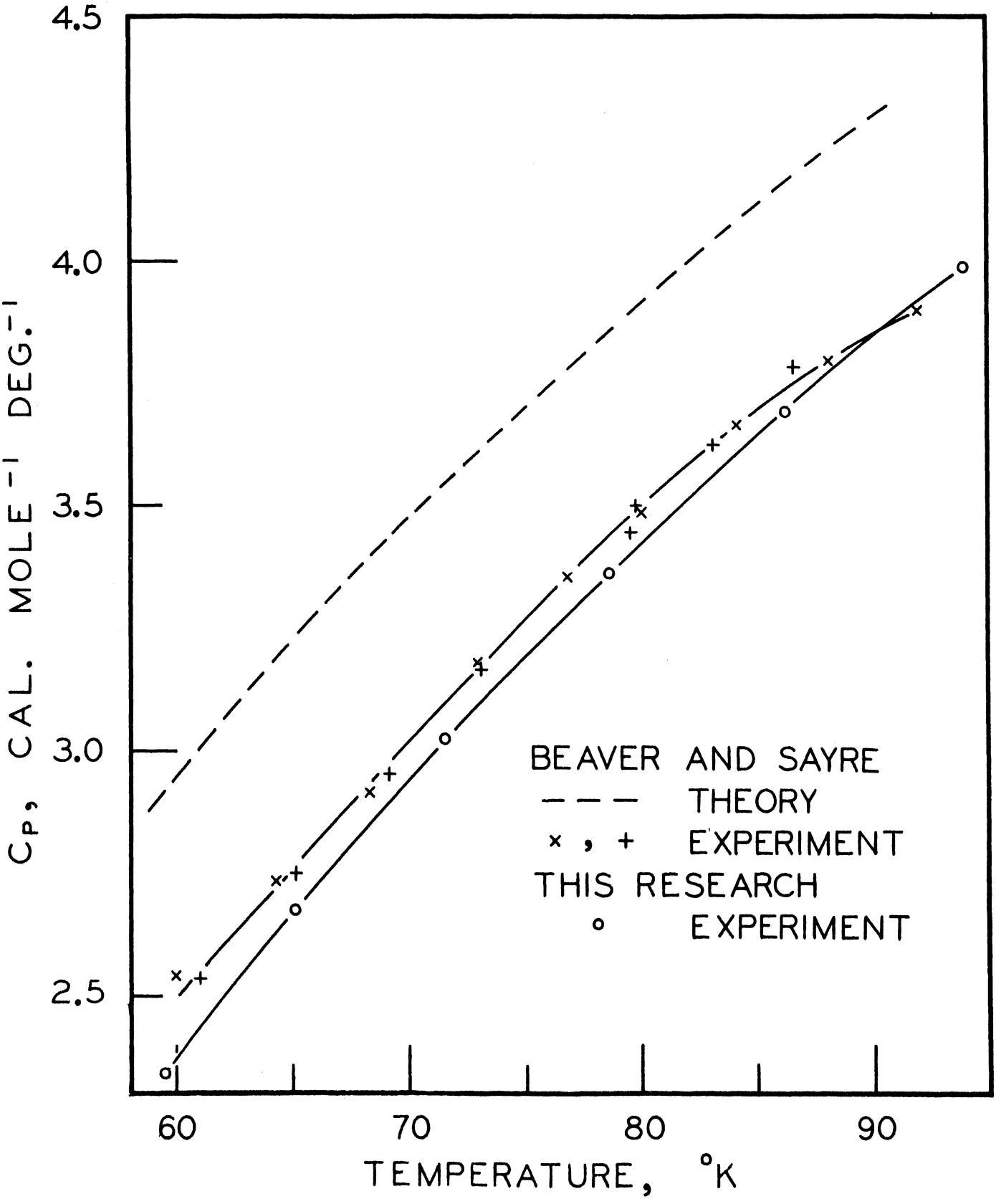

Fig. 10. Comparison of heat capacities of sodium hydride with results of Sayre and Beaver.

TABLE XII

MOLAL THERMODYNAMIC FUNCTIONS
OF SODIUM HYDRIDE

T°, K	C_s cal/deg	$(S^\circ - S^\circ_0)$ cal/deg	$(H^\circ - H^\circ_0)$ cal	$(H^\circ - H^\circ_0)/T$ cal/deg	$-(F^\circ - H^\circ_0)/T$ cal/deg
10	0.0240	0.0080	0.060	0.0060	0.0020
15	0.0604	0.0240	0.263	0.0175	0.0065
20	0.1386	0.0508	0.739	0.0369	0.0139
25	0.2830	0.0959	1.764	0.0706	0.0253
30	0.4991	0.165	3.692	0.123	0.042
35	0.7752	0.262	6.861	0.196	0.066
40	1.087	0.386	11.506	0.288	0.098
45	1.416	0.533	17.753	0.395	0.138
50	1.750	0.700	25.669	0.513	0.187
60	2.382	1.075	46.369	0.773	0.302
70	2.944	1.486	73.074	1.044	0.442
80	3.432	1.912	105.01	1.313	0.599
90	3.839	2.340	141.44	1.572	0.768
100	4.182	2.763	181.59	1.816	0.947
110	4.488	3.176	224.95	2.045	1.131
120	4.769	3.579	271.25	2.260	1.319
130	5.033	3.971	320.27	2.464	1.507
140	5.286	4.353	371.88	2.656	1.697
150	5.528	4.726	425.95	2.840	1.886
160	5.766	5.091	482.42	3.015	2.076
170	6.013	5.448	541.3	3.184	2.264
180	6.262	5.798	602.7	3.348	2.450
190	6.509	6.143	666.6	3.508	2.635
200	6.748	6.483	732.8	3.664	2.819
210	6.980	6.818	801.5	3.817	3.001
220	7.202	7.148	872.4	3.965	3.183
230	7.418	7.473	945.5	4.111	3.362
240	7.624	7.793	1020.7	4.253	3.540
250	7.825	8.109	1098.0	4.392	3.717
260	8.019	8.419	1177.2	4.528	3.891
270	8.206	8.725	1258.3	4.661	4.064
280	8.387	9.027	1341.3	4.790	4.237
290	8.561	9.325	1426.0	4.917	4.408
300	8.732	9.618	1512.5	5.042	4.576
350	9.541	11.026	1969.6	5.628	5.398
273.15	8.264	8.821	1284.3	4.702	4.119
298.15	8.700	9.564	1496.4	5.019	4.545

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