964. *The Preparation and Properties of Some Plutonium Compounds. Part VI.* Plutonium Dioxide.*

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Several different forms of plutonium dioxide have been prepared. That made by ignition at 1200° is stoicheiometric; that prepared by direct ignition of metal at lower temperatures closely approaches stoicheiometric; and that prepared by ignition of plutonium salts at 870° in air has a higher molecular weight. We suggest that the dioxide has a formula in the range $PuO_{2.00-2.09}$ depending upon the starting material and ignition temperature.

SEABORG and WAHL,[1] and Harvey, Heal, Maddock, and Rowley,[2] reported that the only plutonium oxide stable to ignition in air was the dioxide. This observation was based on Zachariasen's *X*-ray diffraction evidence,[3] who found that the oxide had a fluorite-type face-centred cubic structure with a lattice parameter $a = 5{\cdot}386 \pm 0{\cdot}001$ *kX* units (equivalent to 5·396 Å) with four metal atoms per unit cell. The composition was confirmed by a microgravimetric examination of the reaction $Pu(IO_3)_4 \longrightarrow PuO_2$. Cunningham [4] reported that the stoicheiometry of the reaction $PuF_4 + 2H_2O \longrightarrow PuO_2 + 4HF$ verified the formula PuO_2. However, only minute quantities of plutonium were available for these early studies, and the weight changes involved would be insensitive to minor variations in the oxygen content of the oxide. Also the compositions of the iodate and fluoride were not known with certainty. Several authors [5-12] have reported the quantitative use of the dioxide ignited to 700—900° for plutonium determinations, including use in the measurement of specific activity.

Two other oxides of plutonium have been reported, a monoxide and a sesquioxide. No true oxide higher than PuO_2 is known; Westrum [5] reported that neither oxygen at 400°/70 atm., nor ozone at 800°, reacted with the dioxide.

We have now verified many of the early findings and provided new information about the preparation and properties.

The dioxide was produced by the ignition in air or oxygen of plutonium metal; of plutonium hydride, nitride, and carbide; of plutonium-(III) or -(IV) hydroxide, chloride, sulphate, nitrate, oxalate, fluoride, iodate, and peroxide; or of plutonium(VI) nitrate.

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* Part V, *J.*, 1956, 3358.

[1] Seaborg and Wahl, *J. Amer. Chem. Soc.*, 1948, **70**, 1128.

[2] Harvey, Heal, Maddock, and Rowley, *J.*, 1947, 1010.

[3] Zachariasen, "The Transuranium Elements," McGraw-Hill Book Co. Inc., New York, 1949, p. 1442; *Acta Cryst.*, 1949, **2**, 388.

[4] Cunningham, " The Actinide Elements," McGraw-Hill Book Co. Inc., New York, 1954, p. 394.

[5] Westrum, ref. 3, p. 936.

[6] Moulton, Report L.A. 172 (U.S. Atomic Energy Commission).

[7] Hurst, A.E.R.E. C/M.126 (U.K. Atomic Energy Authority).

[8] Hall and Walter, A.E.R.E. C/R.874 (U.K. Atomic Energy Authority).

[9] Allison, P.D.B.60 (Atomic Energy of Canada Ltd.).

[10] Charman and Welch, C.I. Report 81 (U.K. Atomic Energy Authority).

[11] Brown and Charman, WSL/TM.184 (U.K. Atomic Energy Authority).

[12] Farwell, Roberts, and Wahl, *Phys. Rev.*, 1954, **94**, 363.

The physical and chemical properties of the product depend upon the starting material and the temperature of ignition. The variation in appearance is shown in Table 1 for different samples of oxide.

TABLE 1. *Physical properties of plutonium dioxide ignited to* 870°.

Source	Colour	Appearance	Source	Colour	Appearance
Sulphate	Yellow-green to green	Bulky powder	Oxalate	Yellow-buff	Bulky powder
Nitrate	Dull yellow	Bulky solid	Iodate	Buff	Very bulky
Chloride	Dull yellow	Powder	Hydroxide	Black, traces of yellow	Dense shiny particles
Fluoride	Khaki, traces of black	Granules			

In general, the oxide was moderately reactive, and dissolved slowly in boiling mineral acids if it had not been heated above 500°. Highly ignited oxide was attacked only by fused sodium hydrogen sulphate or hot concentrated nitric acid containing a little hydrofluoric acid. The oxide prepared by igniting a plutonium salt at 870° reacted with hydrogen fluoride at 500° to form either the blue trifluoride or pink tetrafluoride, whereas that prepared directly from metal, and any plutonium oxide ignited to 1250°, were more resistant to attack.

Composition.—The variation in properties of different samples of dioxide caused doubt about the constancy of composition. Further, as a reproducible bias was found in the gravimetric assay of plutonium standard solutions by ignition of the sulphate at 700—1000°, the oxide appeared not to be stoicheiometric. The mean plutonium concentration for 15 determinations, the oxide being assumed to be $PuO_{2\cdot00}$, was 0·6% greater than the true value for the standard, which had been prepared from specially purified plutonium metal. The composition of the oxide was examined in order to understand this bias, which is equivalent to an oxide $PuO_{2\cdot10}$. It was not possible to determine the oxygen content directly, and the increase in weight during the conversion of metal into oxide was substituted. Pure, analysed samples of plutonium metal turnings which had been prepared and stored in an inert atmosphere were weighed, burnt in air, and ignited at 870°. The plutonium dioxide which was formed was ignited to constant weight; the average O/Pu atom ratio on 16 results was 2·010. The standard deviation was 0·4% of the ratio (0·05% of the oxide weight).

As this difference from stoicheiometry was insufficient to account for the observed bias in the assay of plutonium solutions, weighed samples of the same quality of plutonium metal were dissolved in sulphuric acid, and the plutonium sulphate was dried and ignited to oxide at 870°. The mean O/Pu atom ratio obtained was 2·07, in contrast to the value by direct ignition of metal. A third value for the ratio, 2·05, was obtained by the ignition of samples of plutonium nitrate, which had been prepared by dissolving plutonium metal in hydrochloric acid and converting the chloride into nitrate. The results are given in Table 2.

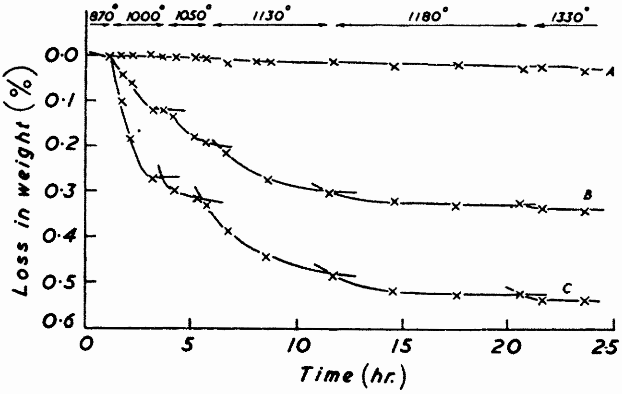
TABLE 2. *The* O/Pu *atom ratio of plutonium dioxide ignited to* 870°.

Material ignited	O/Pu atom ratio	
Plutonium metal	2·002, 2·005, 2·015, 1·999, 2·010, 2·018, 2·012, 2·024, 2·014, 2·011, 2·005, 1·995, 2·021, 2·015, 2·009, 2·002.	Mean = 2·010.
Plutonium sulphate	2·092, 2·059, 2·061, 2·063.	Mean = 2·07.
Plutonium nitrate	2·049, 2·028, 2·070.	Mean = 2·05.

The variation in the O/Pu atom ratio was proved by converting 2·01-oxide into an oxide with a higher ratio. Samples of oxide made directly from metal were weighed and repeatedly evaporated to dryness with sulphuric acid to form some plutonium sulphate, and were then reignited to oxide under the usual conditions. The O/Pu atom ratio always increased according to the percentage conversion into sulphate. The change was many times too great to be caused by impurity added with the sulphuric acid, or by conversion of impurities in the metal into stable sulphates.

As it seemed possible that the variation in the ratio was caused by incomplete decomposition of plutonium sulphate or nitrate through ignition at too low a temperature, each of the three types of oxide was heated to higher temperatures, whereupon the samples lost weight each time the temperature was raised, more markedly if they were derived from plutonium salts, and they approached constant weight on continued heating at any given temperature. The heat-stability curves from 870° to 1330°, for oxide prepared from metal and from sulphate, and for a mixed sample, are reproduced in the Figure. A constant weight corresponding to the stoicheiometric dioxide was reached on ignition at 1180° and no further significant loss was observed on raising the temperature to 1330°. The O/Pu atom ratio at this temperature for the seven results in which the original weight of metal was known was always 2·002 ± 0·008.

The loss in weight on heating to between 870° and 1200° was not due to incomplete decomposition of the salt at the lower temperature, as constant weight was approached at each selected intermediate stage. Also, the necessary amount of oxides of nitrogen or sulphur were not detected by mass spectrometry of the trace of gas evolved during the high-temperature ignition.



The heat stability of plutonium dioxide.

A, Plutonium dioxide made from metal.

B, Mixed plutonium dioxide sample.

C, Plutonium dioxide made from sulphate.

Shimomura, Tsubokawa, and Kojima[13] reported that nickel oxides of similarly high oxygen content can be prepared from nickel nitrate, the composition depending upon the ignition temperature, and approaching stoicheiometric on high-temperature ignition. We deduced that the weight loss which was observed when plutonium dioxide was heated to the stoicheiometric composition was the loss of the excess of oxygen from the system. The loss was measured accurately and gave $PuO_{2\cdot015}$, $PuO_{2\cdot046}$, and $PuO_{2\cdot089}$ as the most reliable formula for the oxides prepared at 870° from metal, nitrate, and sulphate respectively.

The *X*-ray diffraction powder photographs of the different types of oxide were examined for any change in lattice parameter or duplication of lines which might be caused by the variation in oxygen content. However, all samples produced photographs in agreement with the fluorite structure $a = 5\cdot396 \pm 0\cdot001$ Å obtained by Zachariasen, and no other phase was detected in any sample. In contrast, in the uranium–oxygen system at compositions close to UO_2, Alberman and Anderson[14] reported that a variable phase $UO_{2\cdot0}$—$UO_{2\cdot2}$ formed when the dioxide was gently heated in air or oxygen, but that this oxide disproportionated into two distinct cubic phases UO_2 and $UO_{2\cdot2}$ if it was annealed at higher temperatures. Hering and Perio,[15] Grønvold,[16] and Hoekstra and Siegel[17] also reported that annealed UO_2 has no appreciable range of composition.

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[13] Shimomura, Tsubokawa, and Kojima, *J. Phys. Soc. Japan*, 1954, **9**, 521.

[14] Alberman and Anderson, *J.*, 1949, S303.

[15] Hering and Perio, *Bull. Soc. chim. France*, 1952, 351.

[16] Grønvold, *J. Inorganic Nuclear Chem.*, 1955, **1**, 357.

[17] Hoekstra and Siegel, " Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Vol. 7, United Nations, New York, 1956, p. 394.

The diffraction patterns of the oxides prepared from salts at 870° (especially from the nitrate) were less sharp than those from the high-temperature oxides, suggesting that the particle size of the oxides had increased on heating. Particle size may have influenced the physical and chemical properties of the oxides. The samples from plutonium salts ignited at 870° were bulky, hygroscopic, yellow or yellow-green powders which reacted very slowly with hot mineral acids, but the same samples ignited at 1200° all approached a darker, khaki colour, were much more compact, and showed neither affinity for water nor reactivity with acids except nitric acid containing a little hydrofluoric acid. But alternatively the variation in properties may have been due to a change in the oxide from a non-stoicheiometric form with many interstitial oxygen atoms or lattice defects to an ordered crystal structure.

Thorium oxide shows a similar variation of properties depending upon ignition conditions. It is widely reported that thoria requires ignition to more than 1100° to reach constant weight in accurate gravimetric analysis.[18] Like plutonium dioxide, thoria becomes non-hygroscopic and chemically inert at these temperatures. Thorium compounds are almost exclusively quadrivalent and no higher oxides are known, and there are no reports either to confirm or to dispute that a small range of variable composition may exist analogous to that suggested for plutonium dioxide.

For uranium the higher oxides U_3O_8 and UO_3 are well known, and in solution uranium is predominantly sexivalent. By comparison, no oxides of plutonium higher than PuO_2 have been reported, and the most stable valency in solution is Pu^{IV} although it is readily oxidised to the sexivalent state. In a review of the oxide systems of the actinide elements, Katz [19] related the formation of stable compounds over a range of composition to the existence of several oxidation states for the element and to their oxidation–reduction potentials. Such criteria indicate that plutonium dioxide may have a variable composition, and the range $PuO_{2\cdot0}$—$PuO_{2\cdot1}$ is compatible with the overall distribution of actinide oxides noted by Katz. The whole range of plutonium oxides, PuO—$PuO_{2\cdot1}$ is intermediate between the ranges reported for neptunium and americium.

EXPERIMENTAL

The toxicity of plutonium made it desirable to carry out all operations in a totally enclosed glove box, maintained at slightly reduced pressure and fitted with an air filter on the exhaust line. This was not possible however with the large high-temperature muffle furnace, which was placed in a well-draughted fume hood. Samples were first given a preliminary ignition to oxide inside a glove box. The balance was in a separate box and, although glove-box work was slower than normal, most operations were possible with only slight loss of facility.

The O/Pu *Atom Ratio of the* 870° *Oxides.*—Selected turnings of pure plutonium metal, freshly prepared in an inert atmosphere, were analysed for common metallic impurities and corrections were applied to all results in which the error was significant.

In the determination of the O/Pu ratio of oxide prepared by direct ignition, 0·2 g. samples of metal in silica weighing bottles were burned at a controlled rate in air by slowly raising the temperature. The oxide was then ignited to constant weight at 870°. The weight of oxide, which was not hygroscopic, was generally reproducible to within ±0·02% on a semimicro-balance.

When the oxide was prepared *via* plutonium sulphate, the weighed sample of metal was dissolved in dilute sulphuric acid. The solution was evaporated to dryness in a silica weighing bottle and the plutonium sulphate was decomposed to oxide by heating to 870° during 30 min. The oxide was ignited to constant weight at this temperature and was cooled in the closed weighing bottle in air dried by anhydrone [$Mg(ClO_4)_2$]. It was hygroscopic, and the weight was normally reproducible to ±0·05%.

When the oxide was prepared *via* the nitrate, the weighed metal was dissolved in dilute

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[18] *E.g.*, Rodden and Warf, " Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co. Inc., New York, 1950, p. 160.

[19] Katz, *Record Chem. Prog.*, Spring 1951, **12**, 43–53.

hydrochloric acid. The solution was evaporated with an excess of nitric acid to form plutonium(IV) nitrate which was ignited to oxide as above.

The O/Pu *Atom Ratio of the High-temperature Oxides.*—0·2—0·5 g. samples of each of three types of plutonium oxide which had been ignited at 870° in platinum boats were further ignited to constant weight at successive temperatures in the range 1000—1330° in an electric muffle furnace. The samples were cooled over anhydrone and weighed rapidly to prevent adsorption of moisture. The oxides became less hygroscopic as the ignition temperature was raised; the weight of oxide was reproducible to within ±0·02% after ignition at 1200°.

X-*Ray Crystallography.*—All samples submitted for crystallographic examination were powdered and bound with Canada balsam, and were photographed in a 19 cm. powder camera with copper $K\alpha$ radiation.

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