Technical (Third Quarterly) Report

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

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Project 2223

CALLERY CHEMICAL COMPANY
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ABSTRACT

We have prepared samples of high-purity anhydrous crystalline and vitreous sodium tetraborate (Na$_2$B$_4$O$_7$) 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$_0$), 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$_T$ - S$_0$), and enthalpy increment (H$_T$ - H$_0$), 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$_2$B$_4$O$_7$, 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$_2$O-B$_2$O$_3$ 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 tem-
perature 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 Merwin1 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 Na₂O content of the sample was determined by carefully evaporat-
ing 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 B₂O₃ 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 Na₂O was 30.80, 30.78, 30.79;
average, 30.79 ± 0.01%. (Theoretical Na₂O: 30.80%.)

The percent by weight of boron reported as B₂O₃ was 69.26, 69.20,
69.07; average, 69.18 ± 0.04%. (Theoretical B₂O₃: 69.20%.)

The material is, therefore, stoichiometrically anhydrous sodium
tetraborate, Na₂B₄O₇.

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, 0.00 ± 0.1%; Na₂O, 30.73%, 30.79% (theoretical, 30.80%); B₂O₃, 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. 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, from 14 to 373°K. Below 14°K, the scale was obtained by fitting the equation \( R = A + BT^2 + CT^6 \) 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 0.05° 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 )

<table>
<thead>
<tr>
<th>T, °K</th>
<th>AT, °K</th>
<th>C_p</th>
<th>T, °K</th>
<th>AT, °K</th>
<th>C_p</th>
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### Table II

The Molal Heat Capacity of Vitreous Sodium Tetraborate

*(Calories per degree)*

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<th>T, °K</th>
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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. Here the quartz curve rises above the vitreous silica curve only at about 210°K. In another example, the heat capacity of crystalline boron trioxide 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. Using 300°K as the base temperature, the equations for crystalline sodium tetraborate are:

\[ C_p = 21.83 + 0.050T - 2.250 \times 10^5 T^{-2}, \]

\[ H^0 - H^0 = 21.83T + 0.042T^2 + 2.250 \times 10^5 T^{-1} - 11.124.0, \]

and

\[ S^0 = 50.27 \log T + 0.050T + 1.125 \times 10^5 T^{-2} - 105.70. \]


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### TABLE V
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### TABLE VI
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Those for vitreous sodium tetraborate are:

\[ C_p = 27.33 + 0.0720 T - 4.320 \times 10^{5}T^{-2}, \]
\[ H^0 - H_0^0 = 27.33T + 0.360T^2 + 4.320 \times 10^{5}T^{-1} - 13.029.0, \]
\[ S^0 - S_0^0 = 64.09 \log T + 0.0720T + 2.160 \times 10^{5}T^{-2} - 137.96. \]

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.

BIBLIOGRAPHY

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.)
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 ± 0.1% deviation.)
Fig. 3. Comparison of the Heat Capacities of Anhydrous Crystalline Vitreous Sodium Tetraborate.
Fig. 4. Deviation Plot for the Heat Capacities of Sodium Tetraborate Forms.

\[ C_p = C_{p, \text{vitreous}} - C_{p, \text{crystalline}} \]
SODIUM TETRARORATE (VITREOUS-CRYSTALLINE)

Fig. 4