

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

## The Heat Capacity and Thermodynamic Functions of Tetrauranium Nonoxide from 5 to 310°K.<sup>1</sup>

BY DARRELL W. OSBORNE, EDGAR F. WESTRUM, JR., AND HAROLD R. LOHR

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The heat capacity of  $U_4O_9$  was measured from 5 to 310°K., and from these data the entropy, enthalpy and free energy function were calculated. At 298.16°K., the values of  $C_p$ ,  $S^\circ$ ,  $(H^\circ - H_0^\circ)/T$ , and  $(F^\circ - H_0^\circ)/T$  are  $70.11 \pm 0.07$ ,  $80.29 \pm 0.08$ ,  $40.69 \pm 0.04$  and  $39.60 \pm 0.04$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, respectively. In contrast to the behavior of  $UO_2$ , there is no anomaly in the heat capacity of  $U_4O_9$  in the temperature range investigated.

Measurements of the low temperature heat capacity of actinide compounds provide useful thermodynamic data and may afford information concerning the electronic interactions in these substances. In  $UO_2$  and in  $NpO_2$  lambda type anomalies have been observed near 30°K. that are interpreted<sup>2-5</sup> as arising from an antiferromagnetic ordering of the magnetic moments of the cations at lower temperatures.

Uranium dioxide absorbs oxygen at room temperature, forming non-stoichiometric oxides which disproportionate at high temperatures into phases of compositions given by the formulas  $U_4O_9$  and either  $UO_{2+z}$  or  $U_8O_{18-z}$ .<sup>6</sup> The structures of  $U_4O_9$  and  $UO_2$  are very similar,<sup>6-8</sup> the uranium cations in both being arranged in a face-centered cubic array. In  $U_4O_9$  one oxygen anion is added, perhaps interstitially in the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  position, to the four uranium cations and eight oxygen anions contained in each unit cell of  $UO_2$ , and the lattice constant contracts about  $\frac{1}{2}\%$ . The similarity of the structures made it appear desirable to determine whether  $U_4O_9$  has an anomaly in its heat capacity similar to that observed in  $UO_2$ .

**The  $U_4O_9$  Sample.**—The calorimetric sample, which had to be of high purity, well-defined composition, and complete homogeneity, was prepared by Fredrik Grønvold of the University of Oslo. Essentially the same procedure as that recommended by Hönigschmid<sup>9</sup> was used for the purification of uranium and the preparation of pure  $U_3O_8$ . The  $U_3O_8$  was reduced to  $UO_2$  by heating it in alumina boats in a stream of anhydrous hydrogen at 500° until the evolution of water ceased and then heating for an additional four hours at 1200°. The material was cooled in the hydrogen atmosphere. Stoichiometric quantities of this  $UO_2$  and of  $U_3O_8$  prepared by oxidizing  $UO_2$  to constant weight at 800° were mixed and placed in quartz tubes, which were subsequently evacuated and sealed. The mixture was heated for seven days at 800° and then gradually cooled to 20° over a period of two months.

Gravimetric analyses by ignition to  $U_3O_8$  gave

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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$86.81 \pm 0.08\%$  uranium (theoretical, 86.86%). Determinations of uranium by cerate oxidimetry with weight burets gave  $87.04 \pm 0.1\%$ . Dissolution of the sample in  $BrF_3$ <sup>10</sup> revealed an oxygen content of  $13.14 \pm 0.02\%$  (theoretical, 13.14%). Spectrochemical analyses showed the presence of the following elements (in p.p.m.): 10 Al, 0.2 B, 10 Cu, 7 Fe, 5 Mg, 1 Pb, and 70 Si. The following elements were not detected (the numbers indicate the sensitivity limit in p.p.m.): 1 Ag, 10 As, 0.5 Be, 1 Bi, 20 Ca, 4 Ce, 5 Co, 1 Cr, 2 Dy, 0.8 Er, 0.2 Eu, 2 Gd, 4 Ho, 20 K, 0.4 La, 1 Li, 0.8 Lu, 1 Mn, 20 Mo, 2 Na, 4 Nd, 5 Ni, 50 P, 8 Pr, 1 Sb, 4 Sm, 5 Sn, 4 Tb, 20 Th, 50 Ti, 0.8 Tm, 0.1 Y, 0.4 Yb and 50 Zn. Increased sensitivity of detection of rare earth elements was obtained by the extraction of the uranium into tributyl phosphate and the subsequent spectroscopic examination of the raffinate by the copper spark method.<sup>11</sup>

**Experimental Technique.**—The cryostat,<sup>3</sup> calorimeter<sup>4</sup> and the adiabatic method of operation<sup>3</sup> have been described previously. The calorimeter was loaded with the sample, evacuated and filled with helium gas at one atmosphere pressure and 300°K. to improve the establishment of thermal equilibrium.

Temperatures were determined with a capsule type platinum resistance thermometer (Laboratory designation A-1) contained in a central well in the calorimeter. It was calibrated on the temperature scale of the National Bureau of Standards<sup>12</sup> from 14 to 373°K. Below 14°K. the scale was obtained by fitting the equation  $R = A + BT^2 + CT^3$  to the resistance at the boiling point of helium and to the resistance and  $dR/dT$  at 14°K. It is considered that the temperature scale reproduces the thermodynamic scale within 0.1° from 4 to 14°K., within 0.03° from 14 to 90°K. and within 0.05° above 90°K. The ice point was taken as 273.16°K.

Calibrated instruments were used in the determination of all the experimental quantities including the time interval of the energy input. The heat capacity of the empty calorimeter was determined in a separate series of measurements.

**Heat Capacity Results.**—The experimental heat capacity data are presented in chronological sequence in Table I. Corrections for the finite temperature increments employed (which can usually be inferred from the adjacent mean temperatures in Table I) and for slight differences in the amounts of helium and solder in the measurements on the empty and full calorimeter have been applied. The data are presented in terms of 1096.28 g. of  $U_4O_9$  and the defined thermochemical calorie of 4.1840 absolute joules. The calorimetric sample weighed 99.778 g. (*in vacuo*).

(10) H. R. Hoekstra and J. J. Katz, *Anal. Chem.*, **25**, 1608 (1953).

(11) M. Fred, N. H. Nachtrieb and F. S. Tomkins, *J. Opt. Soc. Amer.*, **37**, 279 (1947).

(12) H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **22**, 351 (1939).

No anomaly occurs in the heat capacity of  $U_4O_9$  between 5 and 310°K., in contrast to the behavior of  $UO_2$ . Although the geometric structures and

TABLE I  
MOLAL HEAT CAPACITY OF  $U_4O_9$  (IN CAL. DEG.  $^{-1}$  MOLE  $^{-1}$ )

Mol. wt. = 1096.28; 0°C. = 273.16°K.

T, °K.	$C_p$	T, °K.	$C_p$	T, °K.	$C_p$
Series I					
5.37	0.52	58.72	18.10	178.59	51.44
6.32	.66	64.17	20.06	187.98	53.33
7.23	.73	70.46	22.19	197.33	55.02
8.28	.84	77.61	24.56	206.79	56.75
9.46	.97	77.65	24.59	216.47	58.33
10.42	1.09	85.46	27.15	226.29	59.93
11.71	1.28	93.72	29.69	236.22	61.43
13.05	1.51	102.64	32.31	246.27	63.00
14.44	1.813	Series II		256.46	64.43
15.91	2.111	63.05	19.66	266.75	65.94
17.46	2.489	69.39	21.84	276.88	67.34
18.98	2.910	76.58	24.22	286.92	68.68
20.49	3.380	84.39	26.79	296.88	69.95
22.18	3.927	92.59	29.33	305.82	71.46
24.13	4.626	101.49	31.97	Series III	
26.62	5.558	111.14	34.78	9.28	0.93
29.57	6.699	120.91	37.53	10.65	1.10
32.76	8.002	130.54	40.16	11.98	1.31
36.29	9.447	140.24	42.69	13.26	1.56
40.09	11.00	150.01	45.09	14.56	1.830
44.28	12.65	159.70	47.36	15.99	2.132
48.90	14.45	169.27	49.50	17.53	2.505

interatomic distances of these two compounds are very similar, it appears that the electronic configurations are sufficiently different to modify the exchange interactions that give rise to the anti-ferromagnetic ordering and the thermal anomaly in  $UO_2$ . Since the average oxidation state of the uranium is increased from +4 in  $UO_2$  to +4.5 in  $U_4O_9$ , one would expect that the ground state of the uranium ion would be rather different in the two compounds.

**Thermodynamic Functions.**—The heat capacity read from a smooth curve through the experimental results and some thermodynamic functions computed from the heat capacity are presented at selected temperatures in Table II. The heat capacity values are considered to have a probable error of 0.1% above 25°K., 1% at 14°K., and about 5% at 5°K. Since the measured heat capacities are proportional to the temperature over the range of 5 to 9°K., a linear extrapolation was used below 5°K. Nuclear spin and isotope mixing contributions are not included in the entropy and free energy functions. The estimated probable error in the thermodynamic functions is 0.1% above 100°K., provided that there is no anomaly below 5°K.; but the tabular values include more

TABLE II  
THERMODYNAMIC PROPERTIES OF  $U_4O_9$  AT SELECTED TEMPERATURES

T, °K.	$C_p$ , cal. deg. $^{-1}$ mole $^{-1}$	$S^\circ$ , cal. deg. $^{-1}$ mole $^{-1}$	$H^\circ - H_0^\circ$ , cal. mole $^{-1}$	$-\left(\frac{F^\circ - H_0^\circ}{T}\right)$ , cal. deg. $^{-1}$ mole $^{-1}$
5	0.50	0.50	1.25	0.25
10	1.02	1.00	5.01	.50
15	1.913	1.569	12.16	.758
20	3.224	2.285	24.79	1.045
25	4.946	3.183	45.07	1.380
30	6.869	4.253	74.5	1.768
35	8.919	5.466	114.0	2.208
40	10.96	6.790	163.7	2.697
45	12.93	8.196	223.5	3.230
50	14.87	9.659	293.0	3.799
60	18.57	12.700	460.3	5.028
70	22.04	15.826	663.6	6.346
80	25.36	18.986	900.6	7.729
90	28.55	22.160	1170.3	9.157
100	31.53	25.323	1470.8	10.615
110	34.45	28.465	1800.7	12.095
120	37.27	31.584	2159.3	13.590
130	40.02	34.677	2545.9	15.093
140	42.63	37.739	2959.2	16.601
150	45.09	40.765	3397.9	18.113
160	47.43	43.750	3860.5	19.622
170	49.65	46.693	4346.0	21.128
180	51.73	49.590	4853.0	22.629
190	53.72	52.441	5380.4	24.123
200	55.55	55.244	5926.8	25.610
210	57.27	57.996	6491.0	27.086
220	58.92	60.698	7072.0	28.553
230	60.52	63.353	7669.2	30.009
240	62.04	65.961	8282.0	31.453
250	63.52	68.524	8909.8	32.885
260	64.94	71.042	9552.0	34.303
270	66.39	73.520	10208.7	35.710
280	67.76	75.961	10879.5	37.106
290	69.08	78.361	11563.8	38.486
300	70.34	80.724	12260.9	39.854
273.16	66.82	74.29	10419	36.15
298.16	70.11	80.29	12132	39.60
	$\pm 0.07$	$\pm 0.08$	$\pm 12$	$\pm 0.04$

digits than are justified by the probable error in order to make the table internally consistent.

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LEMONT, ILL.