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

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TABLE OF CONTENTS

	Page
ABSTRACT	iii
OBJECTIVE	iii
INTRODUCTION	1
THE CRYOSTAT AND CALORIMETER	1
THE HEAT CAPACITY OF A STANDARD SAMPLE OF BENZOIC ACID	3
PREPARATION OF ANHYDROUS SODIUM METABORATE	3
HYGROSCOPICITY OF SODIUM METABORATE	4
HEAT CAPACITY OF ANHYDROUS CRYSTALLINE SODIUM METABORATE	5
BIBLIOGRAPHY	9
FIGURES	11

ABSTRACT

Adiabatic measurements of heat capacity have been made on sodium metaborate from about 6 to 350°K. No evidence of anomalous behavior was detected by these measurements. Values of the derived thermodynamic functions are given at rounded temperatures together with the smoothed heat-capacity data. Molal values at 298.16°K of the heat capacity at constant pressure, entropy, enthalpy increment, and free-energy function are: 15.76 cal deg^{-1}, 17.57 cal deg^{-1}, 2780 cal, and -8.25 cal deg^{-1}, respectively.

OBJECTIVE

To obtain chemical thermodynamic data and thermal properties on certain compounds over low- and high-temperature ranges.

INTRODUCTION

The heat capacity of sodium metaborate was determined for chemical thermodynamic purposes. These data permit the calculation of entropy, enthalpy, and free energies useful in the scientific thermochemistry and technical production of certain materials.

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,[1,2,3] sublimation pressures,[4] phase equilibria on the Na_2O-B_2O_3 system,[1] optical properties,[1,2,3] and structural studies and densities based on fragmentary X-ray diffraction data.[2,3,5,6]

THE CRYOSTAT AND CALORIMETER

The cryostat and electrical circuits employed for the heat-capacity measurements are very similar to the equipment described by Westrum, Hatcher, and Osborne.[7] 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 microvolts per millimeter at one meter 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 constants 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[8] 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 0.03° from 14 to 90°K, and within 0.05° from 90 to 373°K.

Essentially adiabatic conditions were achieved by surrounding the 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. For each compound, and the empty calorimeter, at least one series of points was obtained by means of continual runs from 5 to 350°K. During these runs no refrigerant was added to the helium tank after the helium supply had been exhausted, and the helium tank was allowed to warm up and follow the temperature of the calorimeter.

The calorimeter (laboratory designation W-9), 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 grams.

After the calorimeter was filled, weighed, and its top sealed in place with Cerroseal-35 solder,* it was quickly transferred from the dry box

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

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 Cerro-seal 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.

THE HEAT CAPACITY OF A STANDARD SAMPLE OF BENZOIC ACID

In order 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.[9] The heat capacities measured in our apparatus agree excellently with the values reported by the National Bureau of Standards.[10]

PREPARATION OF ANYHYDROUS SODIUM METABORATE

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

to 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, homogeneity, and good crystal development of the calorimetric samples.

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

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.[11,12,13,14,15]

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.[16,17,18,19]

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 stoichiometrically 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-gram 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 minutes after exposure, the

increase in apparent sample weight was 0.24%, at 100 minutes 0.77%, and after 11 hours 3.2%. The necessity of handling this material in an anhydrous atmosphere is readily apparent.

HEAT CAPACITY OF 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. 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 ice point was taken to be 273.16°K, and the gram molecular weight of sodium metaborate ($NaBO_2$) was taken as 65.811 grams. A calorimetric sample of 133.6378 grams (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 entropy, heat content, and free-energy function is 0.1% above 100°K, but in order 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.

The molal heat capacity and thermodynamic functions are extrapolated to the sodium metaborate melting point, 966°C (1239.2°K), and are listed at rounded temperatures in Table III. The formulae for the extrapolation of these functions are predicated on the basis of the method described by Shomate.[20] The equations for molal values (calories) of sodium metaborate using 300°K as a base temperature are:

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

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

and

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

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			

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF SODIUM METABORATE

T, °K	C_p, cal deg^{-1}	S^o, cal deg^{-1}	$H^o - H_0^o$, cal	$-(F^o - H_0^o)/T$, 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
273.16	15.08	16.224	2394.4	7.459
298.16	15.76	17.574	2780.0	8.250

TABLE III

EXTRAPOLATED MOLAL THERMODYNAMIC FUNCTIONS
OF SODIUM METABORATE

T, °K	C_p, cal deg^{-1}	S^o, cal deg^{-1}	$(H^o - H^o_0)$, kcal
400	18.3	22.6	4.52
500	20.5	26.9	6.46
600	22.8	30.9	8.63
700	24.9	34.6	11.0
800	27.1	38.0	13.6
900	29.2	41.3	16.4
1000	31.4	44.5	19.4
1100	33.5	47.6	22.7
1200	35.6	50.6	26.2
1239.2	36.5	51.8	27.5

The extrapolated values have an estimated error of 0.4% below 600°K and 3% at the melting point. However, as with all gross extrapolations, considerable uncertainty as to the validity of the extrapolation procedure is involved. These values, therefore, should be used with due caution as an approximation justified only by the absence of experimental determinations. This limitation is particularly obvious here because the extrapolation is extended over so long a range. No evidence for thermal transformations or anomalies was detected by Morey and Merwin[1] by thermal analysis between 350°K and the melting point.

The molal heat capacity of sodium metaborate is depicted in Fig. 3, and the apparent Debye characteristic temperature per gram atom computed on the basis of one mole equivalent to four gram atoms is diagrammed in Fig. 4.

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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

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

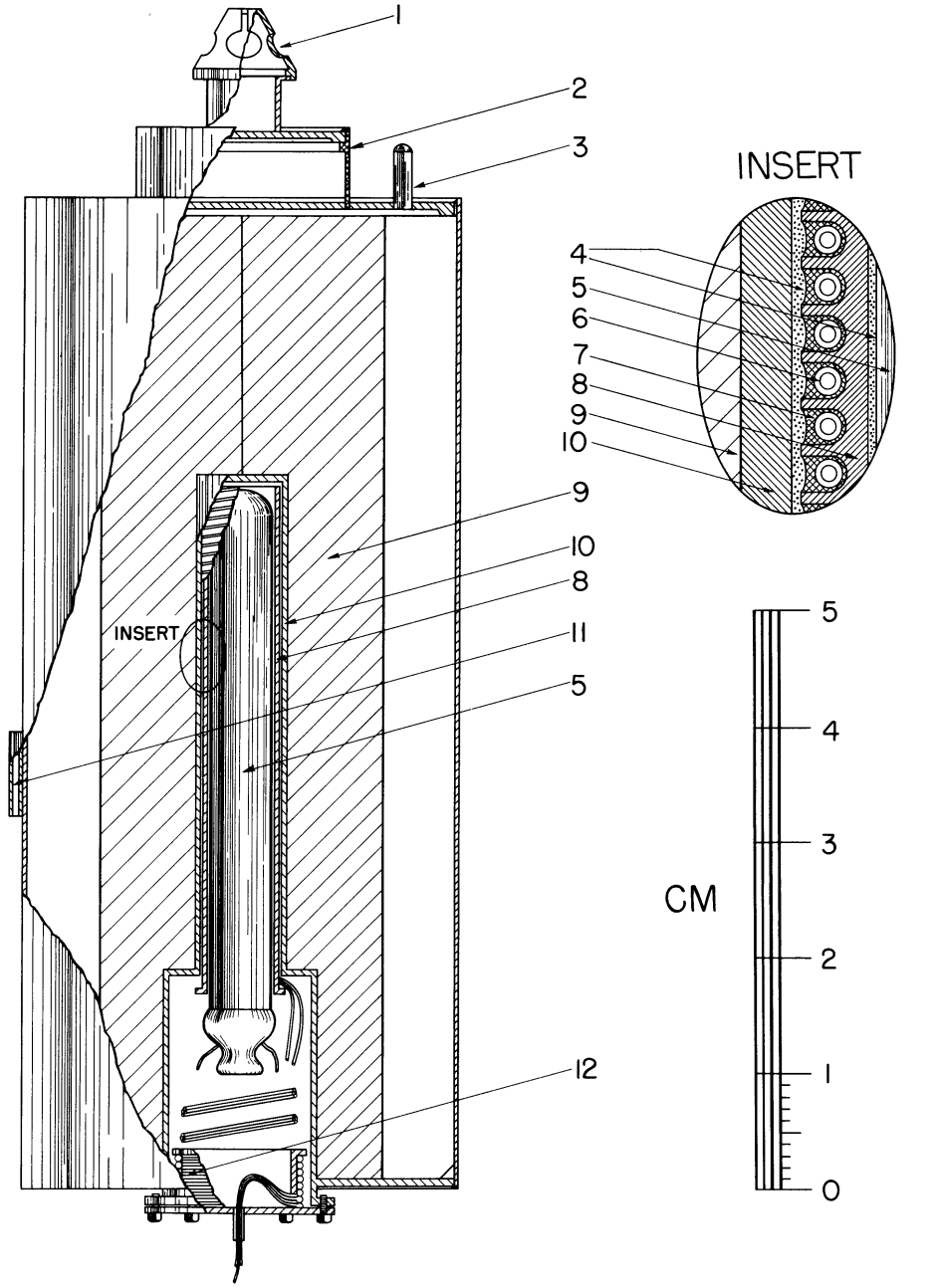

Fig. 2

W-6 CALORIMETER

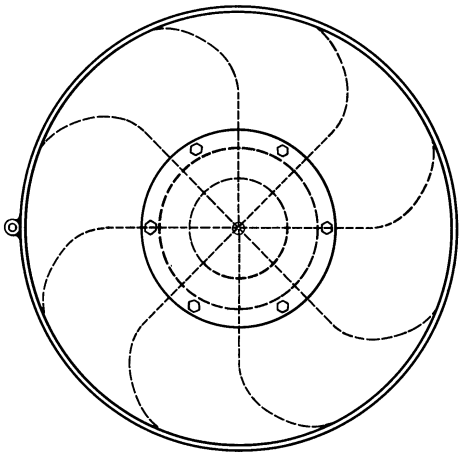

Fig. 3: Molal heat capacity of sodium metaborate as a function of Absolute temperature (6-350°K)

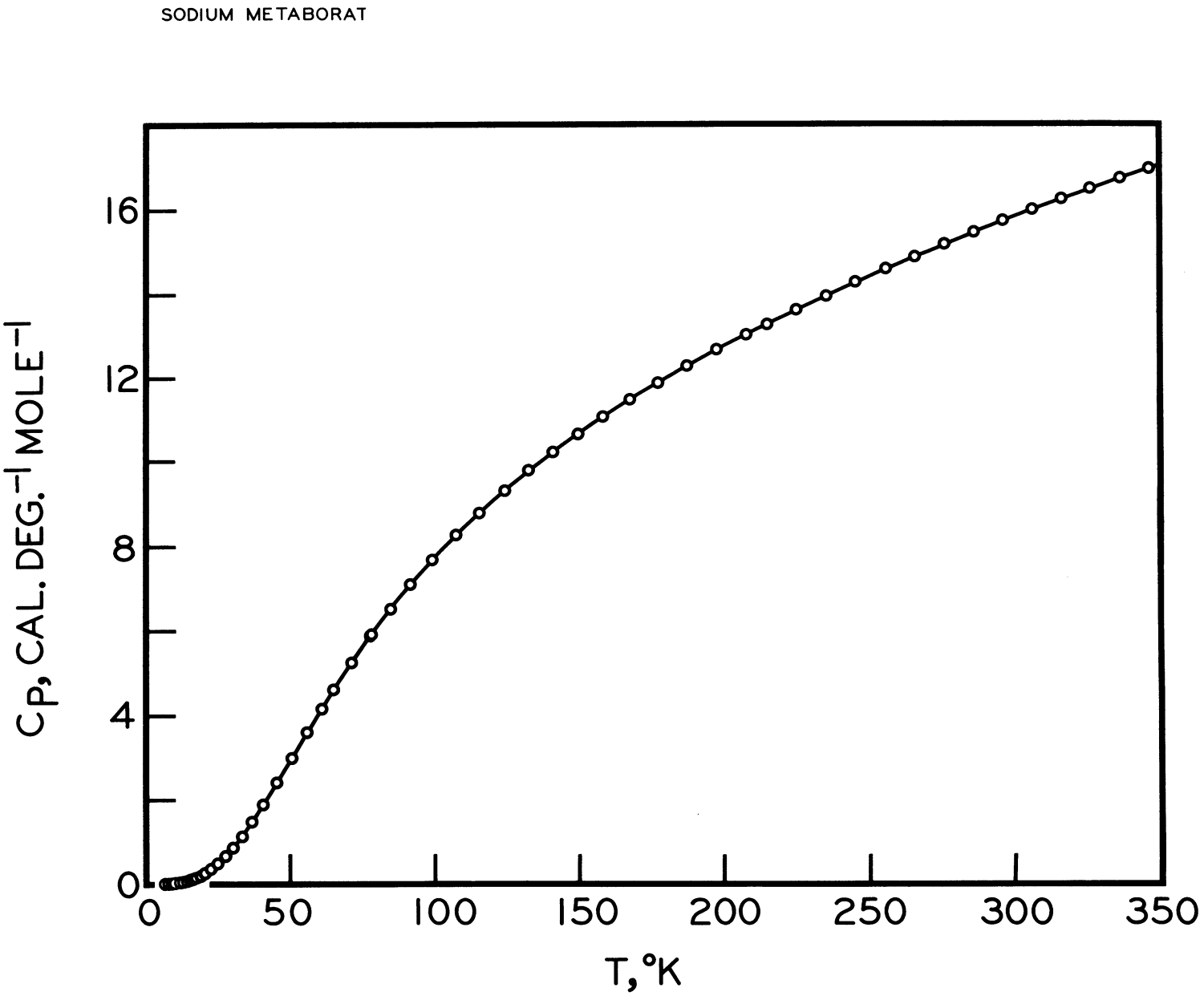
SODIUM METABORAT
C_P, CAL. DEG.$^{-1}$ MOLE^{-1}
0
4
8
12
16
0
50
100
150
200
250
300
350
T, °K

Fig. 3.

Fig. 4: Value of Debye Θ for sodium metaborate as a function of Absolute temperature

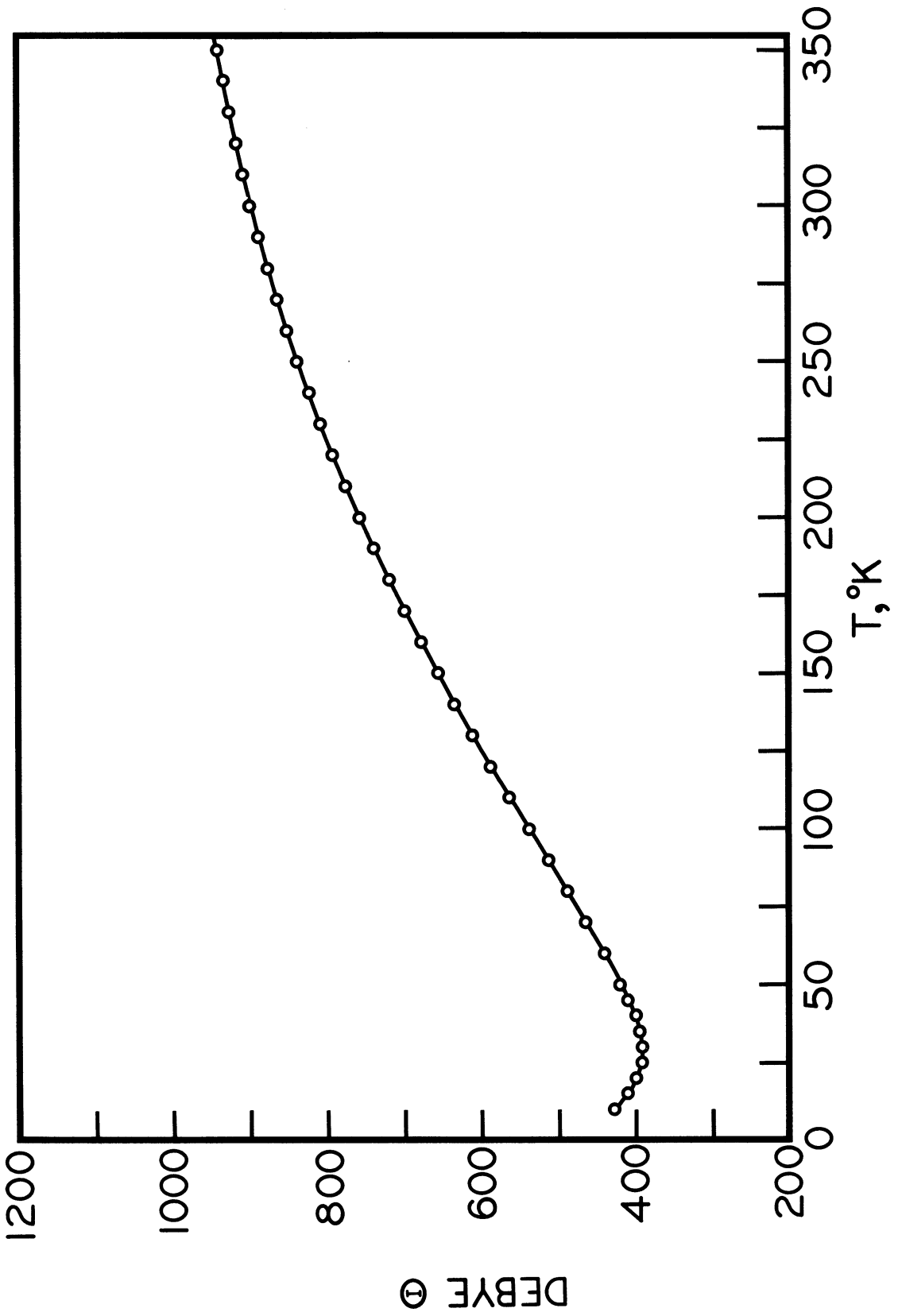
SODIUM METABORAT
DEBYE Θ
T, °K
1200
1000
800
600
400
200
0
50
100
150
200
250
300
350

Fig. 4