pressure. Thus p_1/p represents the mole fraction of the monomer and $k_{1j}p_1{}^j/p$ the mole fraction of the polymers. The total pressure, p, is given by

$$p = p_1 + \sum_{j=2}^{\infty} k_{1j}p_1{}^j \qquad (15)$$

Since z represents the ratio of the number of molecules that exist as a monomer to the number of molecules in the actual gas, we can write

$$z = \frac{p_1}{p} + \sum_{j=2}^{\infty} \frac{jk_{1j}p_1{}^j}{p} \qquad (16)$$

Substituting equations (13), (15) and (16) into equation (14), we get for the entropy of polymerization, ΔS_p which is equal to $S_{HF} - S$

$$12.80 + \frac{1}{z}(57.60) - \frac{1}{z}(70.40)\frac{p_1}{p} +$$

$$\frac{R}{z}\frac{p_1}{p}\ln\frac{p_1}{p} + \frac{R}{z}\sum_{j=2}^{\infty}\frac{k_{1j}p_1{}^j}{p} \times \ln\frac{k_{1j}p_1{}^j}{p} \qquad (17)$$

Since

$$k_{1j} = \prod_{n=1}^{j} k_{n,n+1} \qquad (18)$$

and $k_{n,n+1}$ for $n > 1$ all have the same value; substituting (11) and (12) into the above equation we obtain

$$k_{1j} = 10^{-0.45673}(10^{0.21197})^j \qquad (19)$$

Substituting equation (19) into (15) and summing

$$p = p_1 + \frac{(0.90)p_1{}^2}{(1 - 1.659\,p_1)}$$

For a pressure, p, of 741.4 mm., this leads to a value of $p_1 = 0.428$ atm. Finally, substituting values of p_1, p, k_{1j} and z into equation (17), one obtains $\Delta S_p = 20.2 \pm 2$ e.u. Adding this to the calorimetric data, S^0_{HF} at 741.4 mm. and 292.61°K. becomes 44.10 ± 2 e.u., or S^0_{HF} at 760 mm. and 298.16°K. becomes 44.11 ± 2 e.u. This large

uncertainty arises from errors in computing the equilibrium constants. Nevertheless the value leads to a reasonable agreement between the entropy determined calorimetrically and that from spectroscopic calculations, indicating that this model is probably correct. It should be mentioned that using the data of Breigleb, closer agreement can be attained; however, this is still within the estimated uncertainty.

This model is further substantiated by measurement by Oriani and Smyth[14] of the dielectric constant of the gas which shows that its dipole moment increases with pressure, this being impossible if the polymer exists solely in the ring form. The electron diffraction pattern[16] also indicates that the polymer forms a zigzag chain.

(c) **Zero Point Entropy.**—Finally, it is evident that the residual zero point entropy due to the hydrogen bonding cannot be evaluated from the data, due to the large uncertainty of the entropy of polymerization. There is, however, evidence that the fluorine molecule is located centrally between the hydrogen atoms.[17,18] In view of the fact that the values of the entropy from calorimetric data and from the polymerization calculation are higher than the spectroscopic value, even within the uncertainty limits, this is in agreement with our calculations.

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New Neptunium Compounds

BY IRVING SHEFT AND SHERMAN FRIED

This paper reports the preparation and identification of several new compounds of neptunium. In each case the identity of the compound was established from an analysis of the X-ray diffraction pattern by Prof. W. H. Zachariasen of the Physics Department of the University of Chicago.

Neptunium Carbides.—Neptunium dicarbide, NpC_2, was prepared by the action of carbon on neptunium oxide at high temperature.

A few milligrams of neptunium oxide, prepared by precipitation of the hydroxide from solution with subsequent ignition at 500° was placed in the graphite crucible shown in Fig. 1. The apparatus was flushed with hydrogen for half an hour and the crucible heated to 2660–2800° for five minutes using a high frequency generator. The temperature was determined by means of an optical pyrometer. The product formed was a metallic appearing film which was chipped out of the graphite crucible, freed from adhering fragments of graphite and submitted for X-ray analysis. It proved to be neptunium dicarbide, NpC_2, isomorphous with the corresponding uranium compound.

The conditions under which neptunium dioxide can be converted to a recoverable product seem to be fairly critical. At temperatures below 2500° no reaction seems to take place while at temperatures much above 2800° the product seems either to fuse and "soak" into the pores of the crucible or to volatilize away.

Another method of preparing neptunium carbides yielded lower valent compounds. In this case the fluoride of neptunium was treated with lithium vapor at a high temperature in a graphite crucible.

About 100 micrograms of neptunium trifluoride was placed inside a small graphite crucible which in turn was placed inside an outer crucible of thoria. A small piece of lithium metal was added and the system capped with a thoria plug.

The system was outgassed and heated to 1200° by means of a tantalum-wound resistance furnace. At this temperature the lithium vaporized and reacted with the neptunium trifluoride; the excess passed through the porous thoria crucible and condensed as a dark mirror on the surface of the furnace bulb.

After cooling, the crucible was removed from the vacuum system, the contents of the inner graphite crucible removed and mounted in an X-ray capillary and the sample submitted for X-ray analysis. The product was identified as a mixture of neptunium sesquicarbide, Np_2C_3, and neptunium carbide, NpC, in the proportion of 5 to 1, respectively.

Neptunium Silicide.—A 2-mg. sample of neptunium was precipitated as the hydroxide by addition of ammonium hydroxide to a solution of neptunium(V) in nitric acid. The hydroxide was centrifuged and washed and finally dried in an oven at 70°. The resulting pellet of dried hydroxide was converted to the trifluoride.[1] The neptunium trifluoride with about twice its volume of silicon chips was loaded into the inner crucible of an outgassed beryllia "double crucible system."[2] The inner crucible was placed inside another crucible which was capped, placed in a furnace and evacuated. The reactants were heated at 1500° for five minutes. The reaction probably is

$$4NpF_3 + 11Si \longrightarrow 4NpSi_2 + 3SiF_4$$
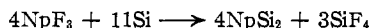
The product, a hard metallic appearing material, was shown by X-ray diffraction to be neptunium disilicide, $NpSi_2$, isomorphous with the corresponding thorium and uranium compounds.

A sample of this material was transferred to a micro centrifuge cone containing 25 microliters of water. There seemed to be no evidence of reaction. On addition of 25 microliters of concentrated hydrochloric acid, a violent reaction accompanied by a crackling noise took place. This is very likely similar to the general reactions of silicides in the formation of silanes.

Neptunium Nitride.—Neptunium nitride, NpN, was the product of the reaction of ammonia vapor and neptunium hydride, presumably according to the equation

$$NpH_3 + NH_3 \longrightarrow NpN + 3H_2$$
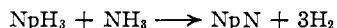
A 1-mg. sample of neptunium metal, prepared by reduction of the trifluoride, was placed in a quartz X-ray capillary and evacuated. Hydrogen, purified by passage over uranium metal heated to 850°, was allowed to react with the neptunium metal at temperatures of 100–150°. The product was a black powder. Ammonia gas, derived from liquid ammonia dried over sodium, was admitted onto the hydride which was then heated to 750–775°. The ammonia gas was evacuated and replaced several times during the heating. No change in appearance of the hydride was observed during this treatment. The product was sealed off *in vacuo* in the original quartz X-ray capillary and was characterized by its X-ray diffraction pattern as NpN, isomorphous with UN and PuN.

Addition of water had no effect on the neptunium nitride. Addition of hydrochloric acid to the solution resulted in the evolution of bubbles of gas. Addition of nitric acid seemed to increase the rate of solution, but the nitride did not completely dissolve. The residue was returned for X-ray analysis but no picture was obtained.

An attempt to prepare neptunium nitride by action of ammonia on neptunium tetrachloride was not successful but instead gave rise to neptunium trichloride, presumably by the reaction

$$6NpCl_4 + 2NH_3 \rightarrow 6NpCl_3 + 6HCl + N_2$$
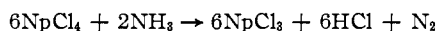
(1) S. Fried and N. Davidson, THIS JOURNAL, **70**, 3540 (1948).
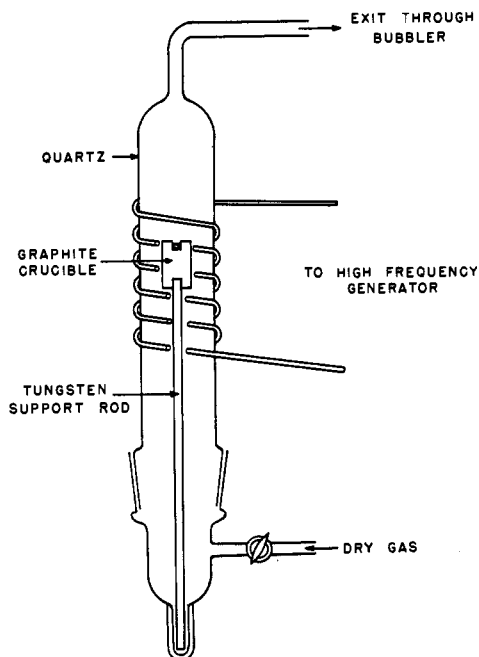(2) S. Fried and N. Davidson, *ibid.*, **70**, 3543 (1948).

Fig. 1.

Neptunium tetrachloride was prepared by action of carbon tetrachloride on a 1-mg. sample of neptunium dioxide in a quartz X-ray capillary and sublimed onto the walls of the capillary. Ammonia gas was allowed to react as above but at 350–400°. The material became green, indicating reduction to neptunium trichloride. In another experiment the neptunium tetrachloride and ammonia were heated to 1000°. The resulting material appeared black and flaked loose from the capillary walls. In both cases the products were identified by their X-ray diffraction patterns as neptunium trichloride. This appears to be a good method for the preparation of larger amounts of neptunium trichloride than have heretofore been possible. It seems likely, however, that further action of ammonia on neptunium trichloride would result in the formation of neptunium nitride since this reaction occurs with uranium tetrachloride.

Neptunium Phosphide.—A 1-mg. sample of neptunium metal was placed in a quartz X-ray capillary with an excess of red phosphorus. After being evacuated and sealed, the capillary was placed in a heavy-walled quartz tube for protection and heated to 750° for 16 hours. The excess phosphorus was removed by sublimation *in vacuo* at 800°. Although the pattern was weak, the product was identified as neptunium phosphide, Np_3P_4, isomorphous with Th_3P_4.

Neptunium. phosphide was unaffected by water. A vigorous reaction occurred with 6 N HCl; gas was liberated and the solution turned dark green. The reaction is probably

$$Np_3P_4 + 12HCl \longrightarrow 3NpCl_4 + 4PH_3$$
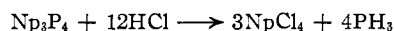
Other Compounds.—Attempts to prepare interstitial compounds of neptunium with selenium and tellurium were not successful. Techniques similar to those of the phosphide preparation were used. In both cases the product was neptunium dioxide.

An attempt to prepare a neptunium boride from a neptunium trifluoride and boron in the apparatus used to prepare the silicide was apparently unsuccessful. The X-ray diffraction pattern showed the product to be mainly NpO_2.

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