copper in the presence of an excess of pyrophosphate ion.

It was possible to evaluate the equilibrium constant for the reaction

$$[Cu(OH)(P_2O_7)]^{-3} + OH^- \rightleftarrows Cu(OH)_2 + P_2O_7^{-4}$$

where $K_{eq.} = C_{P_2O_7^{-4}}/C_{\text{complex ion}}\ C_{OH^-}$. Data obtained in this part of the investigation are listed in Table IV.

TABLE IV

EQUILIBRIUM CONSTANT FOR PRECIPITATION OF $Cu(OH)_2$

| $Na_4P_2O_7$,[a] molar | Complex ion, millimolar | Ionic strength | *p*H of pptn. | $K_{eq.} \times 10^{-3}$ |
|---|---|---|---|---|
| 0.0456 | 0.973 | 0.5 | 12.28 | 2.5 |
| .0461 | 0.973 | .5 | 12.25 | 2.7 |
| .0459 | 2.50 | .5 | 11.67 | 3.9 |
| .0437 | 5.06 | .5 | 11.45 | 3.1 |
| .0437 | 5.06 | .5 | 11.33 | 4.1 |
| .0935 | 5.05 | 1.0 | 11.60 | 4.7 |

[a] Corrected for coördinated $P_2O_7^{-4}$.

Although the equilibrium constant shows nearly a two-fold variation over the range of experimental conditions used, the constancy may be deemed satisfactory in view of the uncertainty of the activity coefficients of multivalent ions, even at a constant ionic strength, and the uncertainty of liquid junction potentials at high *p*H values.

Trial calculations of an equilibrium constant based on the assumed presence of dipyrophosphate cuprate(II) ion in equilibrium with cupric hydroxide gave values varying by twenty-fold.

The dissociation constant for hydroxopyrophosphate cuprate(II), $K_d = C_{Cu^{++}}C_{P_2O_7^{-4}}C_{OH^-}/C_{\text{Complex ion}} = K_{eq}K_{sp}$, was calculated to be $2 \times 10^{-16}$, using the value of $3.3 \times 10^3$ for $K_{eq}$ and the value of $5.6 \times 10^{-20}$ for $K_{sp}$.[12]

## Summary

1. From polarographic data it was shown that cupric ion coördinates two monohydrogen pyrophosphate ions in solutions having more than onefold excess of the complexing ion present. One monohydrogen pyrophosphate ion is coördinated when less than onefold excess of the complexing ion is present. These complex ions were identified in the *p*H range of 3.6 to 5.3. Evidence was given for the existence of pyrophosphate (monohydrogen pyrophosphate) cuprate(II) ion and/or dipyrophosphate cuprate(II) ion in the *p*H range of 7 to 10.

It was shown from data obtained with a glass electrode that hydroxopyrophosphate cuprate(II) ion exists in strongly alkaline solution.

2. Dissociation constants for bis-(monohydrogen pyrophosphate)-cuprate(II) ion and (monohydrogen pyrophosphate)-cuprate(II) ion were calculated from polarographic data. The dissociation constant of hydroxopyrophosphate-cuprate(II) ion was calculated from *p*H measurements.

[12] Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 174.

URBANA, ILL. RECEIVED MARCH 11, 1950

---

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

# Low Temperature Heat Capacities of Inorganic Solids.[1] I. The Heat Capacity of Boric Acid from 16 to 296°K. Description of The Ohio State University Solid Calorimeters

BY HERRICK L. JOHNSTON AND EUGENE C. KERR

## Introduction

This Laboratory is engaged on a program of measuring the low temperature heat capacities and the derived thermal functions of the simple compounds of the lighter elements, including compounds of boron. The present paper deals with boric acid, a compound of thermodynamic interest because of its widespread technological uses. It is also of interest because of the unique type of disorder phenomena that it displays. No previous measurements of the heat capacity of boric acid have been reported in the literature.

## Apparatus

**Calorimeter.**—Measurements were made with a Nernst vacuum calorimeter of the general design developed by Giauque and his co-workers[2] at the University of California, but incorporating some improvements in the cryostat,[3] block, wire, seals and vacuum fittings. In most of its details, the calorimeter assembly is similar to the Ohio State condensed gas calorimeter described in detail in our paper on hydrogen.[4] Seven of these solid calorimeters, constructed and assembled in this Laboratory, are being used in determining the low temperature heat capacities of various inorganic solids, of which this paper describes only boric acid.

Figure 1 is a view of the calorimeter and block assembly with the lower block and vacuum-tight container removed. This instrument is similar to our condensed gas calorimeter[5] with elimination of the monel capillary that served as a filling tube.

The solid calorimeter is suspended from the upper block by three loops of silk thread and is made from 40-mm.

---

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

[2] (a) W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) W. F. Giauque and H. L. Johnston, *ibid.*, **51**, 2300 (1929).

[3] H. L. Johnston, *Rev. of Sci. Instr.*, to be published.

[4] H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, **72**, 3933 (1950).

[5] *Cf.* Fig. 1 of ref. 4.

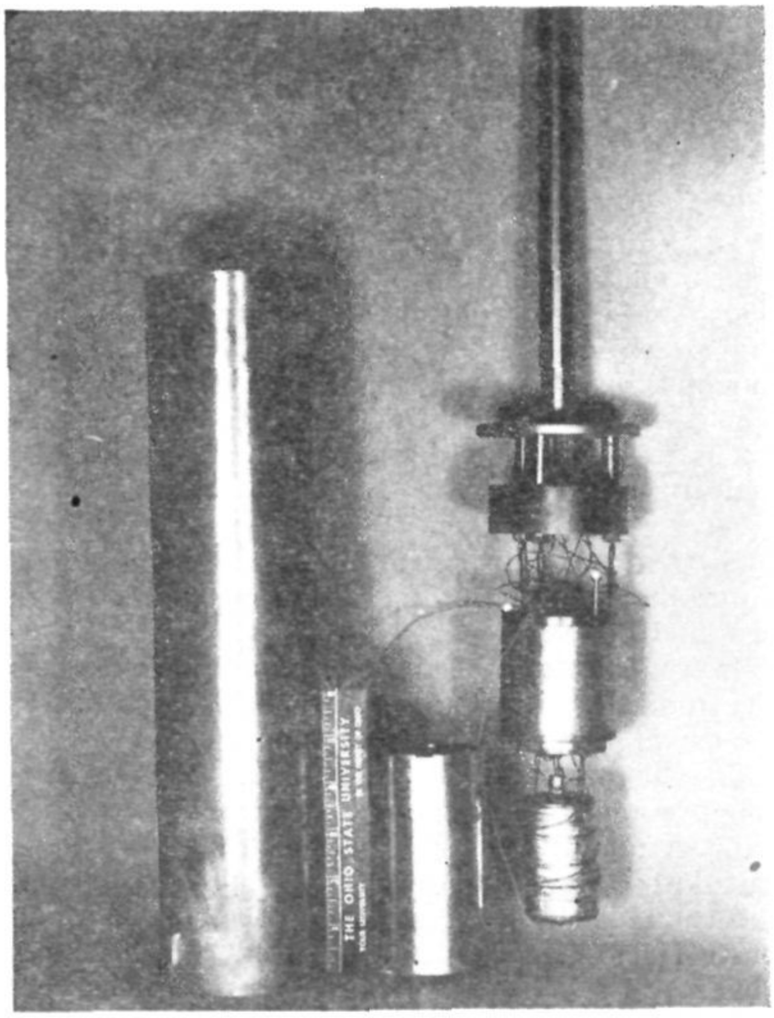


Fig. 1.—Solid calorimeter assembly.

o. d. copper tubing having a 0.127-mm. wall thickness. It is fitted with twelve radial vanes, soft soldered to the walls, to assist in the distribution of heat. The ends of the calorimeter are fitted with spun copper caps silver soldered in place, and the joints are covered with soft solder. A short copper tube, tinned on the inside and filled with cerrobend alloy, is silver soldered to the lower surface of the bottom cap to serve as a thermocouple well. A short piece of 9.5-mm. o. d. copper tubing is silver soldered into a hole drilled in the upper cap to serve as a filling port. This port is closed by a thin copper cap soft soldered to the port, and the cap is removed and resoldered into position when the material in the calorimeter is changed. The length of the calorimeter is 6.5 cm., and its volume approximately 72 cu. cm.

The calorimeter is wound with approximately 200 ohms of No. 40 B. and S. gage, double-nylon covered gold wire alloyed with 0.15% silver, which serves as a combination heater–resistance thermometer. The insulation of the wire is impregnated with General Electric Adhesive No. 7031, while the wire is in position, and is then air-dried. This process serves to improve the insulation between the wire and the calorimeter and to cement the wire to the calorimeter wall. Gold leaf covers the surface of the windings.

The upper and lower blocks are made of lead-filled copper, and the auxiliary block of lead. Dimensions and weights are as follows: upper block, 6.4 cm. o. d. by 7.3 cm. over-all length, weight 2.15 kg.; lower block, 6.3 cm. o. d. by 5.3 cm. i. d. by 11.4 cm. over-all length, weight 1.25 kg.; auxiliary block, 7.0 cm. o.d. by 2.5 cm. thickness, weight 1.06 kg.

The upper and lower blocks are wrapped with double-nylon covered No. 30 B. and S. gage constantan heaters, impregnated with G. E. No. 7031 adhesive, and are fitted with thermocouples for temperature regulation and control. The upper block and the auxiliary block are pierced by holes, 3 mm. in diameter, through which thermocouples and heater leads are passed; good thermal contact is accomplished by the use of paraffin. Thick copper rivets, passing through bakelite inserts, carry the two terminals for the combination heater–resistance thermometer through the upper block. Current and potential leads are soldered to the top rivet heads.

The lower block, which serves both as a sink of heat and as a radiation shield, is heavily gold plated and burnished.

Figure 2a illustrates the means employed for removing lead wires from the high vacuum space with the container and its supporting 19.9-mm. o. d. monel tube. The device consists of a standard 24/40 female ground-glass joint fitted with a lucite plug in whose surface vertical grooves had been machined. The lead wires are laid in these grooves and carefully sealed in position with "Apiezon" W wax so that the plug will form a vacuum-tight seal with the ground-glass joint. This method of removing wires from high vacuum has proven eminently successful. Wires can be removed and replaced with a minimum of injury to their insulation, and vacuum-tight seals are easily obtained.

A side arm near the top of the 19-mm. o. d. monel tube is fitted with a standard ball joint with which connection can be quickly made or broken to a glass high-vacuum system of $10^{-5}$ mm. or better. A short section of flexible, vacuum-tight metal tubing, made from monel bellows of the sylphon type, increases the ease of connecting and disconnecting the calorimeter to the vacuum system.

The cryostat contains a glass dewar, 13-cm. i. d. and 90-cm. long. Slits, 2.5-cm. wide, are left in the silvering of the dewar on opposite ends of a diameter. These slits are aligned with the lucite windows of the cryostat[3] so that the levels of liquid air, liquid nitrogen or liquid hydrogen are visible to the operator.

At each filling, an atmosphere of helium gas is sealed into the calorimeter with the sample. Figure 2b illustrates the brass vessel used to eliminate the danger of contamination by air during the filling process.

The calorimeter, filled with the solid material to be measured, is placed in the brass vacuum chamber and evacuated through a small hole (no. 80 drill) in the top closure of the calorimeter filling tube. When a good vacuum has been attained, the vacuum chamber and calorimeter are filled with pure helium gas to a pressure of 10 to 20 cm. above atmospheric pressure. The lid of the vacuum chamber is then removed, and the small hole immediately soldered shut. This process requires only about 30 seconds, and, since the excess helium pressure causes the helium to stream out through the no. 80 drill hole during this time, air cannot diffuse back into the calorimeter. In order to correct for the heat capacity of helium in the calorimeter, it is assumed that the helium pressure is equal to 760 mm.

**Electric Circuits.**—A Wenner potentiometer having a 10,000-microvolt range is used for thermocouple readings, and a White double potentiometer having a 100,000-microvolt range is used in combination with suitably chosen standard resistances for resistance–thermometer and energy measurements. The resistors were calibrated at the U.S. Bureau of Standards. The electrical circuits are similar in every respect to those used with our condensed gas calorimeter.[4]

Runs are timed to an over-all accuracy of ±0.002 second, including regulator clock accuracy, by an improved form of the electrically controlled switch.[6]

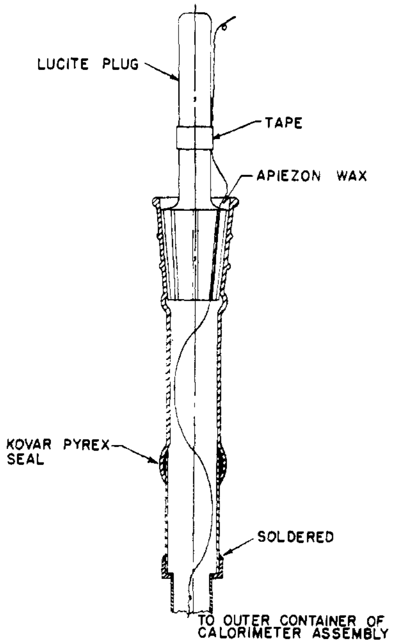
**Temperature Scale.**—Our temperature scale is based on a constant-volume helium thermometer,[7] designed as a temperature standard for this Laboratory in conjunction with work[8] being conducted at this Laboratory concerning

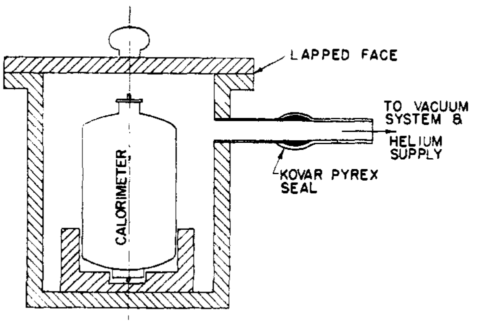
---

[6] H. L. Johnston, *J. Opt. Soc. and Rev. Sci. Instr.*, **17**, 381 (1928).

[7] A description of this standard gas thermometer will eventually be published from this Laboratory.

[8] The temperature scale in use at The Ohio State University Cryogenic Laboratory will be described in a separate paper, in which our scale is compared with that of the U. S. Bureau of Standards on the basis of intercomparisons with two of a group of 30 special platinum resistance thermometers prepared by the Leeds and Northrup Co.





APPARATUS FOR FILLING CALORIMETER WITH HELIUM GAS

Fig. 2b.

Fig. 2a.—Method of sealing lead wires and thermocouples to calorimeter system.

the extrapolation of very accurate $PV$ isotherms for various gases. Two standard copper-constantan thermocouples, designated no. 80 and 93, were soldered to the thermometer bulb under conditions analogous to those in the vacuum calorimeter and were calibrated against our laboratory standard. The several standard thermocouples in use in our solid calorimeters have been compared directly with Primary Standard couple no. 80 to establish temperature scales for the calorimeters. The standard thermocouple in use in our solid calorimeter no. 1, designated no. 112, was used in the measurements on boric acid and was intercompared with primary standard no. 80 in October, 1947. In our experience, a copper-constantan thermocouple, made from selected wire that has passed a severe gradient test, maintains its calibration over a period of years to within its precision of ±0.01° and to within its calibration accuracy of 0.02 to 0.03°K., when it is used under conditions similar to those prevalent during its calibration and when it is not mistreated by allowing the occurrence of sharp bends and kinks. Thus, although the temperatures assigned to the runs may be inaccurate to 0.02 to 0.05°K., the temperature intervals of the heat capacity runs are measured to an accuracy of 0.002 to 0.005°.

**Experimental Corrections and Methods of Data Computations.**—Experimental corrections of small magnitude were applied for (a) heat leaks to or from the surroundings during equilibrium periods, (b) the influence of superheat of the gold heater winding during heat input, (c) the influence of radiation from the lower block on both resistance-thermometer and thermocouple temperatures, (d) drifts in block temperatures during heating periods, (e) potentiometer battery drift, (f) one-half of the heat generated in 25-mm. lengths of no. 40 gold leads connecting the resistance thermometer terminals with the terminals at the bottom of the upper block, (g) the heat capacity of the helium gas sealed in the calorimeter with the samples, and (h) the heat dissipated during heat input in a parallel 30,000-ohm resistor. Similar corrections were applied for the calibration runs on the empty calorimeter. The methods used in making these corrections follow closely those developed by Giauque and his co-workers.[2] A partial description of the methods and of the magnitudes and accuracy of the several corrections is given by Giauque and Johnston[2b] for a condensed gas calorimeter, but their discussion is also appropriate in this case except for those portions that deal specifically with vaporization or with measurement of the amount of material in the calorimeter.

**Preparation and Purity of the Boric Acid.**—Boric acid was recrystallized, from water, from Coleman and Bell C. P. acid which was represented by the manufacturers to have originally contained less than 0.05% by weight of impurities. After recrystallization, the acid was dried over a period of three days at 60 to 70° to a constant weight in a vacuum oven. Using our method of drying, a pilot sample was heated to about 100° and showed no tendency for further dehydration to metaboric acid. The calorimeter was then filled with 49.422 g. (0.7992 mole) of boric acid.

## Experimental Results

The data obtained during these experiments have been plotted and tabulated. Table I and Fig. 3 present the heat capacities obtained for boric acid. The data are expressed in terms of the defined thermochemical calories equal to 4.1833 international joules. The dotted portion of Fig. 3 was calculated from the Debye $T^3$ law, letting $\theta$ equal 167.8. The values of the thermodynamic functions listed in Table II for convenient temperatures were obtained from large graphs of heat capacity *versus* $T$, and *versus* log $T$, with the aid of Simpsons rule.[9] The entropy at 298.16°K. is 21.21 ± 0.1 calories per mole per degree, of which 0.18 E. U. was obtained by extrapolation below 17°K.

**Theoretical Discussion. Disorder Associated with Hydrogen Bonding.**—The question of disorder in the boric acid lattice is of importance in evaluating the proper values of entropy for thermodynamic usage. The disorder enters through hydrogen bonds that bind the planar $BO_3$

---

(9) Contributions from nuclear spin are not included in the entries in the table. These effects can ordinarily be neglected for purposes of applying thermodynamics to chemical processes; *cf.* W. F. Giauque, THIS JOURNAL, **53**, 507 (1931).

TABLE I

MOLAR HEAT CAPACITY OF BORIC ACID ($H_3BO_3$)

Mol. wt., 61.84; 0.7992 mole

| Mean temp., °K. | $\Delta T$ | $C_p$, cal./mole/deg. | Mean temp., °K. | $\Delta T$ | $C_p$, cal./mole/deg. |
|---|---|---|---|---|---|
| 16.72 | 2.666 | 0.449 | 83.54 | 4.758 | 7.529 |
| 18.53 | 1.898 | 0.666 | 88.10 | 4.377 | 7.897 |
| 20.00 | 1.944 | 0.793 | 93.85 | 6.989 | 8.223 |
| 21.82 | 2.285 | 1.014 | 99.23 | 6.413 | 8.508 |
| 24.02 | 1.831 | 1.256 | 106.84 | 8.885 | 8.984 |
| 25.84 | 3.463 | 1.587 | 116.42 | 10.396 | 9.596 |
| 27.71 | 3.488 | 1.686 | 126.18 | 9.277 | 10.10 |
| 30.49 | 3.787 | 2.029 | 136.59 | 11.905 | 10.67 |
| 31.14 | 3.404 | 2.095 | 146.02 | 7.254 | 11.19 |
| 33.54 | 3.445 | 2.387 | 152.97 | 9.496 | 11.59 |
| 34.32 | 3.073 | 2.505 | 166.68 | 8.979 | 12.35 |
| 36.74 | 4.080 | 2.812 | 176.46 | 10.761 | 12.85 |
| 37.17 | 2.657 | 2.850 | 186.36 | 12.251 | 13.34 |
| 39.79 | 2.713 | 3.183 | 196.18 | 11.568 | 13.87 |
| 40.98 | 4.912 | 3.270 | 198.02 | 11.237 | 13.92 |
| 43.44 | 4.640 | 3.595 | 208.71 | 10.414 | 14.49 |
| 48.46 | 5.441 | 4.231 | 217.01 | 9.834 | 15.42 |
| 50.54 | 3.982 | 4.464 | 219.64 | 11.871 | 15.11 |
| 54.27 | 3.412 | 4.933 | 232.39 | 13.234 | 15.79 |
| 57.49 | 3.040 | 5.269 | 245.33 | 12.245 | 16.47 |
| 60.41 | 2.754 | 5.633 | 256.65 | 11.604 | 17.26 |
| 62.47 | 5.314 | 5.829 | 267.68 | 10.099 | 17.77 |
| 67.45 | 4.624 | 6.236 | 277.62 | 9.504 | 18.37 |
| 72.81 | 6.040 | 6.719 | 284.84 | 9.134 | 18.72 |
| 78.50 | 5.284 | 7.160 | 291.66 | 8.795 | 19.10 |
|  |  |  | 301.34 | 4.090 | 19.61 |

TABLE II

THERMODYNAMIC FUNCTIONS FOR BORIC ACID ($H_3BO_3$)

| Temp., °K. | $C_p$, cal./mole/deg. | $S$, cal./mole/deg. | $(H - H_0)$, cal./mole | $-(F - H_0)/T$, cal./mole/deg. |
|---|---|---|---|---|
| 17 | 0.480 | 0.176 | 2.141 | 0.050 |
| 25 | 1.370 | 0.517 | 9.440 | .139 |
| 50 | 4.418 | 2.400 | 81.737 | .765 |
| 75 | 6.888 | 4.702 | 225.76 | 1.692 |
| 100 | 8.585 | 6.927 | 420.15 | 2.726 |
| 125 | 10.025 | 9.002 | 653.25 | 3.776 |
| 150 | 11.42 | 10.95 | 921.17 | 4.811 |
| 175 | 12.80 | 12.82 | 1224.1 | 5.822 |
| 200 | 14.04 | 14.61 | 1559.9 | 6.809 |
| 225 | 15.36 | 16.34 | 1927.2 | 7.772 |
| 250 | 16.76 | 18.03 | 2328.7 | 8.714 |
| 275 | 18.16 | 19.69 | 2765.2 | 9.636 |
| 298.16 | 19.44 | 21.21 | 3200.7 | 10.476 |
| 300 | 19.54 | 21.33 | 3236.6 | 10.542 |

groups in the boric acid layer lattices. Figure 4 illustrates the arrangement of O atoms in a layer, as reported by Zachariasen,[10] who determined the structure by X-ray diffraction. Presumably, the hydrogens lie on the dashed lines between oxygens in the six-membered oxygen rings and form hydrogen bonds, since the O–O distance is 2.71 Å., which corresponds accurately to the O–O distance for oxygens held together by hydrogen bonding. Moreover each hydrogen probably lies much nearer to one of the oxygens in its bond than to the other.[11] If we make the reasonable assumption that boric acid molecules retain their identity in the crystal, which is equivalent to saying that each oxygen possesses one "close" hydrogen, the arrangement of hydrogens in an individual six-membered oxygen ring must correspond to the "permitted" pattern illustrated in Fig. 4, or to its (clockwise) counterpart. However, either of these permitted arrangements is equally probable if weak ordering forces that operate between rings are neglected, since there is no geometric requirement of a coöperative rearrangement between rings to maintain the acid structure $B(OH)_3$. This leads to a condition of complete disorder with respect to the distribution of "clockwise" and "counterclockwise" rings throughout the layer and corresponds to an entropy contribution of 0.69 E. U. = $^1/_2 R \ln 2$ per mole of boric acid since the number of oxygen rings is one-half the number of borons.

The determination of whether or not the disorder entropy of 0.69 E. U. must be added to the values given in Table II depends upon (1) the magnitude of the ordering forces that operate between oxygen rings (or through $BO_3$ groups) and (2) the velocity with which individual rings can reverse the clockwise or counterclockwise arrangements. If the ordering forces are extremely low, so that complete disorder will have been reached below 16°K., to which our measurements were extended, or if the rearrangement velocity is so slow that no appreciable adjustment to thermal equilibrium can occur within the several minutes required for a heat capacity measurement, so that the disorder entropy is "frozen in," the "Third Law" entropies entered in Table II will all be low by 0.69 E. U.

On the other hand, if the ring rearrangements are rapid compared with the time needed to make a calorimetric measurement and if the ordering forces are of such magnitude as to bring the equilibrium curve for the whole transition from complete order to complete disorder within the temperature range 16 to 300°K., the entries in Table II are correct as they stand. In this event, the ordering process should contribute to the heat capacity, as measured, and there should be a superposition of the ordering heat capacity on the curve due to lattice vibrations.

The monomolecular rate constant for the ring rearrangement will be related to the height of the potential barrier that is thought to exist midway between the two oxygens of a hydrogen bond, and should be approximated by the expression

$$K' = K(kT/h)(Q^*/Q) \exp(-V/RT) \quad (1)$$

---

[10] W. H. Zachariasen, *Z. Krist.*, **88** (1934).

[11] This structure corresponds to Paulings description of hydrogen bonding in ice (THIS JOURNAL, **57**, 2680 (1935)), which located each hydrogen at a distance of 0.95 Å. from one oxygen and 1.76 Å. from the other.

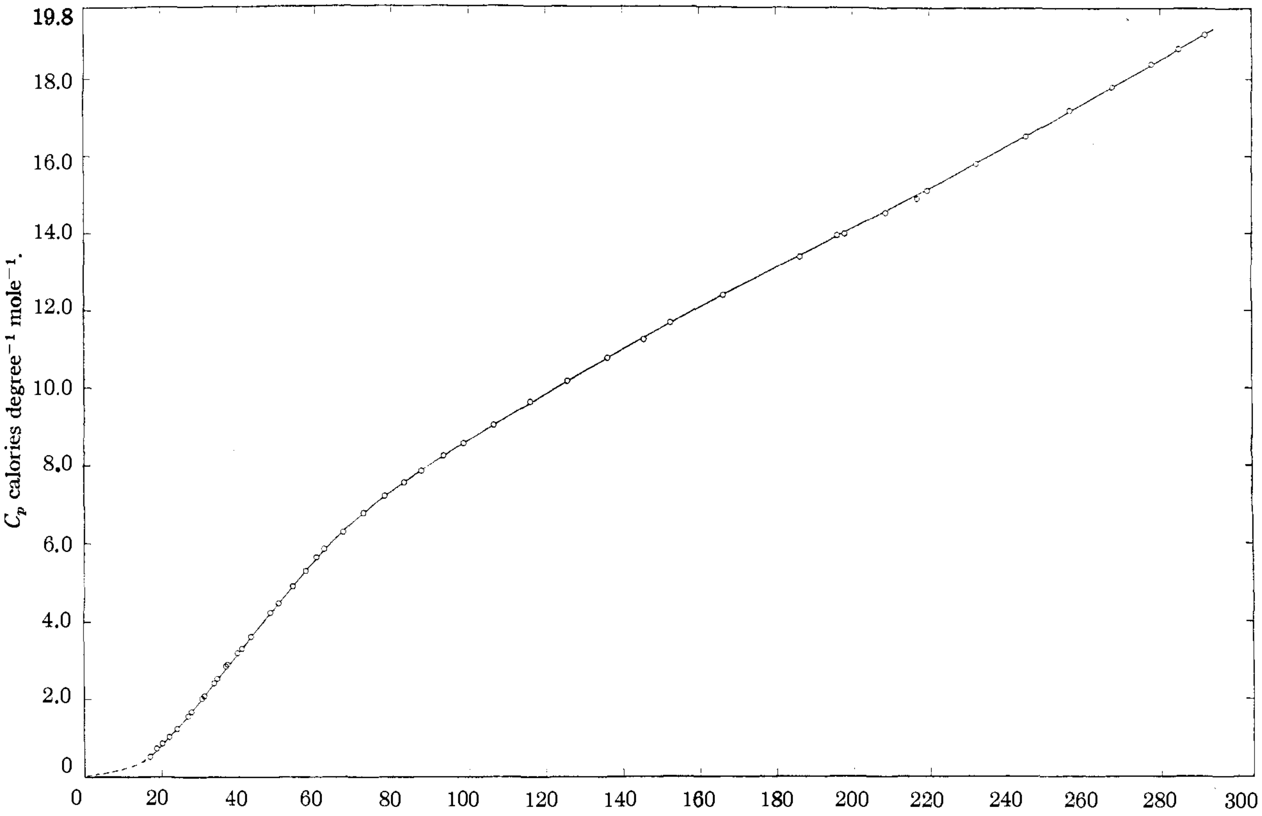


Fig. 3.—Heat capacity of boric acid ($H_3BO_3$).

due to Eyring[12] in which $V$ is the height of the potential barrier, $(Q^*/Q)$ is the ratio of partition functions of the activated and normal states of the hydrogen bond, $K$ is the transmission coefficient, and the other symbols possess their usual significance. For an order of magnitude calculation, both $(Q^*/Q)$ and $K$ can be set equal to unity without significant error, and $V$ can be solved for any chosen values of $T$ and of the half-life (0.69 $K'$). Permitted barrier heights, by this order of magnitude calculation, vary from 1.2 kcal. at 20°K. to 20 kcal. at 300°K. for a 60-second half-life. The actual height of the barrier is unknown. but since the strength of the hydrogen bond is of the order of 5 kcal., the barrier height is probably of the same order of magnitude as the values calculated above as needful to permit attainment of thermal equilibrium in the calorimeter. Tunnelling and the presence of some small amount of ionization in the boric acid lattice may effectively reduce the barrier height so as to reduce the time required for rearrangement.[13]

The heat capacity curve shown in Fig. 3 exhibits a double inflection at about 40°K., where the heat

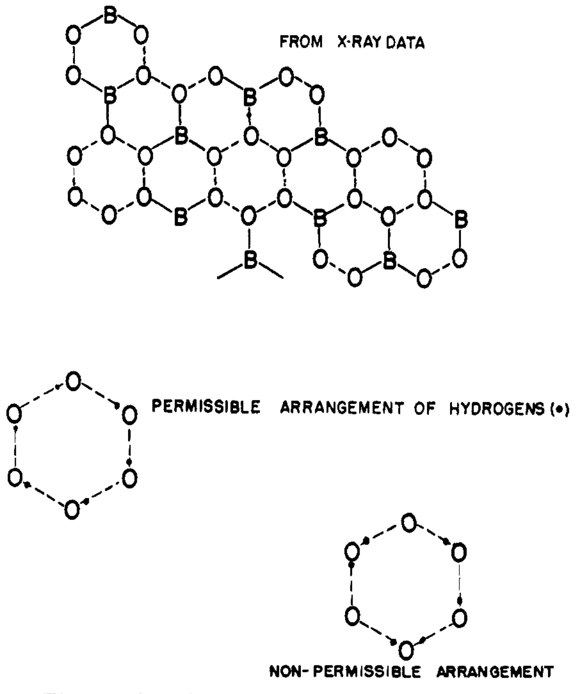


Fig. 4.—Atomic structure of boric acid crystal.

[12] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[13] In a somewhat analogous problem, Bernal and Fowler (*ibid.*, **1**, 515 (1933)) computed the relaxation time for the transfer of a proton between oxygens in adjacent water molecules as only $6.5 \times 10^{-13}$ second, which corresponds to a very much lower barrier for proton transfer than the one we have assumed as a likely magnitude for hydrogen transfer in the hydrogen bond. However, their computations were for an acid medium, and the barrier in boric acid would probably be much higher.

capacity is only 7% of equipartition, and gives the appearance of a spread out hump, from about 20 to 150°K., superimposed on a normal lattice vibration curve. This effect may represent the development of the hydrogen bond disorder discussed above. If so, the entries in Table II are correct as they stand. However it is difficult to separate the contributions due to lattice vibrations from the total heat capacity for a molecule as complicated as boric acid. A decisive treatment of this matter would require a Third Law check through some reaction in which boric acid takes part. Unfortunately there are at present no reliable equilibrium data to which to apply the method.

**Acknowledgment.**—We wish to acknowledge the assistance of Mr. Nathan C. Hallett and Mr. Herbert N. Hersh, who assisted with measurement and calculations.

## Summary

A description has been presented of one of the seven vacuum calorimeters recently constructed and assembled at The Ohio State University Cryogenic Laboratory for measurements of heat capacities of solids. These calorimeters are similar in their general features to those developed by Giauque and co-workers[2] at the University of California, and to the condensed gas calorimeter recently designed and constructed in this Laboratory.

The heat capacities of boric acid, containing less than 0.05% impurities, have been measured between 16 and 296°K. The data yield a value of 21.21 ± 0.1 calories per mole per degree for the entropy at 298.16°K. A table of thermodynamic functions has been prepared for boric acid at smoothed values of the temperature.

Disorder, due to hydrogen bonding in the layer lattice of boric acid has been discussed. This disorder, which makes an entropy contribution of 0.69 E. U., may be responsible for a spread out hump that appears to exist in the heat capacity curve between 20 and 160°K. If this is true, the disorder entropy is contained in the tabulated values derived from the heat capacities.

COLUMBUS 10, OHIO RECEIVED MARCH 6, 1950

---

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

# Low Temperature Heat Capacities of Inorganic Solids.[1] II. The Heat Capacity of Crystalline Boric Oxide from 17 to 300°K.

BY EUGENE C. KERR, HERBERT N. HERSH AND HERRICK L. JOHNSTON

## Introduction

Crystalline boric oxide has been known for only a relatively short time, having been first reliably reported by McCulloch[2] in 1937 and subsequently by Kracek, Morey and Merwin.[3] Low temperature heat capacity data on crystalline boric oxide have been obtained by Kelley[4] in the temperature range of 51 to 298°K.

During the present investigation, the heat capacities of the crystalline form of boric oxide have been measured in the range of 17 to 300°K., to extend the range of the earlier measurements and to better correlate the results of an extensive program of low temperature thermodynamic measurements on boron and several of its compounds. Crystalline boric oxide was studied in solid calorimeter No. 1, which has been described previously.[5]

**Preparation and Purity of Crystalline Boric Oxide.**—Crystalline boric oxide was prepared by one of the methods of Kracek, Morey and Merwin.[3] Boric acid, containing a maximum of 0.05% impurity, was heated for one week at 120 to 130°, after which the temperature was increased 10° per day until it remained at 200° for one day. About 40% additional boric acid (based on the original weight) was added with stirring. The resulting mixture crystallized at 200° over a period of three days. The temperature was then raised to 400° and was maintained at this level for two days under vacuum to complete the removal of water. The hard cake of finely crystalline material was crushed and screened, and finally reheated at 400° for three more days under vacuum to remove any moisture adsorbed during the crushing and screening process.

Analysis was made by hydration to boric acid and controlled drying to a constant weight. A sample of boric acid was similarly moistened and dried as a control blank. The results indicated that the boric oxide crystals were moisture free within the limits of the analytical precision, ±0.1%.

The amount of pure boric oxide used for heat capacity measurements was 69.689 g. or 1.007 moles.

## Experimental Results

The experimental results are summarized in Table I and are plotted in Fig. 1 with the experimental data of Kelley.[4] There are no significant differences between the two sets of data.

Thermodynamic functions derived from the smoothed heat capacity curve are given in Table II at integral values of the temperature. The entropy at 298.16°K. is 12.87 E. U., of which 0.03 E. U. was obtained by a Debye $T^3$ extrapolation with $\theta$ set equal to 329. This value of the entropy at 298.16°K. differs from that given by Kelley[4] by only 0.13 E. U., and 0.08 E. U. of this figure can

---

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

[2] L. McCulloch, THIS JOURNAL, **59**, 2650 (1937).

[3] F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, **35A**, 143 (1938).

[4] K. K. Kelley, THIS JOURNAL, **63**, 1137 (1941).

[5] H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).