

TRIURANIUM HEPTAOXIDES: HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF α - AND β - U_3O_7 FROM 5 TO 350°K*

E. F. WESTRUM, Jr.

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

and

F. GRØNVOLD

Chemical Institute A, University of Oslo, Blindern, Norway

(Received 14 June 1961)

Abstract—Low temperature heat capacities have been measured by adiabatic calorimetry on two phases with composition $UO_{2.33}$ designated α - and β - U_3O_7 . They were obtained by oxidation of UO_2 at 135 and 165°C, respectively. β - U_3O_7 was subsequently heat treated at 225°C. Both substances possess UO_2 -like structures, apparently tetragonally deformed, with $c/a = 0.986$ for the face-centered uranium lattice of α - U_3O_7 and $c/a = 1.031$ for that of β - U_3O_7 . Both have normal and almost equal heat capacities over the measured range, except for a small lambda-type anomaly at 30.5°K in α - U_3O_7 . At 298.15°K the values of the practical entropy, S^0 , and the free energy function, $-(F^0 - H_0^0)/T$, are 19.73 and 9.66 cal gfw⁻¹ °K⁻¹ for α - $UO_{2.333}$, and 19.96 and 9.77 cal gfw⁻¹ °K⁻¹ for β - $UO_{2.333}$, respectively. These new data are correlated with structural and magnetic properties and thermodynamic data for other uranium oxides.

1. INTRODUCTION

THE DISCOVERY of lambda-type heat capacity anomalies in UO_2 ⁽¹⁾ and in NpO_2 ^(2,3) and in U_3O_8 ⁽⁴⁾ (properly designated triuranium octaoxide⁽⁵⁾) but not in U_4O_9 ⁽⁶⁾ (properly designated tetrauranium enneaoxide⁽⁵⁾) has led to further interest in low temperature thermophysical properties of the uranium oxide phases. These anomalies are attributed to the changing population of the uranium 5*f* electrons among the available energy states. Since all the known stable phases between UO_2 and UO_3 ⁽¹⁾ have been examined by cryogenic calorimetry, recourse was had to the study of two metastable phases approximating U_3O_7 in composition obtained by oxidation of UO_2 at temperatures below 200°C.

A compound of composition U_3O_7 was first identified by JOLIBOIS⁽⁷⁾, and shortly afterwards

by GRØNVOLD and HARALDSEN⁽⁸⁾ on oxidation of UO_2 at 150°C. The latter authors observed an increase in density upon oxidation which they related to uptake of oxygen at interstitial positions in the UO_2 structure, but were not able at that time to decide with certainty whether the pseudocubic, UO_2 -like structure of $UO_{2.34}$ belonged to a new phase or was the limiting oxygen-rich member of the UO_{2+x} solid solution. It was interpreted to be part of a solid solution region by ALBERMAN and ANDERSON⁽⁹⁾ and ARONSON *et al.*⁽¹⁰⁾, but the work of HERING and PERIO⁽¹¹⁾ ascertained the presence of U_3O_7 as a separate phase. The same conclusion was reached by GRØNVOLD⁽¹²⁾. Further confirmation is found in the work by BLACKBURN *et al.*⁽¹³⁾, VAUGHAN *et al.*⁽¹⁴⁾, HOEKSTRA *et al.*⁽¹⁵⁾ and in neutron diffraction work by ANDRESEN⁽¹⁶⁾. The phase was characterized by PERIO⁽¹⁷⁾ as tetragonal with a c/a axial ratio of 0.991 ($a = 5.447$, $c = 5.400$ Å). ANDERSON⁽¹⁸⁾ maintains, however, that oxidation products prepared below 180°C show

* This work was supported in part by the Division of Research of the United States Atomic Energy Commission.

cubic structure with unchanged cell dimensions up to the composition $\text{UO}_{2.25}$, except for some asymmetric broadening of the diffraction lines towards higher angles for more oxygen-rich samples than $\text{UO}_{2.1}$. VAUGHAN *et al.*⁽¹⁴⁾ claim that this is only the case for "active" oxide preparations.⁽¹⁹⁾ The phase has been prepared by the present authors by oxidation of UO_2 in air at 135°C. It is designated here as $\alpha\text{-U}_3\text{O}_7$ and gives X-ray photographs corresponding to a tetragonal arrangement of the uranium atoms with axial ratio $c/a = 0.986$ for the face-centered cell.

Some of the earlier investigators^(9,10,13,14,18,20,21) apparently have failed to recognize the differences between this phase and the ones with c/a ratio just above unity, obtainable by oxidizing UO_2 at slightly higher temperatures. One of these phases, designated here as $\beta\text{-U}_3\text{O}_7$, can be prepared by oxidizing UO_2 at temperatures ranging between 150 and 265°C. It has a tetragonal arrangement of the heavy atoms with a c/a ratio of 1.031 and was first found by GRØNVOLD and HARALDSEN⁽⁸⁾ in the composition range $\text{UO}_{2.34}$ to $\text{UO}_{2.43}$. The low density observed for the phase was taken to indicate substitution of oxygen for uranium. It seems, however, as if the oxidation had been carried too far and that the low density (10.00 g cm^{-3}) was due to admixture of more oxygen-rich phases. Thus, determination of the weight increase on a 150 g sample during the present oxidation experiments indicated the composition of the phase to be $\text{UO}_{2.34 \pm 0.01}$, and its pycnometric density was found to be 11.17 g cm^{-3} , in accordance with the assumption of interstitial oxygen uptake. PERIO⁽¹⁷⁾ ascribed the composition $\text{UO}_{2.40}$ to this phase, while ANDERSON⁽¹⁸⁾ favored the composition $\text{U}_{16}\text{O}_{38}$, i.e. $\text{UO}_{2.375}$. ARONSON *et al.*⁽¹⁰⁾ placed the composition at $\text{UO}_{2.34 \pm 0.03}$; other authors^(13-15, 19-22) have placed it at U_3O_7 , i.e. $\text{UO}_{2.333}$.

Several authors^(15,17,18,23,24) claim the existence of one more phase with tetragonal structure, characterized by $c/a = 1.016$ in the composition range $\text{UO}_{2.30}$ to $\text{UO}_{2.33}$. The difference between the phase with $c/a = 1.031$ and the one with $c/a = 1.016$ was related by PERIO⁽²⁴⁾ to differences in temperatures of preparation (180–400°C for the former and 420–460°C for the latter), while ANDERSON⁽¹⁸⁾ ascribed it to differences in composition ($\text{U}_{16}\text{O}_{38}$, i.e. $\text{UO}_{2.375}$ for the former and

$\text{U}_{16}\text{O}_{37}$, i.e. $\text{UO}_{2.313}$ for the latter). HOEKSTRA *et al.*⁽¹⁵⁾ obtained the phase with $c/a = 1.015$ by annealing the $\beta\text{-U}_3\text{O}_7$ phase at temperatures in the range 350–500°C and considered it to have the composition $\text{UO}_{2.30}$. BLACKBURN *et al.*⁽¹³⁾ noted that although the c/a ratio of the tetragonal structure varied between 1.01 and 1.019 on oxidation of UO_2 powder to $\text{UO}_{2.33}$ at 150°C, between 1.016 and 1.032 on oxidation at 200°C, and between 1.029 and 1.032 for UO_2 pellets on oxidation at 250 to 280°C, the unit cell volume was constant. This was taken as evidence of an invariable composition of the U_3O_7 phase, and the small c/a ratios observed on oxidizing the powder with large surface area to be the result of interaction with the UO_2 matrix network. It seems more probable, though, that the matrix would cause the c/a ratio to be less than unity on oxidation, just as has been observed by PERIO⁽¹⁷⁾ and the present authors, and that the varying c/a ratios from 1.01 to 1.032 are due to phases with slightly different compositions or a solid solution.

In addition to the phases already discussed, PERIO⁽²⁴⁾ reported the existence of a fourth phase with tetragonal structure and $c/a = 1.010$ obtained in the temperature range 460–520°C. During the present work a fifth phase was observed in the same composition range. It was obtained by continued heating of $\alpha\text{-U}_3\text{O}_7$ in air at 135°C during a period of six months and was found to have the composition U_8O_{19} or $\text{UO}_{2.37}$ and a structure of lower symmetry than tetragonal (as discussed below).

The relationships of these phases to the stable phases UO_{2+x} , U_4O_{9+y} and U_3O_{8-z} are shown in Fig. 1. The phase boundaries of the stable phases according to GRØNVOLD⁽¹²⁾ are indicated by solid lines and show, as the phase designations indicate, significant variations with temperature. Somewhat conflicting values for the phase boundary compositions have been obtained by electrical conductivity measurements⁽²²⁾ and magnetic measurements⁽²⁵⁾ for example, but this is not surprising in view of the difficulty in reaching true equilibrium in the uranium oxides below 500°C. Gas equilibrium studies by BURDESE⁽²⁶⁾ in the range 500–900°C confirm the unusual temperature dependence of solubility of oxygen in the UO_{2+x} phase. Extensive metallographic work by SCHANER⁽²⁷⁾ differs only slightly with regard to

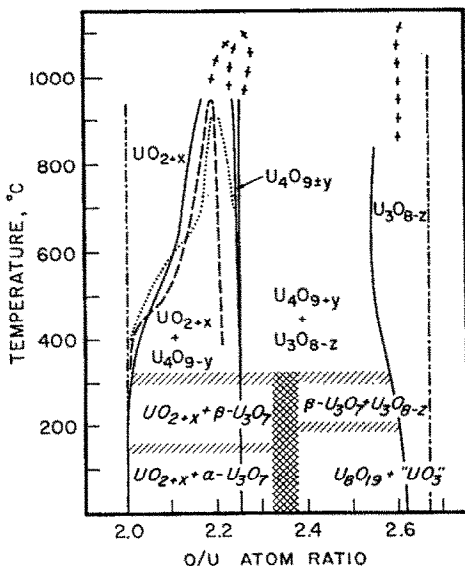


FIG. 1. Diagram of uranium oxide phases in the UO_2 - U_3O_8 region. Phase designations in italics indicate metastable equilibria. Shaded regions indicate approximate conversion temperatures. Solid lines are based on the work of GRØNVOLD⁽¹²⁾, dotted lines on that of BURDESE and ABBATTISTA⁽⁴³⁾, and dashed lines on that of SCHÄNER⁽²⁷⁾, and marked dashes on that of BLACKBURN⁽²⁹⁾.

the UO_{2+x} phase boundary and indicates closing of the solubility loop between the UO_{2+x} and U_4O_{9+y} phases around $950^\circ C$, but results in a surprisingly wide homogeneity range of the U_4O_{9+y} phase. From electrochemical cell measurements by ARONSON and BELLE⁽²⁸⁾ closing of the solubility loop might be inferred to take place at $940^\circ C$, while oxygen pressure measurements by BLACKBURN⁽²⁹⁾ indicate the presence of two uranium oxide phases at $1080^\circ C$ with compositions $UO_{2.228}$ and $UO_{2.249}$, respectively.

Lack of agreement is also present with regard to the existence ranges of the metastable phases obtained by low temperature oxidation of UO_2 . Hence, the shaded lines in Fig. 1 represent the current views of the authors.

2. EXPERIMENTAL

(a) Preparation and purity of the samples

The starting material, Mallinckrodt Analytical Reagent uranyl nitrate, of normal isotopic composition, was purified following in the main lines the

procedure by HÖNIGSCHMID⁽³⁰⁾. The nitrate was first dissolved in water and precipitated with ammonia. The ammonium nitrate formed was dissolved in hydrochloric acid and traces of foreign metals precipitated with hydrogen sulfide gas. After filtration, ammonia was again added, the precipitated ammonium uranate carefully washed, and then dissolved in ammonium carbonate. The carbonic acid was decomposed and uranyl sulfide precipitated by means of ammonium sulfide. The uranyl sulfide was dissolved in nitric acid, crystallized as uranyl nitrate, and dissolved in water. To this solution oxalic acid was first added in a small quantity. After standing overnight the solution was filtered, the precipitate discarded, and oxalic acid added to complete precipitation of the uranium. The uranyl oxalate was converted to triuranium octaoxide by heating at $800^\circ C$ in a platinum dish, the oxide treated with hydrochloric acid and dissolved in nitric acid. The uranyl nitrate formed on evaporation was recrystallized and dissolved in ether, the water layer discarded and the uranyl nitrate converted by heating at $800^\circ C$ to triuranium octaoxide, which in turn was reduced to uranium dioxide by means of dry, purified hydrogen gas. The oxide was placed in an alumina boat inside an alumina tube, heated to $1200^\circ C$ and kept there for four hours. It was then allowed to cool overnight under hydrogen before being transferred for weighing to the dry box filled with nitrogen.

The β - U_3O_7 sample was obtained by heating uranium dioxide in air in a drying oven. The temperature was increased in steps up to $165^\circ C$ and the weight increase observed at suitable time intervals. When the composition U_3O_7 was reached, the heating was stopped and the sample transferred to a pyrex tube. After sealing the sample was homogenized for one week at $225^\circ C$. X-ray photographs of this sample showed the same tetragonal structure as earlier reported by GRØNVOLD and HARALDSEN⁽⁶⁾ for oxides in the range around $UO_{2.40}$ when the oxidation took place above $150^\circ C$. The lattice constants of the face-centered uranium sub-cell are $a = 5.363 \text{ \AA}$, $c = 5.531 \text{ \AA}$, $c/a = 1.031$. R. W. M. D'EYE considers (cf. ANDERSON⁽¹⁸⁾) that the true unit cell dimension should be $A = a\sqrt{2}$ and $C = 2c$. In Table 1 X-ray data for identification of β - U_3O_7 and other oxides in the UO_2 - U_3O_8 region are presented.

Table 1. X-ray data for uranium oxide phases in the UO_2 - U_3O_8 region

UO_2			U_4O_9			α - U_3O_7		
d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
3.158	100	111	3.146	100	111	3.140	100	111
2.735	40	200	2.720	60	200	2.723	30	200
						2.696	20	002
1.934	50	220	1.924	80	220	1.926	20	220
						1.918	25	202
1.649	45	311	1.641	80	311	1.645	20	311
						1.628	15	113
1.579	10	222	1.571	20	222	1.567	15	222
1.368	8	400	1.360	13	400	1.366	5	400
						1.349	5	004
1.255	20	331	1.248	35	331	1.253	10	331
						1.246	10	313
1.223	13	420	1.216	25	420	1.223	10	420
1.117	15	422	1.110	30	422	1.210	10	204

β - U_3O_7			U_8O_{19}			U_8O_8		
d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
3.126	100	111	3.164	30		4.143	100	001
			3.121	100		3.426	100	110
2.767	20	002	3.094	20		3.357	50	200
2.683	35	200				2.639	90	111
			2.755	10		2.501	50	201
1.926	40	202	2.734	25		2.073	30	002
1.895	20	220	2.706	10		1.992	20	020
			2.690	10		1.952	40	310
1.656	20	113				1.795	20	021
1.622	30	311	1.943	10				112
			1.929	10		1.769	60	311
1.563	12	222	1.918	10				202
			1.892	20		1.714	15	220
1.383	3	004	1.650	30		1.678	7	400
1.340	6	400	1.635	8		1.583	20	221
			1.622	15		1.555	9	401
1.249	15	313				1.437	13	022
1.230	10	331	1.584	5		1.421	25	312
			1.566	20		1.382	6	003
			1.548	5				

It was rather more difficult to obtain the low temperature phase α - U_3O_7 in a pure state, and especially without admixture of the β - U_3O_7 phase. To do so required very careful and slow oxidation in air and avoidance of partial superheating of the large sample. Finally a sample was obtained which had the composition $\text{UO}_{2.33}$ and in which neither UO_2 nor β - U_3O_7 could be observed. This sample was prepared by increasing the temperature of the dioxide in small increments from 50 to 135°C over a period of one week. After holding it at this temperature for about three more weeks, the composition $\text{UO}_{2.33}$ was reached. The powder photographs showed line splitting with reversed intensities, characteristic of a tetragonal cell with c/a ratio smaller than unity, as described first by PERIO⁽¹⁷⁾. Data characterizing this phase are also found in Table 1. For the face-centered uranium sub-cell the lattice constants are $a = 5.472 \text{ \AA}$, $c = 5.397 \text{ \AA}$, $c/a = 0.986$.

Further oxidation of α - U_3O_7 at 135°C resulted in the formation of a new phase with composition close to $\text{UO}_{2.37}$ or U_8O_{19} . Its symmetry is apparently lower than tetragonal as evidenced by the splitting of the 111 and 222 reflections into three components (cf. Table 1). This phase seems to occur as an impurity in both the α - and β - U_3O_7 samples of the order of 5 per cent.

A spectrographic analysis of the purified uranium dioxide showed only the presence of the following impurities (in p.p.m.): Al (33), B (10), Mn (< 1), Si (10). The repeated reductions and other handling to produce the α - U_3O_7 sample resulted in an increase of the silicon content and the presence of a small amount of copper while the other impurities remained about as before: Al (33), B (8), Cu (2), Mn (1), Si (100).

Analysis of the β - U_3O_7 sample was kindly carried out at the Los Alamos Scientific Laboratory through the courtesy of Dr. C. E. HOLLEY, Jr. The oxygen content of the oxide was determined by ignition in oxygen at 750°C to be $\text{UO}_{2.330} \pm 0.001$, and the major impurities detected by spectrographic analysis were (in p.p.m.): Al (25), Fe (15) and Si (85). No other elements were reported in amounts greater than 10 p.p.m.

(b) Calorimetric technique

The cryostat⁽³¹⁾ and the adiabatic method employed are being described elsewhere. The copper

calorimeter (laboratory designation W-7) was loaded with the sample and evacuated. Before sealing, purified helium gas of 4.0 cm pressure was added at 300°K to speed the establishment of thermal equilibrium. Temperatures were determined with a capsule-type platinum resistance thermometer (laboratory designation A-3) located in a central well in the calorimeter. The thermometer was calibrated by the U.S. National Bureau of Standards over the range 10–373°K. Below 10°K the provisional temperature scale was established by the equation $R = A + BT^2 + CT^5$ fit to the resistance at the helium boiling point and to the resistance and dR/dT at 10°K. The temperature scale is considered to reproduce the thermodynamic scale within 0.1°K from 4 to 10°K, within 0.03°K from 10 to 90°K, and with 0.04°K above 90°K. The ice point was taken to be 273.15°K. Calibrated instruments were used in the determination of all the experimental quantities including the duration of the energy input. The heat capacity of the empty calorimeter with identical amounts of solder and of Apiezon-T grease for thermal contact was determined in a separate series of measurements. It constituted between 30 and 45 per cent of the total observed heat capacity above 30°K, and a rapidly decreasing amount at lower temperatures.

3. HEAT CAPACITY RESULTS AND DISCUSSION

The experimental heat capacity data are presented in chronological sequence in Table 2. Corrections have been applied for the finite temperature increments employed to obtain the limiting value of $\Delta H/\Delta T$. These experimental temperature increments can usually be inferred from the adjacent mean temperatures in Table 2. The data are presented in terms of a formula weight of $\text{UO}_{2.333} = 275.40 \text{ g}$ in defined thermochemical calories equal to 4.1840 abs. J. The calorimetric sample of α - U_3O_7 weighed 132.078 g; that of β - U_3O_7 weighed 166.233 g (*in vacuo*).

The heat capacities of the two U_3O_7 phases (cf. Fig. 2) are very nearly identical. However, a small lambda-type anomaly with a maximum at 30.5°K occurs in α - U_3O_7 with an enthalpy of 2.5 cal gfw⁻¹ and an entropy of 0.09 cal gfw⁻¹ °K⁻¹ associated with it. If this peak were occasioned by UO_2 , the presence of about 10 per cent of this substance as an impurity would be required to account for the

fractional transition entropy increment of 0.87 cal gfw⁻¹ °K⁻¹ found in UO₂. Since the over-all composition of the sample was represented by the composition UO_{2.33}, the presence of a significant percentage of another phase with higher oxygen content would also be required. X-ray powder photographs failed to reveal such contaminations, except for the presence of about 5 per cent of the U₈O₁₉ phase, even though some of the UO₂ lines should then have shown up with at least $\frac{1}{4}$ of the intensity of neighboring α -U₃O₇ lines. This is a rather unlikely situation, and the peak is therefore tentatively ascribed to the α -U₃O₇ phase. It should also be noted that the heat capacity anomaly in UO₂⁽¹⁾ has its peak at 28.7°K, i.e. 1.8°K lower than found for α -U₃O₇. Since UO₂

and α -U₃O₇ apparently have no mutual solubility (cf. Fig. 1), no elevation in the transition temperature for the UO₂ phase in the presence of α -U₃O₇ would be anticipated. In a partially oxidized UO₂ sample the α -U₃O₇ formed would be expected to introduce compressional strains in the central parts of each particle where UO₂ might still be present. In that case, however, the peak would not be expected to be as sharp as actually observed. On the other hand, the material used by JONES *et al.*⁽¹⁾ was stated to be 99.3 per cent UO₂ and 0.7 per cent UO₃ with traces of other metal oxides, and its transition temperature might thus possibly be lower than for pure UO₂. Although no details of the preparation or thermal history of this sample were reported, it should presumably,

Table 2. Heat capacities of α -U₃O₇ and β -U₃O₇ in cal gfw⁻¹ °K⁻¹

$1/3 \alpha$ -U₃O₇ = α -UO_{2.333}; gram formula weight = 275.40 g.

T (°K)	C _p	T (°K)	C _p	T (°K)	C _p
Series I		Series II—cont.		Series III—cont.	
54.41	4.022	9.98	0.200	291.29	16.87
59.40	4.443	10.96	0.243	300.55	17.12
64.10	4.902	12.25	0.309	309.98	17.30
69.26	5.334	13.63	0.371	319.54	17.51
75.11	5.818	14.97	0.451	329.14	17.71
81.64	6.370	16.32	0.538	338.63	17.91
88.92	6.970	17.69	0.638	346.98	18.06
96.89	7.580	19.26	0.736	Series IV	
105.23	8.199	20.75	0.831	11.64	0.275
113.95	8.830	22.80	1.005	12.85	0.330
122.72	9.478	24.87	1.213	14.05	0.392
129.41	9.927	27.52	1.551	15.27	0.467
138.25	10.52	30.73	2.190	16.57	0.558
147.33	11.09	34.64	2.138	18.02	0.666
156.45	11.65	39.23	2.578	19.63	0.758
165.60	12.17	43.17	2.964	21.42	0.886
174.84	12.64	46.96	3.332	23.28	1.053
184.05	13.10	51.35	3.745	25.02	1.233
193.34	13.54	55.37	4.104	26.20	1.374
202.38	13.93	59.83	4.501	27.23	1.505
211.49	14.31	64.53	4.943	28.34	1.677
220.83	14.68	Series III		29.06	1.834
Series II		227.77	14.96	29.59	2.291
6.14	0.065	237.10	15.27	30.05	2.589
7.04	0.090	246.70	15.60	30.41	3.746
7.53	0.106	255.82	15.86	30.81	1.975
8.27	0.133	264.42	16.12	31.32	1.862
9.07	0.206	273.14	16.38	32.04	1.921
		282.13	16.62	33.58	2.037

Table 2. Heat capacities of α -U₃O₇ and β -U₃O₇ in cal gfw⁻¹°K⁻¹—cont.1/3 β -U₃O₇ = β -UO_{2.333}; gram formula weight = 275.40 g.

T (°K)	C _p	T (°K)	C _p	T (°K)	C _p
Series I		Series III		Series V	
140.54	10.81	74.21	5.853	4.82	0.056
150.65	11.44	81.45	6.474	5.49	0.074
160.35	12.00	88.31	7.046	6.66	0.110
169.87	12.53	95.31	7.586	7.63	0.136
179.92	13.04	102.84	8.159	8.63	0.193
190.37	13.55	110.86	8.762	9.64	0.222
200.32	13.99	119.00	9.351	10.85	0.285
209.71	14.38	127.28	9.937	12.36	0.360
219.07	14.76	135.66	10.50	18.37	0.715
228.42	15.10			20.82	0.855
237.84	15.45	Series IV		22.84	1.028
Series II		7.07	0.114	24.53	1.171
		8.88	0.200	26.00	1.307
231.99	15.23	9.78	0.222	27.32	1.433
241.22	15.55	10.72	0.275	28.52	1.552
250.49	15.86	11.69	0.331	29.62	1.671
259.90	16.15	12.68	0.377	31.13	1.821
269.40	16.43	13.81	0.434	33.54	2.046
278.83	16.68	14.91	0.504	36.26	2.324
288.31	16.93	15.90	0.566	39.20	2.622
297.87	17.17	17.00	0.633	42.92	2.990
307.52	17.38	18.29	0.714	47.17	3.410
316.99	17.59	19.58	0.787	52.12	3.882
326.50	17.78	21.00	0.883	57.88	4.416
336.38	18.00			64.13	4.984
346.41	18.20			70.75	5.560

if quenched, consist of the supersaturated phase UO_{2.01} or, if carefully annealed, consist of UO₂ with about 3 per cent of UO_{2.25} as a contaminant. In the first event, the behavior on transition might be significantly different from that of UO₂, and might also afford an explanation to the rather unusual shape of the heat capacity curve in the transition region. A redetermination of the thermophysical properties of this anomaly in UO₂ of higher purity is desirable.

The anomaly in α -U₃O₇ is thus considered to be a property of the compound and is presumably of magnetic origin. The practically identical dimensions of the UO₂ and α -U₃O₇ structures in the *ab* plane might be a contributing factor for the retention of the transition ($a = b = c = 5.46852 \text{ \AA}$ at 26.5°C for UO₂,⁽³²⁾ $a = b = 5.467 \text{ \AA}$ at 20°C

for α -U₃O₇). The antiferromagnetic-paramagnetic nature of the transition in UO₂ has been confirmed by the magnetic studies of ARROTT and GOLDMAN^(25, 33), and by neutron diffraction work of HENRY⁽³⁴⁾ and of HENSHAW and BROCKHOUSE⁽³⁵⁾. The presence of a related transition in U₃O₈ has been confirmed by magnetic measurements.⁽³⁶⁾ In U₄O₉ and β -U₃O₇ no transitions have been found so far, but it will be noted on inspecting Fig. 2 that the heat capacity of U₄O₉ is diverging from that of the heptaoxides above 275°C. This trend is at present unexplained, but is presumably related to the decrease in the lattice constants of U₄O₉ between 20 and 86°C observed by GRØNVOLD⁽¹²⁾, and perhaps signals the beginning of a transition from an antiferromagnetic to a paramagnetic state.

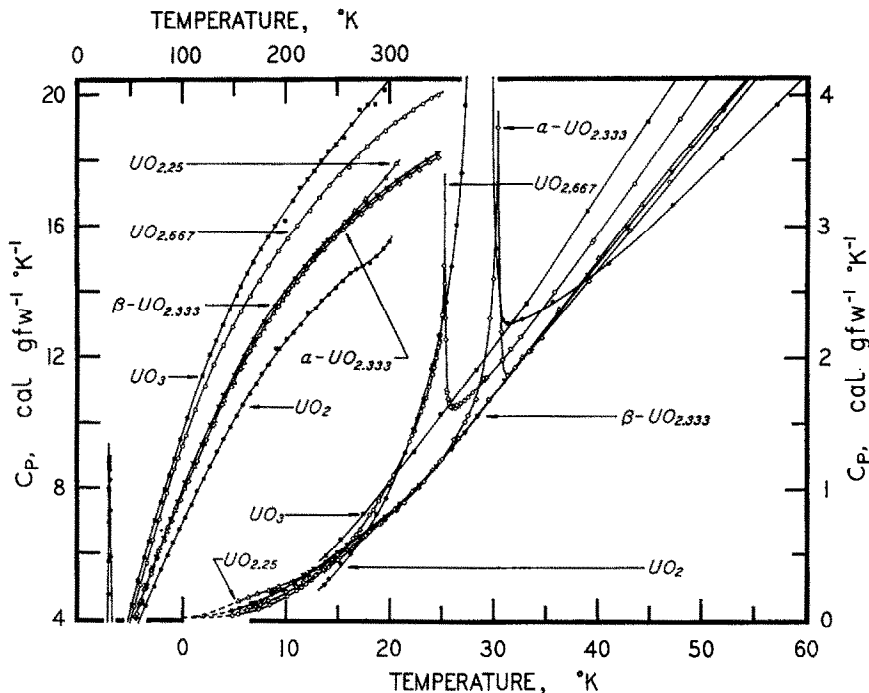


FIG. 2. Heat capacities of uranium oxides; ● represents UO_2 , \triangle : $\text{UO}_{2.25}$, \square : $\alpha\text{-UO}_{2.333}$, \blacktriangle : $\beta\text{-UO}_{2.333}$, \circ : $\text{UO}_{2.667}$ and \blacksquare : UO_3 .

4. THERMODYNAMIC FUNCTIONS

The heat capacities read from a smooth curve through the experimental results, identical with the values obtained by a digital computer least squares fit of the data, are presented together with some thermodynamic functions obtained by the computer integration of the heat capacity in Table 3. The heat capacity values are considered to have a probable error less than 0.1 per cent above 25°K, 1 per cent at 10°K and 5 per cent at 5°K. A Debye T^3 approximation was used to extrapolate the heat capacity 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 per cent above 100°K, but the tabulated values include one more digit than is justified by the probable error in order to make the table internally consistent and to permit interpolation.

The thermodynamics of the uranium oxygen system have been reviewed by BREWER *et al.*⁽³⁷⁾ and discussed by WAGNER⁽³⁸⁾. Additional data are

now available that allow better descriptions of the U_4O_9 and U_3O_7 phases and might be used for testing inconsistencies reported⁽²⁹⁾ to be present in the thermodynamic tables of COUGHLIN⁽³⁹⁾. The thermodynamic values for UO_2 at 298.15°K presented in Table 4 are based upon the low temperature heat capacity data by JONES *et al.*⁽¹⁾ and heat of combustion data for U and UO_2 to U_3O_8 . For the reaction $\text{U}(\alpha) + 1.333 \text{O}_2(\text{g}) = \text{UO}_{2.67}(\text{s})$ HUBER *et al.*⁽⁴⁰⁾ report -284.5 ± 0.5 kcal and POPOV and IVANOV⁽⁴¹⁾ -285.5 ± 1.0 kcal. The value chosen here is $\Delta H_f^0 = -284.8$ kcal at 298.15°K. For the reaction $\text{UO}_2(\text{s}) + 0.333 \text{O}_2(\text{g}) = \text{UO}_{2.67}(\text{s})$ HUBER *et al.*⁽⁴⁰⁾ report $\Delta H = -25.34 \pm 0.03$ kcal, which is adopted here. Other recent values are -25.7 kcal by TOLMACHEV⁽⁴²⁾ and -27.5 kcal by BURDESE and ABBATTISTA⁽⁴³⁾. The resulting value for the molar enthalpy of formation of UO_2 at 298.15°K is $\Delta H_f^0 = -259.5$ kcal. In deriving the entropy of formation, the entropy values $S_{298.15}^0 = 12.00$ cal gfw⁻¹ °K⁻¹ for U by FLOROW and LOHR⁽⁴⁴⁾, and $S_{298.15}^0 = 49.01$ cal

Table 3. Thermodynamic functions of α -U₃O₇ and β -U₃O₇1/3 α -U₃O₇ = α -UO_{2.333}; gram formula weight = 275.40 g.

T (°K)	C_p $\left(\frac{\text{cal}}{\text{gfw}^\circ\text{K}}\right)$	$S^0 - S_0^0$ $\left(\frac{\text{cal}}{\text{gfw}^\circ\text{K}}\right)$	$H^0 - H_0^0$ $\left(\frac{\text{cal}}{\text{gfw}}\right)$	$\frac{-(F^0 - H_0^0)}{T}$ $\left(\frac{\text{cal}}{\text{gfw}^\circ\text{K}}\right)$
5	(0.041)	(0.014)	(0.05)	(0.003)
10	0.200	0.084	0.61	0.023
15	0.452	0.210	2.20	0.063
20	0.793	0.386	5.30	0.121
25	1.218	0.605	10.26	0.195
30	1.698	0.899	18.42	0.285
35	2.172	1.225	28.96	0.398
40	2.656	1.546	41.01	0.521
45	3.145	1.887	55.52	0.653
50	3.617	2.243	72.42	0.795
60	4.523	2.983	113.13	1.097
70	5.404	3.746	162.76	1.421
80	6.244	4.523	221.00	1.760
90	7.040	5.304	287.44	2.110
100	7.809	6.086	361.72	2.469
110	8.558	6.866	443.58	2.833
120	9.281	7.641	532.7	3.202
130	9.970	8.411	629.0	3.573
140	10.63	9.174	732.0	3.945
150	11.26	9.929	841.5	4.319
160	11.85	10.675	957.0	4.694
170	12.40	11.410	1078.3	5.067
180	12.91	12.134	1204.9	5.440
190	13.38	12.844	1336.4	5.810
200	13.83	13.542	1472.4	6.180
210	14.25	14.227	1612.8	6.547
220	14.65	14.899	1757.4	6.911
230	15.03	15.559	1905.8	7.273
240	15.38	16.206	2057.9	7.631
250	15.70	16.841	2213.3	7.988
260	16.00	17.462	2371.7	8.340
270	16.29	18.071	2533.0	8.690
280	16.57	18.668	2697.3	9.035
290	16.83	19.255	2864.4	9.378
300	17.07	19.830	3034.1	9.716
350	18.12	22.544	3914.0	11.357
273.15	16.38	18.26	2585	8.80
298.15	17.03	19.73	3003	9.66

Table 3. Thermodynamic functions of α - U_3O_7 and β - U_3O_7 —(continued) $1/3 \beta$ - $U_3O_7 = \beta$ - $UO_{2.333}$; gram formula weight = 275.40 g.

$T, ^\circ K$	C_p $\left(\frac{\text{cal}}{\text{gfw } ^\circ K}\right)$	$S^0 - S_0^0$ $\left(\frac{\text{cal}}{\text{gfw } ^\circ K}\right)$	$H^0 - H_0^0$ $\left(\frac{\text{cal}}{\text{gfw}}\right)$	$-\frac{(F^0 - H_0^0)}{T}$ $\left(\frac{\text{cal}}{\text{gfw } ^\circ K}\right)$
5	(0.056)	(0.016)	(0.06)	(0.004)
10	0.239	0.096	0.70	0.026
15	0.508	0.240	2.53	0.072
20	0.818	0.427	5.81	0.136
25	1.215	0.653	10.92	0.217
30	1.696	0.917	18.19	0.311
35	2.195	1.214	27.84	0.418
40	2.703	1.538	40.00	0.538
45	3.201	1.884	54.71	0.668
50	3.684	2.246	71.93	0.807
60	4.606	3.003	113.60	1.110
70	5.495	3.784	164.35	1.436
80	6.354	4.574	223.62	1.779
90	7.175	5.367	291.07	2.133
100	7.947	6.161	366.51	2.496
110	8.695	6.954	449.74	2.866
120	9.422	7.743	540.5	3.239
130	10.12	8.527	638.4	3.616
140	10.79	9.302	743.0	3.994
150	11.40	10.067	854.0	4.374
160	11.98	10.821	970.8	4.753
170	12.53	11.563	1093.3	5.132
180	13.05	12.294	1221.1	5.510
190	13.53	13.012	1354.0	5.886
200	13.98	13.718	1491.6	6.260
210	14.40	14.411	1633.7	6.631
220	14.79	15.090	1779.8	7.001
230	15.16	15.757	1929.6	7.367
240	15.51	16.409	2083.0	7.730
250	15.85	17.049	2239.8	8.090
260	16.16	17.676	2399.7	8.447
270	16.44	18.291	2562.7	8.800
280	16.72	18.895	2728.6	9.150
290	16.98	19.486	2897.2	9.496
300	17.22	20.066	3068.2	9.839
350	18.28	22.800	3955.7	11.498
273.15	16.54	18.48	2615	8.91
298.15	17.17	19.96	3036	9.77

Table 4. Thermodynamic functions of the uranium oxides at 298.15°K. Units: cal, gram formula weight, °K

Compound	C_p	S^0	$\frac{H^0 - H_0^0}{T}$	$\frac{F^0 - H_0^0}{T}$	$\Delta Hf^0 \times 10^{-3}$	ΔSf^0	$\Delta Ff^0 \times 10^{-3}$
UO ₂	15.33	18.63	—	—	-259.5	-42.38	-246.9
UO _{2.25}	17.53	20.07	10.17	-9.90	-270	-47.07	-256
α -UO _{2.33}	17.03	19.73	10.07	-9.66	(-273)	-49.46	(-258)
β -UO _{2.33}	17.17	19.96	10.18	-9.77	(-273)	-49.23	(-258)
UO _{2.67}	18.96	22.51	11.42	-11.26	-284.8	-54.82	-268.5
α -UO ₃	20.16	23.57	—	—	-294	-61.95	-275.5

gfw⁻¹ °K⁻¹ for O₂(g) by WOOLLEY⁽⁴⁵⁾ have been used. Apparently, no free energy of formation data are available for checking the derived third law value.

For U₄O₉ the low temperature heat capacity data by OSBORNE *et al.*⁽⁶⁾ have been utilized in combination with the enthalpy for the oxidation reaction UO_{2.25}(s) + 0.208 O₂(g) = UO_{2.67}(s). For this reaction BURDESE and ABBATTISTA⁽⁴³⁾ found $\Delta H = -14.9$ kcal, which results in an enthalpy of formation value for UO_{2.25} of -270 kcal.

The enthalpy of formation of U₃O₇ has not yet been determined, but is assumed to be 3 kcal more negative per gram atom of uranium than for UO_{2.25}, i.e. $\Delta Hf^0 = -273$ kcal.

Using the heat of formation value for U₃O₈ recommended above, and the entropy data by WESTRUM and GRØNVOLD⁽⁴⁾, the free energy of formation of $\frac{1}{3}$ U₃O₈ at 298.15°K is found to be $\Delta Ff^0 = -268.5$ kcal, or very close to the value given by COUGHLIN⁽³⁹⁾ ($\Delta Ff^0 = -268.0$ kcal).

In the U₃O₈-UO₃ region the phase relationships are still quite uncertain but, even so, comparatively reliable data for the different modifications of UO₃ have been derived by HOEKSTRA and SIEGEL⁽⁴⁶⁾. For the hexagonal modification, α -UO₃, they report $\Delta Hf^0 = -294$ kcal gfw⁻¹, which is adopted here. This corresponds to an enthalpy change of -9.2 kcal for the reaction UO_{2.67}(s) + 0.167 O₂(g) = UO₃(hex). For amorphous UO₃ values 3 kcal more positive were reported, which agree with the estimate by BREWER *et al.*⁽³⁷⁾ of

-5.8 kcal for the above reaction, and also with the value -5.4 kcal measured by TOLMACHEV⁽⁴²⁾, while BURDESE and ABBATTISTA⁽⁴³⁾ obtained an intermediate value of -7.6 kcal from heat of solution experiments on an oxide presumably also of amorphous nature (obtained by heating uranium peroxide hydrate in oxygen gas to 380°C).

The free energy of formation data are presented graphically on a gram atom basis in Fig. 3. It will be noticed that the free energies of both α - and β -U₃O₇ lie slightly above the straight line connecting the U₄O₉ and U₃O₈ phases. This gives support to the view that they are of questionable thermodynamic stability and lend their presence to the resistance of UO₂ to more drastic structural changes on oxidation at intermediate temperatures.

It has been assumed here that no transitions take place in the oxides below 5°K, for if this were the case with U₃O₇ and not with the neighboring U₄O₉ and U₃O₈ phases, and amounted to more than about 1 cal gfw⁻¹ °K⁻¹, the stability of U₃O₇ would be established. The possibility of additional transitions cannot, of course, be eliminated at present, but the effective magnetic moments of the oxides have all reached such small values at 5°K (< 0.5 μ_B) that no further transitions involving appreciable entropy are expected.

The possibility of checking the free energy data derived here with equilibrium data is limited by lack of knowledge of the heat capacity behavior of the U₄O₉-phase above room temperature. A

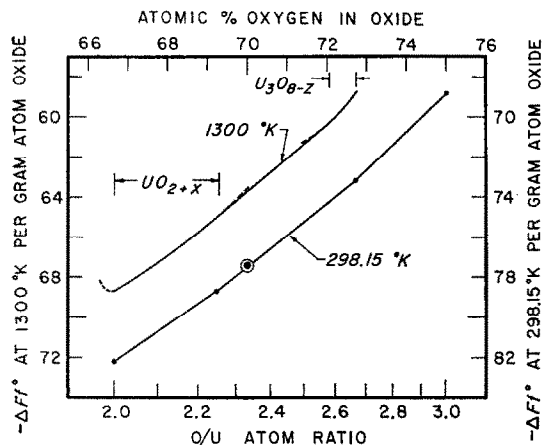


FIG. 3. Free energies of formation of the uranium oxides at 298.15°K and 1300°K. Note shift in energy scales.

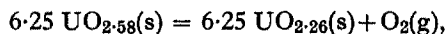
rough estimate can be made on the basis of the heat capacities of the adjacent oxides UO_2 and U_3O_8 . The high temperature heat content of UO_2 was measured by MOORE and KELLEY⁽⁴⁷⁾ up to 1462.5°K, and a heat capacity equation

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

derived. Heat capacities of UO_2 in the range 160–603°C by POPOV *et al.*⁽⁴⁸⁾ are in satisfactory agreement with this equation. For U_3O_8 POPOV *et al.*⁽⁴⁸⁾ gave two equations, one for the temperature range 100–320°C and another for the range 400–600°C. A rough fit with their data and those at lower temperatures by WESTRUM and GRØNVOLD⁽⁴⁾ was obtained with the following equation for $\text{UO}_{2.67}$:

$$C_p = 20.97 + 4.83 \times 10^{-3}T - 3.08 \times 10^5 T^{-2}.$$

The decomposition of the U_3O_{8-z} -phase to U_4O_{9+y} and O_2 gas, as studied by BILTZ and MÜLLER⁽⁴⁹⁾ and BLACKBURN⁽²⁹⁾, was assumed to take place according to the equation



and the heat capacity change was estimated, using available data⁽⁶⁰⁾ for oxygen and heat capacity functions for the oxides (linearly interpolated on the basis of their oxygen content) to be

$$C_p = 1.80 - 8.71 \times 10^{-3}T - 3.07 \times 10^5 T^{-2}.$$

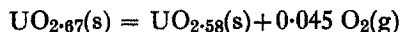
The right hand side of the derived equation

$$\begin{aligned} (\Delta H_0/T) + I = & -4.57 \log p_{\text{O}_2} - 4.14 \log T \\ & - 4.36 \times 10^{-3}T - 1.54 \times 10^5 T^{-2} \end{aligned}$$

was evaluated for all experimental values and plotted against $1/T$. The combined data could not be well fitted by a straight line, since this would result in an excessively high enthalpy of reaction, and systematic errors are probably involved. From BLACKBURN's data the values of the integration constants are $\Delta H_0 = 82,500$ and $I = -24.72$, which lead to the following values for the enthalpy, free energy and entropy of reaction at 298.15°K:

$$\begin{aligned} \Delta H^0 = 83.68 \text{ kcal}, \quad \Delta F^0 = 70.00 \text{ kcal}, \\ \Delta S^0 = 46.01 \text{ cal } ^\circ\text{K}^{-1}. \end{aligned}$$

Including estimates for the reaction



with

$$\begin{aligned} \Delta H^0 = 3.4 \text{ kcal}, \quad \Delta F^0 = 2.9 \text{ kcal}, \\ \Delta S^0 = 1.6 \text{ cal } ^\circ\text{K}^{-1} \end{aligned}$$

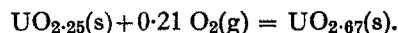
and for the reaction



with

$$\begin{aligned} \Delta H^0 = 0.4 \text{ kcal}, \quad \Delta F^0 = 0.3 \text{ kcal}, \\ \Delta S^0 = 0.2 \text{ cal } ^\circ\text{K}^{-1} \end{aligned}$$

the values for the reaction



are at 298.15°K:

$$\begin{aligned} \Delta H^0 = -17.2 \text{ kcal}, \quad \Delta F^0 = -14.4 \text{ kcal}, \\ \Delta S^0 = -9.2 \text{ cal } ^\circ\text{K}^{-1}. \end{aligned}$$

The agreement with data in Table 4 is not completely satisfactory and suggests either an error in the assumption about the heat capacity increment or in the presumed constant composition of the phases over the temperature range in question, or some slight error in the measured temperature dependence of the equilibrium pressure.

A further test of the U_4O_9 data is possible from studies of the solubility of oxygen in UO_2 at high temperatures by BLACKBURN⁽²⁹⁾ and by ARONSON and BELLE⁽²⁸⁾. For the reaction



the results obtained by BLACKBURN at 1300°K were:

$$\Delta H^0 = -8.45 \text{ kcal}, \Delta F^0 = -4.98 \text{ kcal}, \\ \Delta S^0 = -2.30 \text{ cal } ^\circ\text{K}^{-1}.$$

By integrating the partial molar free energy, entropy and enthalpy values for the solution of oxygen in UO_{2+x} as given by ARONSON and BELLE, the corresponding values at 1300°K are:

$$\Delta H^0 = -8.66 \text{ kcal}, \Delta F^0 = -5.20 \text{ kcal}, \\ \Delta S^0 = -2.77 \text{ cal } ^\circ\text{K}^{-1}.$$

Using the values listed in Table 4 for the formation of UO_2 at room temperature and the enthalpy, free energy, and entropy increase for the substances in question⁽⁶⁰⁾ the data for the formation of UO_2 at 1300°K are:

$$\Delta Hf^0 = -258.7 \text{ kcal}, \Delta Ff^0 = -206.2 \text{ kcal}, \\ \Delta Sf^0 = -40.35 \text{ cal } ^\circ\text{K}^{-1}.$$

Hence, the values for the thermodynamic functions of formation of $\text{UO}_{2.25}$ at 1300°K are:

$$\Delta Hf^0 = -267.3 \text{ kcal}, \Delta Ff^0 = -211.3 \text{ kcal}, \\ \Delta Sf^0 = -43.0 \text{ cal } ^\circ\text{K}^{-1}.$$

These values compare favorably with those calculated from the room temperature data (listed in Table 4) together with the reported data on the enthalpy and entropy increments of oxygen and

uranium between 298 and 1300°K, and estimated values for

$$\text{UO}_{2.25} (\Delta H = 22.2 \text{ kcal}, \Delta S = 30.5 \text{ cal } ^\circ\text{K}^{-1}).$$

This yields:

$$\Delta Hf^0 = -267.6 \text{ kcal}, \Delta Ff^0 = -210.7 \text{ kcal}, \\ \Delta Sf^0 = -43.8 \text{ cal } ^\circ\text{K}^{-1}$$

for the formation of $\text{UO}_{2.25}$. Reasonably good agreement is obtained by evaluating the high temperature thermodynamic data for U_3O_8 (cf. Table 5) and the available data for the reaction



which lead to

$$\Delta Hf^0 = -266.1 \text{ kcal}, \Delta Ff^0 = -210.8 \text{ kcal}, \\ \Delta Sf^0 = -42.5 \text{ cal } ^\circ\text{K}^{-1}$$

for the formation of $\text{UO}_{2.25}$. All these results indicate good consistency in the thermodynamic data for the uranium oxides UO_2 , U_4O_9 and U_3O_8 , although the temperature dependence of the high temperature equilibrium between the U_4O_9 and the U_3O_{8-z} phases seems slightly in error.

A graphical representation of the free energies of the phases in the UO_2 - U_3O_8 region at 1300°K is also presented in Fig. 3 for one gram atom of substance. The concentration dependence of the

Table 5. Thermodynamic functions for $\text{UO}_{2.67}$ at high temperatures (Units: cal. gfw. °K; α , β , and γ indicate phases in uranium.)

$T, ^\circ\text{K}$	$S^0 - S_0^0$	$(H^0 - H_0^0) \times 10^{-3}$	$\Delta Hf^0 \times 10^{-3}$	ΔSf^0	$\Delta Ff^0 \times 10^{-3}$
298.15	22.5	3.40	-284.8	-54.8	-268.5
400	28.4	5.45	-284.4	-53.7	-262.9
500	33.2	7.62	-284.0	-52.7	-257.6
600	37.4	9.89	-283.5	-51.9	-252.4
700	41.0	12.23	-283.1	-51.7	-247.2
800	44.2	14.63	-282.7	-50.7	-242.1
900	47.0	17.07	-282.4	-50.3	-237.2
935 (α)	—	—	-282.3	-50.2	-235.4
935 (β)	—	—	-282.9	-50.8	-235.4
1000	(49.7)*	(19.55)	(-282.7)	(-50.7)	(-232.0)
1045 (β)	—	—	(-282.5)	(-50.5)	(-229.7)
1045 (γ)	—	—	(-283.7)	(-51.6)	(-229.7)
1100	(52.1)	(22.07)	(-283.4)	(-51.4)	(-226.9)
1200	(54.3)	(24.62)	(-282.9)	(-50.9)	(-221.8)
1300	(56.4)	(27.20)	(-282.4)	(-50.5)	(-216.7)

* Values in parentheses are based on extrapolated heat capacities of $\text{UO}_{2.67}$.

free energy within the homogeneity ranges is based upon the results by ARONSON and BELLE⁽²⁸⁾ and BLACKBURN⁽²⁹⁾ for the UO_{2+x} phase and by BILTZ and MÜLLER⁽⁴⁹⁾ for the U_3O_{8-z} phase. The homogeneity ranges of the UO_{2+x} and the U_4O_{9-y} phases overlap, and the composition $UO_{2.26}$ is reached on the oxygen-rich side. On the uranium-rich side the experimental evidence is conflicting,⁽⁵¹⁾ but most probably the partial free energy of oxygen would decrease rather sharply (and that of uranium increase correspondingly) due to interstitial uranium atoms or macroscopic uranium-for-oxygen substitution in the structure of UO_2 . The composition of the U_3O_{8-z} phase in equilibrium with the UO_{2+x} phase at this temperature is assumed to be $UO_{2.58}$, and its decomposition oxygen pressure 0.14 mm Hg. The decomposition pressure reaches the partial oxygen pressure in air at the composition $UO_{2.64}$ and about 18 atm in equilibrium with an oxide of stoichiometric composition U_3O_8 .

Acknowledgements—The authors thank TORKILD THURMANN-MOE for assistance in the preparation and X-ray analysis of the α - U_3O_7 sample, and H. GARY CARLSON and ELFREDA CHANG for assistance with the measurements and calculations. One of the authors (F.G.) expresses his appreciation to the Nansen Foundation for financial assistance. The partial support of the Division of Research of the U.S. Atomic Energy Commission is gratefully acknowledged.

REFERENCES

- JONES W. M., GORDON J. and LONG E. A., *J. Chem. Phys.* **20**, 695 (1952).
- WESTRUM E. F. JR., HATCHER J. B. and OSBORNE D. W., *J. Chem. Phys.* **21**, 419 (1953).
- OSBORNE D. W. and WESTRUM E. F., JR., *J. Chem. Phys.* **21**, 1884 (1953).
- WESTRUM E. F., JR., and GRØNVOLD F., *J. Amer. Chem. Soc.* **81**, 1777 (1959).
- Nomenclature of Inorganic Chemistry*. Butterworths, London (1959).
- OSBORNE D. W., WESTRUM E. F. JR., and LOHR H. R., *J. Amer. Chem. Soc.* **79**, 529 (1957).
- JOLIBOIS P., *C.R. Acad. Sci., Paris* **224**, 1395 (1947).
- GRØNVOLD F. and HARALDSEN H., *Nature, Lond.* **162**, 69 (1948).
- ALBERMAN K. B. and ANDERSON J. S., *J. Chem. Soc.* **1949** S303.
- ARONSON S., ROOF R. B. JR., and BELLE J., *J. Chem. Phys.* **27**, 137 (1957).
- HERING H. and PERIO P., *Bull. Soc. Chim. Fr.* **1952**, 351.
- GRØNVOLD F., *J. Inorg. Nucl. Chem.* **1**, 357 (1955).
- BLACKBURN P. E., WEISSBART J. and GULBRANSEN E. A., *J. Phys. Chem.* **62**, 902 (1958).
- VAUGHAN D. A., BRIDGE J. R. and SCHWARTZ C. M., Battelle Memorial Institute Report BMI-1241 (1957).
- HOEKSTRA H. R., SANTORO A. and SIEGEL S., Paper presented at the American Chemical Society Meeting, Atlantic City, Sept. 1959.
- ANDRESEN A. F., Paper presented at the *Enlarged Symposium on Reactor Materials*, Stockholm, Oct. 1959.
- PERIO P., *Bull. Soc. Chim. Fr.* **1953**, 256.
- ANDERSON J. S., *Australian Atomic Energy Symposium 1958* p. 588. Melbourne University Press, Melbourne (1958).
- VAUGHAN D. A., BRIDGE J. R., ALLISON A. G. and SCHWARTZ C. M., *Industr. Engng. Chem.* **49**, 1699 (1957).
- JOHNSON J. R., FULKERSON S. D. and TAYLOR A. J., *Amer. Ceram. Soc. Bull.* **36**, 112 (1957).
- DEMARCO R. E., HELLER H. A., ABBOTT R. C. and BURKHARDT W., *Amer. Ceram. Soc. Bull.* **38**, 360 (1959).
- WILLARDSON R. K., MOODY J. W. and GOERING H. L., *J. Inorg. Nucl. Chem.* **6**, 19 (1958).
- ANDERSON J. S., *Bull. Soc. Chim. Fr.* **1953**, 781.
- PERIO P., *Bull. Soc. Chim. Fr.* **1953**, 840.
- ARROTT A. and GOLDMAN J. E., *Phys. Rev.* **108**, 948 (1957).
- BURDESE A., *Gazz. Chim. Ital.* **89**, 718 (1959).
- SCHANER B. E., *J. Nuclear Materials* **2**, 110 (1960).
- ARONSON S. and BELLE J., *J. Chem. Phys.* **29**, 151 (1958).
- BLACKBURN P. E., *J. Phys. Chem.* **62**, 897 (1958).
- HÖNIGSCHMID O. and WITTNER F., *Z. anorg. Chem.* **226**, 289 (1936).
- WESTRUM E. F., JR., and BEALE A. F., JR., to be published.
- KEMPTER C. P. and ELLIOTT R. O., *J. Chem. Phys.* **30**, 1524 (1959).
- ARROTT A. and GOLDMAN J. E., *Phys. Rev.* **99**, 1641 (1955).
- HENRY W. E., *Phys. Rev.* **109**, 1976 (1958).
- HENSHAW D. G. and BROCKHOUSE B. N., *Bull. Amer. Phys. Soc.* [2], **2**, 9 (1957).
- WOLF W. P., unpublished communication.
- BREWER L., BROMLEY L. A., GILLES P. W. and LOFGREN N. L., U.S. Atomic Energy Commission Declassified Document MDDC-1543 (1947); cf. *Chemistry of Uranium, Collected Papers*, TID-5290, pp. 219-268, Oak Ridge, Tennessee (1958).
- WAGNER C., U.S. Atomic Energy Commission Unclassified Document WAPD-144 (1955).
- COUGHLIN J. P., *Contributions to the Data on Theoretical Metallurgy*, XII. U.S. Bureau of Mines Bulletin 542, Washington, D.C. (1954).
- HUBER E. J., JR., HOLLEY C. E., JR., and MEIERKORD E. H., *J. Amer. Chem. Soc.* **74**, 3406 (1952).

41. POPOV M. M. and IVANOV M. I., *Soviet J. Atomic Energy* **2**, 439 (1957).
42. TOLMACHEV YU. M., *Trudy Radiovogo Inst. im. V. G. Khlopina, Khim. i. Geokhim.* **7**, 87 (1956).
43. BURDESE A. and ABBATTISTA F., *Ric. Sci.* **28**, 1634 (1958).
44. FLOTOW H. E. and LOHR H. R., *J. Phys. Chem.* **64**, 904 (1960).
45. WOOLEY H. W., *J. Res. Nat. Bur. Stand.* **40**, 163 (1948).
46. HOEKSTRA H. and SIEGEL S., personal communication.
47. MOORE G. E. and KELLEY K. K., *J. Amer. Chem. Soc.* **69**, 2105 (1947).
48. POPOV M. M., GAL'CHENKO G. L. and SENIN M. D., *Zh. Neorg. Khim.* **3**, 1734 (1958).
49. BILTZ W. and MÜLLER H., *Z. anorg. Chem.* **163**, 257 (1927).
50. KELLEY K. K., *Contributions to the Data on Theoretical Metallurgy*, XIII. U.S. Bureau of Mines Bulletin 584 Washington, D.C. (1960).
51. VAUGHAN D. A., MELTON C. F. and GERDS A. F., Battelle Memorial Institute Report BMI-1175 (1957).