[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Thermal Properties of Crystalline and Glassy Boron Trioxide[1]

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Introduction

A study of the thermodynamics of the system crystalline B_2O_3–glassy B_2O_3 furnishes the most direct means of determining the free energy of formation of ordinary glassy B_2O_3. This quantity cannot be determined from low-temperature specific heat measurements because of the well-known inapplicability of the third law of thermodynamics to glasses. The heat of formation of glassy B_2O_3 has been determined by Roth and Börger[3] and the entropy of crystalline B_2O_3 by Kelley.[4] The melting point (450 ± 2°), as determined by Kracek, Morey and Merwin,[5] furnishes a temperature at which the free energies of crystalline and liquid B_2O_3 are the same. There remains, therefore, only determination of the heat of fusion and the heat content above room temperatures to make possible calculation of the free energy of formation of both crystalline and glassy B_2O_3 at any temperature within the range of the data. The purpose of the present work is to determine these quantities.

Methods and Materials

The heat of fusion was not determined directly but calculated from measurements of the heat of the reaction B_2O_3 (cryst.) $\rightarrow$ B_2O_3 (glass) at 298.1° K. This was accomplished by measuring the heats of solution of the two forms in water with a calorimeter described previously.[6] The heat contents above room temperature were measured with a high-temperature calorimeter, also described previously.[7]

The crystalline B_2O_3 used in this work was prepared by G. W. Marks, of the Bureau of Mines laboratory at Berkeley, Calif., by the method of Kracek, Morey and Merwin.[5] As originally prepared, it contained 99.73% B_2O_3 and 0.12% H_2O. The remaining 0.15% impurities could be accounted for largely by those present in the original boric acid and a small amount of nickel oxide taken up from the crucible in which the sample was prepared. By drying the preparation at 375° overnight, the B_2O_3 content was raised to 99.82% and the H_2O lowered to about 0.03%. Two samples of glass were prepared by fusing and quenching a portion of the above crystalline material and grinding to pass on 80-mesh screen. One contained 99.30% B_2O_3 and 0.55% H_2O and the second 99.79% B_2O_3 and 0.06% H_2O. The B_2O_3 was determined by titration with barium hydroxide solution in the presence of a considerable quantity of mannitol, using phenolphthalein as an indicator. The water was determined from the loss of weight on fusion of the crystals. Virtually no additional loss in weight occurred until the preparation was heated above 1250°.

Results

The results of the heat content ($H_T - H_{298.1}$) measurements are given in Table I in degrees absolute (273.1° K. = 0° C.) and defined calories (1 cal. = 4.1833 int. joules). The measurements on the glass extend from room temperature to about 1775° K., while those on the crystals extend to the melting point (about 723° K.). They are shown graphically in Fig. 1. There is little difference in the heat content curves of the glass and the crystals below 560° K., although that of the glass falls slightly *below* that of the crystals in the range 460° to 560° K. This is contrary to usual occurrence but not unprecedented, for W. P. White[8] found that the curve for silica glass fell

TABLE I

HEAT CONTENT ABOVE 298.1°K. OF CRYSTALLINE AND GLASSY BORON TRIOXIDE[a] (G. F. W. = 69.64)

T, °K.	$H_T - H_{298.1}$ cal./ g. f. w.	T, °K.	$H_T - H_{298.1}$ cal./ g. f. w.	T, °K.	$H_T - H_{298.1}$ cal./ g. f. w.
Crystals 1st Series		Glass 1st Series		Glass continued	
692.5	8130	905.9	15740	1532.2	34830
689.4	8070	902.4	15620	1536.5	34940
573.2	5270	794.9	12270	507.3	3750
569.2	5210	791.1	12110	518.4	3960
466.5	3020	694.0	9070	456.1	2710
465.1	2920	685.2	8720	1776.8	42290
409.2	1820	562.1	4950	2d Series	
409.5	1830	569.3	5230	1292.7	27600
373.8	1120	488.9	3480	1282.7	27250
377.5	1190	466.2	2930		
351.1	820	382.2	1330		
350.6	800	381.7	1320		
721.5	9000	562.9	4950		
718.4	8910	1039.7	19900		
2d Series		1036.5	19750		
679.5	7790	1270.6	26980		
681.3	7800	1300.3	27790		

[a] Results in order of the experiments.

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[3] W. A. Roth and E. Börger, *Ber.*, **70B**, 48 (1937).

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

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

[6] J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[7] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

[8] W. P. White, *Am. J. Sci.*, [4] **47**, 1 (1919).

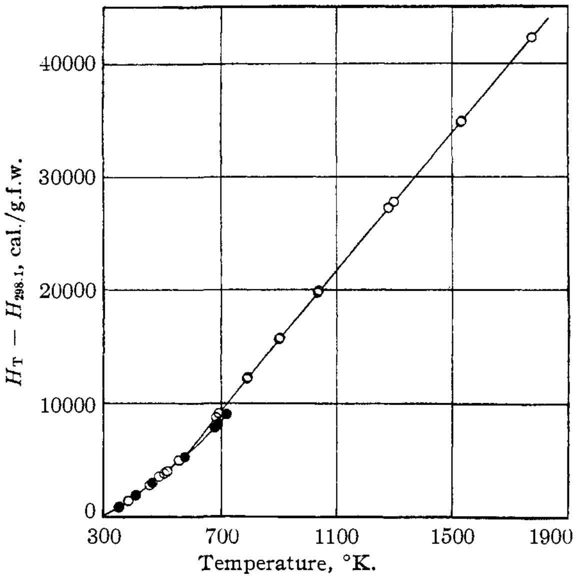

Fig. 1.—Heat content above 298.1°K. of boron trioxide glass ○, and boron trioxide crystals ●.

below that for quartz through a considerable temperature range. At about 560° K., the slope of the heat content curve increases rather abruptly, corresponding to an increase in specific heat. A similar effect was found in the "true" specific heat of B_2O_3 glass at about 525° K. by Thomas and Parks.[9] This sudden increase in heat capacity is a well-known phenomenon, occurring at some temperature for virtually all glasses, and may be said to be the point at which the material changes from a glass to a liquid. A similar change in the slope of the heat content curve occurs at the melting point of the crystals, but it is accompanied by a change in magnitude as well. This may be considered as thermal evidence of the crystalline nature of the sample used in this work.

The heat content of crystalline B_2O_3 between 298.1° K. and the melting point (723° K.) may be represented to about 1% by the equation

(Eq. 1) $H_T - H_{298.1} = 15.75T + 7.49 \times 10^{-3}T^2 + 5.307 \times 10^5/T - 7139$ (298° to 723°K.)

This equation also will hold with about the same accuracy for the glass between 298 and 560° K. The heat content of the liquid may be calculated above 900° K. with an accuracy of about 0.2% from the linear equation

(Eq. 2) $H_T - H_{298.1} = 30.45T - 11{,}820$ (900 to 1800° K.)

(Eq. 2a) $H_T - H_{1000} = 30.45T - 30{,}450$ (1000 to 1800° K.)

This means that the heat capacity of the liquid is constant throughout this range and has a value of 30.45 cal./deg. This agrees almost exactly with the values at the highest temperature (620° K.) of Thomas and Parks,[9] although in the present work the slope of the heat content curve is slightly greater at this temperature.

No previous measurements have been made on crystalline B_2O_3, and the work of Thomas and Parks between 298 and 620° K. constitutes the only extensive measurements on glassy B_2O_3.

The weight of the B_2O_3 in the calorimeter capsule was checked after the measurements near 1300, 1525 and 1775° K., because the capsule was not sealed gas-tight. Virtually no loss in weight occurred until the 1775° K. point, where the sample lost 0.3% in several hours. For this reason no additional points were taken at this temperature. These weight data indicate that anhydrous B_2O_3 has a very low vapor pressure at 1500° K. and below.

The heat of solution measurements made on crystalline B_2O_3 and on the two samples of B_2O_3 glass are summarized in Table II. They were made in water with a final temperature of 298.1° K. ± 0.1° at a concentration of about 1 mole B_2O_3 per 1000 moles H_2O. Approximately 6.9-g. samples were dissolved in about 1790 g. of water in each experiment. Equilibrium was attained in fifteen minutes for the crystals and in less than five minutes for the 80-mesh glass. There was no evidence of delayed heat-of-hydration effects, for on one occasion a constant heat-exchange rate was observed for forty minutes after the normal equilibrium period. Readings were taken every two minutes and gave a rate that agreed within 0.00001° per minute with that determined when no B_2O_3 had been dissolved. On all other experi-

TABLE II

HEAT OF SOLUTION OF 1 G. F. W. B_2O_3 IN 1000 G. F. W. WATER AT 298.1° K. IN CAL./G. F. W. (G. F. W. B_2O_3 = 69.64)

	B_2O_3 crystals 0.03% H_2O	B_2O_3 glass 0.06% H_2O	B_2O_3 glass 0.55% H_2O
	−3471.4	−7818.2	−7607.0
	−3471.9	−7817.8	−7605.9
	−3472.4		−7542.0[a]
Mean	−3471.9	−7818.0	−7606.4
Correction for H_2O	− 6.0	− 20.7	− 190.9
Corrected mean	−3477.9	−7838.7	−7797.3

[a] Not included in average.

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[9] S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **35**, 2091 (1931).

ments, the heat-exchange rate was observed for at least twenty minutes after equilibrium was attained and in no case departed by more than 0.00002° per minute from rates determined when no B_2O_3 had been dissolved. The heat of dilution at the concentration used was determined to be virtually zero.

No previous heat of solution measurements have been made on crystalline B_2O_3. Measurements on B_2O_3 glass at about the same concentration have been made by Roth, Börger and Bertram[10] and by von Stäckelberg, Quatram and Dressel.[11] Roth and co-workers obtained −7,970, −7830 and −7510 cal./mole for final molal concentrations of 0.00250, 0.00105 and 0.00136, respectively, at 19° C. There is no apparent relationship between heat of solution and molality. They give −7850 ± 80 cal./mole as a weighted mean. Roth also corrected the work of von Stäckelberg and co-workers for the several per cent. of water contained, upon the basis that the water was present as HBO_2. The corrected value given was −7720 ± 60 cal./mole, for a concentration of about 1 mole B_2O_3 per 1000 moles water. The same assumption is made here in calculating the corrections listed in Table II. It must be admitted that this assumption is not entirely correct; otherwise the corrected value of the heat of solution for the two samples of glass would be more nearly identical. For this reason, only the results on the glass containing 0.06% H_2O are given any weight in the subsequent calculations. No correction is made for the heat of solution of the remaining 0.15% impurities, for they were identical in all samples. The calorimetric error should not exceed 0.1%, but an additional allowance will be made for possible errors in analysis (which are fortunately compensating to some extent) in the heat-of-reaction calculations.

The results reported above permit calculation of the following thermal data for the reaction

$$B_2O_3 \text{ (crystals)} \longrightarrow B_2O_3 \text{ (glass)}$$

for which a melting point of 450° is adopted from the work of Kracek, Morey and Merwin.[5]

$\Delta H_{298.1} = 4360 \pm 20$ cal./g. f. w.
$(H_{723.1} - H_{298.1})$glass $= 9950$ cal./g. f. w.
$(H_{723.1} - H_{298.1})$crystals $= 9040$ cal./g. f. w.
$\Delta H_{723.1} - \Delta H_{298.1} = 910$ cal./g. f. w.
$\Delta H_{723.1} = 5270$ cal./g. f. w.
$\Delta S_{723.1} = 7.3$ e. u.
$(S_{723.1} - S_{298.1})$glass $= 19.42$ cal./deg. g. f. w.
$(S_{723.1} - S_{298.1})$crystals $= 18.02$ cal./deg. g f. w.
$\Delta S_{723.1} - \Delta S_{298.1} = 1.4$ cal./deg. g. f. w.
$\Delta S_{298.1} = 5.9$ e. u.
$\Delta F_{298.1} = 2600$ cal./g. f. w.

The quantities $H_{723.1} - H_{298.1}$ were determined by interpolation of the experimental results. The quantities $S_{723.1} - S_{298.1}$ were determined by graphical integration of a plot of H/T *vs.* ln T and for the crystals also by analytical integration of the heat content equation (1). To permit comparison of the data of Thomas and Parks with the present work, $S_{620} - S_{298.1}$ was calculated and found to be 14.80 and 14.79 e. u., respectively.

If a melting point 10° higher is assumed, the value of $\Delta F_{298.1}$ becomes 2570 cal./g. f. w.

Calculation of Related Thermal Data

The above results may be combined with data already available in the literature to calculate the entropy and free energy of formation of B_2O_3 glass and the heat and free energy of formation of B_2O_3 crystals, all of which have been unavailable previously. The entropy of B_2O_3 glass at 298.1° K. is calculated to be 18.9 ± 0.3 units from the present value of $\Delta S_{298.1}$ crystals → glass and Kelley's[4] value of $S_{298.1} = 13.0 \pm 0.1$ for the crystals. The free energy of formation of B_2O_3 glass is calculated to be $\Delta F_{298} = -331{,}700$ cal. from Roth and Börger's[3] value of −349,000 cal. for the heat of combustion of amorphous boron at room temperature and the values 18.9, 1.7 and 49.0 for the entropies of B_2O_3 glass, amorphous boron and oxygen gas at 298.1° K. The heat and free energy of formation of crystalline B_2O_3 at 298.1° K. are therefore −353,400 cal. and −334,300 cal., respectively.

The heat and free energy of formation of liquid B_2O_3 at 1000° K. are calculated to be −344,800 cal. and −292,600 cal. These values are based upon those at 298.1° K. using the present high temperature data on B_2O_3, the high temperature heat content measurements of Magnus and Danz[12] on amorphous boron and the tables of Johnston and Walker[13] for gaseous oxygen. ΔS_{1000} of formation is calculated to be −58.2.

The free energy of the reaction

$$2B + 3/2O_2 \longrightarrow B_2O_3 \text{ (liquid)}$$

may be represented above 1000° K. by the equation

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[10] W. A. Roth, E. Börger and A. Bertram, *Ber.*, **70B**, 971 (1937).

[11] M. von Stäckelberg, F. Quatram and J. Dressel, *Z. Elektrochem.*, **43**, 14 (1937).

[12] A. Magnus and H. Danz, *Ann. Physik*, (4) **81**, 407 (1926).

[13] H. S. Johnston and M. K. Walker, THIS JOURNAL, **55**, 183 (1933).

(Eq. 3) $\Delta F_T = -354{,}800 - 12.38T \ln T + 2.24 \times 10^{-3}T^2 + 145.6T$ (1000 to 2000° K.)

Equation (3) is derived from above values for ΔF_{1000} and ΔS_{1000} and the following equations for the heat content of boron (Eq. 4) and oxygen (Eq. 5) in addition to equation (2a) for liquid B_2O_3

(Eq. 4) Boron: $H_T - H_{1000} = 3.01T + 0.96 \times 10^{-3}T^2 - 3970$ (1000 to 2000° K.)

(Eq. 5) Oxygen: $H_T - H_{1000} = 8.034T + 0.213 \times 10^{-3}T^2 - 8247$ (1000 to 3000° K.)

Equation (4) was derived from the values $C_{p_{1000}} = 4.93$ cal./g. f. w. and $C_{p_{2600}} = 8.00$ (estimated); equation (5) was calculated from the values given in the tables of Johnston and Walker[13] at 1000, 2000 and 3000° K.

Equations (4) and (5) are of an abbreviated form intended for use only above 1000° K. They have been used in this high temperature region instead of the longer type ordinarily used by Kelley[14] over the entire range above 273° K.

Summary

1. The heat content above 298° K. has been determined for crystalline B_2O_3 to near the melting point and for glassy B_2O_3 to 1777° K.

2. The heat of the reaction B_2O_3 (crystals) → B_2O_3 (glass) has been determined at 298.1° K. as 4360 ± 20 cal./g. f. w.

3. The free energy of the reaction B_2O_3 (crystals) → B_2O_3 (glass) is calculated to be 2600 cal./g. f. w. at 298.1° K.

4. Entropy of B_2O_3 glass is calculated to be 18.9 ± 0.3 at 298.1° K.

5. An equation has been derived for the free energy of formation of liquid B_2O_3 at temperatures above 1000° K.

(14) K. K. Kelley, *Bur. Mines Bull.*, 371 (1934).

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Entrainment of Cobalt by Tin(IV) Sulfide

BY JOHN F. FLAGG

It has been recognized for some time that the precipitation of tin(IV) sulfide in the presence of cobaltous ion results in contamination of the precipitate with cobalt. Auger and Odinot,[1] who first noted this effect, found that cobalt appeared in the precipitated tin(IV) sulfide at acidities so high that the tin(IV) ion itself was incompletely precipitated. They noted also that the amount of cobalt entrained was almost inversely proportional to the acidity of the solution, and finally concluded that the separation of cobalt and tin by this method was not feasible.

A study in somewhat greater detail was made by Feigl,[2] who determined the amount of cobalt entrained at various concentrations of cobalt and tin. His study was not exhaustive, as the few determinations were part of other work designed to support the "Coördination Theory" of co-precipitation.

The research of Kolthoff[3] and co-workers has made it evident that entrainment is not a simple process, that it is often the result of several processes, and is a function of acid concentration, temperature, time of standing, and concentration of the ions involved to an extent not previously recognized.

From this viewpoint, an investigation of the cobalt—tin problem has seemed desirable. Furthermore, the availability of radioactive isotopes of cobalt provides a convenient tool for attacking such a problem. The use of radioactive cobalt facilitates the quantitative analysis of precipitates for the small amounts of cobalt entrained, and it becomes possible to work at lower concentrations of cobalt than hitherto has been feasible.

The work reported here is a study of the entrainment of cobalt by tin(IV) sulfide from solutions varying in concentrations of tin and cobalt, as well as acidity, time of standing, and temperature of precipitation. Data also are presented to show that this troublesome analytical phenomenon can be successfully eliminated by using acrolein as a flocculating agent. Radioactive cobalt has been used exclusively in these studies.

Experimental Part

Preparation of Reagents.—A solution of tin(IV) chloride was prepared by dissolving Baker Analyzed $SnCl_4$-

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(1) Auger and Odinot, *Compt. rend.*, **178**, 710 (1924).

(2) Feigl, *Z. anal. Chem.*, **65**, 25 (1924).

(3) For review, see Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).