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

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

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.

(14) Rossini, personal communication.
(15) Todd and Miller, THIS JOURNAL, **68**, 530 (1946).
(16) Griveau, Compt. rend., **166**, 993 (1918).

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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.

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.
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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

was purified by heating seventy-nine hours at 550 to 600° in a stream of dry oxygen. During this period, a Dehydrite tube collected from the exit gas an amount of water corresponding to 1.15% of the weight of the sample, in substantial agreement with the above determination. The orange-yellow color of the material did not change noticeably during this treatment, indicating inappreciable decomposition. Final analyses gave 83.02% uranium, as compared with the theoretical 83.22%.

Measurements and Results

The heat contents were determined by the "drop" method in a previously described[4] apparatus. The calorimeter was calibrated electrically in terms of the defined calorie[5] (1 cal. = 4.1833 int. joules).

The uranium was enclosed in silica-glass capsules during the measurements, the capsules having been sealed in an atmosphere of helium. Two series of measurements were made. In the first series, 30.476 g. of uranium was used and the silica capsule weighed 4.110 g. The second series was made with 30.467 g. of uranium in a 4.035-g. capsule. The heat content of the capsule in each instance averaged about 46% of the total measured heat content. Corrections for the capsules were made using the combined data of White,[6] Southard,[4] and Naylor[7] for silica-glass. The possible uncertainty in the correction is large enough to produce a corresponding maximum uncertainty in the uranium results ranging from 1.5% at the lowest temperatures to 0.2% at the highest.

The uranium dioxide measurements were made with a 27.617-g. sample that was sealed by platinum welding in a platinum–rhodium capsule weighing 8.888 g. The heat content of the capsule, which was determined separately, averaged 15% of the total measured heat content.

The uranium trioxide measurements were made with a 20.698-g. sample, sealed by gold soldering in a 8.726-g. platinum–rhodium capsule. The quantity of gold used in soldering was 0.112 g. The heat content of the capsule material was determined separately and available data[8] were employed in computing the heat content of the small amount of gold. The combined heat contents of platinum–rhodium and gold comprised about 17% of the total measured heat content at all temperatures.

The results are assembled in Tables I, II and III, being listed in the order in which they were measured. Figure 1 shows the heat contents plotted against temperature.

(4) Southard, THIS JOURNAL, 63, 3142 (1941).

(5) Mueller and Rossini, Am. J. Physics, 12, 1 (1944).

(6) White, Am. J. Sci., 47, 1 (1919); THIS JOURNAL, 55, 1050 (1933).

(7) Kelley, Naylor and Shomate, Bur. Mines Tech. Paper, 686, 1946, 34 pp.

(8) Kelley, Bur. Mines Bull., 371 (1934) 78 pp.

TABLE I

HIGH-TEMPERATURE HEAT CONTENTS OF URANIUM (AT. WT., 238.07)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
Series I		Series II	
474.9	1250	983.2	6680
472.3	1225	1054.3	8565
657.4	2730	997.3	6825
737.8	3465	1014.8	7010
871.4	4795	1036.8	7315
867.4	4785	1049.2	8505
1070.4	8715	917.8	5320
1065.6	8680	935.1	5965
1173.7	9640	944.7	6285
1160.1	9540	955.1	6385
1269.9	10530	927.4	5440
		798.8	4045
		1276.4	10605

TABLE II

HIGH-TEMPERATURE HEAT CONTENTS OF URANIUM DIOXIDE (MOL. WT., 270.07)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
483.4	3175	1055.7	14440
484.2	3185	1068.2	14680
643.7	6185	1270.3	18875
662.1	6545	1269.9	18875
868.0	10615	758.8	8455
868.1	10615	1424.6	22170
965.9	12595	1462.5	22970

TABLE III

HIGH-TEMPERATURE HEAT CONTENTS OF URANIUM TRIOXIDE (MOL. WT., 286.07)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
415.6	2440	700.8	8850
416.9	2450	775.9	10600
487.7	3985	805.4	11295
486.4	3995	867.0	12765
586.3	6200	885.6	13200
674.9	8260	576.2	5975

Nothing unusual was observed in the behavior of the two oxides, but the metal exhibits two sharp transitions at 935 ± 3°K. and 1,045 ± 3°K., respectively. Results near the transition temperatures were accurately reproducible and there was no evidence of hysteresis. The heat and entropy of the 935°-transition are, respectively, 680 cal./g. atom and 0.73 cal./deg./g. atom. Corresponding values for the 1,045°-transition are 1,165 cal./g. atom and 1.11 cal./deg./g. atom.

The heat content results in Table I to III may be represented by the following relationships for which the temperature range of validity and mean deviation from the measured values are indicated in parentheses.

$$U(\alpha): H_T - H_{298.16} = 3.15T + 4.22 \times 10^{-3}T^2 - 0.80 \times 10^5 T^{-1} - 1046 \ (298°-935°K.; 0.2\%)$$

$$U(\beta): H_T - H_{298.16} = 10.38T - 3525 (935°-1045°K.; 0.1\%)$$

U(γ): $H_T - H_{298.16} = 9.10T - 1026(1045°-1300°K.;$
$\qquad\qquad\qquad\qquad\qquad 0.1\%)$

UO₂: $H_T - H_{298.16} = 19.20T + 0.81 \times 10^{-3}T^2 + 3.957 \times 10^5 T^{-1} - 7124 \ (298°-1500°K.; \ 0.1\%)$

UO₃: $H_T - H_{298.16} = 22.09T + 1.27 \times 10^{-3}T^2 + 2.973 \times 10^5 T^{-1} - 7696 \ (298°-900°K.; \ 0.1\%)$

The heat content equations on differentiation yield the corresponding specific heat expressions listed

U(α): $C_p = 3.15 + 8.44 \times 10^{-3}T + 0.80 \times 10^5 T^{-2}$

U(β): $C_p = 10.38$

U(γ): $C_p = 9.10$

UO₂: $C_p = 19.20 + 1.62 \times 10^{-3}T - 3.957 \times 10^5 T^{-2}$

UO₃: $C_p = 22.09 + 2.54 \times 10^{-3}T - 2.973 \times 10^5 T^{-2}$

Table IV gives even temperature values of the heat content and entropy increments above 298.16°K. The former were read from smooth curves through the measured values. The latter were obtained by graphical integration of the measured values in the case of the metal and by integration of the heat content equations in the case of the oxides. The use of the equations for the oxides was justified as the maximum deviation from experimental values could alter the entropy at any temperature by only 0.01 unit at most.

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	U		UO₂		UO₃	
T, °K.	$H_T -$ $H_{298.16}$, cal./mole	$S_T -$ $S_{298.16}$, cal./ deg./ mole	$H_T -$ $H_{298.16}$, cal./ mole	$S_T -$ $S_{298.16}$, cal./ deg./ mole	$H_T -$ $H_{298.16}$, cal./ mole	$S_T -$ $S_{298.16}$, cal./ deg./ mole
400	690	1.98	1680	4.82	2090	6.01
500	1430	3.63	3470	8.82	4260	10.86
600	2240	5.10	5340	12.24	6510	14.96
700	3110	6.44	7280	15.22	8820	18.51
800	4060	7.71	9250	17.84	11160	21.64
900	5120	8.95	11250	20.21	13540	24.44
935	5500(α)	9.37	...	...		
935	6180(β)	10.10	...	...		
1000	6855	10.80	13280	22.35		
1045	7320(β)	11.25	...	...		
1045	8485(γ)	12.36	...	...		
1100	8985	12.83	15340	24.30		
1200	9895	13.62	17420	26.11		
1300	10805	14.35	19510	27.79		
1400			21620	29.36		
1500			23750	30.83		

There are no previous data with which to compare any of these values. It may be of interest to note that the data indicate that the specific
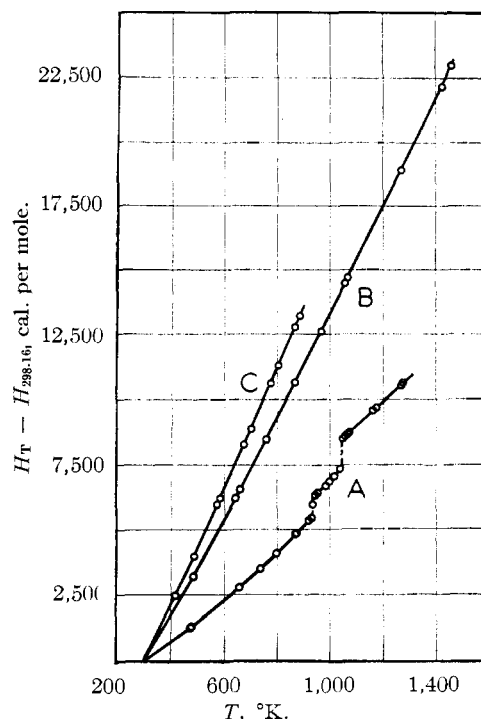

Fig. 1.—High-temperature heat contents: A, uranium; B, uranium dioxide; C, uranium trioxide.

heat of the low-temperature modification of uranium increases from 6.57 cal./deg./g. atom at room temperature to 10.84 at 900°K. Likewise, the indicated trend in the specific heat of the dioxide is from 15.2 to 21.4 cal./deg./mole in the range 298 to 1,500°K.; and for the trioxide, from 19.5 to 24.0 cal./deg./mole in the range 298 to 900°K.

Summary

High-temperature heat contents of uranium, uranium dioxide, and uranium trioxide were measured from 298.16 to 1,300, 1,500 and 900°K., respectively.

Uranium undergoes two sharp transitions, at 935° ± 3° and 1,045° ± 3°K. The heats of transition are 680 and 1,165 cal./g. atom, respectively.

Equations representing the experimental results were derived and a table of heat content and entropy increments above 298.16°K. was compiled.