

The Preparation and Properties of Some Plutonium Compounds.
Part II. Plutonium Nitride.*

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Plutonium nitride has been prepared by two methods: by heating the metal in nitrogen to a high temperature and by heating plutonium hydride in nitrogen to a temperature above 230°. In each case the product was the same, PuN. Unlike the mixture of refractory uranium nitrides obtained under similar conditions, plutonium nitride is quite reactive and very easily decomposed. Complete hydrolysis occurred within a few hours at 80–90° in moist air or within a few days at room temperature. The use of a thermobalance has provided data on the formation and oxidation of the nitride.

IN 1944, Westrum (cf. Abraham, Davidson, and Westrum, jun., "The Transuranium Elements," McGraw-Hill Book Co. Inc., 1949, N.N.E.S., Vol. 14B, paper 6.60) attempted a preparation of plutonium nitride by the action of gaseous ammonia at 250 mm. on plutonium metal at 1000°. This produced a brown coating on the metal which according to Zachariassen's X-ray diffraction analysis (*op. cit.*, paper 20.2; Report A.N.L. 4552, Dec. 8th, 1950, p. 15) consisted of 40% of PuO₂, 35% of PuN, and 25% of unidentified matter. Abraham (*op. cit.*) then heated plutonium trichloride in gaseous ammonia at 900° and obtained a mixture of PuO₂ 50%, PuN 35%, and PuOCl 15%. Finally, Westrum (*op. cit.*) overcame the difficulty of oxide formation by heating plutonium hydride in gaseous ammonia at 650°/250 mm., obtaining a product which was identified by Zachariassen as a single phase, PuN. It was brown with a face-centred cubic sodium chloride structure. No other information on the chemistry of plutonium nitride has been found in the literature or in available classified reports.

We proposed first to study the plutonium–nitrogen system briefly and then to obtain a pure sample of nitride, probably by some other means, for the examination of its properties.

A thermobalance built for use with radioactive materials proved very useful in this work. It was found that plutonium metal reacted with nitrogen to a slight extent at temperatures above about 250°, but that the reaction was only a surface one and even prolonged heating of milligram amounts at 800–1000° did not cause complete conversion into nitride.

* Part I, *J.*, 1955, 3932.

In associated work (*J.*, 1955, 3932) we had found that plutonium metal reacted rapidly with hydrogen at 200°. This finely divided hydride proved to be a much more convenient starting point; at 230° it reacted with nitrogen, forming a practically pure nitride.

The pure nitride was black but became light brown after a few days owing to hydrolysis. (Westrum *et al.* reported a brown nitride prepared from plutonium hydride and ammonia.) It was dense and hard, like the metal, and brittle. It was attacked by mineral acids, both dissolution and oxidation to an insoluble hydrated oxide occurring; the nitrogen was converted quantitatively into ammonium salts. The most notable property was its ease of hydrolysis by heat and moist air. In contrast, uranium under the same conditions of preparation forms a mixture of U_2N_3 and UN_2 which is extremely stable and resistant to hydrolysis (Katz and Rabinowitch, "Chemistry of Uranium," McGraw-Hill Book Co. Inc., 1949, N.N.E.S., Vol. V; Rundle, Baenziger, Newton, Deane, Butler, Johns, Tucker, and Figard, Report A.E.C.D. 2247). The nitride UN, which is obtained only by heating the other nitrides to 1300°, is similarly resistant to attack.

X-Ray diffraction photographs of PuN showed a face-centred cubic system, isomorphous with PuO and identical with that reported by Zachariasen. A faint line due to PuO_2 was detected and was probably due to slight decomposition whilst the nitride was subjected to X-rays for several hours. The formula PuN was confirmed by (a) the weight of nitrogen absorbed by plutonium hydride, and (b) the increase in weight on oxidation of plutonium nitride and ignition of the product to plutonium dioxide.

EXPERIMENTAL

Apparatus.—The apparatus for heating plutonium metal in either hydrogen or nitrogen was very similar to the system described in the related paper reporting the preparation of plutonium hydride (Part I, *loc. cit.*). Inside the glove-box and immediately before the reaction tube was another, smaller tube, also surrounded by a furnace and containing uranium nitride at 600°, for purifying the nitrogen (Newton, U.S.P. 2,487,360/1945). The uranium nitride was made *in situ* by passing nitrogen through the tube packed with cleaned uranium turnings and asbestos wool heated to 800° (Newton and Johnson, U.S.P. 2,544,277/1945). Hydrogen was allowed to by-pass the uranium furnace before entering the reaction tube. As before, precautions were taken to keep an inert atmosphere inside the box when using hydrogen.

The thermobalance was a silica spring type, similar to that constructed at Harwell by Dawson (*J.*, 1954, 558). It was built partly in a glove-box with an inlet tube at the top for applying vacuum or passing in gases. The sensitivity of the balance was 0.909 mm./mg. for any load up to 50 mg. The overall precision ($3 \times$ standard deviation) of the weighings was ± 0.15 mm. *i.e.*, ± 0.17 mg.

Nitrogen for use in the balance was obtained as follows: The gas from a "White Spot" grade cylinder was analysed and found to contain 60 p.p.m. of oxygen. It was purified by adding 120 p.p.m. of hydrogen, and passing the mixture through a "Deoxo" gas purifier (Baker Platinum Ltd.) and then through a sulphuric acid bubbler to remove the water produced. The hydrogen was added by passing the nitrogen through the cathode compartment of a small glass electrolytic cell which was generating hydrogen at a known rate, proportional to the current. The flow rate of the nitrogen (400 ml./min.) was measured with a rotameter, and the current was adjusted accordingly to 6.3 mA, sufficient to generate 120 p.p.m. of hydrogen in the nitrogen. The purified nitrogen was passed into the evacuated balance until atmospheric pressure was reached. To ensure complete freedom from oxygen, the filling process was always repeated twice.

Method of Preparation.—(a) *From plutonium metal.* As in the preparation of plutonium hydride, the surface condition of the metal appeared to affect its rate of reaction considerably. All the following work was carried out with fresh samples of plutonium.

The first experiments were designed to find whether plutonium would react with nitrogen. A 20–50-mg. piece was weighed in a silica boat and placed in the combustion tube in a rapid stream of purified nitrogen. When all the air was displaced, the furnace was moved over the sample to heat it to a measured temperature for a fixed length of time. The sample was then allowed to cool in nitrogen before being removed to measure any increase in weight.

From Table I, showing the results for ten samples of metal, it may be seen that a reaction does occur but is quite slow and incomplete even at 1000°. For 100% conversion into nitride

(PuN; cf. Zachariasen, *loc. cit.*), the increase in weight would be 5.86%. By using this figure and assuming that no other reaction took place, the percentage conversions into nitride were calculated from the increases in weight. Apart from a few inconsistencies due to varying relative surface areas and degree of tarnishing of the metal sample, it appeared that a

TABLE 1. *Summary of results obtained on heating plutonium metal in nitrogen in a combustion tube.*

Temp.	Time of heating (hr.)	Wt. of Pu sample (mg.)	Increase in wt. (mg.)	Calc. % of PuN	N, determined by analysis (mg.)
625°	16	35.0	0.06	3	0.07
800	4	21.7	0.05	2	—
800	16	32.4	0.24	12	—
900	5	11.8	0.29	42	0.23, 0.29
950	16	55.0	0.96	31	—
950	32	16.6	0.33	41	0.32
1000	0.5	25.7	0.16	11	—
1000	6	3.6	0.11	51	—
1000	12	50.7	0.64	22	—
1000	17	15.4	0.70	78	0.60, 0.61

temperature of more than 900° was required for the reaction to proceed to any extent, and even at 1000° the maximum conversion achieved was 78% in 17 hr. In several cases the result was checked by a nitrogen determination carried out by a Conway diffusion method described below. Good agreement was obtained between the nitrogen determined and the increase in weight.

The metal appeared to be altered very little by nitrogen, except for being more tarnished and more brittle than originally. X-Ray diffraction studies of the surface coating of nitride indicated a face-centred cubic system, the same as that found by Zachariasen and attributed to PuN.

One experiment was carried out to see whether sudden admission of nitrogen to plutonium, already heated to a high temperature, above its m. p., in an inert atmosphere, would cause disruption of the metallic structure and complete conversion into nitride. A 60-mg. sample of metal was heated in argon to 900°, then the argon was replaced by a rapid flow of nitrogen. After about 3 min., the sample was allowed to cool in nitrogen and removed for analysis. The metal was tarnished owing to a film of nitride (shown by X-ray diffraction). A nitrogen determination showed the plutonium nitride content to be only 0.8%. Therefore, even under these conditions the reaction is only at the surface.

To obtain more details about the extent of the reaction at various temperatures, plutonium metal was heated in nitrogen on a thermobalance. The increase in weight was measured at regular intervals while the temperature was raised by 30° during each 15 min. Several samples treated in this way gave very similar results: a slight increase in weight began as low as 200° but the reaction remained slow up to 900—1000° where it became more rapid. The increase in extension of the spiral (proportional to the increase in weight) was plotted against temperature, as shown in Fig. 1.

Sample A (Fig. 1) (58.12 mg. of plutonium) was heated to 970° during 4½ hr. and kept at 970° during a further 2 hr. At first there was a very small loss in weight, probably due to a trace of moisture. The overall increase in weight was 1.46 mg., the initial change being at about 200°. When the sample was dissolved in 2N-hydrochloric acid there was a small residue of oxide which was removed and dissolved in nitric acid containing fluoride. The plutonium content was determined radiometrically. The product was calculated to consist of PuO₂ 0.8% (found radiometrically), PuN 43.6% (increase in weight corrected for PuO₂), and Pu metal 55.6% (by difference).

Sample B (49.43 mg. of plutonium) was heated more slowly to 550° during 6 hr., then cooled in nitrogen and dissolved in 4N-hydrochloric acid. The nitrogen was determined by the Conway diffusion method, and the remaining increase in weight was attributed to oxide formation. The obtained results were: PuO₂ 3.7% (increase in weight corrected for PuN), PuN 4.7% (from nitrogen determination), and Pu metal 91.6% (by difference).

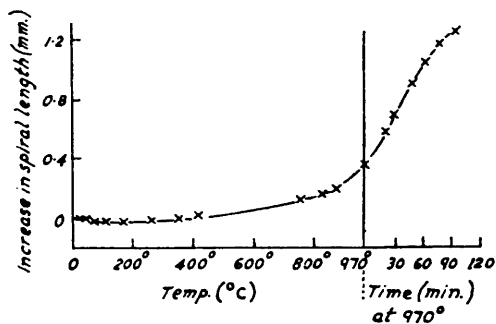
In each case a small amount of oxidation appears to have occurred, due to either moisture from the apparatus or a small leak of air during the 6—8 hours' heating.

Two other samples gave very similar results. It was therefore confirmed that the rate of reaction of plutonium metal with nitrogen is considerably increased above about 800° but is still relatively slow. Some reaction occurs at 300° or less, but is very slight in extent. Pure plutonium nitride, free from oxide and unchanged metal, was not obtained by this means.

(b) *Preparation from plutonium hydride.* The action of hydrogen on plutonium, leading to disintegration and formation of a hydride $\text{PuH}_{2.7}$, was carried out as described earlier (Part I, *loc. cit.*). When the reaction was complete, the temperature was slowly raised to 800° ; at the same time the flow of hydrogen was replaced by that of purified nitrogen. After about 2 hr. the sample was allowed to cool in nitrogen and was then removed for X-ray diffraction analysis. The pattern obtained was that of plutonium nitride, PuN , with a just discernible line due to plutonium dioxide. The oxide impurity could have been due to partial hydrolysis of the nitride whilst being subjected to X-rays, since plutonium nitride was subsequently found to be very unstable.

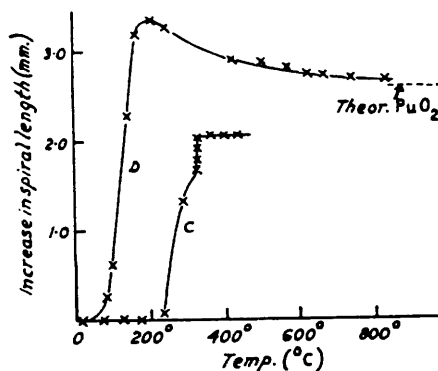
This appeared to be a quite simple and satisfactory method of preparation. To find the temperature at which plutonium hydride reacted with nitrogen, the reaction was carried out on the thermobalance. When heated to 230° during a period of $1\frac{1}{4}$ hr. very little change took place. Then a sudden and rapid increase in weight was observed within 15 min., corresponding to a 63% conversion into plutonium nitride. The rate of heating was reduced and the reaction then became progressively slower, not reaching completion for another 2 hr. Further increase in temperature caused no increase in weight. Fig. 2 (curve C) shows the increase in spiral length (proportional to the increase in weight), plotted against temperature.

FIG. 1. Thermogravimetric curves for plutonium metal heated in nitrogen.



(The increase in spiral length [corresponding to complete conversion into nitride would] be 3.04 mm.)

FIG. 2. Thermogravimetric curves.



C, Plutonium hydride heated in nitrogen.
D, Plutonium nitride heated in air.

The extension due to Pu hydride = 45.68 mm. (50.27 mg.). The total increase in extension = 2.06 mm. The theoretical increase in extension for the reaction $\text{PuH}_{2.7} \rightarrow \text{PuN} = 2.13$ mm. The experimental increase in weight was therefore 3.3% low but the difference represented a very small weight, 0.08 mg. (0.07 mm.), which was within the limits of precision of the balance. These results showed that plutonium hydride reacts with nitrogen at 240° to form the nitride PuN . This confirmed the formula calculated by Zachariassen from X-ray data (Zachariassen, *loc. cit.*). A second sample treated in the same way gave a very similar result.

Properties of Plutonium Nitride.—Like plutonium hydride, the nitride appeared very similar to the metal—black with sometimes a silvery lustre, hard, but brittle enough to be ground to a coarse powder. Whether prepared from the metal or the hydride, there was no apparent change in particle size, volume, or colour on formation.

Plutonium nitride is extremely unstable in air. When kept in a desiccator and removed periodically for weighing, it showed an increase in weight of 1.2% in 5 days. When exposed to moist air it increased its weight by 42% during the same time. The hydrolysis was accompanied by a considerable increase in volume and a change in colour from black to brown, then finally greenish yellow. X-Ray diffraction studies of the brown powder indicated a mixture of plutonium nitride and plutonium dioxide. The final product was plutonium dioxide.

The instability of plutonium nitride was very well illustrated by the results obtained on heating it in air on the thermobalance (Fig. 2, curve D). When heat was applied, a small but immediate increase in weight was observed. The temperature was raised at a rate of about 30° every 15 min., causing the increase in weight to become rapid at about 90° . The reaction was complete within another 45 min., the rate probably depending on the amount of moisture present

in the apparatus as well as on the temperature. The product was a partly hydrated oxide, which gradually lost moisture as the temperature was increased, forming the normal greenish-yellow plutonium dioxide. At 900°, the increase in weight was higher than that expected, by 5% (0.13 mm.), but the oxide was still losing moisture at an extremely slow rate. It appears therefore that plutonium nitride is very readily decomposed in moist air at quite a low temperature, the reaction being particularly fast at about 100°.

Fig. 3 shows the results obtained from two samples of nitride which had been stored in air in a stoppered tube for two weeks and had changed in appearance to a dark brown powder. Instead of the normal increase in weight, there was an initial decrease which, apart from a small increase at 90–100°, continued up to 400° where constant weight was attained. The graph clearly indicated a mixture of hydrated plutonium oxide and plutonium nitride, the hump at 90–100° being due to decomposition of the nitride. This was confirmed by X-ray diffraction data.

In cold water, plutonium nitride was slowly hydrolysed, but in hot water it expanded within a few seconds to a voluminous black mass and the water became alkaline to litmus.

Plutonium nitride, when freshly prepared, was dissolved by 3M-hydrochloric acid or -sulphuric acid in the cold, although a trace of residue was found presumably due to a competitive hydrolysis. The resulting solutions were blue, indicating the presence of trivalent plutonium. The sulphate solution became pink overnight owing to oxidation to more stable plutonium(IV) sulphate.

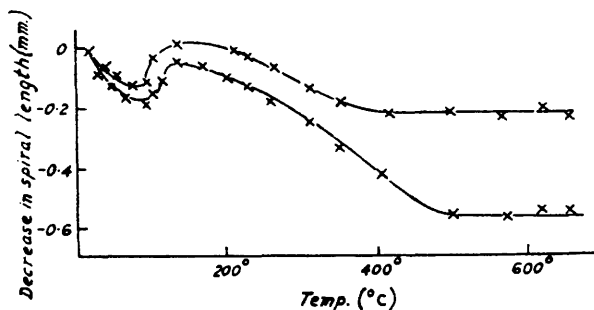


FIG. 3. Thermogravimetric curves for partly decomposed plutonium nitride heated in air.

The reaction with nitric acid was more complicated. The nitride was attacked slowly only on heating, part of it dissolving as nitrate and the remainder being converted into an insoluble, partly colloidal, black hydrated oxide. The relative amounts dissolved or oxidised depended on the concentration of the acid, the particle size of the nitride, the time of heating, and other factors. In one set of experiments, the percentages of nitride dissolved by nitric acid after 30 min. at 90–100° were: 8% in 3M-acid (0.24 mg. of Pu per ml.), 13% in 7.5M-acid (0.46 mg. of Pu per ml.), 35% in 15M-acid (1.11 mg. of Pu per ml.).

All the fresh samples of plutonium nitride gave good X-ray photographs corresponding to a face-centred cubic pattern of lattice parameter $4.905 \pm 0.002 \text{ \AA}$. This agreed well with Zachariassen's reported value of 4.906 Å. A faint pattern due to plutonium dioxide was just visible and was estimated to be due to about 1–2%. On storage, these samples gave progressively stronger oxide patterns and weaker nitride patterns.

Determination of Nitrogen in Plutonium Nitride.—The nitrogen figures quoted in Table 1, for partly nitrated plutonium metal, were found by a method we have used for determining microgram amounts of nitride nitrogen in plutonium metal. This is an adaptation of the Conway and Byrne diffusion method (*Biochem. J.*, 1933, **27**, 419) for determining ammonia and ammonium compounds. Our method consists in placing the sample dissolved in 3N-hydrochloric acid in a Conway diffusion cell (Conway, "Microdiffusion Analysis and Volumetric Error," Crosby-Lockwood, London, 1947) and liberating the nitrogen as ammonia; this diffuses into 0.1 ml. of 0.01N-sulphuric acid, and the excess of acid is then determined by a micro-titration with 0.01N-sodium hydroxide.

The level of nitrogen determined by this method was very low, of the order of 1–5 μg., and it was therefore necessary to take very small aliquot parts (with the consequent low precision) of the dissolved plutonium nitride. However, the results shown in Table 2 agreed within experimental limits with the apparent nitrogen content indicated by the increase in weight during preparation, thus confirming that the increases were due to nitrogen uptake. They also confirmed the conversion of the nitrogen into ammonium salts when the nitride was dissolved in dilute acid.

TABLE 2. *The determination of nitrogen (%) in plutonium nitride by a Conway diffusion method.*

Sample	Calc. from formula PuN	Found by increase in wt. when prepared	Found by Conway diffusion method
1	5.5	5.5	4.9, 4.8, 4.8
2	5.5	—	5.3, 5.2, 5.2, 5.2

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