

517. *Neptunium Pentoxide.*

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Neptunium pentoxide, Np_2O_5 , has been characterized, and its symmetry determined by *X*-ray powder methods.

STUDIES of neptunium oxides by Katz and Gruen¹ and Roberts and Walter² gave no evidence for the existence of intermediate phases between NpO_2 and Np_3O_8 , and until recently no higher oxides were known. The preparations of a quinque- and a sexi-valent neptunium oxide have now been reported,^{3,4} the former being of unknown composition. The neptunium(v) oxide has been identified as Np_2O_5 , and its symmetry determined by *X*-ray powder methods.

The neptunium(v) oxide was prepared in two ways: first by bubbling ozone through molten lithium perchlorate containing NpO_2^+ ion,³ and secondly by the reaction of neptunium metal⁴ with molten lithium perchlorate. This latter reaction is quite slow, unlike the reaction of uranium metal with lithium perchlorate.

The neptunium(v) oxide is dark brown. Dissolution in dilute mineral acids yields only NpO_2^+ ion, identified by spectrophotometry. When Np_3O_8 , which is also dark brown,

¹ Katz and Gruen, *J. Amer. Chem. Soc.*, 1949, **71**, 2106.

² Roberts and Walter, A.E.R.E. report R.3624 (1963).

³ Cohen, *Inorg. Chem.*, 1963, **2**, 866.

⁴ Cohen, Paper, XIXth I.U.P.A.C. meeting, London, 1963.

is dissolved under similar conditions the absorption spectrum shows the presence of NpO_2^+ and NpO_2^{2+} ions in the ratio 2:1. This neptunium(v) oxide was identified by neptunium analysis and determination of the oxygen in excess of NpO_2 .

EXPERIMENTAL

Preparative.—*Neptunium pentoxide.* A novel way of adding neptunium(v) to a melt of lithium perchlorate is to dissolve it in conc. perchloric acid and carefully float this solution on top of the melt. Since conc. perchloric acid boils at $\sim 200^\circ$ and the melt is at 260° , the perchloric acid distills away, leaving the neptunium ions in the melt. The water is then removed from the melt by passing an inert gas through it. When ozone is passed through the melt a dark precipitate forms which is recovered by cooling the melt and dissolving the salt with water. The product is then dried at 100° in an air-oven.

The second method of preparation is the reaction of neptunium metal with molten lithium perchlorate. The neptunium was kindly supplied by Dr. J. Lee of the Metallurgy Division, A.E.R.E., Harwell. A 75 mg. piece of metal was added to molten lithium perchlorate. After a few days the metal had disintegrated into a dark powder at the bottom of the melt. This dark neptunium compound was recovered as described above.

Analysis.—Neptunium was determined by α -counting aliquots of a solution in 6*N*-hydrochloric acid containing a weighed amount of the oxide.

The oxygen in excess of NpO_2 was determined by reduction of a weighed amount of material to NpO_2 in carbon monoxide at 750° , followed by measurement of the pressure of the carbon dioxide produced when contained in a known volume. Previous work² showed that the product of reduction under these conditions is NpO_2 ; stronger reduction conditions led to no further loss of oxygen. PuO_2 is more readily reduced than NpO_2 but is not appreciably reduced under these conditions (Found: Np, 84.9 ± 2 . Calc. for Np_2O_5 : Np, 85.5%. Found: O corresponding to $\text{NpO}_{2.49 \pm 0.02}$). Spectrochemical analyses were carried out on samples from different preparations of Np_2O_5 , at Argonne National Laboratory and at Harwell. Less than 0.01% of lithium was found in each case, and no other metals were detected.

RESULTS

X-Ray diffraction patterns were obtained with the same Guinier-type camera as was used² in the work on Np_3O_8 , and a small amount of ThO_2 was added to the specimens as an internal standard. Samples from each method of preparation gave identical patterns. Cell constants were calculated using $\lambda = 1.54051 \text{ \AA}$ for Cu $K_{\alpha 1}$ radiation, and could be related directly to the lattice parameter of ThO_2 ($a = 5.597 \text{ \AA}$). The patterns of Np_2O_5 were very similar to Np_3O_8 , but some lines were split into two very close lines of equal intensity. These lines could be indexed, assuming a monoclinic unit-cell. A least-squares analysis of the $\sin^2 \theta$ values gave the parameters $a = 4.183 \pm 0.003$, $b = 6.584 \pm 0.005$, $c = 4.086 \pm 0.003 \text{ \AA}$, and $\beta = 90.32 \pm 0.03^\circ$. Comparing these results with those for Np_3O_8 ² ($a = 6.584$, $b = 4.086$, $c = 4.183 \text{ \AA}$) it is seen that the numerical values are unchanged but that a , b , and c must be interchanged to fit the convention for a monoclinic cell. The observed and calculated $\sin^2 \theta$ values for Np_2O_5 are compared in the Table with the observed values for Np_3O_8 .

All the lines which would be expected to split when the orthorhombic Np_3O_8 lattice becomes monoclinic are split into two lines, with values of $\sin^2 \theta$ above and below those for Np_3O_8 . This is so because the equation of each line changes from

$$\sin^2 \theta_{hkl} = (\lambda^2/4a^2)h^2 + (\lambda^2/4b^2)k^2 + (\lambda^2/4c^2)l^2$$

$$\text{to} \quad \sin^2 \theta_{hkl} = (\lambda^2/4a^2)h^2 + (\lambda^2/4b^2)k^2 + (\lambda^2/4c^2)l^2 - Dh$$

$$\text{and} \quad \sin^2 \theta_{hkl} = (\lambda^2/4a^2)h^2 + (\lambda^2/4b^2)k^2 + (\lambda^2/4c^2)l^2 + Dh$$

$$\text{where} \quad D = (\lambda^2 \cos \beta)/(2ac \sin^2 \beta).$$

Only those lines for which neither h nor l is zero are split when the lattice becomes monoclinic. The Miller indices of Np_2O_5 in the Table have been altered to correspond to the monoclinic cell. The space group is $P2_1/a$.

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X-Ray data for Np_2O_5 and Np_3O_8 (ref. 2).

Np_2O_5				Np_3O_8		Np_2O_5				Np_3O_8	
hkl	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	I (obs.)	hkl	$\sin^2 \theta$ (obs.)	hkl	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	I (obs.)	hkl	$\sin^2 \theta$ (obs.)
100	0.0339	0.0339	s	001	0.0338	131	0.1921	0.1922	m	311	0.1928
011	0.0492	0.0492	vs	110	0.0492	131	0.1929	0.1930	m	220	0.1970
020	0.0546	0.0547	s	200	0.0546	022	0.1969	0.1969	m	400	0.2188
111	0.0827	0.0827	vs}	111	0.0828	040	0.2189	0.2190	w	221	0.2308
111	0.0835	0.0835	vs}	201	0.0886	122	0.2297	0.2300	w	401	0.2530
120	0.0887	0.0887	s	002	0.1357	122	0.2317	0.2316	w	022	0.2778
200	0.1355	0.1356	m	020	0.1423	140	0.2532	0.2529	w	231	0.2939
002	0.1421	0.1421	s	310	0.1585	202	0.2768	0.2762	vw	231	0.2950
031	0.1586	0.1587	s	021	0.1759	202	0.2799	0.2793	vw	300	0.3044
102	0.1750	0.1753	m}	112	0.1850	231	0.2939	0.2936	vw	300	0.3052
102	0.1769	0.1768	m}	202	0.1906	231	0.2950	0.2951	vw	222	0.3310
211	0.1840	0.1841	m}	202	0.1906	222	0.3304	0.3310	vw	222	0.3316
211	0.1852	0.1856	m}	202	0.1906	222	0.3339	0.3341	vw	130	0.3337
220	0.1902	0.1904	w			013	0.3335	0.3335			

The first line ($hkl = 100$) was very weak on the pattern of some specimens as prepared, probably owing to crystallization in plates parallel to the "a" axis. On grinding the material, a more random arrangement was obtained and the 100 line was of normal intensity.

Several superstructure lines were found on the pattern for Np_3O_8 but they could not be indexed unambiguously.² Np_2O_5 gave these same lines, and several more, some of quite high intensity. Again it was difficult to choose between an ($a 3b c$) and an ($a 4b 2c$) lattice for these lines (using Miller indices for Np_3O_8), but the ($a 4b 2c$) cell probably yields the better fit.

DISCUSSION

Katz and Gruen¹ found no evidence for the existence of an oxide phase between NpO_2 and Np_3O_8 , from a thermogravimetric study of the decomposition of Np_3O_8 , although there was a slight discontinuity on their decomposition curve at about $\text{NpO}_{2.56}$. The X-ray work of Roberts and Walter² on oxides of intermediate composition, prepared by decomposition of Np_3O_8 , showed the presence of only NpO_2 and Np_3O_8 phases. NpO_2 lines were generally observed for specimens of oxygen content less than $\text{NpO}_{2.60}$, but in one case a composition as low as $\text{NpO}_{2.58}$ showed no NpO_2 lines. The decomposition was not reversible and true equilibrium was not attained. With specimens of large particle size, a layer of NpO_2 which was formed on the surface inhibited further decomposition. On re-examining the diffraction patterns of these partially reduced specimens, no broadening of the Np_3O_8 lines which are split for Np_2O_5 could be observed. However, the present work has shown that the splitting of the lines in the Np_3O_8 pattern on changing to monoclinic Np_2O_5 gives two lines which are so close that the change would not be observed except with well-crystalline specimens. Although the diffraction patterns for Np_3O_8 were not as clear as those for Np_2O_5 , they were sufficiently sharp to show that Np_3O_8 is not monoclinic.

The reduction of the neptunium(vi) atoms in Np_3O_8 to neptunium(v) in Np_2O_5 apparently causes no change in cell volume. The volume of the unit cell of Np_3O_8 (112.5 \AA^3) is larger than that of U_3O_8 (110.9 \AA^3), although, with the dioxides, a steady contraction is observed with increase in atomic number⁵ (the "actinide contraction" effect). This is probably because Np_3O_8 is a less closely packed structure than U_3O_8 .

Bagnall and Laidler,⁶ in a study of the thermal decomposition of NpO_3 monohydrate, have isolated a phase of composition Np_2O_5 , as shown by the absorption spectrum in solution, and neptunium analysis, but the material was not well-crystalline.

This work, together with that of Bagnall and Laidler, has shown that a quinquevalent oxide of neptunium exists as a distinct phase, but preparations made by decomposition of

⁵ Asprey, Ellinger, Fried, and Zachariasen, *J. Amer. Chem. Soc.*, 1955, **77**, 1707.

⁶ Bagnall and Laidler, preceding Paper.

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higher oxides are poorly crystalline and are not distinguishable from Np_3O_8 by X-ray methods. To do this, it is necessary to prepare the Np_2O_5 under conditions which give the quinquevalent oxide as the primary product. Np_2O_5 may not be formed during the decomposition of Np_3O_8 for kinetic reasons.

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