The calorimeter charge was 98.8378 grams (vacuum) or 0.33627 mole of crystalline dipotassium calcium pyrophosphate (formula weight, 292.227) and 0.00224 mole of calcium pyrophosphate (formula weight, 254.103).

Observed molal heat capacities, corrected for the amount of calcium pyrophosphate present, are shown in Table I. The heat capacities at 1° intervals below 10° K. were read from a large-scale plot of the observed values of C_p/T *vs.* T^2 over the range 10° to 30° K. that was extrapolated smoothly to 0° K. The smoothed heat capacities and the corresponding entropy and enthalpy increments are shown in Table II.

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Enthalpy of Formation of Neptunium Dioxide

ELMER J. HUBER, JR., and CHARLES E. HOLLEY, JR.

University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544

The enthalpy of formation of neptunium dioxide has been determined by means of an oxygen bomb calorimeter and found to be $\Delta H^\circ_{f\ 298.15^\circ\ \mathrm{K.}}$ (NpO_2) = −256.7 ± 0.6 kcal. per mole.

OF THE MANY isotopes of neptunium, only Np^{237} has a sufficiently long half life to permit detailed studies of its properties. Only in recent years have sufficient amounts of this material been available for experimental use. Neptunium-237 is a by-product of plutonium production and is recovered and purified by solvent extraction and ion exchange methods. Fluorination of the dioxide followed by reduction with excess calcium in the presence of iodine (*7*) produces a metal of high purity. This paper describes the combustion of such metal in an oxygen bomb calorimeter to determine the enthalpy of formation of neptunium dioxide.

MATERIAL

The neptunium metal was in the form of pellets weighing 1.5 to 2 grams. In addition, Np wire was fabricated for use as a fuse (*9*). Analysis of the metal at this laboratory showed the following impurities: Pu^{238}, 0.02% (by radioassay); C, 0.0055%; H, 0.001%; N, 0.0034%; O, 0.0058%; Si, 0.02%. Thirty-six metallic elements were below the limit of detection by the spectrographic method used. A recasting of a portion of the metal increased the oxygen content to 0.015%. A metallographic examination revealed the presence of a very fine precipitate. An x-ray pattern showed only α-Np with no impurity lines. Mass spectrometer analysis showed essentially m/e of 237 with very small amounts of 235, 238, and 239.

The calculated composition of the material was (weight per cent): Np, 99.62; Pu, 0.02; NpC, 0.114; NpH_2, 0.119; NpO_2, 0.049; NpN, 0.061; Si, 0.02. For the recast sample the values were identical except for Np, now 99.54%, and NpO_2, which was increased to 0.126%.

Spectrographic analysis of the NpO_2 from which the metal was made showed small amounts of Al, Ca, and Si. This oxide was also used in the preparation of disks upon which the combustions were carried out.

METHODS AND RESULTS

The method involved the determination of the amount of heat evolved from the combustion of a weighed sample of neptunium metal in a bomb calorimeter at a known initial pressure of oxygen. The method and equipment have been described (*4, 5*). The energy equivalent of the calorimeter with 25 atm. of oxygen was 2390.0 ± 1.1 cal. per °C. as determined with standard benzoic acid (NBS sample 39i). The calorie is the defined thermochemical calorie, equal to exactly 4.1840 absolute joules. Temperature measurements were made using a platinum resistance thermometer and a type G-2 Mueller bridge. They are believed accurate to 0.001° C. The 2 kg. of water used in the calorimeter were weighed to 0.01 gram.

Because of the neptunium alpha activity and the attendant health hazard the metal was handled through gloves in an enclosed box where it was weighed and loaded into the bomb. The Parr oxygen bomb screwed into an adapter in the floor of the box from the outside, so that the outside surface of the bomb remained uncontaminated. Although the top of the bomb was within the contaminated area of the box, it was protected by means of a molded disposable plastic cap which fitted snugly over the lid of the bomb. The gamma activity of the neptunium was not sufficient to be considered a hazard over the relatively short exposure times. The bomb was flushed and filled with oxygen in a ventilated hood. These precautions were sufficient to prevent contamination of the accessory apparatus.

The neptunium was burned as pellets on sintered disks of NpO_2 supported on a platinum platform weighing 20.8 grams. Two disks of NpO_2 each weighing 25 to 30 grams were used for each run. At room temperature α-Np is a hard (*Dph* ~ 355) brittle material of high density (20.45 grams per cc.). It proved difficult to drill holes through the pellets through which a fuse wire might be threaded. Such operations had to be performed in an inert atmosphere.

Ten-, 20-, and 30-mil diameter Np fuse wires were fabricated in addition to 10-mil magnesium and thorium wires. The 10-mil Np proved too brittle to be mounted on the electrical terminals. The 30-mil Np could not be ignited by any reasonable current flow. The magnesium wire would not ignite the Np. Two successful runs were made with the 20-mil Np and three with the thorium wire. In some cases the Np would not ignite but was heated by the fuse wire to a temperature where it would sustain oxidation over a period of 30 minutes or more. This unusual behavior

Table I. Heat of Combustion of Neptunium Metal

Mass Np Sample, G.		Wt. NpO_2, G.	Wt. Th Fuse Wire, Mg.	Energy Equiv., Cal./Deg. Total	ΔT, °C.	$\Delta E_{\text{ign.}}$, Cal.	$\Delta E_c/M$, Cal./G.
Burned	Unburned						
2.2415	0.0037	59.2	31.74	2394.0	1.0283	3.5	−1078.9
2.5945	0.0089	61.6	34.30	2394.1	1.1923	4.6	−1081.8
1.3158	0.0074	62.2	34.85	2394.2	0.6165	4.5	−1085.0
2.8276	0.0022	53.7	...	2393.6	1.2770	10.5	−1077.3
2.4539	0.0059	55.0	...	2393.7	1.1140	17.2	−1079.7

had not been noted with other metals. Such runs were discarded. The oxygen pressure was varied over a range of 10 to 50 atm., but all the successful runs were made at 25 atm. There was no detectable change in weight of the metal upon exposure to this pressure for an hour. The average initial temperature was 24.95° C.

X-ray powder diffraction analysis was made on each combustion product in addition to microscopic examination. A value of $a_0 = 5.4340 \pm 0.0005$ A. was found for the lattice constant, in good agreement with the value given by Asprey *et al.* (*1*). All samples showed good crystallinity with no extraneous phases. X-ray analysis performed on the oxide formed from the slow oxidation of the metal showed little crystallinity, however.

Each combustion product was ignited at 1000° C. to find the amount of unburned metal. Small amounts of adsorbed water and carbon dioxide were evolved, collected, and weighed, and the change in weight of the sample was noted. A net gain in weight indicated either unburned Np metal or an oxygen-deficient NpO_2. The average formula for the combustion products would have been $NpO_{1.994 \pm 0.003}$, assuming an oxygen-deficient oxide. Because the x-ray lattice constant is almost identical to the literature value for stoichiometric NpO_2, we believe it is more reasonable to assume that a small amount of metal did not burn. On this basis combustion varied from 99.44 to 99.91% of completion. The specific heat of NpO_2 was taken as 0.0564 cal. per gram per degree. The runs are listed in Table I. Column one shows the net amount of metal burned, after subtraction of the unburned metal. $\Delta E_{\text{ign.}}$ is the electrical energy used to ignite the fuse wire. $\Delta Ec/M$ is the total energy evolved corrected for the electrical and fuse wire energy (where thorium was used) divided by the mass of sample burned.

For purposes of calculation, the first three runs were separated from the second two runs for two reasons: the higher oxygen impurity in the Np used in the last two runs and the different fuse wire used, as mentioned above. For the first three runs (average = 1081.9 cal. per gram), the corrected value becomes 1081.0 cal. per gram or 0.09% lower. For the last two runs (average = 1078.5) the corrected value becomes 1078.5 cal. per gram, the same as the uncorrected average. To make these corrections the following enthalpies of formation at 298.15° K. were taken (in kcal. per mole): NpN, −70 (estimated); ThO_2, −293 (*6*); PuO_2, −253 (*5*); NpC, −20 (estimated); CO_2, −94 (*10*); NpH_2, −28 (*8*); $H_2O(g)$, −58 (*10*); NO_2, +8 (*10*); SiO_2, −217 (*10*). It was assumed that each combustible impurity contributed to the over-all heat in accordance with its enthalpy of formation and the enthalpy of formation of its combustion products. A weighted average value of 1080.0 ± 2.2 cal. per gram is found for the combustion of pure Np metal in 25 atm. of oxygen. The uncertainty is increased to ± 2.7 cal. per gram when uncertainties are included for the energy equivalent of the calorimeter and for the correction for the impurities. The 1961 atomic weights were used (*3*) with the atomic weight of Np taken as 237.05 and that of Pu as 238.05.

The heat of combustion of Np metal under bomb conditions was −256.0 ± 0.6 kcal. per mole. Correction to unit fugacity of oxygen and to constant pressure leads to $\Delta H^\circ_{f\,298.15^\circ\,\text{K.}}$ (NpO_2) = −256.7 ± 0.6 kcal. per mole as the enthalpy of formation of neptunium dioxide:

$$\alpha\text{-Np(c)} + O_2\text{(g)} = NpO_2\text{(c)}$$

The uncertainty attached to the value is twice the standard deviation of the mean and is somewhat larger than usual, probably because of the small number of runs. The values for the runs using Th fuse wire are slightly larger than the others, which may indicate an exothermic reaction between ThO_2 and NpO_2. The two averages are well within the combined uncertainties, however.

The above value can be compared only with Brewer's estimate of −246.0 ± 10.0 kcal. per mole (*2*). The value reported above for the enthalpy of formation of the dioxide of neptunium (Atomic No. 93) lies between those reported for uranium (Atomic No. 92), $\Delta H^\circ_f(UO_2)$ = −259.2 kcal. per mole (*6*), and plutonium (Atomic No. 94), $\Delta H^\circ_f(PuO_2)$ = −252.8 kcal. per mole (*5*).

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