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DETERMINATION OF THE LOW-TEMPERATURE HEAT CAPACITY
OF ANHYDROUS AND VITREOUS SODIUM TETRABORATE

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ABSTRACT

We have prepared samples of high-purity anhydrous crystalline and vitreous sodium tetraborate ($Na_2B_4O_7$) and determined their heat capacity from about 6 to 350°K by adiabatic calorimetry. Values of the heat capacity and the derived thermodynamic functions have been computed and tabulated. Molal values at 298.16°K of the heat capacity at constant pressure, entropy, enthalpy increment ($H_T - H_0^O$), and free-energy function are: 44.64 cal deg^{-1}, 45.30 cal deg^{-1}, 7262 cal, and -20.94 cal deg^{-1}, respectively, for the crystalline modification. For the vitreous modification, the molal values at 298.16°K of the heat capacity at constant pressure, the entropy increment ($S_T^O - S_0^O$), and enthalpy increment ($H_T^O - H_0^O$), are: 44.42 cal deg^{-1}, 44.39 cal deg^{-1}, and 7127 cal, respectively.

OBJECTIVE

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

INTRODUCTION

Despite the use of borax and related materials in ceramic technology for many centuries and widespread utilization in current chemical technology, reliable thermodynamic data on alkali borates are relatively rare. This report presents low-temperature heat-capacity data on both crystalline and vitreous sodium tetraborate and the derived thermodynamic functions and thermochemical quantities computed therefrom.

PREPARATION AND ANALYSIS OF CRYSTALLINE SODIUM TETRABORATE

We use the designation sodium tetraborate to refer to the chemical composition $Na_2B_4O_7$, although a contrary usage is occasionally found (e.g., cf. Ref. 1). Data in the chemical literature on the physical properties of anhydrous and crystalline sodium tetraborate are concerned primarily with melting-point and phase-equilibrium studies[1] on the Na_2O-B_2O_3 systems. Two and possibly three distinct crystallographic phases of this material have been claimed.[1] The material prepared for this work is the alpha-form and is that ordinarily obtained and commercially available. No evidence for an enantiotropic inversion between the various forms has been found,[1] despite a careful search from below 500°C to the melting point. The rate of conversion (beta to alpha) is very slow below these temperatures, and the reverse transformation has not been observed.

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.[2] Since rapid cooling or prolonged periods of heating at temperatures appreciably higher than the melting point of 742.5°C[1] 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 ten minutes, 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 ten-hours 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.

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

Determination of water was made by loss in weight on fusion.[3,4] The usual method involving Karl Fischer reagent is unsatisfactory because complicating reactions are involved with borates. Although it is reported by Morey and Merwin[1] 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 $0.01 \pm 0.01\%$ water.

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.[3,4,5,6,7]

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.[7,8,9]

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

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

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

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

PREPARATION AND PURITY OF VITREOUS SODIUM TETRABORATE

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

Analytical data by identical methods on the vitreous material indicated: water, 0.0% $\pm$ 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).

CALORIMETRIC TECHNIQUE

The adiabatic calorimeter, cryostat, and method of operation have been described previously.[10] The calorimeter was loaded in a dry box and after evacuation 2.0 cm of helium gas at 300°K were added to aid in the establishment of thermal equilibrium.

Temperatures were measured with a capsule-type platinum resistance thermometer (laboratory designation A-3) contained in a re-entrant well in the calorimeter. A 160-ohm constantan heater was wound on a cylindrical copper tube surrounding the resistance thermometer. The thermometer was calibrated on the temperature scale of the National Bureau of Standards,[10] from 14 to 373°K. Below 14°K, the scale was obtained by fitting the equation[11] $R = A + BT^2 + CT^5$ to the resistance at the boiling point of helium and to the resistance and dR/dT at 14°K. It is believed that our 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.

The thermometer resistance and the power input were measured with a calibrated White double-potentiometer, calibrated resistances, and a calibrated standard cell. An electric timer operated by a calibrated tuning fork and amplifier was automatically started at the beginning of the heating period and stopped at the end.

EXPERIMENTAL RESULTS

The experimental values of the heat capacity of crystalline sodium tetraborate are presented in Table I and Fig. I, those for vitreous sodium tetraborate in Table II. 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.

TABLE I

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

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

TABLE II

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	260.78	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			

The molal heat capacity and the thermodynamic functions derived from the heat capacity of these substances are listed at rounded temperatures in Tables III and IV. 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 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 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.

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.

The high precision of the data can be seen best in Fig. 2, in which the deviation of the direct experimental values from the smooth-curve values are presented. This precision is also typical of the crystalline data.

A comparison of the heat capacities of crystalline and vitreous sodium tetraborate is depicted in Fig. 3. 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. 4. This contrasts, for instance, with data on the heat capacities of vitreous silica and quartz as determined by Westrum[12]. Here the quartz C_p curve rises above the vitreous silica C_p curve only at about 210°K. In another example, the heat capacity of crystalline boron trioxide[12] exceeds the heat capacity of vitreous boron trioxide at a temperature of about 285°K.

The molal thermodynamic functions extrapolated to the sodium tetraborate melting point, 742.5°C (1015.66°K), are listed at rounded temperatures in Tables V and VI. The formulae for the extrapolation of these functions are derived on the basis of the method described by Shomate.[13] Using 300°K as the base temperature, the equations for crystalline sodium tetraborate are:

$$C_p = 21.83 + 0850T - 2.250 \times 10^5 \cdot T^{-2},$$

$$H^o - H_0^o = 21.83T + .0425T^2 + 2.250 \times 10^5 T^{-1} - 11,124.0,$$

and

$$S^o = 50.27 \log T + .0850T + 1.125 \times 10^5 T^{-2} - 105.70.$$

TABLE III

MOLAL THERMODYNAMIC PROPERTIES OF CRYSTALLINE SODIUM TETRABORATE

T, °K	C_p, cal/deg	S^o, cal/deg	$H^o - H_0^o$, cal	$-(F^o - H_0^o)/T$, 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	4104.0	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
273.16	42.01	41.504	6178.6	18.885
298.16	44.64	45.296	7261.9	20.940

TABLE IV

MOLAL THERMODYNAMIC PROPERTIES OF VITREOUS SODIUM TETRABORATE

T, °K	C_p, cal deg^{-1}	$S^o - S_0^o$, cal deg^{-1}	$H^o - H_0^o$, 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	3.828	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
273.16	41.71	40.620	6050.9
298.16	44.42	44.391	7127.6

TABLE V

EXTRAPOLATED MOLAL THERMODYNAMIC FUNCTIONS
OF CRYSTALLINE SODIUM TETRABORATE

$T,$ °K	$C_p,$ cal/deg	$S°,$ cal/deg	$H° - H_0°,$ kcal	$-(F° - H_0°)/T,$ cal/deg
400	54.4	59.8	12.31	29.01
450	59.0	66.5	15.15	32.81
500	63.4	72.9	18.21	36.51
550	67.8	79.2	21.49	40.08
600	72.2	85.3	24.99	43.60
650	76.6	91.2	28.71	47.05
700	80.9	97.0	32.65	50.41
750	85.2	102.8	36.80	53.71
800	89.5	108.4	41.17	56.95
850	93.8	114.0	45.75	58.13
900	98.0	119.4	50.54	63.28
950	102.3	124.9	55.55	66.39
1000	106.6	130.2	60.78	69.44
1015.16	107.9	131.9	62.40	70.39

TABLE VI

EXTRAPOLATED MOLAL THERMODYNAMIC FUNCTIONS
OF VITREOUS SODIUM TETRABORATE

$T,$ °K	$C_p,$ cal/deg	$S° - S_0°,$ cal/deg	$H° - H_0°,$ kcal
400	53.9	59.0	12.15
450	58.1	65.5	14.95
500	62.1	71.9	17.96
550	66.0	78.0	21.16
600	69.8	83.9	24.56
650	73.6	89.6	28.14
700	77.4	95.2	31.92
750	81.1	100.7	35.88
800	84.8	106.0	40.40
850	88.4	111.3	44.35
900	92.1	116.4	48.87
950	95.8	121.5	53.56
1000	99.4	126.5	58.44
1015.16	100.5	128.1	59.96

Those for vitreous sodium tetraborate are:

$$C_p = 27.83 + .0720T - 4.320 \times 10^5 T^{-2},$$

$$H^{\circ} - H_0^{\circ} = 27.83T + .0360T^2 + 4.320 \times 10^5 T^{-1} - 13,029.0, \text{ and}$$

$$S^{\circ} - S_0^{\circ} = 64.09 \log T + .0720T + 2.160 \times 10^5 T^{-2} - 137.96.$$

The extrapolated values have an estimated error of 0.4% below 600°K and 2.0% at the melting point. As with all 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 serious here because the extrapolation extends over a long range. However, no evidence for thermal transformations or anomalies were detected by Morey and Merwin[1] by thermal analysis between 350°K and the melting point.

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Fig. 1. 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.)

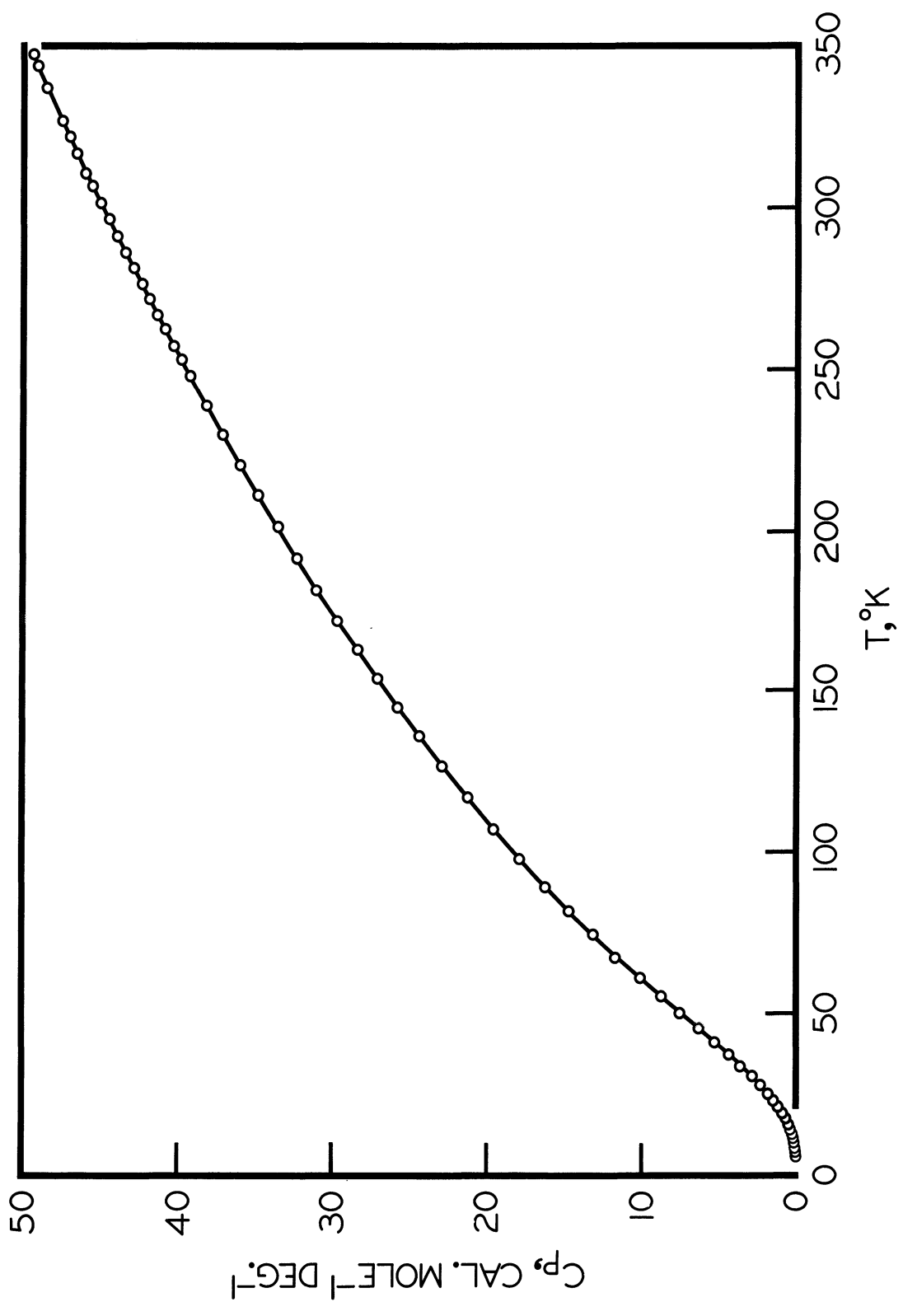CRYSTALLINE SODIUM TETRABORATE

Fig. 1

Fig. 2. Deviation of the Direct Experimental
        Points on Vitreous Sodium Tetraborate
        from the Smoothed Curve.
        (The precision of the data is indicated
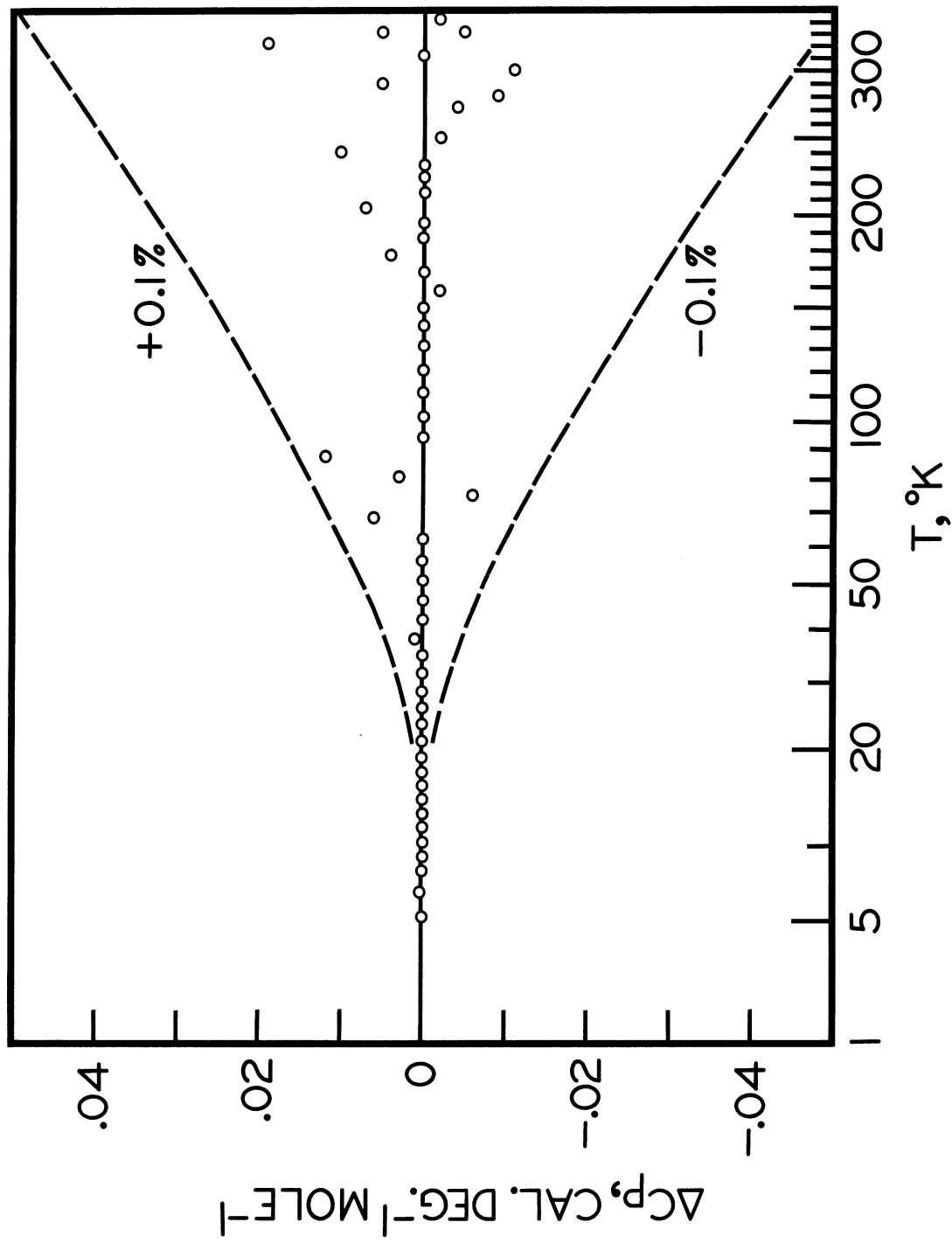   by dashed lines representing $\pm$ 0.1%
        deviation.)

VITREOUS SODIUM TETRABORATE

Fig. 2

Fig. 3. Comparison of the Heat Capacities of
        Anhydrous Crystalline Vitreous Sodium
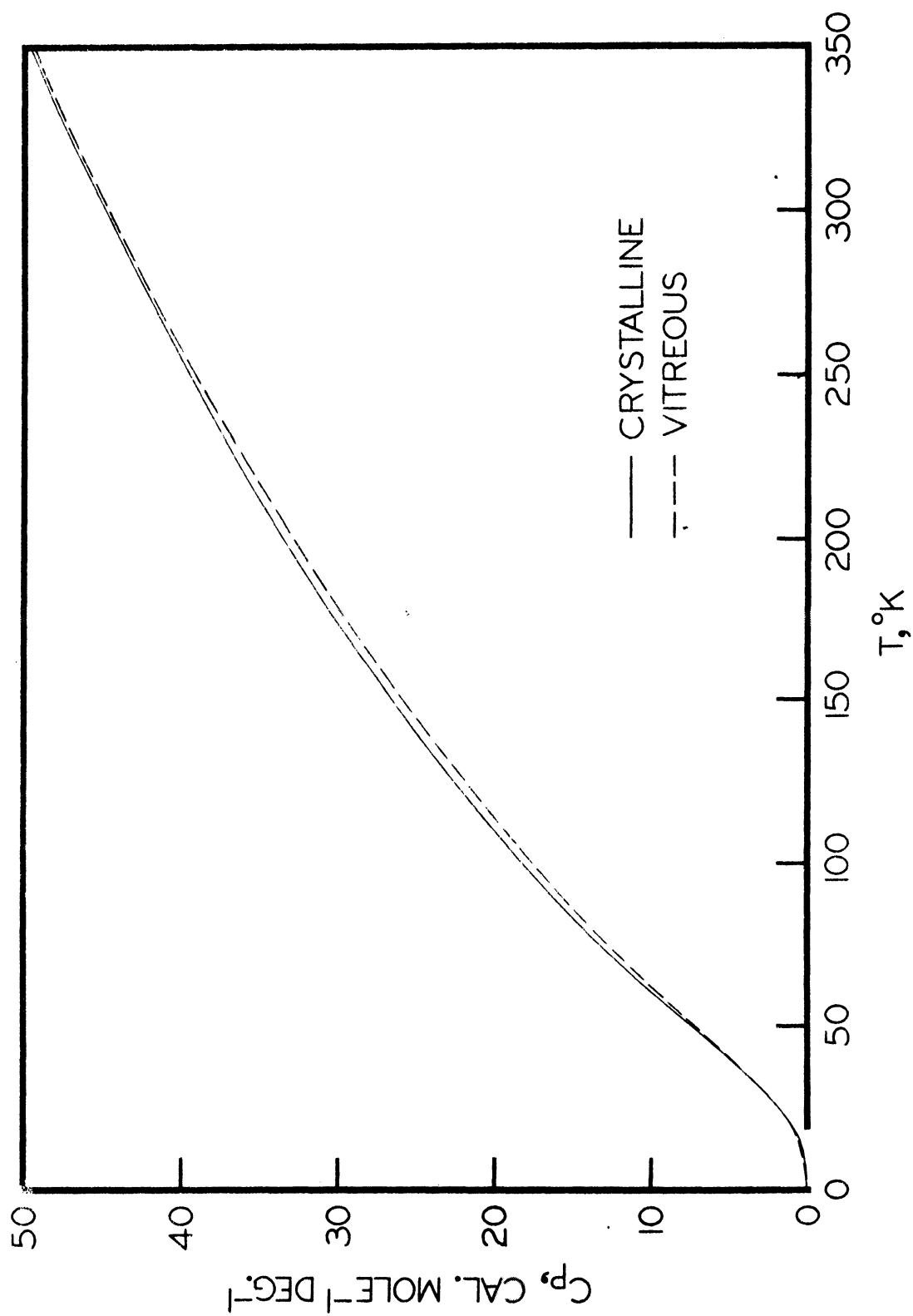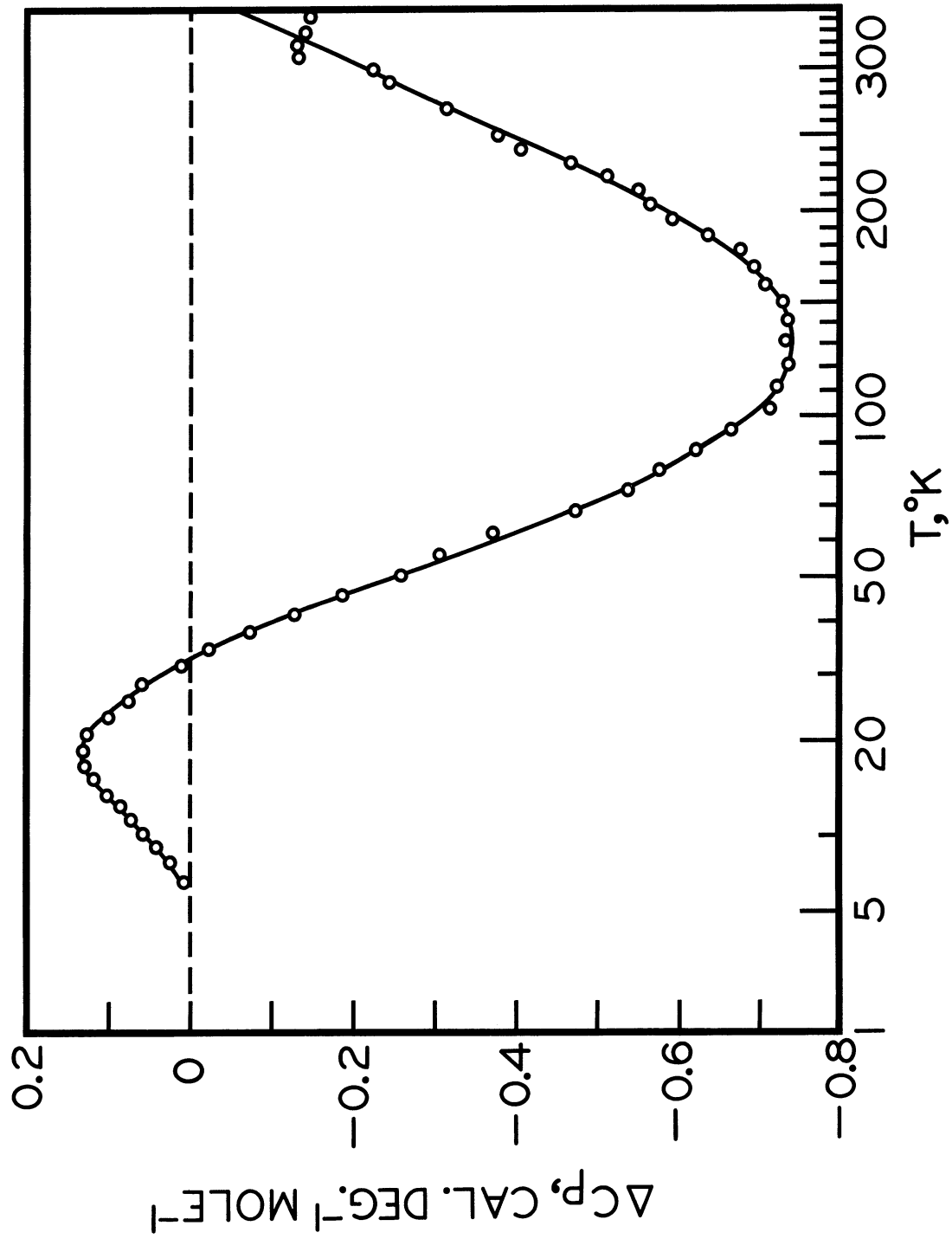   Tetraborate.

SODIUM TETRABORATE

Fig. 3

Fig. 4. Deviation Plot for the Heat
Capacities of Sodium Tetra-
borate Forms.

$$Cp = C_{p, \text{ vitreous}} - C_{p, \text{ crystalline}}$$

SODIUM TETRABORATE (VITREOUS—CRYSTALLINE)

ΔC_p, CAL. DEG.$^{-1}$ MOLE^{-1}

T,$^\circ$K

Fig. 4