THE THERMODYNAMIC PROPERTIES OF CESIUM METABORATE CsBO$_2$ FROM 5 TO 1000 K

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ABSTRACT

The low-temperature heat capacities of cesium metaborate were measured by adiabatic calorimetry from 9 to 346 K. High-temperature enthalpy increments of CsBO$_2$ were measured by drop calorimetry from 414 to 671 K. In addition, the melting data were measured by DSC. The thermodynamic functions $C_p^{\ominus}(T)$, $S^{\ominus}(T)$, $\{H^{\ominus}(T) - H^{\ominus}(298.15 \text{ K})\}$, $\Delta_f H^{\ominus}(T)$ and $\Delta_f G^{\ominus}(T)$ were calculated up to the melting point.

INTRODUCTION

In safety studies of water-cooled nuclear reactors it is suggested that cesium metaborate can be formed as a result of the interaction of the fission product cesium, the cooling water and the boron carbide control rods. In most studies the thermochemical calculations are based on the few data on cesium metaborate which are present in the literature. Khriplovich et al. [1] measured the low-temperature heat capacities, from which the entropy has been derived. The National Bureau of Standards (NBS) tables [2] give a value for the enthalpy of formation which has been derived from an unpublished thesis by Marakov [3].

Recently, we measured the enthalpy of formation by solution calorimetry [4]. The same sample has also been used to measure the low-temperature heat capacities and the melting data, while the enthalpy increments above 298.15 K have been measured on a second sample. The results enable us to calculate the thermodynamic functions of cesium metaborate up to 1000 K.

EXPERIMENTAL

The preparation of CsBO$_2$ from Cs$_2$CO$_3$ and B$_2$O$_3$ has been described previously [4]. In the present work, two different samples were used. The

TABLE 1

Analytical results for $CsBO_2$; mass fraction w [a]

Sample code	$w \times 10^2$ (Cs)		$w \times 10^2$ (B)		$w \times 10^2$ (SiO$_2$)
	Exp.	Calc.	Exp.	Calc.	
4	75.54 ± 0.08	75.64	6.192 ± 0.014	6.15	0.6
6	75.69 ± 0.05	75.64	6.155 ± 0.002	6.15	–

[a] The molar mass of $CsBO_2$ was taken as 175.714 g mol^{-1}.

samples were characterized by X-ray diffraction and chemical analyses. Cs was determined gravimetrically with kalignost, B was determined acidimetrically in the presence of manitol. The results of the analyses are given in Table 1.

For the low-temperature heat-capacity measurements, 24.7588 g of the $CsBO_2$-6 sample was loaded into the gold-plated copper calorimeter (laboratory designation W-9) provided with a screw-type closure with a stainless-steel knife edge and an annealed gold gasket. The loaded calorimeter was evacuated and 2.7 kPa of helium gas was added at 300 K to facilitate thermal contact between sample and calorimeter.

Heat-capacity measurements were made in the range 9–346 K in the Mark II adiabatic cryostat [5]. The calorimeter was surrounded by a shield system provided with automatic temperature control. A Leeds and Northrup capsule-type platinum-resistance thermometer (laboratory designation A-5) was used for temperature determinations. The thermometer was calibrated at the NBS against IPTS-1948 (as textually revised in 1960) [6] for temperatures above 90.2 K, against the NBS provisional scale from 10 to 90 K, and by the calibration technique of McCrackin and Chang [7] below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K from 10 to 90 K and to within 0.04 K above 90 K. Determinations of mass, current, voltage and time are referred to standardizations and calibrations performed at the NBS. The accuracy of a single heat-capacity measurement is considered to be about 0.5% from 10 to 15 K, increasing to about 0.1% between 30 and 350 K. The results are listed in Table 2.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl ether calorimeter which has been described previously [8]. Briefly, the sample is enclosed in a spherical vitreous silica ampoule with a wall thickness of 0.6 mm, a diameter of 20 mm and a volume of 4.2 cm^3. The ampoule is heated in a furnace whose temperature is measured with calibrated Pt–(Pt + 10 mass% Rh) thermocouples to ±0.1 K. After a reasonable equilibration time, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of heat

TABLE 2

Experimental low-temperature heat capacities of $CsBO_2$-6

T (K)	$C_p^{\ominus}(T)$ (J mol^{-1} K^{-1})	T (K)	$C_p^{\ominus}(T)$ (J mol^{-1} K^{-1})	T (K)	$C_p^{\ominus}(T)$ (J mol^{-1} K^{-1})
8.76	1.247	71.55	36.48	202.53	58.63
10.22	1.846	76.63	37.97	209.87	59.48
11.54	2.526	81.61	39.18	217.37	60.56
12.91	3.396	86.51	40.66	224.87	61.54
14.34	4.343	91.48	41.69	232.39	62.40
15.81	5.431	96.48	42.77	234.91	62.69
17.51	6.680	101.51	43.81	242.71	63.76
19.44	8.128	106.56	44.62	250.66	64.53
21.40	9.622	111.62	45.64	258.60	65.26
23.65	11.29	116.69	46.23	266.54	66.23
26.16	13.23	121.77	46.92	274.48	67.12
27.55	14.24	126.83	48.14	282.43	67.92
30.21	16.15	131.91	48.80	290.38	68.87
33.07	18.18	137.22	49.78	296.99	69.25
36.05	20.20	142.90	50.68	298.33	69.52
39.15	22.19	148.72	51.50	305.20	70.14
42.47	24.21	154.55	52.24	306.29	70.33
46.01	26.06	160.78	53.26	313.41	71.14
49.58	27.98	167.43	54.02	321.65	71.80
53.46	29.87	174.08	54.96	329.88	72.86
57.65	31.60	180.99	55.93	338.13	73.54
62.06	33.43	188.17	56.92	345.68	74.00
66.69	35.05	195.35	57.72		

TABLE 3

Calorimetric enthalpy increment measurements of $CsBO_2$-4

T (K)	$H^{\ominus}(T) - H^{\ominus}$(298.15 K) (J mol^{-1})		$\delta \times 10^2$
	Exp.	Calc.	
414.0	8554	8580	−0.30
415.1	8663	8667	−0.05
426.6	9549	9574	−0.26
428.1	9683	9694	−0.11
439.7	10610	10620	−0.09
469.4	13035	13036	−0.01
478.7	13808	13806	0.01
489.9	14735	14741	−0.04
506.2	16162	16117	0.28
532.0	18314	18333	−0.10
561.0	20911	20879	0.15
574.3	22140	22066	0.34
596.0	24017	24030	−0.05
621.4	26303	26368	−0.25
639.5	28013	28062	−0.17
671.2	31127	31082	0.14

input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063 J g^{-1}) and is obtained by calibration with α-SiO$_2$ and compared with the NBS standard reference material (No. 720) synthetic sapphire, Al$_2$O$_3$. Our results with sapphire all agree within 0.2% with the data given by the NBS. The enthalpy contributions of the vitreous silica were determined separately.

For the present measurements 8.5020 g CsBO$_2$-4 was enclosed in an ampoule af about 1.3 g. The results of the 16 measurements are listed in Table 3. A correction was made for the difference in enthalpy between the final calorimeter temperature and the standard reference temperature 298.15 K, using $C_p^{\ominus}(298.15$ K). In addition, the enthalpy was corrected for the presence of 0.6 mass% SiO$_2$.

The melting point of CsBO$_2$ was determined in a Mettler DSC apparatus (type TA-13) by heating the sample (CsBO$_2$-6) in an O$_2$ atmosphere at 10 K min^{-1}.

RESULTS

The smoothed low-temperature properties of CsBO$_2$ are listed in Table 4. The values $C_p^{\ominus}(298.15$ K$) = 69.49$ J mol^{-1} K^{-1} and $S^{\ominus}(298.15$ K$) = 105.38$ J mol^{-1} K^{-1} were derived from the smoothed curve. The individual measurements are plotted in Fig. 1.
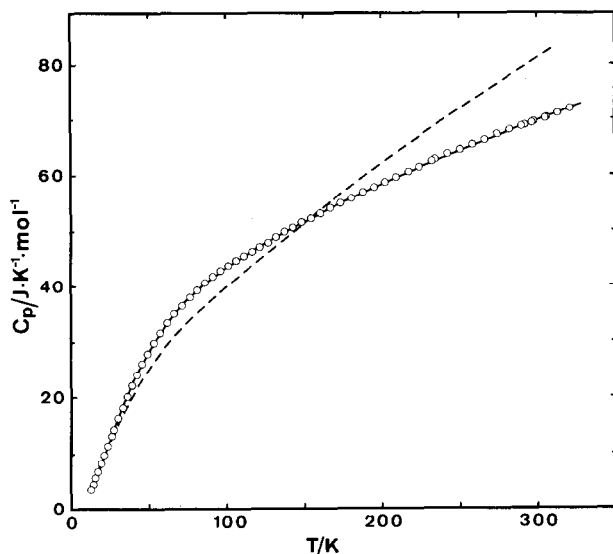

Fig. 1. The heat capacities of CsBO$_2$: — — — Khriplovich et al. [1]; O this work.

TABLE 4

Thermochemical functions of $CsBO_2$ from 10 to 340 K

T (K)	$C_p^{\ominus}(T)$ (J mol^{-1} K^{-1})	$\{S(T)-S^{\ominus}(0)\}$ (J mol^{-1} K^{-1})	$\{H^{\ominus}(T)-H(0)\}$ (J mol^{-1})	$-\{G^{\ominus}(T)-H^{\ominus}(0)\}$ (J mol^{-1} K^{-1})
10	1.742	0.584	4.387	0.313
15	4.797	1.820	20.229	0.472
20	8.556	3.708	53.478	1.031
25	12.377	6.028	105.84	1.796
30	16.026	8.612	176.94	2.712
40	22.657	14.151	371.11	4.872
50	28.201	19.832	626.73	7.297
60	32.583	25.376	931.50	9.851
70	36.077	30.670	1275.4	12.45
80	38.937	35.680	1650.9	15.04
90	41.339	40.409	2052.6	17.60
100	43.407	44.875	2476.6	20.11
120	46.937	53.109	3381.0	24.93
140	50.113	60.585	4351.9	29.50
160	53.089	67.474	5384.3	33.82
180	55.801	73.886	6473.6	37.92
200	58.329	79.897	7615.1	41.82
220	60.848	85.574	8806.8	45.54
240	63.333	90.976	10048.8	49.11
260	65.589	96.137	11338.5	52.53
280	67.626	101.07	12670.8	55.82
300	69.684	105.81	14043.8	59.00
320	71.781	110.37	15458.5	62.06
340	73.725	114.79	16914.3	65.04
273.15	66.938	99.406	12209.9	54.71
298.15	69.490	105.380	13915.0	58.71

The results of the drop calorimetric measurements can be represented by the polynomial equation

$$H^{\ominus}(T) - H^{\ominus}(298.15 \text{ K}) = 52.3364T + 3.31614 \times 10^{-2}T^2$$

$$+ (2.32955 \times 10^5)T^{-1} - 19333.28$$

The boundary conditions $H^{\ominus}(T) - H^{\ominus}(298.15 \text{ K}) = 0$ and $C_p^{\ominus} = 69.49$ J mol^{-1} K^{-1} were applied. The standard deviation is 0.19%.

The melting point of cesium metaborate was found to be 989.7 ± 0.3 K as a sharp and reproducible peak. The enthalpy of fusion, measured in the same runs, is $\Delta_{fus}H^{\ominus} = 34.8 \pm 1.0$ kJ mol^{-1}.

The thermodynamic quantities for $CsBO_2$ from 298.15 K to 989.7 K are given in Table 5. $\Delta_f H^{\ominus}(298.15 \text{ K})$ was taken from Konings et al. [4]. For the calculation of $\Delta_f H^{\ominus}(T)$ and $\Delta_f G^{\ominus}(T)$ the enthalpy increments and entropies of Cs, B and O_2 were taken from Glushko et al. [9].

TABLE 5

Thermochemical functions of CsBO$_2$ from 298.15 to 1000 K

T (K)	$C_p^{\ominus}(T)$ (J mol^{-1} K^{-1})	$S^{\ominus}(T)$ (J mol^{-1} K^{-1})	$-[G^{\ominus}(T) - H^{\ominus}(298)]/T$ (J mol^{-1} K^{-1})	$H^{\ominus}(T) - H^{\ominus}(298)$ (J mol^{-1})	$\Delta_f H^{\ominus}(T)$ (J mol^{-1})	$\Delta_f G^{\ominus}(T)$ (J mol^{-1})
298.15	69.490	105.380	105.380	0	-976 800	-919 917
300	69.645	105.810	105.384	128	-976 808	-919 566
400	77.410	126.933	108.210	7489	-979 137	-899 757
500	84.566	144.981	113.799	15 591	-978 980	-879 920
600	91.483	161.013	120.357	24 394	-978 345	-860 160
700	98.287	175.627	127.222	33 884	-977 201	-840 545
800	105.031	189.193	134.130	44 050	-975 547	-821 129
900	111.739	201.951	140.963	54 889	-973 394	-801 952
989.7	–	212.848	146.988	65 181	-1 031 820	-782 458

DISCUSSION

The low-temperature heat capacity measurements and the enthalpy incre-
ment measurements from 414 to 671 K smoothly join at 298.15 K, as is
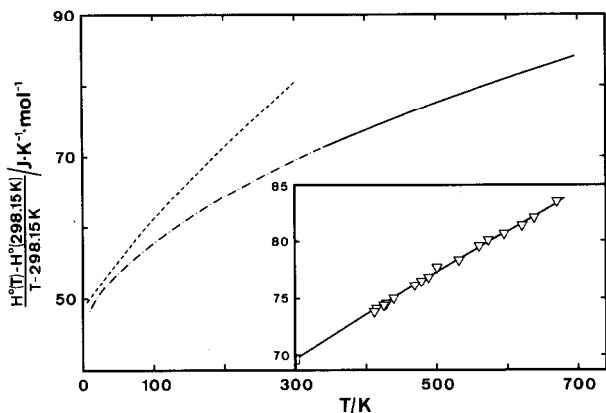

Fig. 2. The reduced enthalpy increment functions, · — · — · smoothed fit from the low-tempera-
ture measurements; ———— smoothed fit from high-temperature enthalpy measurements; ▽
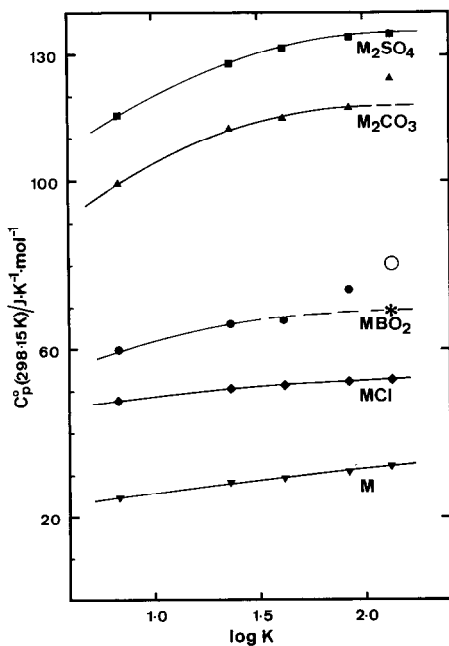experimental points; — — — smoothed fit from the results of Khriplovich et al. [1].

Fig. 3. A plot of $C_p^{\ominus}(298.15\ \text{K})$ versus the logarithm of the mass of the alkali atom ($\log K$).
M = Li, Na, K, Rb, Cs. The open circle indicates $C_p^{\ominus}(298.15\ \text{K})$ of $CsBO_2$ reported by
Khriplovich et al. [1]; the asterisk indicates the result of the present study.

shown in Fig. 2 in a $H^{\ominus}(T) - H^{\ominus}(298.15 \text{ K})/(T - 298.15)$ vs. T plot. The low-temperature heat capacities, reported by Khriplovich et al. [1], deviate considerably from the present results and are apparently in error (see also Fig. 1).

It is interesting to note that, although the value of $C_p^{\ominus}(298.15 \text{ K}) = 80.58$ J mol^{-1} K^{-1} given by Khriplovich et al. [1] differs significantly from the value found by us, the corresponding entropies (104.35 and 105.38 J mol^{-1} K^{-1}, respectively) are in reasonable agreement.

Supporting evidence for the rejection of the Khriplovich et al. [1] data is found in a plot of $C_p^{\ominus}(298.15 \text{ K})$ of the alkali metals and several alkali metal salts (the data were taken from the NBS tables [2]) versus the logarithm of the mass of the alkali atom (log K). The $C_p^{\ominus}(298.15 \text{ K})$ value reported by Khriplovich et al. [1] does not fit into the general relationship found in Fig. 3, while the value from the present study is in perfect agreement. It is hard to judge whether the discrepancy is the result of an impure sample, caused by an incomplete reaction of the starting materials [3], since little information about the preparation and purity is given. An interesting point is nevertheless the fact that the two other deviating points in Fig. 3, RbBO$_2$ and CsCO$_3$, have both been derived from measurements by the same group of investigators.

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