Heats of formation from the component oxides were obtained for magnesium metasilicate, magnesium orthosilicate, and calcium metasilicate by measuring heats of solution and reaction of the pertinent substances in hydrofluoric acid.

BERKELEY, CALIFORNIA RECEIVED JANUARY 30, 1948

CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of $3CaO·B_2O_3$, $2CaO·B_2O_3$, $CaO·B_2O_3$, and $CaO·2B_2O_3$[1]

BY E. G. KING,[2] D. R. TORGESON[2] AND O. A. COOK[3]

In two recent papers,[4,5] heats of formation and low-temperature heat-capacity and entropy data were presented for the four calcium borates, $3Ca·B_2O_3$, $2CaO·B_2O_3$, $CaO·B_2O_3$, and $CaO·2B_2O_3$. These are all the compounds in the $CaO–B_2O_3$ system, according to the work of Carlson.[6] The present paper reports high temperature heat content values, thus completing basic data needed for thermodynamic calculations of reactions of these compounds in both the crystalline and liquid states. The results have additional interest in that this is the first complete series of interoxidic compounds for which high temperature heat content measurements have been carried beyond the melting points so that adequate heat of fusion values are available. No previous high temperature heat content data exist for any of these substances.

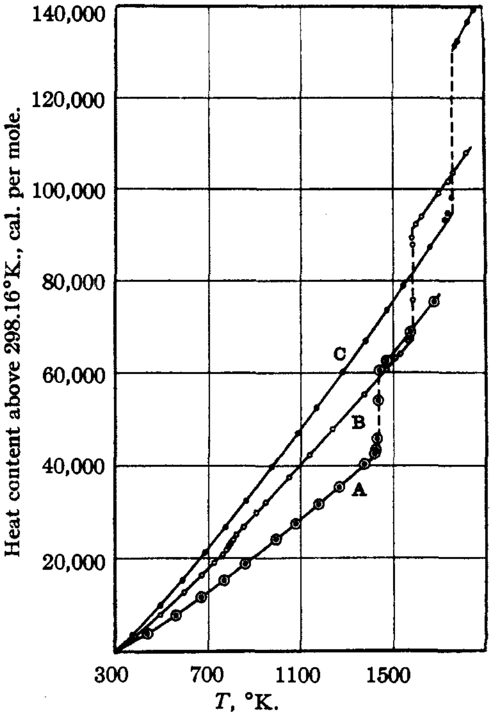

Fig. 1.—Heat contents of calcium borates: A, $CaO·B_2O_3$; B, $2CaO·B_2O_3$; C, $3CaO·B_2O_3$.

Method and Materials

Measurements were made by the "dropping" method, using previously described apparatus.[7,8] During measurement, the samples were enclosed in platinum–rhodium alloy capsules, pure platinum being used in welding shut the capsule necks after evacuating and filling the pore space with helium. The heat contents of the empty capsules were determined by separate experiments. At the highest temperatures, small pinholes developed in the capsules, and it was necessary to weigh capsules and contents after each measurement. The total loss in weight during a complete series of measurements never exceeded 0.5% of the original sample weight. Correction was made on the assumption that boric oxide was lost by volatilization and that the equivalent amount of the borate next higher in calcium oxide had formed. As the net correction always was less than 0.2%, no appreciable error in reported results is involved.

The preparation, analysis, and X-ray diffraction examination of the borates was described by Torgeson and Shomate,[4] whose samples also were used in the present work. It should be noted that the sharpness of the observed melting points and the agreement with results of the National Bureau of Standards[6,9] substantiates the purity of the materials.

Results and Discussion

The experimental heat content values are given in Table I and Figs. 1 and 2, being expressed in defined calories (1 cal. = 4.1833 int. joules)[10] per mole (in vacuum) of borate. Molal weights accord with the 1947 International Atomic Weights. Values marked (t) and (p) show, respectively, effects of pretransition and of premelting or in-

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[4] Torgeson and Shomate, THIS JOURNAL, **69**, 2103 (1947).

[5] Kelley, Todd and Shomate, *ibid.*, accepted for publication.

[6] Carlson, *Bur. Standards J. Research*, **9**, 825 (1932).

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

[8] Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper* **686** (1946), 34 pp.

[9] Flint and Wells, *Bur. Standards J. Research*, **17**, 727 (1936).

[10] Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

complete melting. Table II gives smooth values of heat contents and entropy increments above 298.16° K. at 100° intervals and at transition and melting points.

The compound $2CaO \cdot B_2O_3$ has a transition at 804° K., with a heat absorption of 1,100 cal. per mole and an entropy change of 1.37 e. u.

With the exception of $CaO \cdot 2B_2O_3$, the compounds melted and recrystallized reversibly under the prevailing experimental conditions. The molten diborate solidified completely in the glassy state (single phase) when dropped from the furnace into the calorimeter. It could be reconverted to the crystalline state by heating for a short time in the region just below the melting point of the crystals. This behavior agrees with the ob-

TABLE I

HEAT CONTENT OF $3CaO \cdot B_2O_3$ ABOVE 298.16° K.

Base, crystals at 298.16° K. Mol. wt., 237.88

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
Crystals		1473	73,660
372.5	3,656	1545	78,940
491.1	10,025	1660	87,250
586.0	15,370	1725	93,280(p)
682.2	21,180	1738	94,820(p)
771.7	26,720	1757	98,450(p)
860.7	32,410	Liquid	
973.8	39,750	1771	131,310
1083.7	46,990	1784	132,210
1165.1	52,510	1829	136,500
1281.1	60,260	1856	139,150
1380	66,990		

HEAT CONTENT OF $2CaO \cdot B_2O_3$ ABOVE 298.16° K.

Base, α-crystals at 298.16° K. Mol. wt., 181.80

α-Crystals		1135.2	42,270
381.8	3,295	1137.4	42,340
491.4	7,905	1235.9	47,910
594.3	12,690	1374	55,420
670.4	16,410	1472	60,770
723.3	18,990	1510	63,370
760.2	20,820	1531	64,200
776.4	21,730(t)	1564	67,070(p)
782.2	22,130(t)	1582	89,470(p)
787.9	22,820(t)	1585	87,840(p)
794.3	23,280(t)	1587	75,910(p)
β-Crystals		Liquid	
804.6	23,990	1599	92,300
819.3	25,030	1623	93,970
850.6	26,730	1700	98,980
906.5	29,820	1740	101,630
946.9	32,030	1764	103,600
1048.6	37,460	1821	107,790

HEAT CONTENT OF $CaO \cdot B_2O_3$ ABOVE 298.16° K.

Base, crystals at 298.16° K. Mol. wt., 125.72

Crystals		1375	40,260(p)
435.8.	3,944	1417	42,560(p)
558.2	7,822	1422	43,370(p)
667.3	11,630	1427	45,800(p)
765.7	15,260	1433	54,070(p)
858.3	18,800	Liquid	
990.9	24,090	1439	60,620
1076.8	27,500	1471	62,650
1176.5	31,610	1575	69,020
1265.5	35,350	1678	75,480

HEAT CONTENT OF $CaO \cdot 2B_2O_3$ (CRYSTALS) ABOVE 298.16° K.

Base, crystals at 298.16° K. Mol. wt., 195.36

Crystals		948.9	37,390
369.3	3,045	991.0	40,200
426.9	5,755	1043.5	44,010
433.6	6,155	1076.7	46,250
542.6	11,820	1091.5	47,140
605.1	15,500	1130.0	49,970
645.6	17,810	1173.2	52,870
749.2	24,310	1178.2	53,530(p)
764.8	25,220	1220.7	57,650(p)
874.1	32,330	1259.1	68,790(p)
906.2	34,570		

HEAT CONTENT OF $CaO \cdot 2B_2O_3$ (GLASS AND LIQUID) ABOVE 298.16° K.

Base, glass at 298.16° K. Mol. wt., 195.36

Glass		Liquid	
392.1	4,173	1260.7	73,620
603.2	15,290	1279.3	75,900
794.0	26,970	1296.0	77,540
850.1	31,260	1327	80,670
1005.3	44,620	1355	84,020
1101.1	49,310(m)	1406	89,730
1131.3	50,750(m)	1521	101,850
1143.6	58,920	1645	114,490
1204.7	66,020(m)	1747	124,350

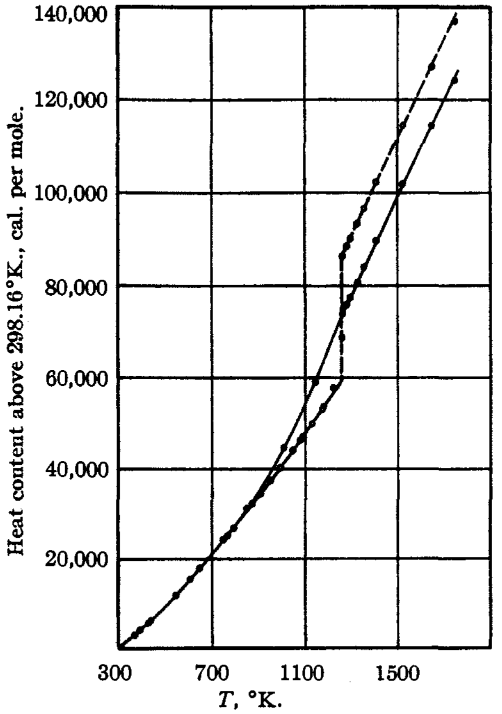

Fig. 2.—Heat content of $CaO \cdot 2B_2O_3$: open circles, crystals and liquid; black circles, glass and liquid.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG./MOLE) ABOVE 298.16° K.

T, °K.	$3CaO \cdot B_2O_3$(c,l)		$2CaO \cdot B_2O_3$(c,l)		$CaO \cdot B_2O_3$(c,l)		$CaO \cdot 2B_2O_3$(c,l)[a]		$CaO \cdot 2B_2O_3$(gl,l)[b]	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	5,180	14.88	4,010	11.53	2,840	8.16	4,470	12.83	4,470	12.85
500	10,520	26.79	8,310	21.11	5,950	15.09	9,500	24.03	9,500	24.05
600	16,250	37.22	12,940	29.55	9,280	21.16	15,130	34.29	15,130	34.28
700	22,220	46.42	17,830	37.08	12,820	26.61	21,170	43.59	21,180	43.59
800	28,410	54.69	22,880	43.82	16,550	31.59	27,510	52.05	27,710	52.30
804	....	...	23,080(α)	44.07	....	...	....	....	....	....
804	....	...	24,180(β)	45.44	....	...	....	....	....	....
900	34,780	62.19	29,410	51.57	20,420	36.14	34,090	59.79	35,210	61.13
1000	41,300	69.06	34,860	57.32	24,410	40.35	40,870	66.94	44,100	70.49
1100	47,950	75.40	40,330	62.54	28,480	44.22	47,820	73.56	54,390	80.29
1200	54,720	81.28	45,840	67.33	32,630	47.84	54,920	79.74	66,080	90.46
1260	....	...	....	....	....	...	59,340(c)	83.33	73,760(gl)	96.71
1260	....	...	....	....	....	...	86,400(l)	104.81	73,760(l)	96.71
1300	61,590	86.78	51,380	71.76	36,870	51.23	90,650	108.11	78,010	100.01
1400	68,540	91.93	56,930	75.87	41,210	54.44	101,280	115.99	88,640	107.89
1435	....	...	....	....	42,740(c)	55.52	....	....	....	....
1435	....	...	....	....	60,410(l)	67.83	....	....	....	....
1500	75,600	96.80	62,490	79.71	64,420	70.57	111,910	123.34	99,270	115.23
1585	....	...	67,260(β)	82.80	....	....	....	....	....	....
1585	....	...	91,350(l)	98.00	....	...	....	....	....	....
1600	82,790	101.44	92,370	98.64	70,590	74.55	122,540	130.19	109,900	122.09
1700	90,110	105.88	99,190	102.77	76,760	78.29	133,170	136.63	120,530	128.52
1760	94,550(c)	108.44	....	....			....	....	....	....
1760	130,040(l)	128.60	....	....			....	....	....	....
1800	133,800	130.71	106,010	106.68			143,800	142.72	131,160	134.62
1900	143,200	135.79	112,830	110.37						

[a] Base = crystals at 298.16° K. [b] Base = glass at 298.16° K.

servations of Carlson.[6] As a consequence, direct measurements were made of the heat content of the crystals with respect to crystals at 298.16° K. as the base, and of the heat content of glass and liquid with respect to glass at 298.16° K. as the base.

Results marked (m) in Table I were obtained under conditions that resulted in partial reconversion of glass to crystals. These values are given no weight and are not plotted in Fig. 2. Results for the glass are, of necessity, sparse in the region just below the melting point and of lower accuracy than the other values.

It was necessary to obtain the heat of fusion of crystalline $CaO \cdot 2B_2O_3$ by an indirect method. This was accomplished by use of the calorimeter described by Southard[11] and Young[12] and also used by Torgeson and Shomate[4] in their heat of formation determinations of the calcium borates. Using 1.000 N hydrochloric acid as solvent, 3.4836 g. of $CaO \cdot 2B_2O_3$-glass was dissolved in 1845.5 g. of acid (identical with procedure of Torgeson and Shomate) and the heat of solution was measured. Three determinations were made, yielding, respectively, −22,720, −22,730, and −22,700 cal. per mole, the mean being −22,720 ± 20 for $CaO \cdot 2B_2O_3$-glass. Torgeson and Shomate obtained −10,080 ± 10 cal. per mole as the heat of solution of $CaO \cdot 2B_2O_3$-crystals. The difference, 12,640 ± 30 cal. per mole, is the heat of transformation of crystals to glass at 298.16° K. Combination of this result and heat content values of crystals and glass from Table II yields 27,060 cal. per mole as the heat of fusion of the crystals at the melting point, 1260° K.

Melting points and heats and entropies of fusion are summarized in Table III. The melting point temperatures are in substantial agreement with determinations of the National Bureau of Standards except in the case of $2CaO \cdot B_2O_3$. The entropies of fusion are remarkably constant when considered on a mean gram-atom basis, 1.69 to 1.83 e. u.

TABLE III

FUSION DATA

Substance	Melting point, °K. This work	Melting point, °K. N. B. S.[5,6]	ΔH (fusion), cal./mole	ΔS (fusion), cal./deg./mole
$3CaO \cdot B_2O_3$	1760	1761	35,490	20.16
$2CaO \cdot B_2O_3$	1585	1571	24,090	15.20
$CaO \cdot B_2O_3$	1435	1427	17,670	12.31
$CaO \cdot 2B_2O_3$	1260	1259	27,060	21.48

Heat content equations for crystals and liquids, derived by the method outlined by Shomate,[13] are listed below. In each instance there are indicated the temperature range of validity and mean devia-

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[11] Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[12] Young, THIS JOURNAL, **67**, 257 (1945).

[13] Shomate, *ibid.*, **66**, 928 (1944).

tion from the experimental data, excluding those marked (t) and (p) in Table I.

$3CaO \cdot B_2O_3(c)$

$H_T - H_{298.16} = 56.44T + 5.21 \times 10^{-3}T^2 + 13.02 \times 10^5T^{-1} - 21{,}658$ (298–1760° K.; 0.4%)

$3CaO \cdot B_2O_3(l)$

$H_T - H_{298.16} = 94.00T - 35{,}400$ (1760–1900° K.; 0.1%)

$2CaO \cdot B_2O_3(\alpha)$

$H_T - H_{298.16} = 43.75T + 5.75 \times 10^{-3}T^2 + 10.69 \times 10^5T^{-1} - 17{,}141$ (298–804° K.; 0.5%)

$2CaO \cdot B_2O_3(\beta)$

$H_T - H_{298.16} = 52.29T + 1.20 \times 10^{-3}T^2 - 18{,}633$ (804–1585° K.; 0.3%)

$2CaO \cdot B_2O_3(l)$

$H_T - H_{298.16} = 68.20T - 16{,}750$ (1585–1900° K.; 0.2%)

$CaO \cdot B_2O_3(c)$

$H_T - H_{298.16} = 31.02T + 4.88 \times 10^{-3}T^2 + 8.07 \times 10^5T^{-1} - 12{,}389$ (298–1435° K.; 0.3%)

$CaO \cdot B_2O_3(l)$

$H_T - H_{298.16} = 61.70T - 28{,}130$ (1435–1700° K.; 0.1%)

$CaO \cdot 2B_2O_3(c)$

$H_T - H_{298.16} = 51.34T + 9.58 \times 10^{-3}T^2 + 17.16 \times 10^5T^{-1} - 21{,}914$ (298–1260° K.; 0.4%)

$CaO \cdot 2B_2O_3(l)$

$H_T - H_{298.16} = 106.30T - 47{,}540$ (1260–1800° K.; 0.2%)

The corresponding molal heat capacity equations are:

$3CaO \cdot B_2O_3(c)$: $C_p = 56.44 + 10.42 \times 10^{-3}T - 13.02 \times 10^5T^{-2}$

$3CaO \cdot BaOO_3(l)$: $C_p = 94.00$

$2CaO \cdot B_2O_3(\alpha)$: $C_p = 43.75 + 11.50 \times 10^{-3}T - 10.69 \times 10^5T^{-2}$

$2CaO \cdot B_2O_3(\beta)$: $C_p = 52.29 + 2.40 \times 10^{-3}T$

$2CaO \cdot B_2O_3(l)$: $C_p = 68.20$

$CaO \cdot B_2O_3(c)$: $C_p = 31.02 + 9.76 \times 10^{-3}T - 8.07 \times 10^5T^{-2}$

$CaO \cdot B_2O_3(l)$: $C_p = 61.70$

$CaO \cdot 2B_2O_3(c)$: $C_p = 51.34 + 19.16 \times 10^{-3}T - 17.16 \times 10^5T^{-2}$

$CaO \cdot 2B_2O_3(l)$: $C_p = 106.30$

Summary

High temperature heat contents of the calcium borates, $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$, were measured from 298.16° K. to temperatures well above their melting points. Melting point temperatures and heats of fusion were determined and also the transition temperature and heat of transition in the case of $2CaO \cdot B_2O_3$.

Heat content and heat capacity equations, adequately representing the measured data, were derived for each borate in the crystalline and liquid states.

Entropy increments above 298.16° K. at 100° intervals and at phase-change points are tabulated, together with smooth values of the heat contents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Electrophilic Attack on Halogen in a Homogeneous Medium: Reaction of Mercuric Nitrate with some Primary and Secondary Alkyl Bromides

BY O. THEODOR BENFEY*

Introduction

In the work of Dostrovsky and Hughes[1] on the series of bromides, methyl, ethyl, *n*-propyl, isobutyl, neopentyl, reactions expected to proceed by the nucleophilic substitution mechanism S_N2 gave the rate sequence

Me > Et > *n*-Pr > *iso*-Bu ≫ Neopentyl

The sharp fall from isobutyl to neopentyl is attributed to a pronounced steric effect, the remaining rate sequence being explainable on the postulation of an inductive effect of methyl groups even on the β-carbon, opposing the approach of the nucleophilic reagent. Steric hindrance is a contributory factor except for methyl.

In order to bring out the alternative ionization mechanism S_N1, the behavior of the halides was studied by these workers both in the highly ionizing solvent formic acid, and in the presence of the electrophilic reagent silver nitrate, which acts by virtue of its affinity for halogen. In these reactions the rate sequence was changed to

Me < Et > *n*-Pr > *iso*-Bu > Neopentyl

Steric hindrance was shown to be absent, and the last member reacted by a pure S_N1 mechanism. The fact that the Me–Et rate sequence is inverted speaks strongly for the idea that the ethyl halide reacts largely by the same mechanism, the inductive effect being operative in assisting the breaking of the carbon-halogen bond. This strongly suggests that the intermediate members also react by this mechanism in spite of the rate sequence Et > *n*-Pr > iso-Bu being opposite to that expected from the influence of the inductive effect. The authors' suggestion that the wrong sequence beyond ethyl is due to an appreciable incursion of mechanism S_N2 is therefore unlikely. An alternative explanation in the case of the silver ion catalyzed reaction is that the catalytic effect of solid silver halide produced during the reaction decreases along this series.

In the reaction of alkyl halides with mercuric

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[1] Dostrovsky and Hughes, *J. Chem. Soc.*, 157 ff. (1946).