Table II. Properties of Sulfur Oxyfluorides

Formula	Name	M.P., ° C.	B.P., ° C.	F^{19} NMR Chemical Shifts[a]
SO_2F_2	Sulfuryl fluoride	−120(?)	−52	−33.5
FSO_2OF	Fluorine fluorosulfonate	−158.5	−31.3	−249, −37
FSO_2OSO_2F	Pyrosulfuryl fluoride	−58	51	−48.5
FSO_2OOSO_2F	Peroxydisulfuryl difluoride	−55.4	67.1	−40.4
FSO_2OOF	Fluorosulfuryl hypofluorite	...	1	−291, −43.0

[a] Measured relative to $CFCl_3$.

chloride to convert the fluorine to chlorine. The chlorine was condensed at liquid nitrogen temperature and measured volumetrically. The oxygen was transferred by means of a Toepler pump to a standard volume and measured. Small but various amounts (as much as 10% of the total gas) of SiF_4 were found, and corrections were made when the amounts were appreciable.

Reactions of O_2F_2. The material to be reacted with O_2F_2 was placed in a small glass tube containing a magnetic stirrer. The O_2F_2 was then distilled into the tube, which was cooled to −196° C. Distillation usually resulted in a slight decomposition of O_2F_2. If a solvent was used in the reaction, it was then distilled into a reactor and used to wash down the O_2F_2 frozen on the side of the tube. The reaction was considered complete upon the disappearance of the red color of O_2F_2.

Separation and Identification of Products. Depending on the complexity of the products, trap-to-trap distillation or the Cady (*1*) codistillation method was used to separate the products. Both infrared and NMR analysis were used to characterize the products, but it was found that F^{19} NMR analysis was usually the best method, since the chemical shifts for all the compounds in question had previously been reported (*4*). The physical properties and NMR data for all of these compounds are given in Table II.

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λ-Type Thermal Anomaly in Triuranium Octaoxide at 482.7° K.

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Heat capacities of U_3O_8 have been measured by adiabatic calorimetry from 300° to 555° K. A reversible λ-type thermal anomaly of uncertain origin, and with an enthalpy of transition of only 41 cal./(mole ° K.), was observed at 482.7° K.

APART from the potential importance of U_3O_8 as a nuclear fuel, its thermophysical properties are of interest because of its polymorphism. The heat capacity of the α-phase was investigated from 5° to 350° K. by Westrum and Grønvold (*12*). A λ-type thermal anomaly, which is presumed to be of magnetic origin, occurs at 25.3° K. Magnetic susceptibility data do indeed show a small anomaly at this temperature but do not reveal the primary nature of the anomaly (*8*). Heat capacity measurements have been made by other workers, covering the temperature regions 477° to 1254° K. (*3*) and 623° to 1273° K. (*7*). The temperature region 350° to 477° K., however, has remained unexplored. The present investigation endeavors to remedy this deficiency.

EXPERIMENTAL

The U_3O_8 sample was prepared in this laboratory eight years ago by purifying uranyl nitrate hexahydrate, A. R. by the well-known procedure of Hönigschmidt (*cf. 12*). 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 hours 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 parts per million): 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 with cell dimensions in accord with the literature (*12*) both before and after the heat capacity determinations.

Heat capacity was determined by the quasi-adiabatic technique using a silver calorimeter (laboratory designation W-22) and platinum resistance thermometer (A-8) in the previously described Mark IV (*11*) cryostat. The calorimeter was sealed after admitting 110 torr of helium gas at 300° K. The total mass of the loaded sample was 164.892 grams in vacuo. A sample density of 8.41 grams per cc. (*10*) was used in making the buoyancy correction. The heat capacity of the sample was greater than 63% of the total at all temperatures. All determinations of mass, temperature, resistance, voltage, and time were referred to calibrations or standardizations made by the National Bureau of Standards.

RESULTS AND DISCUSSION

The experimental heat capacities at the mean temperatures of the determinations are presented in chronological sequence in Table I. These data are given in terms of the defined thermochemical calorie of 4.184 Joules and a gram formula mass (g.f.m.) for U_3O_8 of 842.085. The results have been adjusted for curvature. The probable error of the experimental heat capacities and derived thermodynamic functions is 0.1%.

A λ-type thermal anomaly with a peak temperature of 482.7° K. is evident in the C_p *vs.* T plot of Figure 1. The measurements were repeated six times through the anomalous region, and the results of different series are given in Table II.

The chronological sequence of the ΔHt runs are given in Table I. Each involves a sequence of two or more energy increments which together span the approximate temperature interval 430° to 535° K. Slight adjustments of the actual lower and higher temperatures are made from the smoothed curve but electrical energies added to the calorimeter are summed directly as the major contribution. A lattice contribution is interpolated across the anomalous region and the heat capacity in excess of this is integrated to give the excess enthalpy—i.e., the ΔHt. The average value of ΔHt between 430° and 535° K. is 41 ± 1 calories per g.f.m., and the corresponding entropy increment is 0.084 calorie per (g.f.m. °K.). A sharp break in the slope of the cooling curve occurs at the maximum temperature found in the heat-capacity measurements. This further confirms the reversibility of the transformation (and the absence of undercooling of the high-temperature phase).

ΔHt Runs A, C, E, and G individually encompass so large a temperature region that they yield directly enthalpy increments rather than heat capacities. The ΔH's thus obtained in regions of essentially normal behavior were in excellent accord with those integrated from the heat-capacity determinations.

Table I. Heat Capacity of Triuranium Octaoxide[a]

T	C_p	T	C_p	T	C_p
SERIES I		SERIES III		SERIES V	
303.02	57.39	434.70	64.25	483.20	68.87
311.54	58.06	445.02	64.69	483.97	68.97
320.48	58.82	455.28	64.98	484.74	68.74
329.92	59.56	462.97	65.44	485.51	68.60
339.28	60.27	468.14	65.27	486.28	67.72
348.54	60.98	473.27	65.82	488.72	66.70
358.38	61.49	478.37	66.94	493.35	65.98
368.77	62.08	483.40	68.68	499.06	65.97
379.09	62.48	488.42	66.80	507.67	66.06
389.32	62.94	493.51	65.96	518.62	66.23
399.49	63.36	498.61	65.81	529.50	66.49
409.58	63.73	506.72	65.93		
419.64	64.15	517.75	66.15	SERIES VI	
429.63	64.39	528.73	66.51	ΔH Run C	
439.58	64.63			ΔHt Run D	
		SERIES IV			
SERIES II				SERIES VII	
		ΔH Run A			
432.69	64.34	ΔHt Run B		ΔH Run E	
442.49	64.60	536.38	66.68	458.93	65.35
452.22	65.03			461.95	65.01
461.90	65.39	SERIES V		ΔHt Run F	
472.02	65.95	434.75	64.33	481.25	68.49
482.49	68.26	445.35	64.49	482.02	68.88
492.91	66.27	455.88	64.81	482.51	68.87
503.40	66.12	466.34	65.38	482.99	69.00
513.88	66.24	474.12	66.01	483.48	68.56
524.33	66.40	478.68	67.10	484.25	68.20
534.74	66.67	481.21	68.38	ΔH Run G	
545.10	67.03	482.28	69.23		
555.41	67.49				

[a] Units: calories, g.f.m., ° K.

Table II. Enthalpy of Transformation of Triuranium Octaoxide[a]

Designation	Number of Runs[b]	$H_{535} - H_{430}$
Series II	11	6917
Series III	14	6918
ΔHt Run B	2	6917
Series V	19	6916
ΔHt Run D	2	6917
ΔHt Run F	11	6916

Average value = 6917 ± 1

Lattice, $H_{535} - H_{430}$ = 6876

ΔHt = 41 ± 1

[a] Units: calories, g.f.m., ° K. [b] This represents the number of energy increments used to span the approximate temperature interval, 430° to 535° K.

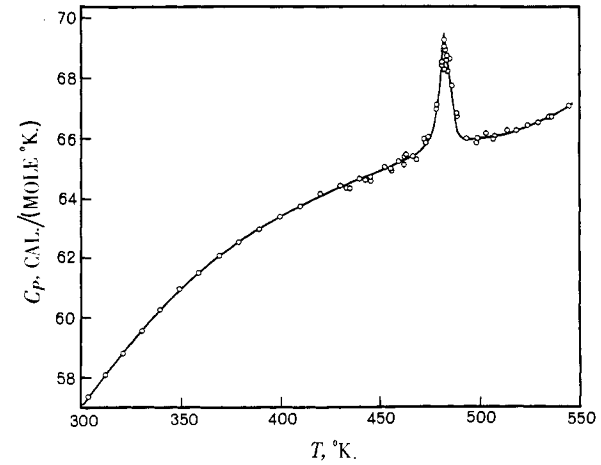

Figure 1. The heat capacity of U_3O_8 from 300° to 550° K.

The smoothed heat capacity and derived thermodynamic functions are given at selected temperatures in Table III. The integrations were performed by a digital computer except in the anomalous region where it was done graphically. These values of thermodynamic functions are predicated on the 273.15° K. values of Westrum and Grønvold (*12*). Near 300° K., both sets of data overlap smoothly and agreement is very good; the accord is everywhere within the estimated precision limits of both sets of data. The contributions due to isotopic mixing and nuclear spin are not included in the entropy and Gibbs energy functions; hence these practical values are suitable for use in chemical thermodynamic calculations. Known transformations of U_3O_8 are summarized in Table IV. Recently George and Karkhanavala (5) prepared δ-U_3O_8 by heating α-U_3O_8 to 1350° C. for about 15 days and cooling it at a rate of 100° per day. They reported studies of the electrical conductivity and differential thermal analysis of the δ phase and

Table III. Thermodynamic Properties of Triuranium Octaoxide[a]

T	C_p	$S°$	$H° - H°_0$	$-(G° - H°_0)/T$
298.15	56.97	67.54	10216	33.27
300	57.13	67.89	10322	33.48
350	60.97	77.00	13279	39.06
400	63.36	85.31	16393	44.33
450	64.83	92.87	19603	49.31
482.7[b]	69.21	97.49	21755	52.42
500	66.03	99.82	22906	54.01
550	67.23	106.15	26231	58.46

[a] Units: calories, g.f.m., °K. [b] At the peak of the lambda-type transformation.

Table IV. Thermal Properties in U_3O_8 Transformations

Transformation	Nature	T_t	ΔHt	ΔSt	Source
$\alpha''' \rightarrow \alpha''$	Magnetic	4.2			(*8*)
$\alpha'' \rightarrow \alpha'$[b]	Reversible	25.3	12	0.56	(*12*)
$\alpha' \rightarrow \alpha$	Reversible	482.7	41.7	0.086	
$\alpha \rightarrow \beta$	Reversible	1043	265	0.254	(*7*)
$\beta \rightarrow \gamma$	Reversible	1213	1105	0.91	(*7*)
$\alpha \rightarrow \delta$	Monotropic	1350	(under optimum conditions)		(*6*)
$\delta \rightarrow \alpha$	Monotropic	393	−1050		(*6*)

[a] Units: calories, g.f.m., °K. [b] The primed quantities are not established as distinct phases.

found that the conductivity *vs.* temperature plot showed a discontinuity at 388° to 398° K. (*6*). Their results also confirmed the presence of the $\delta \rightarrow \alpha$ transformation at 393° K. upon heating. This (endothermic) transformation has $\Delta Ht = 1050 \pm 50$ calories per mole and is irreversible (monotropic). The sample of α-U_3O_8 on which the present investigation was conducted was not treated under conditions productive of δ-U_3O_8. Moreover, the thermal anomaly found in this investigation occurs at 482.7° K. [about 90° higher than that reported by George and Karkhanavala (*5, 6*)]. It is reversible and reproducible with respect to the ΔHt and the peak temperature, T_t. However, scattering of the experimental heat-capacity points within a few degrees of the peak temperature suggests that the crystal lattice transformation is sensitive to the rate of heating. A knowledge of structural parameters, especially in the anomalous regions of temperature, is obviously needed. Ermischer *et al.* (*13*) have shown that the ratio of orthorhombic to hexagonal phase is dependent on the rate of heating and cooling and the atmosphere. Their x-ray diffraction studies on U_3O_8 show a reversible and slow transition in the temperature range of 473° to 523° K. Cordfunke (*14*) has confirmed the existence of the thermal anomaly in U_3O_8 at 383 °K. using a high-temperature x-ray diffraction camera. He considers that the structure of U_3O_8 remains orthorhombic and that the hexagonal pattern occasionally observed on the x-ray films is only a consequence of the approach to coincidence of lattice constants *a* and *b*.

Chodura and Malý (*4*) proposed the presence of two different coexisting structures in α-U_3O_8, one orthorhombic and the other monoclinic. More recently Blinova *et al.* (*2*) found that their x-ray diffraction data are inconsistent with the existence of such structures. Neutron diffraction investigations on powdered U_3O_8 made by Andresen (*1*) show 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. To resolve the discrepancies between the x-ray and neutron diffraction studies of U_3O_8, Loopstra (*9*) investigated a polycrystalline sample of α-U_3O_8 by neutron diffraction with improved resolution and found that the uranium atoms are surrounded by six oxygen atoms in close contact at distances between 2.07 and 2.23 A. with a seventh oxygen at 2.44 A. for one type of U atom and at 2.71 A. for the other type of U atom. The minute entropy increment observed may thus be due to slight, but abnormal expansion of the crystal lattice and changes in the distances of the neighboring oxygen atoms from the central U atom.

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