DECLASSIFIED

33921

Master Copy

This document contains restricted information within the meaning of the Atomic Energy Act and/or information affecting the National defense of the United States within the meaning of the Espionage Act, 50 U.S.C. 31 and 32 as amended. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited and may result in severe criminal penalty.

CLASSIFICATION CANCELLED

DATE 9-1-50
FOR THE ATOMIC ENERGY COMMISSIONWilbur A. Stansbury
CHIEF, DECLASSIFICATION BRANCH *fm*

THE ENTROPY AND LOW TEMPERATURE HEAT CAPACITIES OF
NEPTUNIUM DIOXIDE

This report has been photostated to fill your request as our supply of copies was exhausted. If you should find that you do not need to retain this copy permanently in your files, we would greatly appreciate your returning it to TIS so that it may be used to fill future requests from other AEC installations.

E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne

July 28, 1950

DECLASSIFIED

8-203-1

~~SECRET~~

Abstract

The Entropy and Low Temperature Heat Capacities of Neptunium Dioxide

R. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne

Argonne National Laboratory, Chicago, Illinois

33073

May 27, 1950

An adiabatic semi-microcalorimeter for measuring low temperature heat capacities of 0.01 mole samples of neptunium compounds was constructed. The cryostat was a modification of the design of Rueshrwein and Huffman¹

¹ R. A. Rueshrwein and H. M. Huffman, Jour. Am. Chem. Soc. 65, 1620 (1943)

but employed only liquid helium and liquid nitrogen as refrigerants for measurements in the range 4°K to 320°K. Temperature measurements were made with a strain-free platinum resistance thermometer which was an integral part of the calorimeter. Calibration of the thermometer was made possible by the kind assistance of H. M. Huffman, G. B. Guthrie, Jr., and others at the Bureau of Mines Petroleum Experiment Station. Heat capacity determinations were made on 2 grams of neptunium dioxide prepared by Sherman Fried, J. C. Hindman, and J. G. Halm in this laboratory. There is a pronounced hump in the heat capacity curve at 25°K similar to the hump in the heat capacity curve of uranium dioxide at 29°K. The entropy and the interpretation of the anomaly in the heat capacity curve will be discussed.

CLASSIFICATION CANCELLED

DATE 6-9-50
FOR THE ATOMIC ENERGY COMMISSION

Anthony C. Kallala
CHIEF, DECLASSIFICATION BRANCH

This document contains restricted data within the meaning of the Atomic Energy Act of 1946 and/or information affecting the National defense of the United States within the meaning of the Espionage Act, 50 U.S.C. 21 and 23. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited and may result in severe criminal penalty.

SECRET

Acco-286

Abstract

The Entropy and Low Temperature Heat Capacities of Neptunium Dioxide

R. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne

Argonne National Laboratory, Chicago, Illinois

33073

May 29, 1950

An adiabatic semi-microcalorimeter for measuring low temperature heat capacities of 0.01 mole samples of neptunium compounds was constructed. The cryostat was a modification of the design of Rueshrwein and Huffman¹

1 R. A. Rueshrwein and H. M. Huffman, Jour. Am. Chem. Soc. 65, 1620 (1943)

but employed only liquid helium and liquid nitrogen as refrigerants for measurements in the range 4°K to 320°K. Temperature measurements were made with a strain-free platinum resistance thermometer which was an integral part of the calorimeter. Calibration of the thermometer was made possible by the kind assistance of H. M. Huffman, G. B. Guthrie, Jr., and others at the Bureau of Mines Petroleum Experiment Station. Heat capacity determinations were made on 2 grams of neptunium dioxide prepared by Sherman Fried, J. C. Hindman, and J. G. Malm in this laboratory. There is a pronounced hump in the heat capacity curve at 25°K similar to the hump in the heat capacity curve of uranium dioxide at 29°K. The entropy and the interpretation of the anomaly in the heat capacity curve will be discussed.

CLASSIFICATION CANCELLED

DATE 6-9-50
FOR THE ATOMIC ENERGY COMMISSION

Anthony P. Vellardi
CHIEF, DECLASSIFICATION BRANCH

DECLASSIFIED

0-203-2

(Contribution from the Argonne National Laboratory, Chicago, Illinois)

The Entropy and Low Temperature Heat Capacities of Neptunium Dioxide

E. F. Westrum, Jr., J. D. Hatcher, and D. W. Osborne

The availability of a sample of approximately 2 grams of pure neptunium dioxide has made possible the measurement of the low temperature heat capacities of this compound. To carry out the investigation on such a small amount of material, an adiabatic semi-microcalorimeter and a cryostat were constructed. The cryostat employs only liquid nitrogen and liquid helium as refrigerants for measurements in the range 4 °K to 320 °K. No liquid hydrogen is necessary.

Experimental

Neptunium Dioxide.— The neptunium was isolated and purified by Dr. Sherman Fried, Dr. J. C. Hindman, and Mr. John Malm. The neptunium dioxide was prepared by Dr. Sherman Fried by precipitating the hydroxide from hydrochloric acid solution with ammonia and igniting to constant weight in air in a platinum boat at 700° C. The mass of the sample was 1.9250 grams. The identity of the dioxide was established by Professor W. H. Zachariasen by x-ray analysis. Spectrochemical analysis showed only the following impurities in detectable amounts: Chromium, iron and calcium in amounts less than one-tenth of a percent.

Cryostat.— The cryostat was a modification of the design of Ruehrwein and Huffman¹, and details may be seen by reference to

¹ R. A. Ruehrwein and H. M. Huffman, Jour. Am. Chem. Soc., 65, 1620 (1943).

Figure 1. The cryostat is enclosed in an evacuated brass can, (A). (B) is a highly-polished, chrome-plated copper radiation shield. A copper tank, (C), to which is attached another radiation shield, contains liquid or solid nitrogen. A 1.3-liter container for liquid helium (or nitrogen), with its attached radiation shield, is shown at (D). In order to utilize the refrigeration of the vaporized helium, there is an "economizer", (E), connected to the exit tube from (D). Suspended below (D) are two concentric adiabatic shields, (F) and (G), which surround the calorimeter, (H). Cooling of the calorimeter and the adiabatic shields is accomplished by bringing them into thermal contact with the helium can, (D), by means of a nylon thread and windlass. The bundle of lead wires makes thermal contact successively with (C), (E), (D), (F) and (G). Approximately 1.5 liters of liquid helium is required to cool the apparatus from 55 °K to 4 °K, and the rate of loss of liquid helium after cooling is 13 cc./hr.

Calorimeter.- The calorimeter is shown in Figure 2. The sample is contained within an inner platinum well, which is sealed at the top by a conical copper cap sealed with low-melting Cerroseal-35 solder (50% Sn, 50% In). A sealed, helium-filled platinum shell contains the heater and the thermometer. The heater consists of approximately 150 ohms of B. and S. No. 40 gauge glass-insulated constantan wire, wound on a thin layer of mica. A strain-free resistance thermometer of B. and S. No. 47 gauge bare platinum wire (ice point resistance 83 ohms) is bifilarly wound on six slotted mica spacers. The platinum leads to the thermometer and heaters were brought through the case through beads of Pyrex Corning .0100 glass. A platinum tube with a gold "pinch-off" end permitted evacuation, admission of a known pressure of helium and

0-203-4

3

sealing of the sample compartment. The entire mass of the calorimeter was 10.4 grams. The calorimeter junction of the difference thermocouple was closely clamped to a short seal-off tube with a weighed length of bare copper wire.

Shield Control. Two adiabatic shields of a cylindrical design completely surround the calorimeter. Non inductive, glass insulated, advance wire heaters are bifilarly wound on the top, the bottom, and the cylindrical portion of these shields and on the bundle of lead wires connecting the outer adiabatic shield to the helium can. The heaters are connected to a variable source of alternating current through appropriate series and parallel resistors and variacs on the panel. Separate copper-constantan thermocouple junctions attached to the top, bottom, and cylindrical portion of each shield and to the calorimeter are used to indicate the differences of the temperature between the calorimeter and the various parts of the shield. These differential couples are connected to a high sensitivity galvanometer, the deflections of which are magnified by a five meter light path. Selection of the appropriate couple is made through a Leeds and Northrup ten point selector switch on the shield control panel. One operator is used to maintain zero temperature differential between the calorimeter and its enclosing adiabatic shields. The control of the inner shield was greatly simplified by maintaining the outer shield at a convenient, slightly lower, temperature than the inner one. The heater wound around the bundle of wires (analogous to the ring heater in the Huffman-Ruchrwein cryostat) was actually seldom used.

The control and measurement of the energy input and the temperature of the calorimeter and sample are accomplished by another operator using a White double potentiometer and a high sensitivity galvanometer together with a suitable control panel. The voltage for operating the calorimeter heater is obtained from a battery of low discharge wet storage cells, the potential of which is suitably adjusted with a series resistance. The current used by the calorimeter heater is obtained by measuring the potential drop across Leeds and Northrup 10 or 100 ohm resistors certified by the Bureau of Standards. The voltage is obtained by measuring the potential drop across a similar 100 ohm resistor in parallel with the heater and in series with a shunting volt box of 30,000 ohms. The volt box leads are soldered to the current leads to the heater at a point halfway between the calorimeter and the inner adiabatic shield. Consequently, no correction is required for the energy lost to the leads. Simultaneous with the initiation and end of the energy run, the master switch activates a precision timer, which was operated on a 60 cycle frequency, amplified from a precision tuning fork, and frequently checked against time signals broadcast by the National Bureau of Standards. The energy input in each run was calculated in the usual manner from the current, voltage, and time measurements. The resistance of the thermometer was determined by comparing the potential drop of the thermometer with that across the Leeds and Northrup resistors certified by the Bureau of Standards: 10 ohms was used for very low temperatures, 100 ohms for higher temperatures. A current of two ma. was used with the smaller resistance and 0.75 ma. across the 100 ohm resistor. Calibrated Eppley (Weston Type) cells provided a standard potential.

Calibration of the Resistance Thermometer. The calibration of the thermometer built into the calorimeter was accomplished by comparing its resistance with that of a 25.5 ohm platinum resistance thermometer (A-1) of the platinum capsule type made by Leeds and Northrup. We gratefully acknowledge the considerable assistance of the late Drs. H. H. Hoffman and G. B. Guthrie of the Thermodynamic section, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma, who assisted greatly in the comparison of thermometer A-1 with their laboratory standard thermometer H-25 which had previously been calibrated by the National Bureau of Standards. The comparison between thermometer A-1 and our calorimeter thermometer was made by inserting thermometer A-1 into the sample space of the calorimeter by means of a suitable massive copper sleeve. Thermal contact was established with the Apiezon greases. The resistance of the two thermometers was then compared at frequent intervals over the temperature range. Dr. Guthrie again assisted us greatly in the actual calculation of a temperature scale.

Manner of Operation. The small heat capacity of the calorimeter and sample made exactly adiabatic conditions highly desirable in obtaining a zero temperature drift for the calorimeter. Because of slight stray thermoelectromotive forces in the difference couple circuits and because of a drift in the thermometer current, it was found most convenient to operate in a quasiadiabatic fashion; that is, the temperature drift of the calorimeter was observed for a matter of ten or fifteen minutes during the fore period of the

run; then energy was put into the calorimeter for five to ten minutes, and then the afterdrift was observed until a small constant value was obtained. It was possible to obtain small or zero drifts over practically the entire temperature range, and only at the lowest temperatures, where the sensitivities of the differential couples decreased markedly, did the drift corrections (or the extrapolation of temperature to the mid point of the run) become significant.

Data. The experimental heat capacity data are given in Tables 1 and 2, the latter giving the best values at rounded temperatures. These data are also shown graphically in Figures 3 and 4.

The first series of measurements revealed the existence of a region of high energy absorption over the range from about 11° to 40°K , with a very pronounced maximum at a temperature of 25.3°K . The subsequent measurements of series B were made to confirm the original measurements using relatively small temperature intervals in the region of rapid change of heat capacity. These measurements establish satisfactorily the shape of the curve. We observe no evidence of poor thermal equilibrium in the transition region and no hysteresis effects. The heat capacity curve rises smoothly to a maximum value of about 6.2 calories per mole per degree at 25.3° and then falls rapidly but not discontinuously on the high temperature side of the maximum. There was no evidence of a discontinuity in the slope of the heat capacity curve.

Although no hysteresis or irreproducibility of the transition at 25° was noted, as a matter of record it is of interest to note that for the Series A runs the calorimeter was cooled from below

0.203-8

TABLE I

MOLAL HEAT CAPACITY OF SEPTIMIUM DIOXIDE

Molecular Weight = 269.07

0° C. = 273.16° K

T, °K	ΔT, °K	C _p cal./deg.	T, °K	ΔT, °K	C _p cal./deg.	T, °K	ΔT, °K	C _p cal./deg.
Series A			Series B					
10.87	0.714	0.257	11.11	1.432	0.296	123.87	9.000	8.54
12.46	0.855	0.495	13.14	2.013	0.612	133.28	9.635	9.14
14.10	1.458	0.833	15.40	2.414	1.176	143.35	10.322	9.74
15.91	1.411	1.289	18.10	2.803	1.968	153.87	10.595	10.37
17.67	1.663	1.825	20.54	1.973	2.973	164.38	10.273	10.96
19.19	1.122	2.330	22.47	1.530	4.053	174.89	10.643	11.54
20.39	0.947	2.860	23.89	1.125	5.021	185.78	10.993	12.12
21.42	0.824	3.285	24.76	0.484	5.774	196.70	10.688	12.59
22.44	0.837	3.995	25.27	0.387	6.064	207.36	10.459	13.10
23.29	0.588	4.560	25.71	0.273	4.267	217.73	10.872	13.48
23.98	0.510	5.074	26.08	0.277	2.407	228.55	10.625	13.87
24.63	0.497	5.655	26.52	0.407	2.143	239.12	10.420	14.26
25.21	0.466	6.084	27.11	0.605	1.960	249.80	10.838	14.45
25.84	0.565	3.430	27.99	0.823	1.863	260.69	10.844	14.86
26.60	0.612	2.137	52.43	4.975	3.328	271.48	10.628	15.28
27.38	0.595	1.909	57.52	5.029	3.726	282.04	10.417	15.54
28.41	1.126	1.832	62.78	5.368	4.14	292.42	10.257	15.73
30.13	1.963	1.835	68.40	5.718	4.56	302.64	10.124	15.78
32.71	2.667	1.944	74.18	5.681	4.96	312.69	9.941	16.14
35.62	3.006	2.099	80.73	7.285	5.43			
39.07	3.718	2.355	88.10	7.304	5.96			
42.99	3.886	2.617	96.52	7.643	6.56			
47.44	4.729	2.935	104.79	8.760	7.18			
52.27	4.671	3.207	113.97	9.455	7.82			

O-203-9

TABLE II

MOLAL HEAT CAPACITY OF NEPTUNIUM DIOXIDE
AT ROUNDED TEMPERATURES(Values read from a smooth curve through
the experimental observations)

T, °K	Cp cal./deg.	T, °K	Cp cal./deg.
15	1.056	160	10.72
20	2.725	170	11.27
25	6.00	180	11.82
30	1.832	190	12.31
40	2.409	200	12.76
50	3.129	210	13.18
60	3.924	220	13.58
70	4.67	230	13.94
80	5.37	240	14.28
90	6.10	250	14.59
100	6.80	260	14.88
110	7.53	270	15.15
120	8.26	280	15.40
130	8.93	290	15.64
140	9.56	300	15.85
150	10.15	310	16.06

O-203-10

liquid nitrogen temperatures down to helium temperatures over a period of approximately 12 hours. The sample was cooled even more slowly prior to the Series B run. For this cooling the calorimeter and adiabatic shield assembly was not contacted with the helium can and the cooling in the helium temperature range therefore was allowed to take place over a period of several days, and the sample was maintained at liquid helium temperature for approximately two days before the series of measurements were begun.

The total entropy was evaluated in the following fashion. The entropy from zero to 11°K was obtained by means of a single Debye function fitted to the lowest measured point on the experimental heat capacity curve. A Debye theta of 132° was used and the entropy at 11° is calculated to be 0.092 entropy units. Graphical quadrature of the heat capacity versus the logarithm of the temperature between 11 and 298.16°K yielded a value of 19.073 entropy units. The total entropy at 298.16°K is, therefore, 19.17 entropy units.

The dotted line on figure 4 represents our best estimate of the "normal" heat capacity of the crystalline NpO_2 . This curve was obtained by fitting a single Debye function to our experimental data between 45° and 90°K and corresponds to a Debye temperature of 191°. The total entropy at 50°K obtained by graphical quadrature of the experimental data extrapolated below 11° as already indicated yielded 3.38 entropy units. The lattice or "normal" entropy at 50°K (obtained by the integration of the Debye function, $\theta = 191^\circ\text{K}$) was 1.70 entropy units. The difference or the entropy in excess of the lattice entropy is therefore 1.68 entropy units. The corresponding

8-203-11

enthalpy excess over that of the lattice is 34.52 calories per mole. Graphical integration of the experimental heat capacities plotted against the temperature yielded ($H^{\circ}_{298.16} - H^{\circ}_0$) of 2769 calories per mole.

It is to be noted that the Debye extrapolation of the experimental data and the estimation of the lattice heat capacity by use of a Debye curve is a somewhat arbitrary process. However, we believe that the extrapolation selected contributes a possible error smaller than the experimental uncertainty of the data. Because so small an amount of neptunium dioxide was available for the experiment, the heat capacity of the calorimeter represents a correspondingly larger fraction of the total heat capacity, than is normally the case in calorimetry of this type. Thus we find that at 11° the heat capacity sample is about 33% of that of the empty calorimeter, at 52° it diminishes to a minimum of about 13%, and at 300° it is about 20% of the entropy heat capacity. At the height of the transition the sample heat capacity reaches a maximum or is equal to about 89% heat capacity of the empty. The correction for solder is also more serious here than with a larger sample and varies between .3% to 1%. We believe the precision of the individual determinations of the heat capacities of the empty calorimeter and of the loaded calorimeter are reliable to about 0.1% and that the entropy figure is accurate to within a tenth of an entropy unit. The calculation of the enthalpy difference and the absolute entropy between 0°K and the temperature of interest has been summarized at 50° temperature intervals in Table 3.

0-203-12

TABLE III

MOLAL ENTROPY AND HEAT CONTENT OF IRP-
TUNGSTUM DIOXIDE AT ROUNDED TEMPERATURES

T, °K	S° cal./deg.	H°-H° ₀ Calorie
50	3.38	94.3
100	6.71	344.7
150	10.13	772
200	13.43	1348
250	16.48	2035
300	19.26	2798
298.16	19.17	2769

8-203-13

Discussion. The thermal behavior of NpO_2 is very similar to that found by Earl A. Long, Wesley H. Jones, and Joseph Gordon in the study of a heat capacity of uranium oxide. Uranium oxide shows a similar transition at 28.6° to that which we found at 25.3° for the NpO_2 . They find, however, that the entropy in excess of the lattice entropy is 0.87 entropy units compared to the figure of 1.68 entropy units found for NpO_2 . Their total entropy at 298.1°K was $18.63 \pm .1$ of an entropy unit. The structure of both the dioxides is of the fluoride type and the similarity, therefore, is not particularly surprising. One would deduce by comparison other paramagnetic substances that at a sufficiently high temperature the magnetic ions of UO_2 or NpO_2 are distributed among the several states available to each ion. As the temperature is lowered the distribution of the magnetic ions among these states would be expected to change until at absolute 0 we would reasonably expect complete ordering of the magnetic moment of the ions. We believe as did Long, Jones, and Gordon (for UO_2) that the maximum in the heat capacity curve near 25° in NpO_2 is associated with this loss of magnetic entropy. In the case of UO_2 where one might postulate three spin states per ion the magnetic entropy contribution would be $R \log 3$ or 2.18 entropy units, that is, the total magnetic entropy present at high temperatures. For NpO_2 the assumption of four spin states might be reasonable corresponding to a magnetic entropy contribution of $R \log 4$ or

2.75 entropy units. The entropy in excess of the Debye or "lattice" entropy would correspond roughly to 40% in the case of UO_2 or 60% in the case of NpO_2 of the maximum theoretical amount. The theoretical contribution is

0-203-14

calculated on the assumption that the orbital coupling has been frozen out. Long, Jones, and Gordon* suggest two possibilities to explain the fact that only a partial amount of the magnetic entropy appears in the region of anomalous heat capacities. They suggest either that there is a gradual increase in the magnetic entropy of temperatures above the region of the maximum so spread out that the magnetic contribution of the heat capacity cannot be distinguished from that due to the lattice vibration. They believe that this is the case for uranium dioxide. Secondly, they suggest another possibility, which is very unlikely, that at 13°K there remains a large contribution of magnetic entropy which would be lost at lower temperatures. We believe that the effect in NpO_2 is of analogous origin to that of UO_2 and suggest the virtue of further investigation of other compounds of elements which would be expected to show similar behavior, possibly together with a study of the temperature dependents of the paramagnetic susceptibility.

Acknowledgement. The co-authors of this paper express their deep appreciation especially to Dr. Sherman Fried for his preparation of the NpO_2 , his assistance in the construction of the apparatus, and in the operation thereof. We acknowledge also the assistance of Drs. H.H. Huffman and G.B. Guthrie of the Petroleum Experiment Station for their assistance in enabling us to construct a temperature scale and thus complete the measurements in the relatively short time during which the neptunium was available to us.

* Long, Jones, and Gordon A-329 (1942) the data on the heat capacity and entropy and heat capacity anomaly appear in the declassified NNES Uranium volume in the chapter on Uranium oxides. 9-203-15

The following figures are attached hereto and are a part of this report:

Figure 1. Schematic Cross Section through Cryostat

Figure 2. Detail of Calorimeter

Figure 3. The Heat Capacity of NpO_2

Figure 4. The Heat Capacity of NpO_2 and UO_2 in the Region of Anomalous Heat Capacity.

8-203-16

G-203-17
FIGURE I

Q-203-18

Figure 2
Calorimeter

C_p
cal/mole/deg

Q-203-19

Figure 3

C_p of NpO_2

Fig. 4.

C_p of NpO_2 at Low Temperatures
(INCLUDING UO_2 DATA BY LONG, JONES,
AND (2nd CON.))

D-203-20