MDDC - 1332

UNITED STATES ATOMIC ENERGY COMMISSION
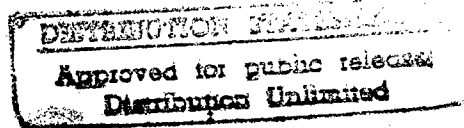

THE BASIC DRY CHEMISTRY OF NEPTUNIUM

by

S. Fried
N. R. Davidson

Argonne National Laboratory

Date Declassified: July 18, 1947

19960920 075

THE BASIC DRY CHEMISTRY OF NEPTUNIUM*

By S. Fried and N. R. Davidson

ABSTRACT

A description of the microtechniques used in the preparation of neptunium compounds is given. Neptunium dioxide and sodium neptunyl acetate have been prepared and identified.

Neptunium trifluoride and tetrafluoride have been prepared by the reactions:

$$NpO_2 + 1/2 \ H_2 + 3HF \longrightarrow NpF_3 + 2H_2O$$
$$NpF_3 + 1/4 \ O_2 + HF \longrightarrow NpF_4 + 1/2 \ H_2O$$
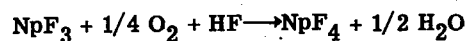
The NpF_3, as observed with about 250 micrograms of material, was dark purple. The NpF_4 was a light green material.

Neptunium tetrachloride was prepared by the reaction of CCl_4 vapor upon Np(IV) oxalate or NpO_2 at 500°C in a Pyrex x-ray capillary. The $NpCl_4$ is formed as a yellow sublimate.

Hydrogen reduction of $NpCl_4$ at 450°C gave rise to $NpCl_3$.

The action of chlorine gas on $NpCl_4$ at elevated temperatures failed to yield any higher chlorides of neptunium.

Neptunium tetrabromide was prepared by the action of $AlBr_3$ on NpO_2, and the tribromide by the same reaction in the presence of excess aluminum.

Neptunium triiodide was prepared by the action of AlI_3 on NpO_2.

The reaction of an H_2S-CS_2 mixture on NpO_2 at 1000° for two hours gave rise to NpOS. Prolonged treatment under the same conditions yielded Np_2S_3.

Ignition of Np(IV) nitrate in 28 atmospheres of O_2 at 400°C gave rise to NpO_2, not a higher oxide. Under the same conditions U_3O_8 is converted to UO_3.

A tabular survey of the dry chemistry of U, Np, and Pu is given, and the relationship between the stability of the different oxidation states in solution and in dry compounds is discussed. In general, it is easier to obtain the higher oxidation states of the elements under discussion in solution than in dry compounds. Among the pure compounds (solid or gaseous) the small positively charged ions of the various oxidation states must be stabilized by coordination to the anions of electronegative atoms. The small and difficultly polarizable anions, $O^=$ and F^- in general form compounds of higher oxidation number than do the more readily polarized anions, Cl^-, Br^-, $S^=$, and I^-.

* * * * * *

---

*This paper is based largely on work reported in CN-3381

Identification of solid reaction products by means of an analysis of their x-ray diffraction patterns can be carried out rapidly, and in favorable cases, with less than 10 micrograms of material. This is particularly true when the compound produced is isomorphous with known compounds of other elements. Accordingly, the identification of the compounds of neptunium was in most cases by the x-ray method in the laboratory of Dr. W. H. Zachariasen, and the composition inferred from a consideration of the crystalline form and lattice dimensions.

By use of the x-ray method, together with the development of techniques for handling microgram quantities of solids and a consideration of the methods of preparation, it has been possible to elucidate the structure and/or composition of the several neptunium compounds known in the dry state.

TECHNIQUES

It is appropriate at this point to describe some of the more common techniques used in the handling of solids on the ultramicro scale. Some of the techniques described were developed by P. L. Kirk and his group early in the work on this project, while others were developed by various members throughout their own work.

A great deal of effort was expended in developing methods for the preparation of samples for x-ray diffraction analysis, since, as mentioned above, many of the analyses were done by this method. This involved the preparation of samples of the order of 5 micrograms in a suitable form and mounted in very thin-walled glass capillaries.

A brief discussion of the basic techniques is presented in the following paragraphs.

1. Preparation of Capillaries for X-ray Samples

In order to obtain satisfactory x-ray diffraction patterns of microgram quantities of a solid in a glass capillary, the wall thickness of the capillary must be not greater than 0.030 mm. One of the most satisfactory methods of obtaining capillaries with this specification is as follows: a four-inch length of well-cleaned 10 to 12-mm diameter Pyrex tubing is drawn down by means of a sharp oxygen-gas flame as shown in Figure 1. The constricted tube is heated with an air-gas flame at point A until sufficiently soft and is then rapidly drawn out to a thin capillary. Capillaries of 0.100-mm inside diameter and a wall thickness as low as 0.010 mm may be readily produced by means of this technique. The cutting of capillaries of these dimensions may be accomplished by gently rubbing the capillary at the desired point with a small fragment of clay chip. It will be found that a light pressure will cause the capillary to break cleanly at the point scatched by the chip. The end of the capillary may be satisfactorily sealed by using a very small flame. Care should be taken to prevent over-thickening of the glass at the bottom of the capillary, since an increase in wall thickness enhances the diffuse scattering of the x-ray beam and thus intensifies background darkening on the film.

Quartz capillaries are much more difficult to make. Ten millimeter quartz tubing with a 1-mm wall may be drawn into satisfactory x-ray capillaries by means of a sharp oxyhydrogen flame in the same manner as previously described, except that a "soft" oxy-hydrogen flame is used for the final drawing instead of an air-gas flame, as in the case of Pyrex. These capillaries are generally not circular in cross section, nor are they of uniform wall thickness.

2. Filling X-Ray Capillaries

Since these tubes are very fragile and of small diameter, it is generally preferable to leave the stem attached rather than to try to fill the narrow tube directly, though this may be done under low magnification. The x-ray capillary, with attached stem, will have the appearance indicated in Figure 2. These tubes may be held for observation on the stage of a dissecting microscope by means of a lump of modeling clay placed at C. Particles of the solid may be introduced into the larger tube in any convenient way, but care should be taken not to put in too much material at one time or to add particles
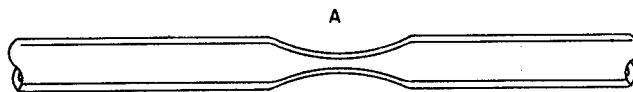
A

Figure 1. Constricted 12-mm Pyrex tubing for use in preparing x-ray capillaries.
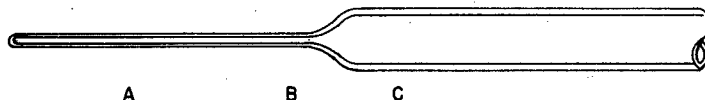

A   B   C

Figure 2. X-ray capillary with attached stem.

too large to fall to the bottom of the capillary. In general, powders may be persuaded to fall to the bottom of a fine capillary by holding it in a vertical position and tapping sharply at C. Sometimes light rubbing at B with a knurled edge or file will shake the powder loose from the walls into the capillary. Vibration should not be attempted at points lower than B because of the danger of breaking the capillary.

After the particles have been satisfactorily packed into the end of the capillary, it may be sealed off at A. If desirable, the stem of the capillary may end in a ground joint, so that it may be evacuated before sealing.

3. Emptying Capillaries

It is frequently necessary to reuse material submitted for x-ray analysis. In such case, the capillary (usually 1/2 to 3/4 inches long) is held lightly in the fingers and opened by scratching with a clay chip. The opened capillary is then attached to a stout wire with a bit of clay, as shown in Figure 3. The wire is then tapped sharply at A, causing the contents of the capillary to fall out into the container.

4. Preparation of Solids from Solution

The preparation of solids from solutions involves either evaporation of the solvent or precipitation from solution by a chemical reagent. Evaporation may be done from small platinum boats. These boats are usually rectangular in shape, 6 by 3 mm by about 3 mm deep. A solution of a heavy metal nitrate can be placed in a boat such as this, the solution evaporated to dryness, and if necessary, the nitrate ignited to an oxide. Samples of the oxide or nitrate can be removed from the boat by means of a needle and introduced into an x-ray capillary for examination. Alternatively, the oxide can be treated with other reagents to produce new compounds. These operations can very easily be carried out on the 50-microgram scale.

In precipitation of solids from solution the following technique was found very satisfactory in the case of substances precipitating in a bulky gelatinous form (such as certain hydroxides). These hydroxides can be precipitated, washed, and centrifuged in a microcone. This leaves the desired product tightly packed at the bottom of the cone. The supernatant liquid is removed, and the cone and contents are dried slowly at about 70°C. It is found that the precipitate has a tendency to shrink away from the walls of the cone under these conditions so that if forms a loose single piece, or at most a few pieces. Various dry operations can now be performed on these small amounts of material in situ, or the material may be transferred to an x-ray capillary made from a ground joint. When such a system is connected to a vacuum line various chemical reactions, such as the action of gaseous substances on the hydroxides, may be studied.

This type of manipulation lends itself to the preparation of halides that may later be sublimed on the walls of the capillary. The capillary may then be sealed off to the proper length, and the contents (both the sublimate and residue) studied by x-ray diffraction methods.
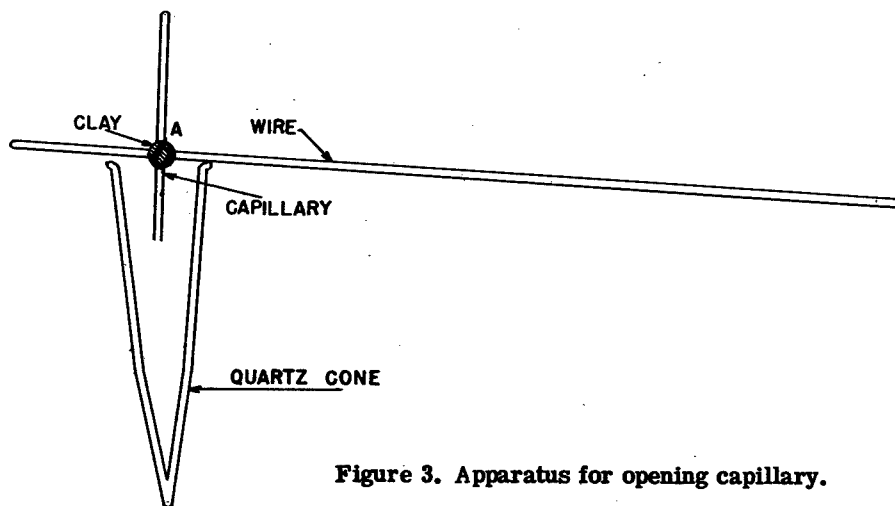
Figure 3. Apparatus for opening capillary.

4.1. Neptunium Dioxide and Sodium Neptunyl Acetate.—These two compounds were the first identifiable neptunium compounds prepared. They were both prepared by Magnusson and LaChapelle[1] —the oxide by ignition of a hydroxide precipitate, and the neptunyl acetate by a method similar to that used for the preparation of the analogous uranium and platonium salts.

Neptunium dioxide is a brownish material that has a cubic structure and is isomorphous with UO_2 and PuO_2.[2] Sodium neptunyl acetate, $NaNpO_2Ac_3$, is pink under 30X magnification (transmitted light), pale green by reflected light, and is isomorphous with the corresponding plutonium and uranium compounds.[3]

4.2. RNp_2F_9—This compound also was prepared by LaChapelle and Magnusson by adding HF to a Np(IV) solution containing ammonium ion. This compound is isomorphous with KTh_2F_9 and KU_2F_9.

4.3. Preparation and Properties of NpF_3 and NpF_4.—Neptunium trifluoride and neptunium tetrafluoride were prepared by the reactions:[4]

$$NpO_2 + 1/2\ H_2 + 3HF \longrightarrow NpF_3 + 2H_2O \tag{1}$$

$$NpF_3 + 1/4\ O_2 + HF \longrightarrow NpF_4 + 1/2\ H_2O. \tag{2}$$
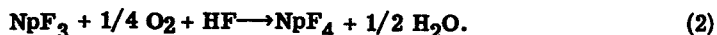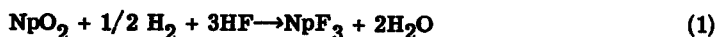
For the preparation of NpF_3, Np(IV) hydroxide was precipitated in a microcone with gaseous NH_3 from a solution containing 50 micrograms of Np(IV) at a concentration of 1 g/liter in dilute sulfuric acid. The gelatinous precipitate was washed and then dried to a pellet, in an oven at 70°C. The pellet was transferred to a platinum vessel made from the cover of a 1-ml J. Lawrence Smith crucible, with a platinum holder spotwelded to it. The platinum vessel was placed in an all-platinum hydrofluori- nation apparatus and treated with an H_2-HF (about 1:1) mixture for one and one-half hours at 500°C.* The system was cooled in the HF-H_2 mixture, which was then pumped out and replaced with nitrogen. The reaction product was crushed and transferred to an x-ray capillary for examination by Dr. W. H. Zachariasen. He reported that the sample contained about 25 per cent Pt and 75 per cent NpF_3, isomorphous with PuF_3, UF_3, and LaF_3.[5]

After a metallic-looking flake of Pt was removed from the sample of NpF_3, the rest was transferred back to the platinum crucible and treated in the hydrofluorination apparatus with an O_2-HF mixture for one hour at 500°C. The light green reaction product proved to be NpF_4.[6]

---

* The authors wish to acknowledge the valuable assistance of A. S. Florin in this stage of the preparation.

The NpF_3, as observed with about 25 micrograms of material, was black in appearance, reminiscent of the "black fluoride," PuF_3, which was encountered so frequently when the plutonium fluorides were being prepared on the microgram scale. Preparations on the 250-microgram scale, which were free of platinum, appeared dark purple—darker than PuF_3. The NpF_4 was a light green material.

These reactions for the preparation of the neptunium fluorides are analogous to reactions for the preparation of PuF_3 and PuF_4 from PuO_2 and PuF_3, respectively. It may be inferred that the direct synthesis of NpF_4 from NpO_2,

$$NpO_2 + 4HF \rightarrow NpF_4 + 2H_2O \qquad (3)$$

will take place with HF that is free of H_2. Reaction 1 does not take place for UO_2. At 500°C, the action of an H_2-HF mixture gives rise to UF_4. Neptunium tetrafluoride also has been synthesized directly from the oxide by the action of an O_2-HF mixture at 500°C.[7]

One incidental observation on the properties of NpF_4 has been made. It was desired to convert the sample to NpO_2 for further experiments. The NpF_4 was placed in a microcone with 50 micro-liters of concentrated HNO_3 and evaporated to dryness at 70°C. The sample retained its color and shape and had evidently not been attacked.

4.4. Neptunium Hexafluoride. — This compound was prepared by A. E. Florin according to the following reaction:[8]

$$2NpF_3 + 3F_2 \rightarrow 2NpF_6.$$
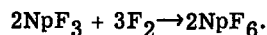
The reaction was carried out by heating a sample of NpF_3 on a nickel filament in a stream of fluorine and condensing the volatile NpF_6 in a thin-walled capillary "U" tube. The walls of the U tube were thin enough so that when it was sealed off, both below and above the mass of collected material, it could be submitted directly for x-ray examination.

The NpF_6, as prepared by this method from 0.5 mg NpF_3, consisted of a mass of browish-white crystals which were shown to be isomorphous with UF_6.[9] The melting point was determined as 53°C under its own pressure at that temperature. This substance seemed to be quite volatile and could be sublimed from one end of the capillary to the other by slight warming. Even cooling one end of the capillary while the other remained at room temperature was sufficient to cause sublimation.

The ingenious apparatus used in this preparation is shown in Figure 4.

4.5. Preparation and Properties of $NpCl_3$ and $NpCl_4$. — It was of interest to investigate the reaction of a neptunium compound with carbon tetrachloride. Uranium dioxide or oxalate reacts with CCl_4 vapor at 450 to 500°C according to the reaction

$$UO_2 + 2CCl_4 \rightarrow UCl_4 + 2COCl_2. \qquad (4)$$
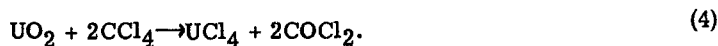
The UCl_4 slowly sublimes out of the reactor. Plutonium dioxide, on the other hand, does not react completely with CCl_4 below 750 to 800°C. At this temperature, the reaction is

$$PuO_2 + 2CCl_4 \rightarrow PuCl_3 + 2COCl_2 + 1/2\ Cl_2. \qquad (5)$$
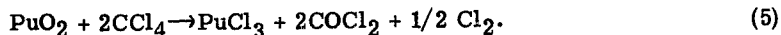
The $PuCl_3$ is obtained as a green sublimate.

It has been found that Np(IV) oxalate (or the dioxide) reacts with CCl_4 vapor at 500°C to give a yellow sublimate of $NpCl_4$.[10] In this respect, therefore, the Np is more like uranium than Pu in its chemical behavior. Just as UCl_4 may be reduced with hydrogen to form UCl_3, so $NpCl_4$ may be reduced to $NpCl_3$.

Many anhydrous chlorides are extremely hygroscopic and it was believed that transferring 50-microgram samples of neptunium chlorides, even in the relatively anhydrous atmosphere of a
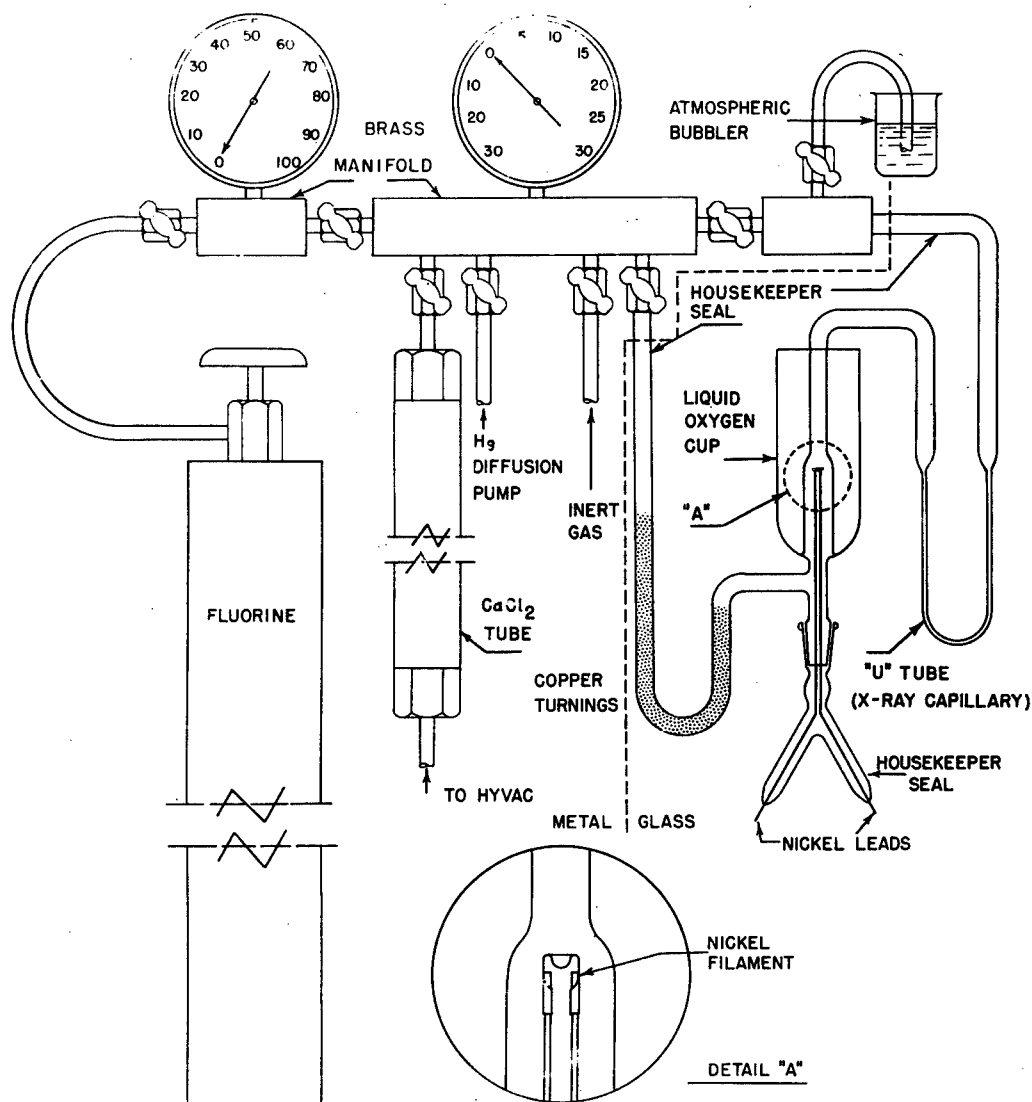
Figure 4. Apparatus for the preparation of neptunium hexafluoride.

"dry box," would result in hydration. Therefore, the preparations were carried out directly in an x-ray capillary. The apparatus used is diagrammed in Figure 5. By manipulation of stopcocks B and C it is possible alternately to admit CCl_4 vapor onto the neptunium compound at the bottom of the capillary and to pump it out along with the volatile reaction products. During the time when the capillary is evacuated, any volatile neptunium chloride formed has an opportunity to sublime up to the cold portion of the capillary. The heating block was wound with resistance wire and the temperature determined by means of a thermocouple.

The reaction and apparatus were tested with a sample of about 50 micrograms of UO_2. The temperature of reaction was 530°C, and the CCl_4 was alternately admitted and pumped off every few minutes. This was continued for about one-half hour. Some dark material was observed to collect in the capillary just outside the hot nickel block. The capillary was sealed off in two parts, one containing the residue and the other the sublimate. Dr. Zachariasen reported that the sublimate was UCl_4 and the residue primarily UO_2. The reaction system is evidently rather inefficient, since only a small fraction of the UO_2 was converted to sublimed UCl_4 (perhaps 1 to 2 micrograms).
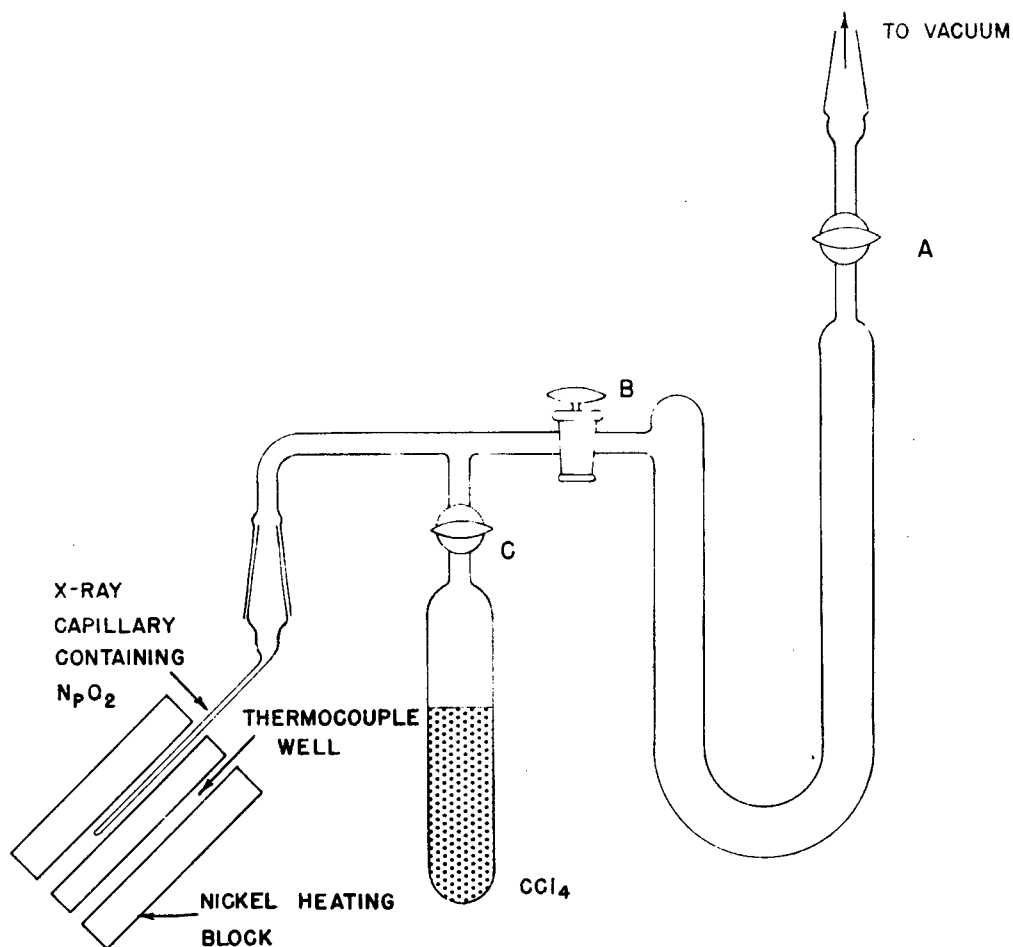
Figure 5. Apparatus for preparing anhydrous chlorides.

Fortunately, the small amount of material synthesized was disposed as a thin layer on the walls of the x-ray capillary in such a position as to be maximally effective in producing diffraction. Hence, an interpretable, although weak, pattern was produced by these few micrograms.

In the experiment with Np, about 20 micrograms of oven-dried (70°) Np(IV) oxalate* were treated in the same manner described above. After a short time, a yellowish sublimate formed in the capillary just above the hot nickel block. The sublimate was only a small portion of the total amount of Np, perhaps 1 to 2 micrograms. The capillary was sealed off in two portions and Dr. Zachariasen reported that the residue was NpO_2 and the sublimate $NpCl_4$, isomorphous with UCl_4 and $ThCl_4$.[11]

In later syntheses, on about the same scale, a larger fraction of the NpO_2 was converted to sublimed $NpCl_4$ by prolonged treatment with CCl_4 vapor at 530°C.

The mode of synthesis and the volatilization of $NpCl_4$ also indicate its close similarity to UCl_4 and suggest similar volatility, melting-point characteristics, etc. A comparison of some of the physical properties of the isomorphous tetrachlorides is shown in Table 1.

---

* The oxalate was precipitated from a solution that was 0.8M HNO_3, 0.1M $H_2C_2O_4$, containing about 1 g Np/liter. The Np was believed to be in the (IV) state, because it was obtained from a Np sulfate solution which was saturated with SO_2 for a period of 12 hours. The Np was precipitated with gaseous NH_3 and redissolved in HNO_3 for the oxalate precipitation. The oxalate precipitated slowly as a crystalline material when an ammonium oxalate solution was added. The observed solubility (assay by Dr. J. C. Hindman) was 200 mg/liter.

Table 1. Comparison of the isomorphous tetrachlorides of thorium, uranium and neptunium.

	Lattice constants (tetragonal)				Temperature °C at which vapor pressure is 10^{-3} mm
	a_1	a_3	Mp °C	ΔH Subl.	
$ThCl_4$	8.473 ± 0.003[12]	7.468 ± 0.003[12]	770°[14]	59,000[14]	473°[14]
UCl_4	8.296 ± 0.009[12]	7.487 ± 0.009[12]	590°[15]	38,600[16]	360°[16]
				47,000[17]	373°[17]
$NpCl_4$	8.25 ± 0.01[13]	7.46 ± 0.01[13]	(?)	(?)	. .

On the basis of the data in Table 1, it seems reasonable to predict that $NpCl_4$ will prove to be somewhat more volatile and lower-melting than is UCl_4.

The reduction of $NpCl_4$ to $NpCl_3$ was carried out directly in the x-ray capillary in which the $NpCl_4$ had been formed. Several micrograms of yellow sublimed $NpCl_4$ were obtained as previously described. The nickel furnace was moved up to surround the $NpCl_4$ and was maintained at 450°C. Hydrogen, purified by passing through hot copper and a liquid air-cooled charcoal trap, was admitted to one atmosphere pressure into the reaction system through the stopcock B (Figure 5). The hydrogen was allowed to react for 10 minutes and was then pumped out to remove the HCl formed as a reaction product. Hydrogen was admitted twice more, with subsequent pumping. Calculations indicated that these three treatments should provide a more than adequate supply of hydrogen to reduce several micrograms of $NpCl_4$ to $NpCl_3$, provided the $NpCl_4$ is no more difficult to reduce to $NpCl_3$ than is UCl_4 to UCl_3.[18] The material in the capillary had diminished in quantity, suggesting that some sublimation of $NpCl_4$ had occurred. Dr. Zachariasen identified the residue as $NpCl_3$, isomorphous with UCl_3 and $PuCl_3$.[19]

The yellow color of the material had disappeared and the solid appeared white but somewhat iridescent. It is possible that $NpCl_3$ may be more highly colored, since observations on such minute quantities of material are unreliable.

In later preparations of this compound the difficulty due to volatilization of the $NpCl_4$ during the treatment with hydrogen was circumvented by treating the oxide with a mixture of hydrogen and carbon tetrachloride at relatively low temperatures (350° to 400°C). When the reaction was completed the $NpCl_3$ was sublimed out at 750 to 800°C. For this reaction it is necessary, of course, to use quartz capillaries.

Table 2 gives the lattice dimensions of the isomorphous hexagonal trichlorides of uranium, neptunium, and plutonium.

4.6. $NpOCl_2$. — This compound resulted when a sample of $NpCl_4$ was heated to 450°C in vacuo in a sealed capillary. Apparently residual oxygen (or water) adsorbed on the walls was present in sufficient quantity to oxidize (or hydrolyze) the $NpCl_4$ to $NpOCl_2$. This compound appeared as clusters of light yellow needles which could be sublimed at 550°C. An x-ray diffraction pattern of this material showed it to be isomorphous with $UOCl_2$. Attempts to reduce this compound to NpOCl with hydrogen at 450° failed, probably because of impurities in the hydrogen (H_2O) and the product was NpO_2.

Table 2. Lattice dimensions.

	a_1	a_3
UCl_3[20]	7.428 ± 0.003	4.312 ± 0.003
$NpCl_3$[21]	7.405 ± 0.010	4.273 ± 0.005
$PuCl_3$[22]	7.384 ± 0.004	4.234 ± 0.004

4.7. Neptunium Tribromide and Neptunium Triiodide.— It has been shown that NpO_2 reacts with $AlCl_3$ at 250° to 500°C to form $NpCl_4$ according to the equation

$$3NpO_2 + 4AlCl_3 \longrightarrow 3NpCl_4 + 2Al_2O_3. \tag{6}$$
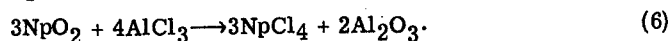
A modification of this method in which neptunium oxide was treated with aluminum metal and the appropriate halogen, resulted in the formation of the corresponding trihalides.[24]

The reaction may probably be represented by the following equation, with the qualification that any excess Al aids in reduction to the trivalent state:

$$6NpO_2 + 8AlX_3 \longrightarrow 6NpX_3 + 4Al_2O_3 + 3X_2. \tag{7}$$
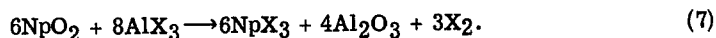
Ninety micrograms of neptunium oxide, prepared by the precipitation of the hydroxide with gaseous ammonia from an acid sulfate solution, was dried at 70°C for 12 hours, so that it formed a small pellet at the bottom of a microcone. A quartz 19/38 joint was drawn into a capillary about 0.1 mm in diameter with a wall thickness of 0.015 mm. The capillary was sealed at the end, and the pellet of NpO_2 was introduced. A small amount of aluminum metal (about 50 micrograms) was added on top of the oxide and the system connected to a vacuum line, where the contents were dried by heating the tip of the capillary to 400°C for 15 minutes in vacuo.

At this point bromine vapor that was free of chlorine and iodine was admitted to the mixture of the oxide and aluminum metal. The aluminum slowly reacted with the bromine at slightly elevated temperatures to form aluminum bromide that condensed as a crystalline solid just beyond the warm zone of the tube. When the lumen of the capillary was almost closed by the slug of $AlBr_3$, the excess bromine was pumped out and the capillary was sealed off so that its length was about 4 inches.

The capillary was then placed inside a heavy-walled glass tube that was sealed at both ends and contained air at atmospheric pressure. This system was inserted in a steel jacket which was heated in a tube furnace to 350° to 400°C for 12 hours. The air inside the heavy-walled tube tended to equalize the strain on the thin-walled quartz capillary as the pressure of the aluminum bromide developed. A sketch of this "micro-bomb tube" is shown in Figure 6.
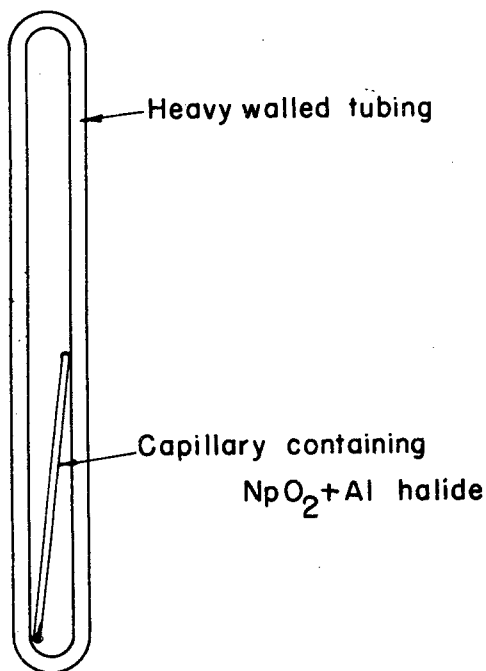

Figure 6. Micro bomb tube.

At the end of the heating period the heavy glass tube was opened and the capillary was found to contain a greenish melt. The excess $AlBr_3$ was separated by heating to 250°C and driving it to the cool end of the capillary, where it condensed. The portion of the capillary containing the $AlBr_3$ was sealed off from the end containing the relatively nonvolatile residue.

On heating the residue to 600°C a silvery material, which was shown by the x-ray method to be aluminum metal, sublimed out. On further heating (to 800°C) a green material distilled, which was shown by the same method to be $NpBr_3$, isomorphous with UBr_3. The composition of the residue not volatile under these conditions has yet been determined.

Neptunium triiodide was prepared in an analogous manner from NpO_2, Al, and iodine.[25]

After removal of the excess AlI_3, the triiodide was sublimed at 800°C. It proved to be a brownish material (probably slightly contaminated with iodine), which was shown by the x-ray method to be isomorphous with PuI_3 and UI_3.

Table 3 gives the lattice dimensions of the isomorphous orthorhombic triiodides of uranium, neptunium. and plutonium.

Table 3. Lattice dimensions.

	a_1	a_2	a_3
UI_3[27]	13.98 ± 0.02	4.33 ± 0.02	9.99 ± 0.02
NpI_3[28]	13.93 ± 0.04	4.31 ± 0.03	9.94 ± 0.05
PuI_3[29]	$13.9 \ \pm 0.1$	4.29 ± 0.04	9.90 ± 0.01

4.8. Neptunium Tetrabromide.— It was found that NpO_2 reacts with $AlBr_3$ in the absence of excess aluminum metal to give $NpBr_4$.[26] Fifty micrograms of neptunium oxide were placed in a thin-walled quartz capillary and dried in vacuo at 400°C for 1 hour. Approximately 250 micrograms of anhydrous $AlBr_3$ were added on top of the oxide* and the system evacuated and sealed off so that the length of the capillary was about 4 inches. The capillary was placed inside a heavy-walled glass tube, as previously described, and heated to 350°C for 12 hours.

At the end of the heating period the capillary was removed from the tube, and excess $AlBr_3$ was removed by sublimation at 250°C, and the portion containing it was sealed off. On heating the remainder of the capillary to 500°C, a reddish brown substance sublimed out, whose x-ray diffraction pattern showed it to be $NpBr_4$, isomorphous with UBr_4. On further heating (to 800°C) a green material ($NpBr_3$) distilled out, and at slightly higher temperatures, a yellow one. The yellow substance has not been identified. The amount of $NpBr_4$ obtained was approximately 20 to 25 per cent of the total volatile material.

A consideration of the results shows that equation 7 does not completely account for the formation of the trivalent neptunium bromide, and that the free aluminum metal that was present in the experiment in which $NpBr_3$ was first produced performed a definite, though accessory, function in the reduction of the tetrabromide to the tribromide.

The apparent partial stability of $NpBr_4$ when sublimed in vacuo at 500°C is somewhat surprising, in view of the calculations made by Brewer et al.[30]

The existence of $NpBr_4$ in the solid state constitutes an additional piece of evidence that neptunium is more like uranium than plutonium and tends to confirm the evidence already deduced from a study of its chemistry in solution.

4.9. Preparation and Properties of Neptunium Metal.— Neptunium metal was prepared by the reaction of Ba vapor with NpF_3 at 1200°C in a beryllia "double-crucible" system.[31]

Because only a limited amount of neptunium was available for this purpose (about 250 micrograms),

---

*This operation was carried out in a dry box.

many practice reductions using UF_4 and PuF_4 as stand-ins were carried out in an attempt to deter-mine conditions favorable for the production of Np metal. The reductions were carried out in beryllia "double-crucible" systems and the conventional tantalum-wound furnaces described for the production of plutonium on the microgram scale.[32]

The inner crucibles were "vitrified" by heating in vacuum at 1500° to 1800°C for an hour, in order to minimize the chances of metal soaking into the crucible. Before making a run the system was thoroughly outgassed at about 1400°C for 1 hour or until the pressure was reduced to 10^{-6} mm Hg.

Attempts to prepare uranium and plutonium metal on the 50-microgram scale by reduction of the tetrafluorides with barium metal at about 1200°C were uniformly successful, but two attempts to prepare neptunium metal from NpF_4 under similar conditions failed completely. When the crucibles were opened they were found to be empty but somewhat alpha-active, suggesting that either the fluoride or metal had soaked into the crucible. These results led to the possibility of two choices: (1) the use of a more volatile reductant, such as magnesium, that would minimize the tendency for the metal or fluoride to soak in by permitting the reaction to take place at a lower temperature, or (2) the use of NpF_3 instead of NpF_4 as the starting material. Neptunium trifluoride would be expected to have a higher melting point than the tetrafluoride and thus would be less likely to soak into the crucible.

Tests of magnesium as a reducing agent for uranium and plutonium fluorides under these con-ditions were not encouraging in that the appearance of metal produced was not as good as that ob-tained in the barium reductions. Therefore it was decided to use NpF_3 as the starting material.

Accordingly the remainder of the NpF_4 (about 150 micrograms) was converted to the trifluoride by the action of HF and H_2 at 500°C, this material was used in the preparation of Np metal after x-ray analysis showed it to be essentially pure NpF_3.

Three runs of about 50 micrograms each were made using barium as a reductant at a maximum temperature of about 1200°C for 1.5 to 2 minutes. Each of these reductions was successful and yielded several pieces of metal weighing from 10 to 40 micrograms. The metal was silvery in color and about as malleable as uranium prepared under the same conditions. The metal is not particularly affected by air during the time intervals necessary for manipulations (one-half hour).

The method used for the determination of the density of neptunium metal was the same as that used earlier on plutonium.[33]

The displacement of a piece of metal weighing 40.32 micrograms was measured to two different capillary pycnometers whose diameters were 0.231 and 0.333 mm. The measured densities were 17.8 g/cc and 17.6 g/cc, respectively.

The x-ray diffraction pattern obtained by Dr. W. H. Zachariasen from some flattened pieces of metal was complex and has not been interpreted.

The observation that the neptunium apparently soaked into the crucible during the attempted reduction of NpF_4, whereas the reductions of UF_4 were successful, suggests that the melting point of NpF_4 is less than the melting point of UF_4 (960°C), and that the NpF_4 melted and soaked into the crucible before the reductant vapor attacked it. By extrapolation the melting point of PuF_4 is ex-pected to be still less. However, since PuF_4 readily decomposes in vacuo to PuF_3,[34] PuF_4 may be prevented from melting and soaking into the crucible during a vapor-phase reduction by the formation of a trifluoride skin around the tetrafluoride.

4.10. The Preparation of Neptunium Hydride.—Neptunium hydride was prepared by the action of H_2 on the metal.[35] The apparatus used was that developed by Baumbach for the preparation of plutonium hydride on the microgram scale.[36]

The metal weighed 20.88 micrograms and did not react with hydrogen when this gas was ad-mitted at a pressure of one atmosphere, but after a few minutes heating to 50°C it rapidly absorbed gas.

Examination of the hydride under the microscope showed that the metal had broken up into a black flaky material very similar in appearance to uranium or plutonium hydride. The volume of H_2 absorbed corresponded to the formula $NpH_{3.6-3.8}$. However, no great accuracy is claimed for this formula.

X-ray diffraction patterns of this compound exhibited lines which could not be assigned to any neptunium hydride, but according to Zachariasen are very probably due to the lower oxide NpO. A small amount of oxygen adsorbed on the walls of the capillary could easily account for appearance of this compound.

4.11. Attempted Preparation of a Higher Chloride of Np.—Since neptunium in aqueous solution forms ions of oxidation number 5 and 6 as well as 3 and 4, it was of interest to attempt the preparation of the higher chloride in the solid state. The experiment described here was an unsuccessful attempt to prepare these higher chlorides of neptunium by the action of chlorine gas on $NpCl_4$ at elevated temperatures. A sketch of the apparatus is given in Figure 7.

The chlorine used in this and the following experiments was tank chlorine that was passed through an H_2SO_4-bead tower, condensed in liquid N_2, distilled into a $-120°C$ bath (solid ethyl bromide) with pumping to remove O_2, and finally distilled into the receiver.

It was decided to test this apparatus by using UO_2 as a stand-in. Accordingly a small quantity of UO_2 was placed in the x-ray capillary and the system evacuated. Carbon tetrachloride vapor was admitted onto the heated UO_2 and then pumped off. It was found that the optimum temperature range for the formation of UCl_4 in this apparatus was 510° to 530°C. After sufficient UCl_4 was formed, the furnace was moved up so that the UCl_4 could be heated. The stopcocks were manipulated so that
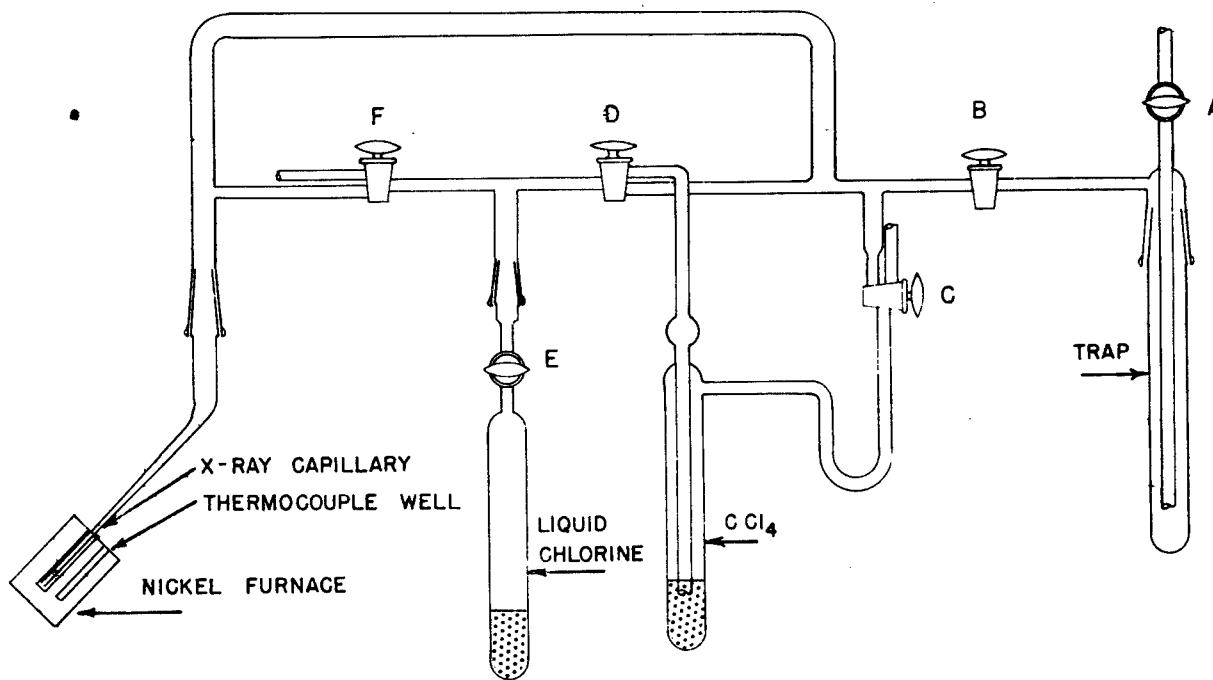

Figure 7. Apparatus for the preparation of higher chlorides.

the CCl_4 was saturated with chlorine gas and this mixture passed over the UCl_4 heated to 390° to 400°C. It was observed that a red zone formed in the cool portion of the capillary, and beyond that, a black zone. When sufficient material had been collected the reaction was stopped and the capillary sealed off. Figure 8 shows the appearance of the capillary.

The zones of condensation were about 1 mm wide and were separated from each other by about 0.5 mm. The boundaries were quite sharp and it was possible to obtain x-ray diffraction patterns of the individual zones. The zone nearest the hot portion of the tube consisted of UCl_4. The red zone was UCl_5, and the black zone, which had condensed in the coolest portion of the tube, was UCl_6.[37]

When this experiment was repeated with $NpCl_4$, the vaporized material failed to condense in distinct zones. Examination of the condensed material under the microscope showed it to consist of transparent yellow bipyramids. In thicker layers or in reflected light the crystals appeared reddish. A study of the x-ray diffraction pattern showed that this substance was $NpCl_4$.

4.12. Preparation and Properties of NpOS and Np_2S_3.[38] — The reaction of H_2S on ThO_2 or UO_2 at 1000°C gives rise to ThOS or UOS, according to results obtained at the Berkeley project,[39] and it

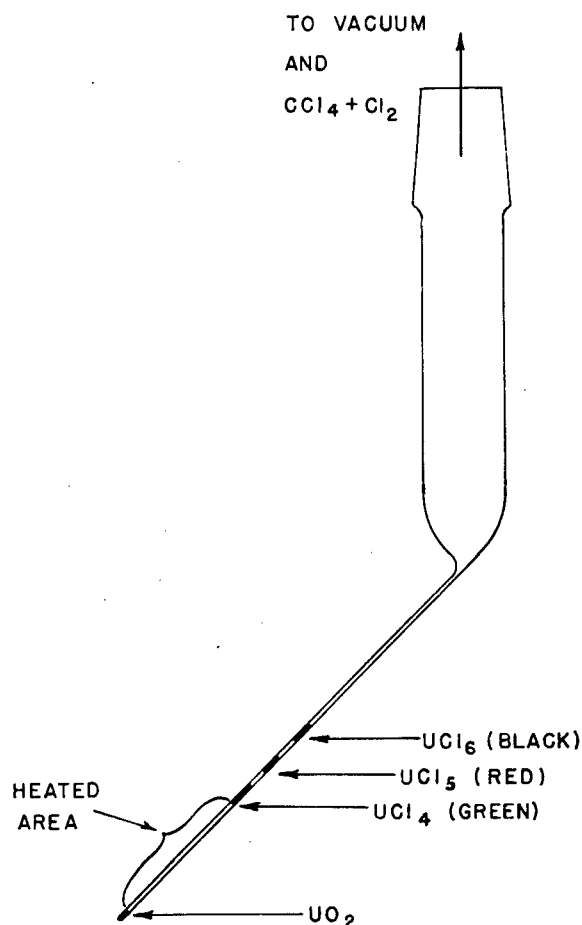Figure 8. Appearance of capillary used to test apparatus for the preparation of higher chlorides.

was of interest to attempt a similar reaction with NpO_2. The results obtained at Berkeley indicate that an H_2S-CS_2 mixture is a more potent "sulfiding" agent at high temperature than is H_2S by itself. Accordingly, our experiments were carried out with the gas mixture obtained by bubbling H_2S through CS_2 at 30°C. The H_2S was dried by passage over P_2O_5 before entering the CS_2 bubbler.

A quartz microcone containing about 50 micrograms of Np as Np(IV) hydroxide was placed in a quartz tube and treated with the H_2S-CS_2 stream for two hours at 1000°C. The black brittle reaction product was crushed and submitted for x-ray analysis. Dr. Zachariasen identified it as NpOS.[40]

The NpOS was combined with some NpO_2 obtained by the ignition of an NpF_4 sample in air. The mixture was maintained in the H_2S-CS_2 stream at 1000° for about 12 hours. The product was still a black brittle material. Dr. Zachariasen reported that this substance gave only a weak x-ray diffraction pattern, but he finally succeeded in showing that it was Np_2S_3, isomorphous with U_2S_3 and Th_2S_3.[41]

The chemistry of the neptunium-sulphur system seems to be intermediate in a rather interesting way between that of the uranium sulfides and that of the plutonium sulfides.[42]

The oxysulfide of neptunium is NpOS like UOS but differs from Pu_2O_2S. In the fully sulfided product, however, the oxidation number of the neptunium is reduced to 3. When U_3O_8 is converted to a sulfide by H_2S at 1300° to 1400°C in a graphite system, the product is US_2, with some decomposition to U_2S_3. The U_2S_3 reverts to US_2 as the reaction product is cooled in H_2S.[43]

In such a reaction PuO_2 is converted to Pu_2S_3.[44] While Pu_2S_3 is presumably like Co_2S_3, which is a "normal-valent" sulfide that does not show metallic conductivity, U_2S_3 is a "reduced" sulfide showing semimetallic conductivity, and US_2 is a "normal-valent" sulfide.

Since Np_2S_3 was prepared under conditions such that, in general, "normal" rather than "reduced" sulfides are obtained, it is presumably a "normal-valent" sulfide. However, its crystal structure is isomorphous with that of the "reduced" sulfide U_2S_3 rather than that of the "normal" sulfide Pu_2S_3.

It would be of great interest to synthesize a neptunium sulfide at 1400°C in a graphite system and determine if Np_2S_3 with the Pu_2S_3 structure would be obtained. It would also be of interest to treat Np_2S_3 with sulfur, at a relatively low temperature, in an attempt to prepare NpS_2.

4.13. Attempted Preparation of a Higher Oxide of Np. — On the basis of the similarity of Np to U, it was decided to attempt the preparation of a crystalline higher oxide (higher than NpO_2) of this element by ignition of a neptunium salt in a high pressure of oxygen. The apparatus used in this experiment is diagrammed in Figure 9. The inside diameter of the heavy-walled bomb tubing was 4 mm, and the inside diameter of the capillary was 1 mm. The neptunium salt was contained in the cone. The tube was connected by means of a stopcock to a vacuum line filled with tank oxygen, and oxygen was condensed in the small capillary by means of a liquid nitrogen bath. The amount condensed was measured as a length in the capillary and was chosen to give a pressure of 28 atmospheres at 400°C after sealing off at the proper point. These capillary bombs were annealed in an oven before use and if carefully sealed off were found to withstand about 30-atmospheres pressure. They were enclosed in steel jackets when heated in a tube furnace. The application of this apparatus to a synthesis of UO_3 from U_3O_8 is described in a separate report.[45]

The neptunium as Np(VI) in HCl was evaporated to dryness at 70°C, taken up in 6M HNO_3, and evaporated to dryness again. From previous observations by L. B. Magnusson, it was probably Np(IV) nitrate at this stage. The cone was placed in the bomb, which was filled with O_2 to give a pressure of 28 atmospheres at 400°C, and the system sealed off. When heated to 400°C the bomb burst at the top "seal-off." The sample was intact and was placed in another bomb, where it was maintained at 350°C for 5 hours, 250°C for 12 hours, and 125°C for 4 hours. Dr. Zachariasen reported that the sample gave the diffraction pattern of NpO_2 and a few other weak unidentifiable lines.

The conditions used in the attempted formation of a crystalline-neptunium higher oxide were
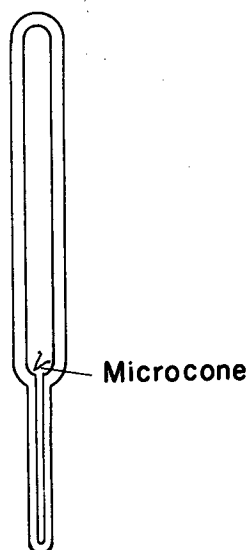
Figure 9. Oxygen bomb tube.

unfavorable in that (1) it would have been better to start with a Np(VI) nitrate, and (2) at 400°C any higher oxide of neptunium might have irreversibly decomposed to NpO_2, especially if the tube burst and the pressure was released, even though at a lower temperature at the high pressure the higher oxide was stable.

4.14. Survey of the Dry Chemistry of U, Np, and Pu.—The elements uranium, neptunium, and plutonium exhibit the oxidation numbers 3, 4, 5, and 6 in aqueous solution and among "dry" compounds. They therefore form an interesting series in which to observe the relationship between the stability of the different oxidation states in solution and in dry compounds.

The higher oxidation states in aqueous solution are stabilized by solvation and complex formation. Among the pure compounds (solid or gaseous) the small positively-charged ions of the various oxidation states must be stabilized by coordination to the anions of electronegative atoms (F^-, $O^=$, Cl^-, Br^-, I^-, $S^=$, etc). The small and difficultly polarizable anions $O^=$ and F^-, in general form compounds of higher oxidation number than do the more readily polarizable anions Cl^-, Br^-, $S^=$, I^-. It is interesting to observe that in general it is easier to obtain the higher oxidation states of the elements under discussion in solution than among dry compounds. Thus, the free energies of solution of UO_3, UF_6, and UCl_6 are more negative than the free energies of solution of UO_2, UF_4, and UCl_4. Similarly, Pu(III) may be oxidized to Pu(IV) in aqueous solutions by Cl_2 or Br_2, but evidently anhydrous $PuCl_4$ or $PuBr_4$ do not exist.

Table 4 lists a comparison of the potentials between the various oxidation states in hydrochloric acid solution. In Table 5 an attempt has been made to summarize the available information as to the existence and stability of compounds of U, Np, and Pu of various oxidation states. Guesses as to the possibility of existence of certain compounds of Np and Pu are indicated by enclosing the compound in brackets. The reasoning underlying these guesses is generally rather obvious when account is taken of the principles stated above and the trends apparent in the two tables.

Table 4. Formal potentials of couples in aqueous solution
of U, Np, and Pu.

Couple	Uranium	Neptunium	Plutonium
III, IV	0.63[46]	-0.14[47]	-0.95[48]
IV, V	-0.6 ?	-0.7[49]	-1.10[50]
IV, VI	-0.54[51]	-0.9[52]	-1.05[53]

Table 5. Survey of the "dry" chemistry of U, Np, and Pu.[*]

Coordinating Anion	Uranium	Neptunium	Plutonium
$O^=$	UO_3 decomposed to U_3O_8 on ignition above 700°C		
	Uranyl salts, uranates. U_3O_8: a mixture of U(IV) and U(VI)[54]	Neptunyl salts. $NaNpO_2 Ac_3$, ($CaNpO_4$? ?)	Plutonyl salts $NaPuO_2 Ac_3$ ($CaPuO_4$)
	UO_2: by H_2 on U_3O_8, not by thermal decomposition	Only NpO_2 and PuO_2 obtained by ignition of Np, Pu salts in high pressure O_2 or air, resp.[55,56]	
	No U_2O_3	(Np_2O_3 ? ? : probably not in view of the difficulty in reducing PuO_2 to Pu_2O_3)	Pu_2O_3: by C or Ba reduction of PuO_2, not by H_2 at 1000°C (6)[57]
F^-	UF_6: very stable relative to decomposition into UF_4 or $UF_5 + F_2$	NpF_6	PuF_6: experiments indicate that it probably exists, but quite unstable[58]
	UF_5: U(IV) U(VI)? exists only in solid state	(NpF_5: very probable)	PuF_5 ?
	UF_4: reduced by H_2 (1000°C) to	NpF_4: reduced by H_2 in presence of HF to	PuF_4: very readily reduced by H_2 or apparently thermally decomposes to[60]
	UF_3[59]	NpF_3	PuF_3

Table 5. (Continued).

Coordinating Anion	Uranium	Neptunium	Plutonium
Cl^-	UCl_6, UCl_5: readily decomposes thermally to	($NpCl_5$: not formed when $NpCl_4$ sublimed in Cl_2)	
	UCl_4: reduced by H_2 to	$NpCl_4$: reduced by H_2 to	Evidently no solid $PuCl_4$: may exist in gas phase in presence of Cl_2[61]
Br^-	No UBr_5: UBr_4: reduced by H_2 to	$NpBr_4$: by reduction with Al and also, probably by thermal decomposition, yields $NpBr_3$[62]	
	UBr_3		$PuBr_3$
I^-	UI_4: some tendency to decompose thermally to	(NpI_4 ? : probably not)	
	UI_3[63]	NpI_3	PuI_3
Oxyhalides	UO_2Cl_2, $UOCl_2$, etc; attempts to make UOCl in this laboratory unsuccessful.[64]	$NpOCl_2$	($PuOCl_2$?)
		($NpOCl$, $NpOBr$, $NpOI$?)	$PuOCl$, $PuOBr$, $PuOI$
$S^=$	US_2: U_2S_3 is conducting and may contain U(IV) and free electrons. US_2 is said to be unstable in presence of H_2 + CS at 1400° C, decomposing to U_2S_3.[65]	NpS_2 ?? Np_2S_3 Np_2O_2 S??	Pu_2S_3
	UOS	NpOS	Pu_2O_2S

* The authors have attempted to judge which of the facts in Table 5 are sufficiently well known and described in summary references not to require detailed documentation.

BIBLIOGRAPHY

1. Magnusson, L. B. and T. J. LaChapelle, CN-2159, Sept. 1944, p 16; CN-1764 (A-2471), July 1944, p 9.

2. Zachariasen, W. H., MUC-FWHZ-31, June 22, 1944, p 1.

3. Zachariasen, W. H., MUC-FWHZ-54, Aug. 29, 1944, p 1.

4. Fried, S. and N. R. Davidson, CN-2689, Feb. 1945, p 1.

5. Zachariasen, W. H., MUC-FWHZ-94, Dec. 29, 1944, p 1; CN-2610, Dec. 1944, p 4.

6. Zachariasen, W. H., MUC-FWHZ-95, Jan. 2, 1945, p 1; CN-2610, Dec. 1944, p 5.

7. Fried, S., CN-3053, July 1945, p 6.

8. Florin, A. E., MUC-GTS-2165, Jan. 23, 1946, p 1.

9. Zachariasen, W. H., MUC-FWHZ-166, Jan. 22, 1946, p 1.

10. Fried, S. and N. R. Davidson, CN-2689, Feb. 1945, p 2.

11. Zachariasen, W. H., MUC-FWHZ-101, Jan. 18, 1945, p 1.

12. Zachariasen, W. H., CC-2768, Mar. 1945, p 6.

13. Zachariasen, W. H., MUC-FWHZ-101, Jan. 18, 1945, p 1.

14. Fisher, et al, Zeits. Anorg. Allgem. Chem. 242:161 (1939).

15. Butler, T. and A. Newton, CC-1500 (A-2083), May 1944, p 7.

16. Schelberg, A. and R. W. Thompson, A-809, p 5.

17. Mueller, M., RL-4.6.257, May 1944, p 24.

18. Macwood, G. E. and D. Altman, RL-4.7.600, p A-4.

19. Zachariasen, W. H., MUC-FWHZ-102, Jan. 25, 1945, p 1.

20. Zachariasen, W. H., CC-2768, Mar. 1945, p 6.

21. Zachariasen, W. H., MUC-FWHZ-102, Jan. 25, 1945, p 1.

22. Zachariasen, W. H., CK-1367, Feb. 1944, p 12.

23. Fried, S., MUC-FWHZ-152, Oct. 12, 1945, p 1.

24. Fried, S., MUC-FWHZ-162, Dec. 7, 1945, p 1.

25. Ibid.

26. Fried, S., CN-3381, Dec. 1945, p 21.

27. Zachariasen, W. H., CC-2768, Mar. 1945, p 7.

28. Zachariasen, W. H., MUC-FWHZ-163, Dec. 10, 1945, p 1.

29. Zachariasen, W. H., MUC-FWHZ-39, July 1944, p 2.

30. Brewer, L., L. Bromley, P. Gilles, and N. Lofgren, CN-3306, Oct. 1945, p 3.

31. Fried, S., CN-3053, June 1945, p 6.

32. Westrum, E. F., Jr., CK-1586 (A-2251), May 1944, p 20; CN-2495, Jan. 1945, p 12.

33. Kirk, P. L., R. S. Rosenfels, S. Fried, and H. L. Baumbach, CK-1145 (A-1631), Dec. 1943, p 15.

34. Fried, S. and N. R. Davidson, CN-2159, Oct. 1944, p 5; CN-2495, Jan. 1945, p 1.

35. Fried, S., CN-3053, June 1945, p 7.

36. Baumbach, H. L. and S. Fried, CK-1145 (A-1631), Dec. 1943, p 17.

37. Zachariasen, W. H., MUC-FWHZ-113, Feb. 28, 1945, p 1.

38. Fried, S. and N. R. Davidson, CN-2689, p 6; CN-3053, July 1945, p 8.

39. Lofgren, N., CK-941, p 7.

40. Zachariasen, W. H., MUC-FWHZ-98, Jan. 5, 1945, p 1; CN-2610, Dec. 1944, p 1.

41. Zachariasen, W. H., MUC-FWHZ-129, Apr. 14, 1945, p 1.

42. Fried, S. and N. R. Davidson, CN-3053, July 1945, p 8.

43. Brewer, L., L. A. Bromley, P. W. Gilles, and N. Lofgren, CT-2290, Nov. 1944, p 3.

44. Davidson, N. R., CN-2431, Dec. 1944, p 2.

45. Fried, S. and N. R. Davidson, CN-3053, July 1945, p 9.

46. Howland, J. J. and L. B. Magnusson, CN-2888, Apr. 1945, p 21.

47. Magnusson, L. B., T. J. LaChapelle, and J. C. Hindman, CN-3053, July 1945, p 27.

48. Hindman, J. C., CN-2289, Nov. 1944, p 6.

49. Magnusson, L. B., J. C. Hindman, and T. J. LaChapelle, CN-2767, Mar. 1945, p 22.

50. Connick, R. E., W. H. McVey, and G. E. Sheline, CN-1912 (A-2800), July 1944, p 12.

51. Howland, J. J., CN-2495, Jan. 1945, p 31.

52. Magnusson, L. B., J. C. Hindman, and T. J. LaChapelle, CN-2767, Mar. 1945, p 22.

53. Hindman, J. C., CN-2289, Nov. 1944, p 1.

54. Zachariasen, W. H., CK-2267, Jan. 1945, p 11.

55. This paper, p 26.

56. Moulton, G. H., LA-172, Nov. 1944, p 2.

57. Westrum, E. F., Jr., CN-2159, Oct. 1944, p 2.

58. Florin, A. E., CN-2159, Oct. 1944, p 5.

59. Spencer-Palmer, H. J., British Report (422) (CT), p 10.

60. Fried, S., CN-2159, Oct. 1944, p 5; S. Fried, and N. R. Davidson, CN-2495, Jan. 1945, p 1.

61. Davidson, N. R., CN-3001, May 1945, p 4.

62. Fried, S., CN-3381, Dec. 1945, p 21.

63. Macwood, G. E. and D. Altman, RL-4.7.600, p A-7.

64. Abraham, E. H., private communication.

65. Brewer, L., L. A. Bromley, P. W. Gilles, and N. Lofgren, CT-2290, Nov. 1944, p 3.

END OF DOCUMENT