[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Molar Heats of Solution of Boric Oxide and Boric Acid[1]

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It became necessary to know the heats of formation and solution of boric oxide and boric acid in connection with a program of investigation of the thermochemistry of certain boron compounds. We have determined the heat of hydration of boric oxide to boric acid from the heats of solution of the two compounds at corresponding concentrations. This value can be combined with the heat of formation of boric oxide to give the heat of formation of boric acid and in a later paper we will report our determination of the heat of formation of boric oxide. Although several investigators have measured the heats of solution of boric oxide and boric acid, we felt it was desirable to carry out a complete set of measurements under carefully controlled conditions, in part because of the unreliability of the earlier data.[2,3] One of the prime difficulties in calorimetric studies with boric oxide has been preparation of boric oxide of known high purity free from traces of moisture. Failure to have moisture absent unquestionably led to erroneous results in the earlier work. Much of the recent work was done for special cases, thus Stackelberg, Quatram and Dressel[4] were interested in volatility of boric acid, Southard[5] was comparing glassy and crystalline boric oxide and Katz[6] made rough measurements to be used in some second order corrections to heats of combustion. We further felt it was necessary to have, for our purposes, measurements made at corresponding concentrations and to investigate the concentration dependence of the heats of solution.

Table I gives a compilation of some previous determinations as well as our own. It is to be noted that only Roth and Börger[7] gave an estimate of precision of their work.

TABLE I

Investigator	ΔH of solution (kcal./mole) B_2O_3	H_3BO_3
Ditte[2a]	−3.16	3.2
Berthelot[3b]	−7.3	4.8
Stackelberg, *et al.*[4]	−8.0	5.3
Roth and Börger[7]	−7.85 (±0.08)	5.10 (±0.05)
Southard[5]	−7.839 (glassy) −3.478 (cryst.)	
Katz[6]	−7.5	5.3
Smisko and Mason[6a]	...	5.27
This work	−7.93 (±0.03)	5.17 (±0.04)

Apparatus.—A submarine isothermal calorimeter operating in a well-stirred constant temperature water-bath controlled to 25.00 ± 0.002° was used. The calorimeter vessel was a silvered dewar flask of approximately 500 ml. capacity with a female standard taper ground joint for mouth into which there fitted a mating composite brass stopper carrying openings for stirrer, heater, thermometer and breaker. This stopper was permanently affixed to a brass superstructure on which was mounted a small synchronous motor and gear train for driving the stirrer. The stopper was composed of two brass pieces separated by a thermally insulating fiber plastic to minimize heat flow. The stirrer was a multibladed impeller of stainless steel which rotated in a well to provide thorough and rapid mixing. The stirrer shaft was in three sections, the middle section located above the liquid level in the calorimeter being lucite for thermal insulation. Two precision bearings above the calorimeter vessel permitted good alignment and smooth rotation of the stirrer. A 4-lead copper resistance thermometer, having a resistance of approximately 27.3 ohms at the ice point, was wound on the tube constituting the well in which the stirrer rotated and was covered by a thin brass shield with the leads carried out through a tube into the bottom of the calorimeter stopper, all joints being soldered water tight so that no leakage to the thermometer occurred. A manganin heater of 18.2638 ohms at 25° was wound on a brass mandrel and encased in a Pyrex tube which dipped into the liquid in the calorimeter. One opening in the insulated stopper was provided for a Pyrex rod used to break the sample bulbs, which were held in a basket arrangement soldered to the outside of the stirrer well. All metal parts of the calorimeter, with the single exception of the stainless steel stirrer, were heavily nickel plated and did not show any corrosion in the course of our measurements.

The copper resistance thermometer was used in conjunction with a Leeds and Northrup G-2 Mueller bridge, which was calibrated against a Leeds and Northrup certified standard resistor, and a high sensitivity galvanometer with a scale to mirror distance of approximately 7 meters and read with a high power telescope. Sensitivity was such that temperature differences of 0.0001° could be measured. Reproducibility of the system was very good. This resistance thermometer was calibrated *in situ* against a Leeds and Northrup platinum thermohm which was recalibrated by the National Bureau of Standards during the course of these investigations.

The manganin heater served two purposes; first, it was for calibration of the calorimeter and second, by its use the temperature within the calorimeter could be raised conveniently to the desired value. For calibrating the calorimeter a direct current of known magnitude was caused to flow through the heater for some carefully measured time interval and the energy input computed in calories. The rectifying part of an Army surplus radar unit operating from the laboratory 115 volt a.c. line was used as our source of direct current, a practice we believe to be unique in precision calorimetry. As received this voltage regulator had an output of 325 ma., but the addition of 2 power tubes in parallel with the existing 3 plus insertion of a 62 Kohm resistor made it possible to draw 500 ma. at approximately 300 volts d.c. The output was run through an appropriate size resistance (*ca.* 550 ohms) wound of 29 B & S cotton covered Advance wire which was immersed in a large well stirred oil-bath, and then through a "standard" manganin resistor which was immersed in the same constant temperature bath as the calorimeter. The circuit was constructed so that the current could be passed through either the calorimeter heater or an almost exactly equivalent dummy or ballast heater maintained in the constant temperature bath. The potential drop across the heater was about 9 volts. Measurement of current flowing in the circuit was accomplished by determining the potential drop across the "standard" resistor with a type K potentiometer and high sensitivity Rubicon box galvanometer. The resistance of the "standard" resistor at 25.00° was determined with the G-2 Mueller bridge and found to be 13.5667 ohms. It was determined that this mode of supply of direct current to the calorimeter was extremely stable over calibration periods. In general voltage fluctuations were not over 1 part in 6000 and never exceeded 3 parts in 6000 after a 30 minute "warm up" period using the dummy heater.

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(1) In part from the Ph.D. thesis of Keith P. Anderson, Cornell University, 1950.

(2) A. Ditte, *Ann. chim. phys.*, [5] **13**, 67 (1878).

(3) M. Berthelot, *ibid.*, [5] **15**, 185 (1878); [5] **17**, 132 (1879).

(4) Stackelberg, Quatram and Dressel, *Z. Elektrochem.*, **43**, 14 (1937).

(5) J. C. Southard, THIS JOURNAL, **63**, 3147 (1941).

(6) C. Katz, M.S. Thesis, Cornell University, 1949.

(6a) Smisko and Mason, THIS JOURNAL, **72**, 3679 (1950).

(7) Roth and Börger, *Ber.*, **70**, 48, 971 (1937).

All time interval measurements were made on a tape recorder connected to a precision electric clock in such a way that pips were placed on the tape at second intervals by a very high speed pen. Times of various operations or galvanometer readings were marked on the tapes by closing an appropriate key. However, for precise measurement of duration of heating, timing keys were interlocked with the heating current switches, thereby removing the human factor. Varying precision in timing could be obtained by changing the speed of the tape. We normally operated it at about 2 cm. per second so that time intervals could be measured easily to 0.05 second.

Materials.—Baker and Adamson reagent grade crystalline boric acid was used both in the heat of solution measurements on boric acid and also for preparation of boric oxide. Samples of the acid analyzed 100.0% when titrated with 0.1 *N* NaOH in the presence of excess mannitol by a procedure standard in this Laboratory. The finely ground crystalline boric acid was stored in a desiccator over P_4O_{10} for 8–12 days. However, the same titer was found for fresh crystals which had not been so stored. Appropriate size samples of dried boric acid were sealed into small, thin wall glass ampules for the calorimetric measurements.

Preparation of boric oxide, free of water, from crystalline boric acid presents some problems. We are convinced that much previous work resulted in incomplete conversion to the oxide. The method we followed was a modification of that of Lange[8] who recommends vacuum dehydration of boric acid at 200° for the preparation of porous boric oxide. The literature indicates that boric acid begins to lose water of constitution at 50° and that 95% is gone at equilibrium at 100° but that dehydration is not complete below 250°.[9,10] In agreement with this we found it necessary to heat boric acid in a vacuum of 1–4 mm. well above the 200° recommended by Lange in order to dehydrate completely. Our procedure was to place finely crushed crystalline boric acid in small porcelain boats in a Pyrex tube in a tube furnace, connect to a vacuum to hold about 1–2 mm. and gradually raise the temperature of the furnace over a period of 2 hours to 260–270° where it was held for an additional 6 hours under vacuum. Analyses proved that within quite small experimental error boric acid was dehydrated completely under these conditions. However, too rapid heating or heating at pressures above 40 mm. caused the mixture to puff up and sinter sufficiently to prevent eventual complete dehydration. After breaking the vacuum the hot product was bottled quickly in small previously weighed glass ampules and sealed off in a micro flame. These ampules were used directly in the heat of solution measurements. X-Ray diffraction patterns showed that boric oxide obtained in this way was amorphous. It dissolved very quickly in water, making a slight hissing sound much in the manner of P_4O_{10}.

Calibration of the Calorimeter.—All calibrations were made with 520.0 g. of water plus an ampule of either boric acid or oxide in the calorimeter, to be used in a subsequent heat of solution measurement. A carefully standardized procedure was used which was entirely comparable with heat of solution runs in terms of rating periods, etc. A small correction (generally less than 0.001°) for the introduction of the ampule breaker was determined experimentally over the range of temperature studied and applied to every measurement. Because of the exact symmetry of the calibration heating curves the 50% point of total temperature rise was used in evaluating the exact temperature change, though it was shown that the 60% point gave the same values. The energy input into the calorimeter was calculated from measurements of the current flowing in the heater and its duration as described above. The conversion factor 1 calorie equals 4.1833 international joules was used. From 33 calibration runs the thermal equivalent of the calorimeter was found to be 588.2 cal./deg. with a probable error of ±1.9 cal./deg. or ±0.32%. We define our probable error as $r = 0.6745\sqrt{\Sigma d_i/n - 1}$ where d_i is an individual deviation and n is the number of observations.[11]

A simple experimental check was made by determining the heat of solution of $Na_2S_2O_3$ at 0.016 molal which we found to be 11220 cal./mole with a probable error of ±20. By combining this deviation with the probable error of calibration we obtain by the usual methods 11220 ± 41 cal./mole for heat of solution of $Na_2S_2O_3$. Zimmerman and Latimer[12] report 11300 ± 60 cal./mole at 0.0107 molal.

Experimental Results.—A common procedure in evaluating the temperature change in a calorimetric measurement is one employed by Dickinson[13] which makes the assumption that the rate of temperature change is exponential with time and chooses the 60% point for determining temperature change. A very accurate but laborious graphical method described by Sturtevant[14] was used by us. Effectively this method integrates the area under the time *vs.* temperature curve and finds the midpoint of area for determining the temperature change. This procedure gave agreement with the Dickinson method for the heat of solution of B_2O_3, but did not agree in the case of H_3BO_3. This was to be expected since the rate of heat absorption on dissolving H_3BO_3 was neither exponential nor symmetric with time.

It was decided to determine heats of solution to give approximately 0.05 molal solutions of H_3BO_3, whether H_3BO_3 or B_2O_3 were being dissolved. Actually the range of final concentrations was about 0.015 *m* above and below the nominal 0.05 *m*.

The dissolution of crystalline H_3BO_3 in water is a rather slow endothermic process. From 15 determinations we find the heat of solution to be −5166 cal./mole with a probable error of ±32 (±0.61%) to give an average final concentration of 0.0508 *m*. With the probable error of calibration given above we arrive at

$$H_3BO_3(c) + Aq. = H_3BO_3(0.05\ m)$$
$$\Delta H = 5166 \pm 36 \text{ cal./mole}$$

A slight trend in heat of solution of H_3BO_3 with changing final molality is discernible and by making an extrapolation one can estimate that the value of ΔH at infinite dilution is about 5063 cal./mole. Davis, Mason and Stegeman[15] report that the heat of dilution of 0.925 *m* to 0.006 *m* H_3BO_3 is 68 cal./mole. Four determinations were made of the heat of solution of H_3BO_3 in solutions of H_3BO_3 and these are shown in Table II.

TABLE II

Moles H_3BO_3 (per 1000 g. H_2O)	Initial concn. (molal)	Final concn. (molal)	ΔH (cal./mole)
0.0510	0.1705	0.2215	5226
.0562	.1687	.2249	5264
.0673	.1585	.2258	5253
.0672	.1790	.2462	5226

Boric oxide made by our vacuum dehydration technique goes into solution so readily that the temperature *vs.* time curve is sufficiently steep to prevent obtaining points during much of its rise. We found that the 50% point, 60% point and the Sturtevant procedure gave essentially identical results. Our measurements for 12 determinations

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[8] W. Lange, *Inorganic Syntheses*, vol. 2, McGraw-Hill Book Co., New York, N.Y., 1946, p. 22.

[9] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1922, p. 101.

(10) L. Hackspill and A. P. Kieffer, *Ann. Chim.*, [10] **14**, 227 (1930).

(11) Margenau and Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943.

(12) Zimmerman and Latimer, THIS JOURNAL, **61**, 1554 (1939).

(13) H. C. Dickinson, *Natl. Bur. Standards, Bull.*, **11**, 189 (1915).

(14) J. M. Sturtevant, "Calorimetry, Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N.Y., 1945, pp. 337–339.

(15) Davis, Mason and Stegeman, THIS JOURNAL, **71**, 2775 (1949).

give for the heat of solution 7928 cal./mole with a probable error of ±15 (±0.19%) to give an average final concentration of 0.0495 *m*. Combining with the probable error of calibration we write

$$B_2O_3\text{(amorph.)} + \text{Aq.} = H_3BO_3(0.05\ m)$$
$$\Delta H = -7928 \pm 29 \text{ cal./mole}$$

The trend in heat of solution of B_2O_3 with changing final molality is smaller than with H_3BO_3. An extrapolation to infinite dilution gives for ΔH about −7960 cal./mole.

Two determinations were made of the heat of solution of glassy B_2O_3 prepared by fusion of H_3BO_3 in a platinum crucible. The average value of these was $\Delta H = -7963$ cal./mole at an average concentration of 0.0218 *m*.

The experimental results obtained for the molar heats of solution of B_2O_3 and H_3BO_3 may be combined to give the heat of conversion of B_2O_3 into H_3BO_3. We then obtain

$$^1/_2B_2O_3\text{(amorph.)} + {}^3/_2H_2O = H_3BO_3\text{(c)}$$
$$\Delta H = -9130 \pm 39 \text{ cal./mole}$$

Summary

1. An isothermal calorimeter for measuring heats of solution and reaction in solution has been described. A unique feature is the use of a radar rectifying unit to supply the d.c. heating current for calibration.

2. Vacuum dehydration of crystalline H_3BO_3 to amorphous B_2O_3 has been described.

3. The molar heats of solution of H_3BO_3 and B_2O_3 to give 0.05 *m* solutions have been determined to be −5166 ± 36 and 7928 ± 29 cal./mole, respectively.

4. The heat of conversion of amorphous B_2O_3 to crystalline H_3BO_3 has been computed from these results to be 9130 ± 39 cal./mole of H_3BO_3.

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Equilibrium Measurements in the System C–CH_4–H_2[1]

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The carbon–hydrogen–methane equilibrium has been the subject of a number of investigations.[2,3,4,5,6] The experimental data are widely scattered, the disagreement being ascribed to such factors as temperature uncertainty, thermal diffusion and the use of different forms of carbon. Apparently the most reliable data are those[7] calculated from the thermodynamic properties of carbon (β-graphite), hydrogen and methane.

In the course of experiments relative to the iron–iron carbide–methane–hydrogen equilibria,[8] it was found that the carbon formed by the decomposition of iron carbide reacted readily with hydrogen at temperatures as low as 400°, the iron catalyzing the reaction. It therefore seemed worthwhile to study the carbon–hydrogen–methane equilibrium using carbon formed by this method, and to compare the results with those for the calculated equilibrium involving β-graphite. The present paper reports equilibrium constants for the reaction

$$CH_4 = C + 2H_2 \quad K_p = (H_2)^2/CH_4 \qquad (1)$$

in the range 380–838°.

Experimental

A synthetic ammonia iron catalyst was reduced at 500° in a stream of dry hydrogen. The iron was then carbided with normal butane at 275° to about 6% carbon and heated to 500° for 72 hours. Any Fe_3C remaining was removed by passing dry hydrogen over the sample at 275° at which temperature the Fe_3C is reduced rapidly while free carbon reacts relatively slowly. The 10-gram sample of iron catalyst after the above treatment contained about 0.57 g. of free carbon.

The apparatus and experimental procedure were essentially the same as those described in a previous paper.[7] At temperatures above 500° in the present case a clear quartz catalyst container was used instead of Pyrex glass, and a calibrated Pt–Pt, 10% Rh thermocouple was used for temperature measurement instead of a chromel–alumel couple. Also, provision was made for carbon dioxide analysis since it was found that at the higher temperatures the carbon reacted with a small amount of oxygen remaining on the iron to form CO and CO_2. The CO was converted to CO_2 by hot copper oxide during the hydrogen analysis, and the CO_2 determined by absorption on Ascarite. Correction was then made for the small amount of CO or CO_2 present in calculating the partial pressure of methane in the equilibrated gas sample.

Results and Discussion

The experimental values of log K_p are shown plotted against $10^3/T$ in Fig. 1. Some of the results obtained by other authors, and a curve representing the values as given by Rossini[7] are also included in Fig. 1.

If ΔC_p for reaction (1) is assumed to be the same as that for the reaction in which β-graphite is used as carbon, the variation of ΔC_p with temperature may be represented by the equation[9]

$$\Delta C_p = 9.18 - 5.96 \times 10^{-3}\,T - 0.051 \times 10^5\,T^{-2} \quad (2)$$

or, performing the proper integrations, the standard free energy for reaction (1) may be represented by the equation

$$\Delta F^\circ = \Delta H_0 - 21.14T \log T + 2.98 \times 10^{-3}T^2 + 0.026 \times 10^5T^{-1} + IT \quad (3)$$

The integration constants ΔH_0 and I may be ob-

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[1] Joint contribution from the Gulf Research & Development Company's Multiple Fellowhsip, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Pa.

[2] (a) Bone and Jerden, *J. Chem. Soc.*, **71**, 41 (1897); (b) Pring and Hutton, *ibid.*, **89**, 1591 (1906).

[3] Coward and Wilson, *ibid.*, **115**, 1380 (1919).

[4] Pring, *ibid.*, **97**, 498 (1910).

[5] Schenck, *Z. anorg. allgem. Chemie*, **164**, 313 (1927).

[6] Randall and Mohammed, *Ind. Eng. Chem.*, **21**, 1048 (1929).

[7] Rossini, *et al.*, Circular of the National Bureau of Standards C 461 (1946).

[8] Browning, DeWitt and Emmett, THIS JOURNAL, **72**, 4211 (1950).

[9] Kelley, Bull. of Bur. of Mines No. 407 (1937).