suming no falling off of intensity with q_k,[10] and a is chosen so that $\exp(-aq_k^2) = 0.1$ for the maximum value of q_k.

The prominent maximum at 2.52 Å. and the smaller one at 3.80 Å. may be taken as representing the Te–Br and Br–Br distances, respectively; ∠Br–Te–Br is then 98°. The asymmetric peak at about 5 Å. is without significance; false peaks at abscissas about twice those of prominent features are common[9] in radial distribution summations made with only one term for each feature of the diffraction pattern.

Theoretical curves (A to E of Fig. 1) for the correlation treatment were calculated with the use of the formula

$$I(q) = \frac{2}{2.51}\frac{(Z-f)_{\mathrm{Te}}}{(Z-f)_{\mathrm{Br}}}\sin(2.51\ \pi q/10) + 1/r \sin(\pi r q/10)$$

where Z is the atomic number, f the atom form factor, r the Br–Br distance, and $q = 40/\lambda \sin \theta/2$; account was taken of the variation of f with θ. The Te–Br distance was taken as 2.51 Å. in all cases.

The third, fifth and seventh minima are observed to be shallow (decreasingly in the order named) in comparison with the second, fourth, sixth, and eighth minima. The sixth maximum is a little more prominent than the fifth and seventh maxima. These features are best represented by a curve intermediate between B and C but very close to B, and we have, therefore, chosen as most probable the angle 98°, which is also given by the radial distribution curve. To this value we assign a limit of error of ± 3°. Comparison with C gives the same value for the tellurium–bromine distance as comparison with B. This distance is the sum of the covalent radii.[11] Curve E, with ∠Br–Te–Br = 155°, and curves for models with wider angles show regularly spaced strong maxima and do not correspond to the appearance of the photographs.

Summary

A redetermination of the structure of tellurium dibromide by the electron diffraction method has been carried out. The Te–Br distance 2.51 ± 0.02 Å. found agrees within experimental error with that found by Grether[3] in an earlier electron diffraction investigation (2.49 ± 0.03 Å.), but the molecule has been shown to be triangular with ∠Br–Te–Br = 98 ± 3°, rather than nearly linear with ∠Br–Te–Br ≥ 150° as reported by Grether.

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[10] The coefficients were chosen according to the recommendations of V. Schomaker, A. C. S. Meeting, Baltimore, April 1939.

[11] Linus Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 165.

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

Heats of Formation of $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$[1]

BY D. R. TORGESON[2] AND C. H. SHOMATE[3]

The system calcium oxide–boron oxide was investigated by Carlson[4] who established existence of four compounds: $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$. Present interest in calcium borate slags enhances the desirability of having adequate thermal data for these substances. This paper presents measurements of heats of solution in hydrochloric acid from which heats of formation of the four borates are obtained.

Materials

The calcium borates were prepared[5] by repeatedly heating, followed by grinding, stoichiometric mixtures of calcium and boric oxides. The heating periods were of two to three hours duration. The materials were analyzed between heatings and small additions of boric oxide were made to compensate for boric oxide lost by volatilization. Table I lists the temperature of preparation and actual and theoretical analyses of the borates. The method of analysis for calcium and boric oxides was that described by Carlson.[4]

TABLE I

ANALYSES OF CALCIUM BORATES

Substance	t, °C.	Actual analyses CaO, %	Actual analyses B_2O_3, %	Theoretical analyses CaO, %	Theoretical analyses B_2O_3, %
$3CaO \cdot B_2O_2$	1200–1350	70.76	29.32	70.72	29.28
$2CaO \cdot B_2O_2$	1200	61.71	38.31	61.69	38.31
$CaO \cdot B_2O_2$	1200	44.67	55.36	44.61	55.39
$CaO \cdot 2B_2O_2$	950–970	28.58	71.12	28.71	71.29

The calcium diborate contained a measured 0.42% insoluble impurity, formed by superficial reaction with the nickel crucible in which it was prepared. This was not observed for the other borates.

X-Ray diffraction examination[6] was made of the borates. Each gave a distinct diffraction

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[3] Formerly chemist, Pacific Experiment Station, Bureau of Mines.

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

[5] These compounds were prepared and their densities determined by R. J. O'Dea, formerly chemist, Pacific Experiment Station, Bureau of Mines.

[6] The X-ray diffraction pictures were taken by A. E. Salo, formerly metallurgist, Pacific Experiment Station, Bureau of Mines.

TABLE II

HEATS OF SOLUTION AT 298.16°K. IN 1.000 *N* HYDROCHLORIC ACID (CAL. PER MOLE)

Result no.	Heats of solution				
	$3CaO\cdot B_2O_3$ ΔH_1	$2CaO\cdot B_2O_3$ ΔH_2	$CaO\cdot B_2O_3$ ΔH_3	$CaO\cdot 2B_2O_3$ ΔH_4	CaO ΔH_5
1	−82413	−50252	−20261	−10075	−46394
2	−82425	−50287	−20249	−10095	−46355
3	−82398	−50301	−20255	−10089	−46377
4	−82435	−50298	−20258	−10085	−46375
5	−82434	−50316	−20257	−10069	−46388
6	−82432	−50270	−20276	−10069	−46388
Mean	−82423 ± 12	−50287 ± 20	−20259 ± 8	−10080 ± 10	−46380 ± 11

pattern in which it is notable that the strong lines of calcium and boric oxides were absent.

Unpublished high-temperature heat content measurements of $3CaO\cdot B_2O_3$ and $2CaO\cdot B_2O_3$ have been made. Each showed only small premelting effects, again indicative of high purity.

Calcium oxide was made by calcining special reagent grade calcium carbonate at 1,200°. Analysis indicated 99.7% CaO, the remainder being largely inert material.

The boric oxide was the crystalline material previously used for low-temperature heat capacity[7] and high temperature heat content[8] measurements. It was redried for twenty-six hours at 400° before use. The previous analysis was checked, 99.8% B_2O_3.

The 1.000 *N* hydrochloric acid was made by dilution of reagent grade 36% acid with distilled water in three batches of about 40 liters each. The basis of standardization was titration against sodium carbonate, prepared by heating reagent grade sodium bicarbonate to constant weight at 290°. The normality of one batch was further confirmed by gravimetric determination of chloride by silver chloride precipitation.

Method and Results

The apparatus employed in the heat of solution measurements was that described by Southard,[9] including minor modifications by Young.[10]

In all heat of solution measurements, 1.000 *N* hydrochloric acid was employed as the solvent. The amounts of materials dissolved were such that the final concentration of calcium ion was that obtained by dissolving 1 g. of calcium oxide in 1845.5 g. of 1.000 *N* hydrochloric acid. In other words, the amounts dissolved in 1845.5 g. of acid were: 1.0000 g. of CaO, 1.4139 g. of $3CaO\cdot B_2O_3$, 1.6209 g. of $2CaO\cdot B_2O_3$, 2.2418 g. of $CaO\cdot B_2O_3$, and 3.4836 g. of $CaO\cdot 2B_2O_3$. In the case of crystalline boric oxide, it was necessary to cover the range of concentrations equivalent to the solutions of the borates. This was accomplished by dissolving various amounts of boric oxide in 1845.5 g. of 1.000 *N* hydrochloric acid to which had been added 1 g. of calcium oxide, as will be seen later.

TABLE III

HEAT OF SOLUTION AT 298.16°K. OF CRYSTALLINE B_2O_3 IN 1.000 *N* HCl (CAL. PER MOLE)

Result	Measured values		Interpolated values	
	B_2O_3 dissolved, g.	Heat of solution	B_2O_3 dissolved, g.	ΔH_6
1	0.4045	−3295	0.4139	−3286 ± 7
2	.4098	−3308	.6209	−3289 ± 7
3	.3891	−3269	1.2418	−3298 ± 7
4	.4763	−3291	2.4836	−3316 ± 7
5	.6120	−3279		
6	.6811	−3284		
7	1.2938	−3303		
8	1.2447	−3302		
9	2.4558	−3317		
10	2.4097	−3318		
11	2.4734	−3313		

The time required for solution and attainment of equilibrium was short, three to five minutes, except for $CaO\cdot 2B_2O_3$ which required forty-eight minutes, even after grinding to −200 mesh.

The results are expressed in defined calories[11] (1 cal. = 4.1833 int. joules) per gram formula weight, the latter being in accordance with the 1941 International Atomic Weights. Corrections of weighings to vacuum basis were made with the aid of the following densities[5]: $3CaO\cdot B_2O_3$, 3.08; $2CaO\cdot B_2O_3$, 2.81; $CaO\cdot B_2O_3$, 2.71; $CaO\cdot 2B_2O_3$, 2.69; B_2O_3, 2.46; and CaO, 3.30 g./ml.

The results appear in Tables II and III. The method of Rossini and Deming[12] was used in calculating the precision uncertainties.

No corrections were necessary in the measured results for $3CaO\cdot B_2O_3$, $2CaO\cdot B_2O_3$ or $CaO\cdot B_2O_3$. The results for $CaO\cdot 2B_2O_3$ were corrected for the previously mentioned 0.42% insoluble impurity, equivalent to 42 cal. per mole. A correction of 69 cal. per mole is involved in the calcium oxide results, to take account of impurities. Likewise, a correction of 21 cal. per mole was made in the boron oxide results for an estimated 0.1% water content.

It is noted that the boron oxide values show a trend with solution concentration. The results are represented within an average precision uncertainty of ±7 cal. per mole by the equation

$$\Delta H_6 = -3280 - 14.60\ C$$

in which *C* is the amount in grams of boron ox-

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

[8] Southard, *ibid.*, **63**, 3147 (1941).

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

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

[11] Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

[12] Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

ide dissolved in 1845.5 g. of 1.000 *N* hydrochloric acid. The equation yields the interpolated values in Table III.

Heats of Formation

The data of Tables II and III are sufficient for obtaining the heat of formation of each calcium borate from the component oxides, care being taken to use the proper heat of solution value for boric oxide. For example, for the reaction $3CaO + B_2O_3$ (crystalline) $= 3CaO{\cdot}B_2O_3$, $\Delta H_{298.16} = 3\Delta H_5 + \Delta H_6 - \Delta H_1 = -3 \times 46{,}380 - 3{,}286 + 82{,}423 = -60{,}000 \pm 40$ cal. per mole. Results, computed in this manner, are in Table IV.

TABLE IV

HEATS OF FORMATION (CAL. PER MOLE)

Substance	From oxides, $\Delta H_{298.16}$	From elements, $\Delta H_{298.16}$
$3CaO{\cdot}B_2O_3$	-60000 ± 40	-858200
$2CaO{\cdot}B_2O_3$	-45760 ± 30	-692100
$CaO{\cdot}B_2O_3$	-29420 ± 20	-524000
$CaO{\cdot}2B_2O_3$	-42930 ± 20	-880200

To obtain the heats of formation from the elements (also in Table IV), there are needed the heats of formation of calcium and boric oxides. For the former, the result given by Bichowsky and Rossini[13] is adopted, $\Delta H_{291} = -151{,}800$ cal. per mole; the error in assigning this value to 298.16°K. is inconsequential. Rossini[14] has re-evaluated Todd and Miller's[15] heat of formation result for boric oxide glass, obtaining $\Delta H_{298.16} = -338{,}400$ cal. per mole. Southard[8] found $\Delta H_{298.16} = -4{,}360$ cal. per mole for the transformation of glassy boric oxide to crystalline boric oxide. Combining these figures, there is obtained $\Delta H_{298.16} = -342{,}760$ cal. per mole as the heat of formation of crystalline boric oxide. This value is used in deriving the column labelled "from elements" in Table IV. It is not possible at this time to assign precision uncertainties to values in this column.

It does not appear worthwhile to attempt to compare with heats of formation from the elements listed by Bichowsky and Rossini.[13] Their results are based on a greatly different value for the heat of formation of boric oxide and on rather crude heat of solution measurements of the borates by Griveau.[16]

Summary

Heats of solution of $3CaO{\cdot}B_2O_3$, $2CaO{\cdot}B_2O_3$, $CaO{\cdot}B_2O_3$, $CaO{\cdot}2B_2O_3$, CaO and B_2O_3 (crystalline) in 1.000 *N* hydrochloric acid were measured at 298.16°K.

The results are used to obtain heats of formation of the four calcium borates from the component oxides and from the elements.

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[13] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

[14] Rossini, personal communication.

[15] Todd and Miller, THIS JOURNAL, **68**, 530 (1946).

[16] Griveau, *Compt. rend.*, **166**, 993 (1918).

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

High-Temperature Heat Contents of Uranium, Uranium Dioxide and Uranium Trioxide[1]

BY G. E. MOORE[2] AND K. K. KELLEY[3]

In the autumn of 1942, the Pacific Experiment Station of the Bureau of Mines undertook the measurement of the high-temperature heat contents of uranium, uranium dioxide, and uranium trioxide, at the request of Professor H. C. Urey of Columbia University. The data were needed in connection with a then current National Defense Research Committee project and, as the Bureau of Mines had the only equipment for such measurements known to be in operating condition at the time, this arrangement was the most expeditious way of obtaining the desired values. The results of this work are the subject of the present paper. No previous, similar measurements of these three substances have been reported.

Materials

The materials came to us from E. A. Long, who was associated with Professor Urey at the time. The metal and the dioxide were of high purity but the trioxide required a purification treatment before use in the measurements.

The uranium sample consisted of two solid chunks of metal, semi-circular in cross-section, which together formed a circular cylinder of 1.3 cm. diameter and 1.3 cm. height. The uranium content, according to our analyses, was 99.71%.

The uranium dioxide was in the form of powder and was composed of well-crystallized particles. Our analyses gave 88.26 per cent. uranium, as compared with the theoretical 88.15 per cent.

The uranium trioxide also was in powder form. As received, it contained 1.17% water not removable at 120°. This was determined by heating a weighed portion to 1,000° and absorbing the expelled water in Dehydrite. The material

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