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PuO₂

HEAT CAPACITY OF PLUTONIUM DIOXIDE BELOW 325°K*

by

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Abstract-- The low temperature heat capacity behavior of PuO_2 was found to be anomalous and irreproducible, changing slightly after every one of seven liquid helium coolings. Data obtained from a second series of liquid helium coolings, made after refiring three of four original PuO_2 wafers in air, were consistent with the last run of the first series. The final low temperature heat capacity vs temperature curve was more like that reported for ThO_2 than it was for similar curves reported for UO_2 and NpO_2 .

A least squares equation relating heat capacity and temperature is given for the low temperature region. Values of heat capacity, entropy and enthalpy are listed for several temperatures.

1. INTRODUCTION

The low temperature heat capacity of PuO_2 was studied in order to provide thermodynamic data for this plutonium compound. It was initially suspected that PuO_2 would have a spike in the low temperature region of its heat capacity (C_p) versus temperature (T) curve, since heat capacity spikes have been found in similar curves for NpO_2 ⁽¹⁾ and UO_2 .⁽²⁾ Heat capacity peaks (spikes) found at 25°K and ~ 30°K in these latter oxides have been attributed to antiferromagnetism. SANDHAN and GIBNEY⁽³⁾ have speculated that plutonium metal was antiferromagnetic below 100°K.

2. SPECIMEN DESCRIPTION

Before it was placed in a copper calorimeter can for the first series of low temperature heat capacity measurements, the PuO_2 was initially processed by being compressed, fired, and milled with nonmetallic balls in a rubber-lined ball mill. This was done to obtain a higher density on final pressing and firing. The material was next pressed at 50,000 psi into four wafers having a diameter of ~ 1/2 in. and a thickness of ~ 0.1 in. The four wafers were fired in an air atmosphere in a covered platinum dish at 1650°C to 1700°C. Two hours were taken to reach this temperature at which the wafers were held for 5 hr. Cooling back to room temperature took 2 hr.

"Canning" of the wafers was deemed necessary because of danger of radio-active contamination of the vacuum system of the heat capacity calorimeter. The four wafers were Heliarc-welded into a cylindrical copper calorimeter can having a wall thickness of 10 mil. Each wafer was separated from its neighbors by a 5 mil thick star-type copper washer whose points

made positive contact with the inner wall of the copper container. The combination of an atmosphere of dry helium exchange gas (a consequence of Heliarc-welding) and star-type copper washers was considered sufficient provision for conducting heat from the specimens to the copper can wall for temperature measurements. The proof that the canning would give satisfactory values for specific heat was obtained when the rate of heat generation of the oxide was determined with the canned material by the method of Sandenav.⁽⁴⁾

A 1 to 2 mil thick nickel coat was deposited on the copper container before the first specific heat determinations were started because of a slight alpha count detected in one of the Heliarc-welds. The weld was found to be satisfactory on examination, so it was assumed that the inner can wall had been touched with the radioactive PuO_2 wafers during insertion.

The first two heat capacity runs showed an unexpected peak at $\sim 69^\circ\text{K}$ (see Section 3) so seven low temperature runs were made, each after the calorimeter can was cooled with liquid helium. Many more runs were made commencing with liquid nitrogen cooling and at points intermediate between 76°K and 300°K . This comprised the first series of runs.

The copper container was opened after the first series of heat capacity runs, and one wafer was pulverized for representative material for an X-ray study and chemical analysis. The determination of the lattice constants by X-ray analysis was made within 20 hr after the container was opened. The remaining three wafers were fired again in the manner described above for compacted material. Edge material from one pallet was sampled for X-ray analysis of crystal structure just after firing.

The three wafers were canned again in a copper container as described above. For the second series, three heat capacity runs beginning with liquid helium cooling were performed plus more runs with liquid nitrogen cooling, before each of the three wafers was submitted for a final X-ray determination of lattice parameters. Table 1 shows the lattice spacings of the PuO_2 material as indicated by X-ray analysis at the various stages of sampling. Normal PuO_2 lattice spacing is from Ref. 5.

Table 2 lists the impurities present in the PuO_2 when freshly made (in ppm by weight). Analysis showed the oxide material to be 87.30% plutonium by weight, when sampled after the first series of heat capacity measurements. Impurities present after the PuO_2 was compressed twice in steel dies are also shown. Only the elements that showed an appreciable increase as a consequence of ball-milling and compressing are compared in the two columns. It is believed that much of the iron, nickel, and chromium impurity increase was surface contamination from being compacted twice in steel dies.

The canned PuO_2 was loaded with additional copper for the first four liquid helium runs in order to lower the rate of temperature rise. Weights of materials making up the canned assembly for the first four liquid helium runs of the first series were: PuO_2 , 25.720 g; Cu, 18.740 g; Ni, 1.705 g; and for the last runs of the first series the PuO_2 and nickel weights remained the same, while the weight of copper was reduced to 4.925 g. The weight of PuO_2 was 19.638 g and of Cu was 4.634 g for all runs of the second series.

Calculated average density of the wafers was 9.45 g/cm^3 after the

Table 1. Lattice spacing at various stages of processing and heat capacity measurement.

<u>Sampling stage</u>	Lattice spacing <u>(Å)</u>	<u>Remarks</u>
Normal for PuO ₂ *	5.396 ± .001	--
After seventh liq He cooling	5.4029	PuO ₂ lines sharp and clear. No extra lines.
After refiring, before second series	-	Lines fuzzy. Supposedly a mixture of PuO ₂ and oxygen- deficient PuO ₂ .
After second series (ave)	5.3988 ± 0.0001	PuO ₂ lines sharp and clear. Well-crystallized. No extra lines.

* See Ref. 5.

Table 2. Impurities present in PuO_2

<u>Element</u>	<u>ppm by weight</u>	
	<u>After initial preparation</u>	<u>Compressed twice in steel die</u>
C	40	—*
Si	80	300
Cu	4	25
Ni	100	2400
Cr	< 20	1300
Mn	4	200
Fe	40	3200
Am	—*	550
Other elements	43	196

* No analysis made

first series of heat capacity runs and 10.17 g/cm^3 after firing but before the second series of determinations. The rate of heat generation was determined to be 1.967 mw/g .

3. HEAT CAPACITY APPARATUS AND PROCEDURE

The heat capacity values of the PuO_2 material were determined by following the rate of temperature rise during self-heating. This had been the procedure followed with plutonium metal, for which experimental techniques have been described.⁽⁶⁾ The experimentally determined specific heat values of the can assembly were corrected for the specific heats of nickel as reported in the literature.⁽⁷⁾

The apparent specific heat of the copper jacket in the calorimeter can assembly was calculated through the differing rates of rise in temperature of the assembly due to different copper loading, assuming that the specific heat of the PuO_2 material was always the same at any temperature in a spike-free region. The rate of rise in temperature with 4.925 g of Cu (25.702 g PuO_2 and 1.705 g Ni) was roughly twice that found with 18.740 g Cu and the same weights of PuO_2 and Ni. The shape of the calculated heat capacity versus temperature curve deviated slightly from a similar curve plotted from the data of Giaugue and Meads.⁽⁸⁾

The processing procedures before the first two runs of the first series starting at $\sim 4 \text{ K}$ were made as follows: The specimen container was slowly cooled with 15 to 20 mm Hg pressure of dry helium exchange gas in the inner dewar of a double dewar assembly, and liquid nitrogen in the outer surrounding dewar. This cooling was usually accomplished overnight; then

enough liquid nitrogen was transferred into the inner dewar to immerse the specimen completely. The liquid nitrogen was pumped to cool the assembly down to $\sim 48^\circ\text{K}$ and then the system was allowed to warm back to $\sim 76^\circ\text{K}$ at a rate determined by heat leaks and radiation losses. The liquid nitrogen was removed by pumping through a permanently installed transfer tube; and then pumping was continued, utilizing a diffusion pump and cold trap, until specimen and shields had warmed up to 82°K to 85°K . Liquid helium was added slowly; and 140 min were taken to cool to $\sim 4^\circ\text{K}$ for the first run and 56 min for the second. The liquid helium was cooled to below its lambda point by pumping. Holding time at the temperature of boiling liquid helium was $3\text{--}3/4$ hr for the first run and $1\text{--}1/4$ hr for the second.

It was suggested that the liquid nitrogen precool might be responsible for the unexpected spike at $\sim 69^\circ\text{K}$ in the first two runs (see Section 4.1). Because of this, three more runs were made with which liquid helium alone was used to precool the specimen. The liquid nitrogen precool was again used in the last two liquid helium runs of the first series. The transfer of liquid nitrogen around the heat capacity specimen was done only for the first of the three liquid helium runs making up the second low temperature series.

4. EXPERIMENTAL RESULTS

4.1 Heat capacity curves

The C_p vs T curves resulting from the first, third, fifth, and seventh liquid helium runs of the first series are shown in Fig. 1. The peak found at 34°K during the first run was expected because of the low temperature

behavior of $\text{NpO}_2^{(1)}$ and $\text{UO}_2^{(2)}$ but the second peak at $\sim 69^\circ\text{K}$ was very puzzling, so the experiment was repeated. Two peaks again appeared. The first was sharper and shifted to a lower temperature, while the second shifted to a higher temperature. Values of $\frac{C}{T}$ at the crests decreased, and continued to decrease with each succeeding heat capacity run; and the peak first found at 69°K had completely disappeared by the fifth run. Slight evidence of a crest at 30°K was still apparent on the seventh run. The consistent trend, in the absence or presence of a liquid nitrogen precool (discussed in Section 5), seems to rule out the possibility of a spurious peak at $\sim 69^\circ\text{K}$ due to trapped solid or liquid nitrogen.

The solid line of Figure 2 is a composite curve for the heat capacity of PuO_2 as a function of temperature. The portion of the curve below $\sim 115^\circ\text{K}$ represents data obtained during the second series of measurements after the PuO_2 wafer had been refired in air. Three liquid helium runs checked rather well below 100°K and there was only slight evidence of peaking at 29°K in the first one of the three. Slight humping was seen in the last two of the three liquid helium runs.

The $\frac{C}{T}$ vs T curve (solid line) above $\sim 115^\circ\text{K}$ represents the best average of all data taken for PuO_2 above this temperature. The data for ThO_2 reported by OSBORNE and WESTRICH⁽⁹⁾ is shown as the broken line on Figure 2. The two curves are roughly parallel up to $\sim 112^\circ\text{K}$ where they cross. The PuO_2 curve runs below the similar curve for ThO_2 up to $\sim 205^\circ\text{K}$, where they cross again with the curves rapidly diverging above this temperature.

4.2 Equation for heat capacity data

The equation for the $\frac{C}{T}$ vs T curve in the temperature region between

11.9°K and 28.8°K was determined by a least squares analysis of data from three liquid helium runs of the second series to be:

$$\frac{C}{2} = \underline{AT} + \underline{BT}^3 \quad (11.9^\circ\text{K to } 28.8^\circ\text{K})$$

where

$$A = 1.350 \times 10^{-2}$$

$$B = 2.877 \times 10^{-5}$$

$$\sigma \text{ (standard deviation)} = 3.0 \times 10^{-2}$$

Table 3 lists values of heat capacity in terms of gfw (gram formula weight) at intervals from 13°K up to 325°K.

The standard deviation of data in Table 3 is considered to be 1 per cent, as a maximum, at any temperature above 130°K.

4.3 Thermodynamic properties

The use of an IBM 704 electronic data processing machine and a trapezoidal rule for calculation of enthalpy (H) and entropy (S), and summed up to and including the last experimentally determined $\frac{C}{2}$ value, has been described.⁽⁶⁾ Values of enthalpy and entropy, as summed up to several temperatures, are given in Table 4. Heat capacity and entropy were assumed to be zero at 0°K. The atomic weight of plutonium was taken to be 239.11 (chem scale) and the gram calorie was taken to be equivalent to 4.184 abs j.

5. DISCUSSION OF RESULTS

5.1 Argument for a phase transition through thermal cycling

The anomalous heat capacity behavior between 11°K and 100°K, as shown in Fig. 1, suggests the presence of metastable plutonium oxide phases at the commencement of the low temperature heat capacity measurements. The gradual

Table 3. Heat capacity of PuO_2 at rounded temperatures (per gfu).

T (°K)	$\frac{C_p}{2}$ (cal/°K)	T (°K)	$\frac{C_p}{2}$ (cal/°K)	T (°K)	$\frac{C_p}{2}$ (cal/°K)
13	0.24	100	6.4	230	13.4
15	0.29	110	7.0	240	13.9
20	0.48	120	7.6	250	14.4
25	0.80	130	8.1	260	14.9
30	1.13	140	8.7	270	15.3
35	1.42	150	9.3	280	15.7
40	1.80	160	9.8	290	16.1
45	2.22	170	10.4	298.15	16.4
50	2.62	180	10.9	300	16.5
60	3.42	190	11.4	310	16.9
70	4.20	200	12.0	320	17.2
80	4.93	210	12.4	325	17.4
90	5.67	220	12.9		

Table 4. Values of $\bar{S}$ and ΔH at different temperatures.

T (°K)	$\bar{S}_T$ (cal/deg°K)	$\bar{H}_T - \bar{H}_0$ (cal/deg)
25	0.45 ± .03	7.0 ± 0.5
50	1.50 ± .04	48 ± 1
75	2.94 ± .05	139 ± 2
100	4.50 ± .05	276 ± 3
150	7.64 ± .07	668 ± 7
200	10.68 ± .10	1200 ± 10
250	15.61 ± .15	1858 ± 15
298	16.35 ± .16	2600 ± 26
300	16.45 ± .16	2632 ± 26
320	17.52 ± .20	2969 ± 30

change in low temperature heat capacity behavior with processing, coupled with the clear, sharp lines typical of PuO_2 found on X-ray analysis after the first series of liquid helium coolings, would seem to indicate an almost complete conversion of originally metastable states over to room-temperature stable PuO_2 .

Because of his experience with mixtures of actinide element dioxides, ELLINGER⁽¹⁰⁾ believes that any other phase present in excess of 2% would be detectable. Although there was no indication of any other phase, the lattice spacing of 5.4029 Å supposedly indicated an appreciable oxygen deficiency in the PuO_2 as sampled.

In contradiction, the chemical analysis made after the seventh liquid helium cooling of the first series of tests indicated an O/Pu ratio of just slightly less than 2.0 if detectable impurity elements were all considered to be present as their respective oxides. The PuO_2 material was Heliarc-welded into the copper container with air excluded, i.e., in an atmosphere of helium gas, but adsorbed and interpose air was not pumped from the vafers so there was very slight source of oxygen.

An initial oxide phase mixture would seem to be a possibility by analogy to the oxides of uranium. ARROTT and GOLDMAN⁽¹¹⁾ interpret their magnetic analysis of the uranium-oxygen system to be in favor of oxygen interstitials rather than the presence of uranium-ion vacancies. They⁽¹¹⁾ indicate that there may be some difficulty in preparing homogeneous samples, i.e., there is not only just a range of compositions, but there may be a mixture of phases in the uranium-oxygen system.

BRETT and RUSSELL⁽¹²⁾ report that there is evidence of a phase transformation in $\text{PuO}_{1.77}$ in the temperature region 600°C to 700°C. They also

report that changes have been observed in electrical resistivity and differential thermal analysis of this reduced material at about 620°C. Their X-ray pattern of $\text{PuO}_{1.77}$ showed approximately equal amounts of PuO_2 and $\alpha\text{-Pu}_2\text{O}_3$ at room temperature. Recent dilatometric measurements made on PuO_2 by GHEKALIA⁽¹³⁾ show a smooth expansion curve to 1000°C, while $\text{PuO}_{1.97}$ shows a hysteresis at 600°C. $\text{PuO}_{1.99}$ shows the hysteresis at 270°C and 650°C. As indicated by Table 1, there was no detectable evidence for any $\alpha\text{-Pu}_2\text{O}_3$ in Los Alamos PuO_2 material as sampled after each of the two series of heat capacity measurements.

ELINGER⁽¹⁰⁾ states that one normally cannot get $\alpha\text{-Pu}_2\text{O}_3$ (cubic Pu_2O_3) to stoichiometric composition and that the material is also known as $\text{PuO}_{1.62}$. OLSEN et al⁽¹⁴⁾ have found an oxide of plutonium to be either ferrimagnetic or ferromagnetic with a Curie temperature of about 92°K. Ferromagnetism is favored in explaining the magnetic behavior. The oxide showing the 92°K Curie temperature was found by X-ray analysis to be predominately $\text{PuO}_{1.62}$ (cubic).

The retention of the high temperature structure by plutonium oxides, under certain unspecified conditions of cooling, does seem to be a possibility from the experimental evidence when considered in the light of other published data.

There appear to be two contradictions in X-ray and chemical analysis. The lattice spacing of 5.4029 Å, indicating an appreciable oxygen deficiency, seems to be regulated by the chemical analysis made for total plutonium on the same sample. Again the oxygen deficient PuO_2 , shown by X-ray analysis after refiring, seems to be regulated by the final lattice spacing of 5.3988 Å obtained on the material after final heat capacity measurements. This final

lattice spacing should indicate an O/Pu ratio as near to 2.0 as is shown by the results from calculations using the total plutonium found to be present by chemical analysis.

One can speculate that one of the following alternatives is correct:

(1) the presence of retained high temperature stoichiometric PuO_2 along with room temperature phase stoichiometric PuO_2 results in the expanded lattice spacing that has been attributed to oxygen-deficient PuO_2 . Processing between 300°K and 42°K converts the phase mixture into a single phase. (2) Adsorbed and inter pore oxygen may be present in a large enough amount to convert oxygen-deficient PuO_2 into nearly stoichiometric PuO_2 through radiation induced diffusion processes at very low temperatures.

5.2 Possible influence of radiation damage on phase transitions in PuO_2

Work of OLSEN and ELLIOTT⁽¹⁵⁾ and SANDERAW⁽¹⁶⁾ has indicated the importance of self-induced radiation damage from radioactive decay in plutonium metal at very low temperatures. Calculations of VINEYARD⁽¹⁷⁾ have indicated that there is a very high concentration of displacements in plutonium metal and that "spike" effects must be important. Also according to VINEYARD, formation of large clusters of defects and production of phase transformations (at low temperature) in plutonium metal can be expected in thermal spikes. By analogy to plutonium metal, one can surmise that the gradual change in low temperature heat capacity behavior of the PuO_2 during temperature cycling (first series) was influenced by self-induced radiation damage. The thermal spikes seemingly influenced the conversion of retained high temperature phase(s) as indicated by X-ray crystallography. The effect

seems to be one of radiation-induced diffusion or homogenization. The possibility of radioactive disintegrations in plutonium influencing ordering of atoms in a plutonium alloy has been previously suspected by SANDERSON⁽¹⁸⁾.

5.3 Comparison of thermal properties with those of other actinide element oxides

Table 5 compares published values of heat capacity and entropy and enthalpy (at 298°K) for ThO_2 ,⁽⁹⁾ PaO_2 ,⁽⁹⁾ UO_2 ,⁽²⁾ and NpO_2 ,⁽¹⁾ with values for PuO_2 reported here. The value of E_{298} for the actinide series oxides increases with increasing atomic number through element 93 (neptunium), then drops back again at element number 94 (plutonium). Since entropy, summed up to room temperature, will be partially dependent upon electronic or magnetic contributions to low temperature heat capacity, one can concede that entropy is influenced by the effective magnetic moment of the actinide element ion. SELWOOD⁽¹⁹⁾ shows the effective magnetic moment of some actinide ions. Values for effective magnetic moment of Pu(III) and Pu(IV) are less than those for Np(IV), Np(V), or Np(VI). A plot of entropy (298°K) vs atomic number for the dioxides listed in Table 5 gives a figure strikingly similar to the plot of effective magnetic moment vs atomic number for the first six of the trivalent ions of the rare earths.⁽²⁰⁾ This similarity has been pointed out by OLSEN.⁽²¹⁾

5.4 General discussion

The peak-free, low temperature heat capacity curve of PuO_2 shown in Figure 2 must be considered as the correct one for PuO_2 material with an O/Pu ratio of very slightly less than 2.0.

Table 5. Values of ΔH_{298}° , ΔG_{298}° , and ΔF_{298}° for oxides of actinide elements.

Material	Element No.	ΔH_{298}° (cal/grm/°K)	ΔG_{298}° (cal/grm/°K)	ΔF_{298}° (cal/grm/°K)	$\Delta H_{298}^\circ - \Delta F_{298}^\circ$ (cal/grm)
ThO_2	90	14.76	15.59	2524	
PaO_2	91	-----	17.80(9)	-----	
UO_2	92	[15.32]*	18.63	[2757]*	
NpO_2	93	[15.82]*	19.19	2770	
PuO_2	94	16.4	16.3	2600	

* Estimated from published data.

The fact that the C_p vs T curve of PuO_2 is parallel to but slightly above the similar curve for ThO_2 at temperatures below 100°K , probably indicates some slight additional electronic or magnetic contribution to heat capacity, but does not appear to be a clear-cut indication of antiferromagnetism. It should be noted that the temperature of the shift in heat capacity of PuO_2 , at $\sim 110^\circ\text{K}$, is only 18° above the Curie temperature of $\text{PuO}_{1.62}$.⁽¹⁴⁾ We are aware that the behavior below $\sim 110^\circ\text{K}$ could be due to the presence of a small quantity of $\text{PuO}_{1.62}$. We are also aware that the double peaking in the original low temperature C_p vs T curve could be due to the appearance of both antiferromagnetism and ferrimagnetism in an intimate mixture of room temperature and retained high temperature phases.

Holding times at the temperature of boiling liquid helium were varied randomly from $1\frac{1}{4}$ to $3\frac{3}{4}$ hr, but had no apparent effect on the heat capacity peaks shown in Figure 1; the crests of the peaks just dropped with each subsequent processing during the first series.

Although radiation damage with subsequent annealing, was suspected as the cause of the odd behavior at $\sim 110^\circ\text{K}$, examination of rate of rise curves for all runs gave no indication of any annealing.

The experimentally determined values of S_{298} and $H_{298} - H_0$ for solid PuO_2 , as given in Tables 4 and 5, are considerably lower than estimates used by MILFORD and LAMAR⁽²²⁾ in making thermodynamic calculations.

ACKNOWLEDGMENTS

The writer wishes to thank the following people of the Los Alamos Scientific Laboratory for their assistance: V. O. Struebing, CMF-5, for fabrication of the PuO_2 wafers, firing, sampling, refiring and final sampling; R. R. Gilmore, CMB-11, for fabrication of copper cans and Heliarc welding of wafers in the copper cans and opening them for sampling; P. Vigil and F. H. Ellinger, CMF-5, for X-ray analyses of PuO_2 material at various stages of the experiment; J. H. Muntz, CMB-1, for spectrographic analyses; J. Bubernak, CMB-1, for americium analyses; A. Zerwekh, CMB-1, for Fe and total Pu analyses; and Louise C. Owen, D-5, for editorial comments and corrections. Stimulating discussions with R. N. R. Mulford, CMF-5, and with R. B. Gibney and C. E. Olsen, CMF-13, are also sincerely appreciated.

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FIGURE CAPTIONS

FIG. 1. Heat capacity of PuO_2 below 100°K showing gradual disappearance of peaks with repeated liquid helium cooling during first series of measurements.

After first liquid helium cooling; _____

After third liquid helium cooling; - - - - -

After fifth liquid helium cooling;

After seventh liquid helium cooling. - - - - -

FIG. 2. Comparison of low temperature heat capacities of PuO_2 and ThO_2 .

$\underline{C_p}$ vs $\underline{T}$ curve of PuO_2 below 115°K represents average of results after three liquid helium coolings of the second series. Above 115°K , the PuO_2 curve is the best average of all data.

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Figure 1.

Figure 2.