The Preparation and Properties of Some Plutonium Compounds. Part I. Plutonium Hydride.

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Plutonium hydride with the approximate composition $PuH_{2\cdot7}$ has been obtained by direct combination of the metal with pure hydrogen at temperatures between 150° and 250°. Its chemical properties have been found to be very similar to those of the metal. By means of a thermobalance the hydride has been found to be stable in air up to 150°. *X*-Ray diffraction photographs showed two patterns, one of which was cubic and similar to that of plutonium dioxide, and the other hexagonal.

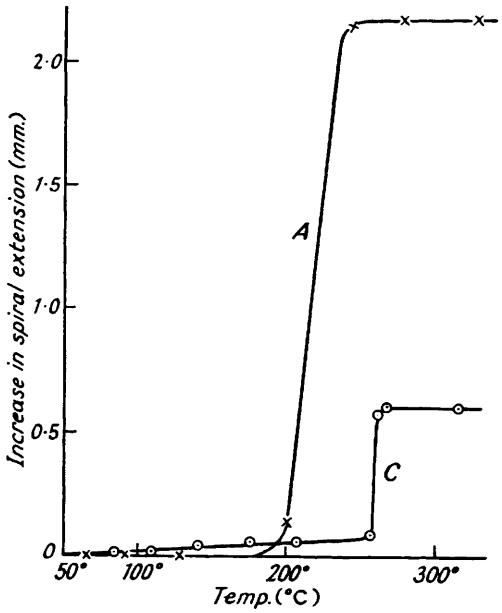
According to Burke (A.E.C.D. 2124, May 1944, declassified July, 1948) and Bakes and Johns (reported by Johns in L.A.D.C. 277, September 1944; M.D.D.C. 717, February 1947, declassified February 1947; reported by Kennedy and Smith L.A.M.S. 101, June 1944), plutonium and hydrogen react together at room temperature. Disintegration and powdering of the metal occur owing to the formation of a hydride. The method was to admit hydrogen slowly into an evacuated vessel containing plutonium and to measure the volume of hydrogen taken up. Burke (*loc. cit.*) reported three attempts, resulting in (*a*) no reaction, (*b*) $PuH_{2\cdot55}$ at 50°. (*c*) $PuH_{2\cdot75}$ at room temperature. Bakes and Johns (*locc. cit.*) in a more thorough investigation found the hydrogen to plutonium ratio by measuring the volume of hydrogen taken up and pumped off, several successive times, from samples of metal. They reported an average ratio (H/Pu) of 2·95 at 26·4°.

These workers published very few data on the chemical and physical properties of plutonium hydride and we have prepared and investigated it more fully.

Experimental

Preparation.—Bright plutonium metal (50—200 mg.) in a silica boat was placed in a silica combustion tube in a slow stream of dry oxygen-free (<1 p.p.m. of oxygen) hydrogen and the temperature of the sample was raised by means of an electric furnace until reaction occurred. Precautions were taken to prevent air from being sucked into the tube owing to rapid uptake of hydrogen. When the reaction was complete the hydride was allowed to cool in hydrogen.

In contrast to Burke, and to Bakes and Johns, we were unable to convert plutonium quantitatively into hydride at room temperature. A black coating formed on the outside of the metal and prevented any further action even after 16 hr. At temperatures between 150° and 200° darkening took place within about 30 min., then the metal rapidly disintegrated to coarse, black, still metallic-looking particles. In one case the sulphuric acid in the bubbler immediately following the combustion tube began to suck back for a few seconds owing to the sudden absorption of hydrogen. In several cases some particles of the hydride were projected out of the sample boat.



The reaction was followed more closely by heating plutonium in hydrogen on a thermobalance of silica-spring type similar to that described by Dawson, Elliott, Hurst, and Truswell (*J.*, **1954**, **558**). The increase in extension of the spring, which was measured by observing the movement of an index fibre by means of a cathetometer, was proportional to the increase in weight, the sensitivity being 0·909 mm./mg. The precision (3 × standard deviation) of any weighing at any temperature was calculated to be ±0·15 mm. or ±0·17 mg.

A platinum boat containing plutonium (about 40 mg.) was hung on the silica spring in hydrogen and the temperature was raised by about 30° every 15 min. Graph C in the Figure shows the increase in spiral length, plotted against temperature. It was believed that the sudden and complete increase in weight at 270° indicated that the point of reaction depended rather on an induction period than on temperature, especially since the hydride was normally prepared at a *lower* temperature.

Properties of Plutonium Hydride.—Appearance. The hydride was an almost black metallic-looking substance and appeared to occupy approximately the same volume as the original metal. It was hard, although grinding with a glass rod reduced it to a coarse powder with occasional sparking.

Action of water. In cold water there was no apparent reaction but on heating to 90°, a slow, steady flow of bubbles appeared and the solid partly broke down to a fine black oxide or hydroxide.

Action of mineral acids. In most respects plutonium hydride behaved very similarly to the

metal. It was virtually insoluble in 3M- or 16M-nitric acid, less than 10 μg. of plutonium per ml. of acid being dissolved even after prolonged heating. It dissolved readily with effervescence in hydrochloric acid (0·1—10M) and more slowly in sulphuric acid (3M) to give violet-coloured plutonium(III) salt solutions.

Hydrogen : plutonium ratio. This was determined by measuring the volume of hydrogen evolved on dissolving a known weight of hydride in 4N-hydrochloric acid. Corrections were made for temperature, pressure, water vapour pressure, and the volume of air displaced by the acid. Eight determinations on three different batches of plutonium hydride gave the results shown in the Table, the mean ratio being 2·69.

The hydrogen : plutonium ratio in plutonium hydride (calculated from the volume of hydrogen evolved with acid).

Sample	Mg.	Vol. of gas evolved (ml. at N.T.P.)	Ratios: H : hydride	H : Pu
Pu hydride (Batch No. 1)	33·8	8·83	5·66	2·67
	31·8	8·36	5·68	2·69
	34·5	9·18	5·75	2·76
	30·9	8·03	5·62	2·63
	34·7	9·15	5·70	2·71
Pu hydride (Batch No. 2)	32·7	8·48	5·61	2·62
	31·1	8·25	5·73	2·74
Pu hydride (Batch No. 3)	32·6	8·61	5·70	2·71
Pu metal	59·8	8·40 (2·99 equiv.)	—	—

Mean value = $PuH_{2\cdot69}$.

The apparatus was tested and found to be very satisfactory, 2·99 equiv. of hydrogen being obtained from pure plutonium metal.

Effects of air and heat. The hydride is fairly stable in air. In three weeks at room temperature, its weight only increased by 0·1% in dry air and by 1·3% in normal moist air. When heated in an open tube a sample glowed dully and changed into a greenish-yellow oxide. This oxidation was then followed on the thermobalance. It may be seen from the graph (curve *A*) that, when heated to 150° during 1½ hr., the hydride remained unchanged. Rapid oxidation then occurred, and further increase in temperature caused no change in weight. The product occupied several times the volume of the original hydride. A very similar curve was obtained with a second sample, B, except that the reaction was rather slower. The measurements were as follows :

	Sample A	Sample B
Extension due to hydride (mm.)	17·77	27·70
Maximum increase in extension (mm.)	2·19	3·25
Theoretical increase for the reaction $PuH_{2\cdot7} \longrightarrow PuO_2$ (mm.)	2·16	3·36

The deviations were only +0·03 mm., and −0·11 mm., both within the precision limits of the balance, *viz.*, ±0·15 mm.

Reaction with nitrogen. When the hydride was heated in nitrogen at 250°, a nitride, PuN, was formed. Its properties will be published in a subsequent paper.

Crystal structure. *X*-Ray diffraction photographs of a number of different samples of plutonium hydride (McDonald and Fardon, to be published) were essentially identical whether the sample had been exposed to air for only a few minutes, between preparation and photography, or for several days. A strong, face-centred cubic structure, very similar to that of plutonium dioxide, and a fainter hexagonal pattern were identified. Since the oxide content of the samples was known to be no more than 1—2% (see below) and there were small differences between this cubic structure and that found for PuO_2, the cubic phase was believed to be plutonium hydride. The hexagonal phase was too diffuse to be measured accurately but was attributed to about 5% of another hydride phase or an unidentified impurity. The density of the cubic phase was calculated to be 10·6 from *X*-ray data. This is considerably lower than the density of 19 reported for plutonium metal (Lord, *Nature*, **1954**, **173**, 534; Ball, Robertson, Mardon, Lee, and Adams, *ibid.*, p. 535).

Discussion

The reaction between plutonium and hydrogen occurred at 100—200° after an induction period of 20—30 min. This was contrary to the results of Bakes and Johns (*locc. cit.*)

who found the reaction to take place at room temperature after an induction period of only a few minutes. Our observations show that plutonium behaves more like uranium (Katz and Rabinowitch, " The Chemistry of Uranium," McGraw Hill Book Co. Inc., New York, 1951, N.N.E S. VIII, Vol. 5), which reacts most rapidly with hydrogen at 250°. Uranium exhibits an induction period if the oxide layer is not removed from the surface of the metal or if the hydrogen is not rigorously freed from oxygen. It is probable that the induction period observed with plutonium was also due to the oxide film which forms immediately on the metal surface and is not easy to remove chemically.

As with uranium, the reaction, once it began, was completed rapidly. There was disintegration to a coarse dark powder and a slight increase in volume, but the change was small compared with that of uranium reacting under the same conditions to form a voluminous, fine, black powder.

The properties of plutonium hydride, particularly the reactions with air and mineral acids, were very similar to those of the metal.

The hydrogen to plutonium ratio was found to be 2·7. Bakes and Johns (*locc. cit.*) reported a value of 2·95, but, since the plutonium left after pumping off the hydrogen in their experiments would have been very finely divided and reactive, their results are not strictly comparable with those from massive metal. From the pressure–hydrogen-to-plutonium ratio isotherms they concluded that PuH_2 is formed, which in the presence of an excess of hydrogen reacts to give PuH_3 which remains in solid solution with the PuH_2. By extrapolation of these curves they predicted a ratio of about 3·0 at room temperature and 350 mm. pressure. Higher temperatures or lower pressures would give mixtures of PuH_2 and PuH_3.

The volume of hydrogen measured in our experiments was 5% lower than the amount required for a formula of PuH_3. There are four possible explanations for this low result :

(1) The hydride contained 5% of PuO or PuO_2, or other impurity which would not evolve hydrogen with hydrochloric acid. However, the amount of impurities in the original metal was very small and impurities formed during or immediately after preparation of the hydride were confined to oxides. The complete solubility of the hydride in dilute hydrochloric acid, the purity of the plutonium nitride resulting from the reaction with nitrogen, and the lack of plutonium monoxide lines in the *X*-ray diffraction patterns permit a limit of 1—2% to be given for these.

(2) The hydride contained 10% of unattacked plutonium metal which would liberate 3 equiv. of hydrogen instead of 6. This is unlikely since no plutonium metal pattern was detected in the *X*-ray diffraction photographs of the hydride, more prolonged heating in hydrogen caused no increase in the hydrogen to plutonium ratio, and hydride of smaller particle size did not give a higher ratio.

(3) The hydride consisted of a mixture of approximately 30% of PuH_2 and 70% of PuH_3. Two crystal structures were identified, one cubic and the other hexagonal, but only about 5% of the hexagonal phase was present. From Bakes and Johns's conclusions (*locc. cit.*) it seems likely that this mixture could occur although the PuH_2 should have been converted into PuH_3 on cooling in hydrogen.

(4) The hydride was a non-stoicheiometric compound. This is contrary to Bakes and Johns's theory of PuH_2 and PuH_3 in solid solution. However, examination of their isotherms reveals no proof of the existence of PuH_3 as a separate compound; they only show that hydrogen is being dissolved in PuH_2, forming a solid solution which appears to approximate in composition to PuH_3 under certain conditions. Therefore, if it is assumed that the solid solution was one of hydrogen in PuH_2, it is reasonable to suggest that plutonium hydride ($H/Pu > 2$) is a non-stoicheiometric compound.

Plutonium hydride is obviously a member of the transitional-metal group of hydrides, having definite similarities with the hydrides of the rare earths, thorium, and uranium. Like them it has a considerably lower density than the metal, it is an exothermic, reactive compound with a crystal structure different from that of the metal, and has no simple stoicheiometric formula. Hurd (" Chemistry of the Hydrides," Chapman and Hall Ltd., London, 1952) has described how some transitional metals may form compounds with hydrogen and how the new structure formed physically absorbs more hydrogen. Zhukov

(*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 2073) found evidence for the existence of CeH_2 from dissociation-pressure measurements. With higher hydrogen to cerium ratios the dissociation pressure of hydrogen was dependent upon the hydrogen content. The usual compound at atmospheric pressure is $CeH_{2\cdot69}$ (Hurd, *op. cit.*). This is analogous to the plutonium–hydrogen system. Other hydrides formed by the "lanthanide" and "actinide" elements are $PrH_{2\cdot84}$, Gd_2H_3, GdH_2, ThH_2, $ThH_{3\text{-}4}$, PaH_3, UH_3, $NpH_{3\cdot7}$, and $AmH_{2\cdot7}$. The chemistry of these compounds has been reviewed by Hurd (*op. cit.*) and Seaborg and Katz ("The Actinide Elements," McGraw-Hill Book Co. Inc., New York, 1954). Rundle (*J. Amer. Chem. Soc.*, 1951, **73**, 4172) suggests that in uranium hydride the hydrogen atoms which lie in distorted tetrahedra, equidistant from four uranium atoms, are in holes which are larger than necessary and must result from the reaction. A similar observation has been made with ThH_2 (Rundle, Shull, and Wollan, *Acta Cryst.*, 1952, **5**, 22). This type of structure may occur in other similar hydrides, for example, plutonium hydride, where an exothermic reaction between the metal and hydrogen results in a change in crystal structure and an increased unit-cell volume. It is also possible that these reactions take place in two stages, the first giving the change of crystal structure, possibly resulting in a lower hydride, with a simple stoicheiometric formula, and the second being the expansion of the new structure by entry of more hydrogen atoms. The number of extra atoms added would depend upon the space available and on physical conditions such as temperature and pressure. This would give rise to the increased dissociation pressure with increased hydrogen content which has been observed with some transitional-metal hydrides and to their non-stoicheiometric formulæ.

All the *X*-ray work here recorded was carried out by B. J. McDonald and J. B. Fardon who will report their detailed results later. Their help is gratefully acknowledged. Thanks are offered to A.E.R.E., Harwell, for the silica spiral used in the thermobalance, and to J. K. Dawson of A.E.R.E. for full details of the construction of his balance. Thanks are also offered to the Managing Director of this Group for permission to publish this paper.

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