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THE HEAT CAPACITY ANOMALIES IN URANIUM DIOXIDE
AND NEPTUNIUM DIOXIDE

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CHEMISTRY DIVISION

July 1953

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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Darrell W. Osborne and Edgar F. Westrum, Jr.*

The heat capacity of thorium dioxide was determined from 10 to 305°K in an adiabatic calorimeter. As expected, no anomaly was observed in the heat capacity. The enthalpy, entropy, and free energy were calculated from the heat capacity data and are tabulated for several temperatures. At 298.16°K the entropy and the enthalpy are, respectively, 15.593 ± 0.02 cal deg⁻¹ mole⁻¹ and 2524.4 ± 3 cal mole⁻¹. By assuming the lattice entropy of uranium dioxide and of neptunium dioxide to be equal to the entropy of thorium dioxide, the magnetic entropy contributions at 298.16°K were evaluated as 3.0 cal deg⁻¹ mole⁻¹ for uranium dioxide and 3.6 cal deg⁻¹ mole⁻¹ for neptunium dioxide. These values are somewhat greater than the spin-only values ($R \ln 3 = 2.18$ cal deg⁻¹ mole⁻¹ for uranium dioxide and $R \ln 4 = 2.75$ cal deg⁻¹ mole⁻¹ for neptunium dioxide). The entropies of the other isomorphous actinide dioxides at 298.16°K are estimated to be (in cal deg⁻¹ mole⁻¹) 17.8 for PaO₂, 19.7 for PuO₂, 20.0 for AmO₂, 20.3 for CmO₂, 20.6 for BkO₂, and 20.3 for CfO₂.

Anomalies have been observed in the heat capacity of uranium dioxide at 28.7°K¹ and of neptunium dioxide at 25.3°K² that are presumably related to the magnetic behavior of these substances. In order to obtain an estimate of the contribution of the lattice vibrations to the heat capacities of uranium dioxide and of neptunium dioxide, so that the magnetic contributions can be resolved, measurements have been made of the heat capacity of thorium dioxide.

Inasmuch as the electronic structure of the Th⁺⁴ ion is of the rare gas type, with a ¹S₀ ground state, and thorium dioxide is diamagnetic,³ the heat capacity of thorium dioxide arises entirely from the lattice vibrations and should not show an anomaly. Further, the dioxides of thorium, uranium, and neptunium, as well as those of protactinium, plutonium, and americium, all have the fluorite structure. The lattice parameter⁴ is 5.597 Å for thorium dioxide, 5.468 Å for uranium dioxide, and 5.436 Å for neptunium dioxide, and the masses of the isotopes of the cations employed are 232, 238, and 237,

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

¹Jones, Gordon, and Long, J. Chem. Phys. 20, 695 (1952).

²Westrum, Hatcher, and Osborne, J. Chem. Phys. 21, 419 (1953).

³W. Trzebiatowski and P. W. Selwood, J. Am. Chem. Soc. 72, 4504 (1950).

⁴W. H. Zachariasen, Acta Cryst. 2, 388 (1949).

respectively. Because of the similar structure and the small percentage differences between the lattice dimensions and between the atomic masses, it seems reasonable to assume that the heat capacity of thorium dioxide is a good approximation for the lattice contribution to the heat capacities of uranium dioxide, neptunium dioxide, and the other actinide dioxides.

THORIUM DIOXIDE SAMPLE

A very pure sample of electrically fused thorium dioxide that had been ground and sieved to 200 mesh was ignited to constant weight at 800°C in a platinum dish, and then weighed directly into the calorimeter. Gravimetric analyses on the thorium dioxide (before ignition) by A. R. Mendenhall, Jr., indicated 750 p.p.m. of water and 40 p.p.m. of carbon. It is believed that the traces of water and carbon were removed by ignition. Thorium determinations by K. J. Jensen using gravimetric oxalate precipitation were 87.93, 87.54, and 87.88 per cent thorium (theoretical, 87.88 per cent). Spectrochemical analyses by J. P. Faris and J. A. Goleb revealed the following impurities in p.p.m.: 50 of Al, 10 of Fe, 50 of Si, less than 5 of B, Be, Bi, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, Pb, Sb, and Sn.

Analyses for the rare earth elements were performed by K. J. Jensen and J. P. Faris by a procedure involving extraction of the thorium into thenoyltrifluoro-acetone and spectroscopic examination of the raffinate for the rare earths. Checks were made to determine the validity and sensitivity of the method. The only rare earth element detected was lanthanum (40 p.p.m.). The upper limit of the sum of all the other rare earth elements was 150 p.p.m.

The mass of the sample used in the calorimeter was 185.504 g.

CRYOSTAT AND CALORIMETER

The cryostat used in these measurements has been previously described² and was modified only by substitution of a copper "floating" ring⁵ for the outer adiabatic shield and by increasing the dimensions of the remaining adiabatic shield to inside diameter 4.8 cm, length 12 cm, and thickness 0.75 mm, in order to accommodate a larger calorimeter.

The gold-plated copper calorimeter, 2.8 cm in diameter and 6.4 cm long, is shown in schematic section in Figure 1. The thickness of the shell is 0.25 mm. A carefully machined copper cone (A) at the top provides thermal contact with the adiabatic shield when it is desired to cool the calorimeter. The lid of the calorimeter is soft-soldered in place after filling. Six vanes (C) of 0.1 mm copper foil, soft-soldered to the re-entrant well, aid in establishing temperature equilibrium. Pure helium gas, at a pressure of one atmosphere at 25°C, is used to provide thermal conductivity between the sample and the calorimeter. A small hole drilled in the end of a thin-walled monel tube (B) serves for evacuation and filling with helium. The amount of solder used for soldering the lid and closing the hole in the tube (B) is determined by reweighing the closed calorimeter.

⁵Yost, Garner, Osborne, Rubin, and Russell, J. Am. Chem. Soc. 63, 3488 (1941).

Figure 1

The calorimeter

- A Cone for cooling
- B Monel tube
- C Copper vanes
- D and G Platinum resistance thermometer
- E Thermocouple well
- F Constantan heater
- H Spool for leads

The re-entrant well contains a 25-ohm capsule type platinum resistance thermometer⁶ (D) (Laboratory designation A-1) within a cylindrical copper heater tube (F). The heater tube is wound bifilarly with 160 ohms of B. and S. no. 40 double glass insulated constantan wire, which is cemented in place with baked Formvar. The glass head (G) through which the thermometer leads are sealed is entirely within the enlarged portion of the well, and the lead wires to both the thermometer and the heater are brought to temperature equilibrium with the outside of the calorimeter by means of a small copper spool (H) around which the leads are wound and cemented with baked Formvar. The spool is bolted in place with 00-90 brass cap screws. A copper-constantan differential thermocouple junction coated with baked Formvar makes a snug fit in a small tube (E) soldered to the calorimeter. A weighed amount of Lubriseal stopcock grease is used to establish thermal contact between the calorimeter, thermometer, heater, thermocouple, and spool. The amount of stopcock grease is carefully maintained constant to a few tenths of a mg in the heat capacity measurements on the empty and on the full calorimeter. The mass of the empty calorimeter including thermometer, heater, spool, and grease is 45.7 g.

The calibration of thermometer A-1 and the method of making the heat capacity measurements have been described previously.²

EXPERIMENTAL RESULTS

The molal heat capacities are listed in Table I in chronological sequence. The temperature intervals can usually be estimated from the difference between the average temperatures for successive runs. A correction for curvature, amounting at most to $0.001 \text{ cal deg}^{-1} \text{ mole}^{-1}$, has been made. Also, small corrections were made for the difference in the amount of helium and of solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The molecular weight of thorium dioxide was taken to be 264.12, and the ice point was taken to be 273.16°K .

The rate of heating was 1 deg/min or less, except in a few duplicate runs where it was varied intentionally. For example, the runs at mean temperatures of 61.63 and 61.39°K had a temperature rise of 5.9° and a rate of 1.2 deg/min; the run at 61.43°K had the same temperature rise but half the rate. The run at 74.95°K had an abnormally high rate (2.1 deg/min) and a large temperature rise (10.1°). The duplicate runs of varying heating rate agree within 0.1 per cent and indicate that the shield control was satisfactory.

⁶H. J. Hoge and F. G. Brickwedde, J. Research Natl. Bur. Standards, 22, 351 (1939).

Table I

HEAT CAPACITY OF ThO_2
Molecular Weight = 264.12; $0^\circ\text{C} = 273.16^\circ\text{K}$

$\bar{T}$ ($^\circ\text{K}$)	C_p (cal deg $^{-1}$ mole $^{-1}$)	$\bar{T}$ ($^\circ\text{K}$)	C_p (cal deg $^{-1}$ mole $^{-1}$)	$\bar{T}$ ($^\circ\text{K}$)	C_p (cal deg $^{-1}$ mole $^{-1}$)
10.19	0.034	61.43	3.340	166.27	10.43
11.85	0.048	67.15	3.786	175.73	10.90
13.44	0.070	72.93	4.230	185.75	11.36
15.15	0.099	79.41	4.722	195.89	11.80
17.09	0.142	86.35	5.257	185.66	11.35
19.14	0.207	61.39	3.337	195.64	11.78
21.18	0.290	67.11	3.784	205.69	12.19
23.27	0.394	74.95	4.380	215.83	12.56
25.46	0.521	84.37	5.103	226.06	12.91
27.83	0.674	92.34	5.697	236.26	13.24
30.52	0.865	99.61	6.219	246.35	13.54
33.59	1.100	106.97	6.745	256.45	13.81
37.00	1.369	114.43	7.269	266.58	14.07
40.93	1.693	122.30	7.804	276.62	14.31
45.48	2.061	130.77	8.359	286.58	14.53
50.49	2.470	139.55	8.924	296.52	14.73
55.86	2.898	148.37	9.450	305.40	14.91
61.63	3.356	157.30	9.956		

Values of the molal heat capacity at selected temperatures, read from a smooth curve through the experimental points, are presented in Table II. These values are considered to have a probable error of 0.1 per cent above 25°K ; at 14°K the probable error may be 1 per cent, and at 10°K it may be 3 per cent as a consequence of the decreased sensitivity of the resistance thermometer and the provisional nature of the temperature scale below 14°K .

The heat content or enthalpy was calculated by numerical quadrature of the heat capacity versus the temperature, the entropy by numerical quadrature of the heat capacity versus the logarithm of the temperature, and the free energy from the relation $F = H - TS$. The extrapolation below 10°K was made with a Debye function. The values of these thermodynamic functions at 50° intervals are given in Table II. The estimated probable error in each function is 0.2 per cent at 50°K and 0.1 per cent at temperatures above 50°K , but in order to make the table internally consistent, one more figure is given for some of the values than is justified by the experimental accuracy.

Table II

THERMODYNAMIC PROPERTIES OF ThO_2

T (°K)	C_p (cal deg ⁻¹ mole ⁻¹)	$H^\circ - H_0^\circ$ (cal mole ⁻¹)	S° (cal deg ⁻¹ mole ⁻¹)	$-\frac{F^\circ - H_0^\circ}{T}$ (cal deg ⁻¹ mole ⁻¹)
10	0.032	0.08	0.011	0.003
15	0.096			
20	0.240			
25	0.492			
30	0.827			
40	1.614			
50	2.430	38.60	1.068	0.296
60	3.226			
70	4.006			
80	4.767			
90	5.525			
100	6.246	257.3	3.948	1.375
110	6.960			
120	7.649			
130	8.315			
140	8.951			
150	9.546	655.1	7.129	2.762
160	10.10			
170	10.62			
180	11.10			
190	11.55			
200	11.97	1196.5	10.227	4.244
210	12.35			
220	12.71			
230	13.04			
240	13.35			
250	13.64	1839.1	13.088	5.732
260	13.90			
270	14.15			
280	14.38			
290	14.60			
300	14.80	2551.6	15.683	7.159
298.16	14.76 ±0.015	2524.4 ±3	15.593 ±0.02	7.126 ±0.01

DISCUSSION

The heat capacities of thorium dioxide, uranium dioxide,¹ and neptunium dioxide² are presented graphically in Figure 2. As anticipated, thorium dioxide, unlike the other two dioxides, does not have an anomaly in its heat capacity.

On the assumption that the lattice heat capacity of the actinide dioxides is equal to the heat capacity of thorium dioxide, the magnetic contributions to the heat capacities of uranium dioxide and of neptunium dioxide can be obtained by taking the difference between the thorium dioxide curve and the other curves in Figure 2. The magnetic heat capacity curves resemble those calculated for a cooperative transition from an ordered antiferromagnetic state at low temperatures to a disordered state at temperatures above the anomaly,⁷ except that they are appreciably different from zero at temperatures far above the anomaly.

Similarly, the magnetic contributions to the entropies can be obtained by subtracting the entropy of thorium dioxide from the entropies of uranium dioxide¹ and of neptunium dioxide.² The results are shown in Figure 3.

It is of interest to compare these results with the magnetic entropies calculated on the basis of the spin-only and the free ion approximations and also to compare them with the magnetic susceptibility data. In uranium dioxide, with two unpaired electrons, the magnetic entropy at high temperatures is $R \ln (2S+1) = R \ln 3 = 2.18 \text{ cal deg}^{-1} \text{ mole}^{-1}$ if the orbital contribution to the magnetic moment is completely quenched. On the other hand, the magnetic entropy of free U^{+4} ions at high temperatures is $R \ln (2J+1) = R \ln 5 = 3.20 \text{ cal deg}^{-1} \text{ mole}^{-1}$ if the ground state is $6d^2 {}^3F_2$, or $R \ln 9 = 4.37 \text{ cal deg}^{-1} \text{ mole}^{-1}$ if the ground state is $5f^1 6d^1 {}^3H_4$ or $5f^2 {}^3H_4$. (Hund's rules are assumed. The term symbols are given for LS coupling, but J in the ground state will be the same for jj coupling as for LS coupling.) It can be seen from Figure 3 that the magnetic entropy of uranium dioxide attains the spin-only value of $R \ln 3$ at about 73°K and increases steadily with temperature. At 298.16°K it is $3.04 \text{ cal deg}^{-1} \text{ mole}^{-1}$, corresponding to partial but not complete quenching of the orbital angular momentum. Extrapolation indicates that the magnetic entropy exceeds $R \ln 5$ above 370°K , and this may be an argument against the $6d^2$ electronic configuration for the ground state.

The effective magnetic moment of uranium dioxide derived from susceptibility measurements extending down to 80°K is 3.20 Bohr magnetons.^{3,8} This magnetic moment is intermediate between the spin-only value (2.83 Bohr magnetons) and that for the free ions with a $5f^2 {}^3H_4$ or $5f^1 6d^1 {}^3H_4$ ground state (3.58 Bohr magnetons), and it is much larger than the magnetic moment for

⁷ R. Kikuchi, Phys. Rev. 81, 988 (1951).

⁸ J. K. Dawson and M. W. Lister, J. Chem. Soc. 2181 (1950).

Figure 2

Heat capacities of ThO_2 , UO_2 , and NpO_2 .

Figure 3

Magnetic entropies of UO_2 and of NpO_2 , obtained by subtracting the entropy of ThO_2 from the entropies of UO_2 and of NpO_2 .

the free ions with a $6d^2\ ^3F_2$ ground state (1.63 Bohr magnetons). Hence, the magnetic moment of uranium dioxide corresponds to a $5f^2$ or $5f^16d^1$ configuration and partial quenching of the orbital angular momentum. However, Trzebiatowski and Selwood⁵ and Dawson⁹ have found that in UO_2 - ThO_2 solid solutions the magnetic moment of U^{+4} approaches the spin-only value at infinite dilution. On the assumption that quenching would occur for $6d$ but not for $5f$ electrons, they concluded that the configuration in the ground state is $6d^2$. The magnetic entropy curve, on the other hand, seems to indicate that the configuration is $5f^16d^1$ or $5f^2$ rather than $6d^2$.

The only measurement of the magnetic susceptibility of uranium dioxide below $80^\circ K$ is a single determination by Trapnell and Selwood¹⁰ at $20^\circ K$. It would be desirable to have further measurements to give the shape of the magnetic susceptibility curve in the region of the heat capacity anomaly ($29^\circ K$), in order to determine whether uranium dioxide is antiferromagnetic below $29^\circ K$, as suggested by Jones, Gordon, and Long.¹

In neptunium dioxide, with three unpaired electrons, the spin-only value for the magnetic entropy at high temperatures is $R \ln 4 = 2.75 \text{ cal deg}^{-1} \text{ mole}^{-1}$, whereas the magnetic entropy of free Np^{+4} ions at high temperatures is $R \ln 10 = 4.58 \text{ cal deg}^{-1} \text{ mole}^{-1}$ if the ground state is $5f^3\ ^4I_{9/2}$, and $R \ln 4 = 2.75 \text{ cal deg}^{-1} \text{ mole}^{-1}$ if it is $6d^3\ ^4F_{3/2}$. Other possible ground states for free Np^{+4} ions and the corresponding magnetic entropies at high temperatures are $R \ln 12 = 4.94 \text{ cal deg}^{-1} \text{ mole}^{-1}$ for $5f^26d^1\ ^4K_{11/2}$ and $R \ln 8 = 4.13 \text{ cal deg}^{-1} \text{ mole}^{-1}$ for $5f6d^2\ ^4H_{7/2}$. As shown in Figure 3, the spin-only value of $R \ln 4$ is attained at $95^\circ K$, and at $298.16^\circ K$ the magnetic entropy of neptunium dioxide is $3.60 \text{ cal deg}^{-1} \text{ mole}^{-1}$. These results seem to indicate that there is partial quenching of the orbital angular momentum and that the configuration in the ground state is not $6d^3$.

Susceptibility measurements have not been made on neptunium dioxide, but data on another quadrivalent neptunium compound, $KNpF_5$, indicate partial quenching of the orbital angular momentum.¹¹

It would be difficult to measure the low temperature heat capacities and thus obtain the entropies of the other actinide dioxides, because the half-lives of the available isotopes are too short. The rate of energy liberation by radioactive decay is so large that it would be difficult to achieve thermal equilibrium between the sample, calorimeter, and thermometer. For example, if the heat capacity of $Pu^{239}O_2$ is approximately the same as that of NpO_2 the radioactive decay would cause the temperature to rise more than 3 deg/min at $30^\circ K$. Therefore, it is desirable to attempt to estimate the entropies of the other actinide dioxides.

⁹J. K. Dawson, J. Chem. Soc. 2889 (1951).

¹⁰B. M. W. Trapnell and P. W. Selwood, Nature 169, 840 (1952).

¹¹D. M. Gruen, Dissertation, University of Chicago, 1951.

It will be noted that at 298.16°K the magnetic entropy of uranium dioxide exceeds the spin-only value for two unpaired electrons by 0.86 cal deg⁻¹ mole⁻¹, and the magnetic entropy of neptunium dioxide exceeds the spin-only value for three unpaired electrons by 0.85 cal deg⁻¹ mole⁻¹. We assume that the difference between the magnetic entropy and the spin-only value is roughly constant for the isomorphous actinide dioxides, and accordingly estimate that the entropy of each actinide dioxide at 298.16°K is given approximately by the entropy of thorium dioxide at this temperature (i.e., the lattice contribution) plus $R \ln (2S + 1)$ plus 0.86 cal deg⁻¹ mole⁻¹. In this manner the following estimates were obtained for the entropies at 298.16°K, in cal deg⁻¹ mole⁻¹: PaO₂, 17.8; PuO₂, 19.7; AmO₂, 20.0; CmO₂, 20.3; BkO₂, 20.6; and CfO₂, 20.3. For completeness, the experimental entropies of ThO₂, UO₂¹, and NpO₂² at 298.16°K are listed here also, in cal deg⁻¹ mole⁻¹: ThO₂, 15.59 ± 0.02; UO₂, 18.63 ± 0.1; and NpO₂, 19.19 ± 0.1.