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Low Temperature Heat Capacity and Thermodynamic Functions of Triuranium Octoxide[1]

BY EDGAR F. WESTRUM, JR., AND FREDRIK GRØNVOLD

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The heat capacity of U_3O_8 has been measured over the range 5 to 350°K. A small λ-type anomaly was observed with a maximum at 25.3°K. and an entropy increment of 0.56 e.u. per mole of U_3O_8. The transition is presumed by its similarity with that in UO_2 to be of magnetic origin. Thermodynamic functions have been calculated by numerical quadrature of the heat capacity and the values of C_p, $S°$, $H° - H°_0$, and $-(F° - H°_0)/T$ at 298.15°K. are: 56.87 cal. deg.$^{-1}$ mole^{-1}, 67.534 cal. deg.$^{-1}$ mole^{-1}, 10216 cal. mole^{-1} and 33.572 cal. deg.$^{-1}$ mole^{-1}, respectively.

Low temperature heat capacity measurements of the structurally-related uranium oxides UO_2[2] and U_4O_9[3] have shown the presence of a λ-type transition only in the former, associated with an antiferromagnetic ordering[4] of the uranium atoms below 30°K. Therefore it seemed of interest to study other uranium oxides to gain further insight in the conditions under which such transitions occur, and for this purpose the heat capacity of U_3O_8 has been measured in the low temperature range. There is, furthermore, a need for precise data on the thermodynamic properties of U_3O_8, as the only existing heat capacities are average values from drop calorimetric data by Russell[5] over three regions in the range 82.7 to 314.6°K., one very old set of measurements[6] in the range 0 to 100° and a more recent one[7] in the range 25 to 100°.

Reasonable extrapolations or interpolations have been made, however, on the basis of the data obtained[2] for UO_2 and UO_3, but they are likely to be in some error because of the rather different structures for the oxides and the occurrence of λ-type transformations. The existence of an additional crystalline form of U_3O_8, a metastable orthorhombic β-modification[8] obtained by oxidation of $UO_{2.64}$ in oxygen to 750°, has been claimed. Subsequently evidence for still another modification with cubic structure has been obtained[9] by heating U_3O_8 and silica in a sealed gold capsule at about 700° under a pressure of 4000 atm.

The structure of the ordinary orthorhombic U_3O_8 (or α-U_3O_8) studied here is not as closely related to either that of α-UO_3 or ReO_3 as supposed by earlier investigators,[10-12] in that the oxygen atoms do not surround the uranium in the form of staggered hexagons and deformed hexagonal double pyramids or octahedra with anion vacancies. Recent neutron diffraction work by Andresen[13] has shown that two-thirds of the uranium atoms are surrounded by seven oxygen atoms at the corners of a pentagonal double pyramid and one-third by six oxygen atoms at the corners of an octahedron. X-Ray single crystal studies by Chodura and Maly[14] indicated the presence of two different kinds of U_3O_8 crystals, one

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[1] This work was supported in part by the Division of Research, U. S. Atomic Energy Commission.

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orthorhombic, the other monoclinic in the form of twins. These structures have a close relationship to that proposed by Andresen,[13] confirming the slight movement of some of the uranium atoms from special to more general positions, but superstructure reflections were observed which require a doubling of the *c*-axis. The scattering ratio of uranium to oxygen is considerably greater for neutrons than for X-rays; hence, the coördinates of the oxygen atoms found by neutron diffraction are considered to be more reliable in establishing the main features of the U_3O_8 structure.

U_3O_8 Sample.—The U_3O_8 sample was obtained by purifying uranyl nitrate hexahydrate, A.R., following essentially the procedure used by Hönigschmid.[15] This U_3O_8 was reduced to UO_2 by heating it in dry, purified hydrogen gas at 500° until the formation of water ceased. The temperature was raised to 1200° and the sample kept at this temperature for 4 hr. before cooling to room temperature. It then was oxidized in air at 800° to constant weight, transferred to a vitreous silica tube which was evacuated and sealed, heated at 800° for seven days and gradually cooled to room temperature over a period of two months.

Spectrographic analysis of the U_3O_8 sample showed the presence of these impurities (in p.p.m.): Al 60, B $<$ 0.08, Cu 3, Fe 10, Mg 30, Ni 20 and Si 200. The weight increase upon oxidation of UO_2 to U_3O_8 corresponded to the theoretical value within 0.01 O/U atom, and X-ray powder photographs showed only the presence of the U_3O_8-phase described earlier.[16]

Experimental Technique.—The Mark I cryostat and the technique employed in low temperature adiabatic calorimetry are described elsewhere.[17] The copper calorimeter (laboratory designation W-9) has a capacity of 90 cc.; it is gold-plated inside and out and has six vanes. The heat capacity of the empty calorimeter was determined separately, using the same thermometer and heater and exactly the same amount of indium-tin solder for sealing. The calorimeter, thermometer and heater represented from 15 to 39% of the total heat capacity observed. Corrections for a slight difference in the amount of Apiezon-T grease on the empty and loaded calorimeter were applied. The platinum resistance thermometer (laboratory designation A-3) has been calibrated by the National Bureau of Standards, and the temperatures are judged to correspond with the thermodynamic temperature scale within 0.1°K. from 5 to 10°K., within 0.03°K. from 10 to 90°K., and within 0.04°K. from 90 to 350°K. Precision is considerably better, and the temperatures are probably correct to 0.001°K. after corrections for quasi-adiabatic drift.

The calorimeter was loaded with sample and evacuated, and helium was added at 4 cm. pressure at 25° to provide thermal contact between sample and calorimeter. The mass of the calorimetric sample was 267.942 g.

Results

The heat capacity determinations are listed in Table I in chronological order, expressed in terms of the thermochemical calorie, defined as 4.1840 absolute joules. The ice point was taken to be 273.15°K. and the atomic weight of uranium as 238.07. The data are presented in terms of one mole of U_3O_8, *i.e.*, 842.21 g. An analytically-determined curvature correction was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments usually can be inferred from the adjacent mean temperatures in Table I.

TABLE I

HEAT CAPACITY OF U_3O_8 IN CAL. DEG.$^{-1}$ MOLE^{-1}

Molecular weight = 842.21; 0°C. = 273.15°K.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		36.93	7.960	18.09	2.395
		39.63	8.681	19.96	3.123
95.80	26.78			21.92	4.084
103.64	28.85	Series IV		23.07	4.770
112.78	31.13			23.46	5.050
122.11	33.29	13.80	1.174	23.83	5.331
131.23	35.28	15.07	1.473	24.18	5.639
140.23	37.08	16.76	1.949	24.51	5.974
148.76	38.68	18.43	2.516	24.83	6.362
157.14	40.16	20.36	3.311	25.13	6.922
165.91	41.57	22.33	4.324	25.42	6.396
175.01	43.03	24.21	5.737	25.76	4.935
184.09	44.40	26.45	5.228	26.12	4.873
193.22	45.68	29.37	5.542	26.50	4.903
202.34	46.91	32.59	6.461	26.87	4.942
211.63	48.12	35.90	7.485	27.23	5.001
221.06	49.29	39.52	8.613	27.58	5.072
		43.56	9.960	28.01	5.181
Series II		47.96	11.444		
		52.85	13.117	Series VI	
214.07	48.41	58.24	14.953		
223.37	49.43	64.29	17.03	17.11	2.059
232.88	50.62	70.92	19.20	18.94	2.707
242.51	51.76	77.69	21.38	22.17	4.224
251.93	52.72	84.49	23.50	23.22	4.885
261.09	53.64	91.87	25.71	24.17	5.626
270.15	54.39	99.98	27.90	24.73	6.222
279.15	55.28			24.96	6.493
288.06	56.10	Series V		25.11	6.950
296.92	56.77	4.77	0.078	25.24	8.087
305.72	57.44	5.36	.114	25.35	7.675
314.45	58.07	6.25	.155	25.41	6.883
323.32	58.66	7.32	.221	25.49	5.261
332.11	59.20	8.37	.314	25.58	5.175
340.03	59.67	9.22	.437	25.65	5.030
346.86	60.07	10.11	.510	25.73	4.994
		10.99	.633	25.81	4.893
Series III		11.95	.794	25.90	4.863
		13.06	1.016	26.00	4.852
24.80	6.321	11.46	0.703	26.15	4.867
26.78	4.977	12.44	0.877	26.34	4.840
29.16	5.483	13.59	1.126	26.48	4.985
31.62	6.178	14.96	1.461	26.68	4.880
34.24	6.820	16.47	1.857	27.97	5.188

The heat capacity *versus* temperature curve is shown in Fig. 1 over the low temperature region, where a λ-type transition is encountered at about 25°K. This transition resembles that found in UO_2, but it is not as large and its maximum lies about 4°K. lower.

Values of C_p, $S°$, $H° - H°_0$, and $-(F° - H°_0)/T$ for U_3O_8 at selected temperatures are listed in Table II. The enthalpy, entropy and free-energy increments were computed by numerical integration, using graphically-interpolated values of heat capacity. The heat capacity values are considered to have a probable error of about 5% at 5°K., 1% at 10°K. and 0.1% above 25°K. Values below 5°K. were extrapolated with a T^3 function. The effects of nuclear spin and isotopic mixing are not included in the entropy and free-energy values. The estimated probable error in the thermodynamic functions is 0.1% above 100°K., but some of the values are given to an additional digit for comparison purposes.

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TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF U_3O_8

T, °K.	C_p, $\frac{\text{cal.}}{\text{deg. mole}}$	$S°$ $\frac{\text{cal.}}{\text{deg. mole}}$	$H° - H°_0$ $\frac{\text{cal.}}{\text{mole}}$	$\frac{-(F° - H°_0)}{T}$, $\frac{\text{cal.}}{\text{deg. mole}}$
10	0.49	0.196	1.42	0.054
15	1.47	0.558	6.06	.154
20	3.16	1.188	17.23	.326
25	6.72	2.192	40.14	.587
30	5.73	3.163	66.78	.937
35	7.21	4.155	99.07	1.324
40	8.77	5.219	139.0	1.745
45	10.45	6.348	187.0	2.193
50	12.15	7.537	243.4	2.668
60	15.55	10.052	381.9	3.417
70	18.90	12.701	554.2	4.784
80	22.10	15.436	759.3	5.945
90	25.16	18.218	995.8	7.154
100	27.89	21.011	1261.1	8.399
110	30.46	23.791	1553.0	9.673
120	32.82	26.544	1869.5	10.965
130	35.00	29.257	2208.7	12.267
140	37.01	31.926	2568.8	13.577
150	38.87	34.543	2948.3	14.888
160	40.61	37.108	3345.7	16.197
170	42.24	39.619	3760.0	17.501
180	43.79	42.078	4190.3	18.799
190	45.25	44.484	4635.5	20.087
200	46.62	46.841	5095	21.367
210	47.92	49.148	5568	22.636
220	49.14	51.405	6053	23.892
230	50.30	53.616	6550	25.137
240	51.40	55.779	7059	26.368
250	52.47	57.900	7578	27.588
260	53.49	60.100	8107	28.916
270	54.45	62.013	8648	29.985
280	55.35	64.011	9197	31.166
290	56.21	65.968	9754	32.332
300	57.01	67.887	10321	33.485
350	60.25	76.933	13256	39.058
273.15	54.74	62.647	8819	30.360
298.15	56.87	67.534	10216	33.572

Discussion

It is interesting to compare the present results with the only existing low temperature enthalpy data, obtained by Russell[5] in 1912 by drop calorimetry. The mean values from his work are presented in Table III. The agreement between the first set of values is very good, while that for the other two is poorer. The drop calorimetry value by Donath[6] in the range 0 to 100° and the NBS value[7] in the range 25 to 100° are considerably higher than those obtained by extrapolation of the present results.

TABLE III

COMPARISON WITH EARLIER ENTHALPY MEASUREMENTS

T_1, °K.	T_2, °K.	$H_{T_2} - H_{T_1}$, cal./mole Russell[5]	This research
82.7	195.0	4052	4044
196.1	273.2	3997	3906
275.7	314.6	2322	2205

The enthalpy and entropy increments associated with the λ-type transition at 25.3°K. are 12 cal. mole^{-1} and 0.56 cal. deg.$^{-1}$ mole^{-1} of U_3O_8, respectively. They were evaluated by subtracting the lattice contribution from the total increment in the range 10 to 40°K. The lattice heat capacity values were estimated on the basis of a linear change in Debye θ's with temperature from 218 at 10°K. to 324 at 40°K. This is indicated in Fig. 1 by a dashed line. The entropy increment associated with the λ-type transition is about 21% of the entropy increment observed per uranium atom for UO_2 (0.87 e.u. per mole UO_2).[2] and because of the proximity of the transition temperatures, one might be led to assume that the U_3O_8 sample contained UO_2. Further consideration shows that this is unlikely because (1) the weight increase upon oxidation of the UO_2-sample to U_3O_8 had the expected value, (2) X-ray powder photographs of the sample showed only lines from the U_3O_8-phase and (3) if the sample were deficient in oxygen, U_4O_9 should be formed (as is known to be the case under the same heating conditions)[3] as it does not show a λ-type transition. Nevertheless, a new U_3O_8-sample was made up from uranyl acetate dihydrate which was first ignited over a Bunsen burner and then heated in air to constant weight in an electric muffle furnace at about 1000° and cooled to room temperature. A sample weighing 142.296 g. was loaded into the calorimeter as before, and 18 runs were made in the region from 21.05 to 27.86°K. which showed the presence of the transition at the same temperature and the same enthalpy increment within a few tenths of 1%.

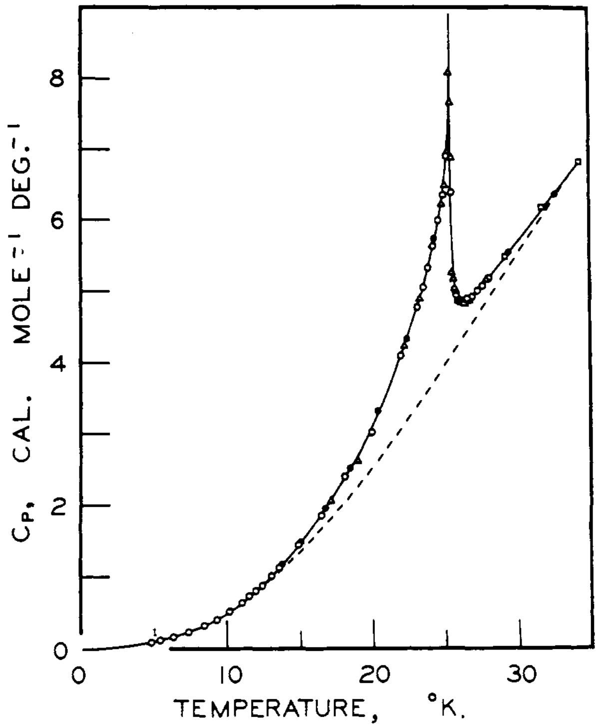

Fig. 1.—Molal heat capacity of U_3O_8 from 5 to 35°K. Data from series III, IV, V and VI are indicated by □, ●, ○, and △, respectively. The dashed line indicates the estimated lattice heat capacity.

With respect to its magnetic properties, U_3O_8 behaves as if it consists of U^{5+} and U^{6+} ions, and not of U^{4+} and U^{6+} ions,[18] on the assumption of spin-only magnetism. The same conclusion was reached by Dawson and Lister,[19] but deviations from the Curie–Weiss law were observed. The U^{6+} ions have no unpaired electrons, while U^{5+} has one, supposedly in a 5f orbital, which gives rise to the paramagnetism of U_3O_8. For spin-only magnetism the magnetic entropy should thus amount to $2R \ln 2$, or 1.84 e.u. per mole U_3O_8, but apparently only a fraction of this is associated with the effective magnetic moment of U_3O_8, decreases considerably as the temperature is lowered, and only amounts to 0.6 Bohr magneton per uranium atom at 25°K., and the magnetic entropy might therefore be spread over a rather large temperature region. In the crystal structure of U_3O_8 infinite linear –U–O–U– chains are present in the *c*-direction, a situation which should favor superexchange.[20] Since magnetic susceptibility measurements[4] have not indicated significant changes in the magnetic properties of U_3O_8 around 25°K. no conclusion concerning the mechanism can be drawn at present.

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α-Ferric Oxide: Low Temperature Heat Capacity and Thermodynamic Functions[1]

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The heat capacity of synthetic α-Fe_2O_3 was determined from 5 to 350°K. No heat capacity anomaly was observed at the magnetic transition about 250°K. Thermodynamic functions have been calculated and the values of C_p, $S°$, $H° - H°_0$, and $-(F° - H°_0)/T$ at 298.15°K. are: 24.80 cal. deg.$^{-1}$ mole^{-1}, 20.889 cal. deg.$^{-1}$ mole^{-1}, 3718.9 cal. mole^{-1} and 8.416 cal. deg.$^{-1}$ mole^{-1}, respectively.

Ferric oxide exists in two crystalline modifications, alpha and gamma, of which alpha is considered the stable form, but there are indications that it might transform into gamma under special conditions.[2] The heat capacity of α-ferric oxide previously has been measured[3] over only four narrow regions between 90 and 290°K., and it was considered of interest to extend the measurements to lower temperatures and obtain more accurate thermodynamic data for this compound. Moreover, α-Fe_2O_3 is a substance of rather complex magnetic properties,[4] having a weak ferromagnetism, which disappears below about 250°K., superimposed on its antiferromagnetism.

In the study by Parks and Kelley[3] two different samples were used, one consisting of large crystals of specular hematite, the other of a finely divided powder prepared from iron oxalate (Kahlbaum). The heat capacity of the synthetic sample was considerably higher (3.8% at 90°K., 2.4% at 275°K.) than of the mineral, which was explained on the basis of its somewhat amorphous state, as inferred from X-ray powder photographs. The lower values of the specular hematite were adopted, and the resulting entropy at 298°K. found to be 21.5 ± 0.5 e.u. Apart from these data a series of enthalpy measurements on a synthetic sample have been made[5] over three regions in the range 81 to 317°K.

Neutron diffraction[6] work on α-Fe_2O_3 in the range 80 to 1000°K. confirmed earlier X-ray data[7-9] leading to a rhombohedral unit cell containing two formula units, with the oxygen atoms forming a slightly distorted close packing and $^2/_3$ of the octahedral interstices filled by iron atoms. The structure consists of sheets of iron atoms parallel to the (111) plane and sheets of oxygen atoms in between. In concordance with the view expressed by Néel,[4] the neutron diffraction data indicated the existence of an antiferromagnetic structure. All four iron atoms in the unit cell are located on the space diagonal. The neutron diffraction data suggest that they are non-equivalent and have relative spin orientation (+ − − +). At room temperature the moments seem to be parallel to the (111) plane and directed toward one of the three nearest neighbors, while at lower temperatures they are oriented normal to the (111) plane or, in other words, in the (111) direction.

This change in the direction of the moments causes the parasitic ferro- or ferrimagnetism to disappear below about 250°K. according to the magnetic susceptibility data by Morin[10] and in the

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