965. *The Preparation and Properties of Some Plutonium Compounds. Part VII.* Plutonium Carbides.*

By J. L. DRUMMOND, B. J. McDONALD, HEATHER M. OCKENDEN, and G. A. WELCH.

Plutonium monocarbide, PuC, has been prepared by the reaction of graphite with plutonium metal or hydride at about 900°. A sesquicarbide, Pu_2C_3, was formed, in addition to the monocarbide, by the reduction of plutonium dioxide with graphite at 1800—1900°. Both carbides are reactive and easily hydrolysed by dilute acid or boiling water. Strong chemical and *X*-ray evidence suggests that a higher carbide exists but it has not been identified unequivocally.

CARBIDES of plutonium with the formulæ PuC and Pu_2C_3 have been reported, but there is very little information on their preparation and properties. They were identified by *X*-ray diffraction methods alone. Zachariasen[1] showed the presence of three distinct phases in the product from a micro-scale reduction of plutonium trifluoride with lithium in a graphite crucible. There were two face-centred cubic phases, corresponding to plutonium monoxide,[2] with the parameter $a = 4{\cdot}948 \pm 0{\cdot}002$ *kX* units (equivalent to 4·958 Å) which had been found in earlier work, and to plutonium monocarbide,[3] $a = 4{\cdot}910 \pm 0{\cdot}005$ *kX* units (4·920 Å). The third phase[1] was body-centred cubic, $a = 8{\cdot}11 \pm 0{\cdot}01$ *kX* units (later quoted as $8{\cdot}129 \pm 0{\cdot}001$ Å [4]), and was tentatively identified as the sesquicarbide by volume considerations. The composition was confirmed when the isostructural uranium sesquicarbide was prepared by Mallet, Gerds, and Vaughan.[5]

We have prepared these carbides by different methods and studied their chemical properties. As the carbon impurity in plutonium metal is likely to be present as carbide, these compounds may be of metallurgical significance.

Plutonium Monocarbide.—Preparation. Plutonium monocarbide was prepared by heating powdered graphite in an inert atmosphere with (*a*) plutonium hydride at 800° for 4 hr.,

---

* Part VI, preceding paper.

[1] Zachariasen, "The Transuranium Elements," McGraw-Hill Book Co. Inc., New York, 1949, Vol. II, p. 1449.

[2] Mooney and Zachariasen, *op. cit.*, p. 1442.

[3] Zachariasen, *Acta Cryst.*, 1949, **2**, 388.

[4] *Idem, ibid.*, 1952, **5**, 17.

[5] Mallet, Gerds, and Vaughan, *J. Electrochem. Soc.*, 1951, **98**, 505.

or (*b*) plutonium metal at 1000° for 5 hr., or (*c*) plutonium dioxide at 1800° for 10 min. In the last case sufficient graphite was used for the reaction $PuO_2 + 3C \longrightarrow PuC + 2CO$. The product was always a sintered, coke-like mass which could be broken into pale-grey crystalline fragments. The purest monocarbide was that prepared from plutonium hydride although, owing to the difficulty of mixing the reactants, the product contained small amounts of unchanged graphite and plutonium metal (which is formed on thermal decomposition of the hydride). Samples free from plutonium metal were prepared from intimate mixtures of the dioxide and graphite, but at the higher temperature required for this reaction some sesquicarbide was also formed. Where this contamination was found to be small by *X*-ray diffraction photography, the carbon content varied from 4·5 to 4·8% (PuC requires C, 4·78%).

Properties. Plutonium monocarbide began to oxidise slowly when heated to 200—300° in air, and it burned brightly in oxygen at 400°. In an inert atmosphere it melted at about 1850°. On cooling, the melt formed brittle pellets which sparked vigorously when broken, to expose shiny metallic surfaces. These surfaces remained bright even after two months in air at room temperature. Plutonium metal in the same circumstances would have been considerably oxidised. Samples prepared from hydride decomposed more rapidly in air, perhaps owing to their more porous nature.

The monocarbide was not attacked by cold water, but it effervesced steadily in hot water and precipitated plutonium(III) hydroxide. It was readily hydrolysed by cold dilute hydrochloric or sulphuric acid. The gas evolved in every case contained hydrogen and methane together with smaller quantities of ethane, butanes, acetylene, ethylene, and butenes, which were identified by mass spectrometry. There was only slight attack by nitric acid, but when the monocarbide was heated with concentrated nitric acid containing a little sodium fluoride there was a steady evolution of gas and carbon was deposited. A similar deposit of carbon was observed when uranium carbides were treated with nitric acid.

The *X*-ray diffraction patterns of eleven preparations of the monocarbide indicated a face-centred cubic system with a lattice parameter varying from 4·959 to 4·973 Å, as shown in the Table.

The lattice parameter of plutonium monocarbide.

Reactant	Temp.	Parameter (Å)	Reactant	Temp.	Parameter (Å)
Pu	1000°	4·969 ± 0·001	PuO_2	1650°	4·972 ± 0·001
$PuH_{2\cdot7}$	800	4·9695 ± 0·0005	PuO_2	1800	4·971 ± 0·003
$PuH_{2\cdot7}$	800	4·974 ± 0·0005	PuO_2	1800	4·972 ± 0·001
$PuH_{2\cdot7}$	800	4·959 ± 0·001	PuO_2	1800	4·973 ± 0·001
$PuH_{2\cdot7}$	1000	4·9705 ± 0·0005	PuO_2	1880	4·965 ± 0·002
$PuH_{2\cdot7}$	1650	4·969 ± 0·001			

The variation may be due to small amounts of plutonium monoxide or graphite existing in solid solution in the carbide, or possibly to a deficiency of carbon in the lattice. The fact that plutonium monocarbide and monoxide can exhibit mutual solubility was shown by heating a mixture of the two at 1650°. Although neither reactant was pure, their diffraction patterns were both visible in the mixture. In the sintered product they were replaced by one pattern with a parameter intermediate between the two. (The plutonium monoxide for this work was prepared by reducing the dioxide with plutonium hydride at 1800° in a tantalum crucible.) The corresponding uranium compounds have been more extensively studied and the lattice parameter of the isomorphous uranium monocarbide [6] is reported to vary from 4·948 to 4·995 Å. The monocarbide and monoxide form mutual solid solutions, but neither uranium nor carbon is appreciably soluble in the monocarbide.[7, 8]

[6] Katz and Rabinowitch, " The Chemistry of Uranium," McGraw-Hill Book Co. Inc., New York, 1951, Vol. I, pp. 215, 249.

[7] Rundle, Baenzinger, Wilson, and McDonald, *J. Amer. Chem. Soc.*, 1948, **70**, 99.

[8] Mallet, Gerds, and Nelson, *J. Electrochem. Soc.*, 1952, **99**, 197.

The parameter $a = 4{\cdot}920$ Å reported by Zachariasen for plutonium monocarbide was obtained from a diffraction pattern in which three separate phases were identified and attributed to PuC, PuO, and Pu_2C_3 respectively. There was no reported chemical evidence for attributing the 4·92 phase to *pure* monocarbide, and it is likely that it had a different composition from the 4·97 phase found in this work. It is interesting to note that the plutonium monoxide mentioned above gave parameters $a = 4{\cdot}917$ and 4·938 for two preparations.

Plutonium Sesquicarbide.—Preparation. *Plutonium sesquicarbide* was prepared by heating an intimate mixture of plutonium dioxide and powdered graphite at 1850° for 10 min. The components were mixed in the ratio required to satisfy the equation $2PuO_2 + 7C \longrightarrow Pu_2C_3 + 4CO$. A slight excess of graphite or oxide was taken to allow for side reactions, depending upon whether a tantalum or a graphite crucible was used. The product melted at about 1900°; it closely resembled the monocarbide described above and often contained some of this compound or of a suspected higher carbide. The carbon content of the purer samples ranged from 6·2 to 7·1% (Pu_2C_3 requires C, 7·0%).

Properties. The chemical properties of the sesquicarbide differed from those of the monocarbide only in degree. Thus the former seemed slightly less stable to hydrolysis in the atmosphere, but more stable to oxidation on heating. The sesquicarbide was rather less easily hydrolysed by boiling water and by acids, the product containing solid or liquid hydrocarbons in the form of a wax in addition to a mixture of gaseous hydrocarbons similar to that from the monocarbide.

The *X*-ray diffraction powder photographs of the sesquicarbide gave a reproducible, body-centred cubic pattern with lattice spacing identical with those attributed to Pu_2C_3 by Zachariasen.[4]

Higher Carbides of Plutonium.—The existence of at least one higher carbide was strongly suspected although it was not possible to make a definite identification. Several preparations at temperatures above 2000°, made in graphite crucibles from mixtures rich in graphite, gave a new *X*-ray diffraction pattern whose stronger, distinguishing lines had "*d*" values of 3·31 (100), 3·08 (60), 1·56 (60), 1·52 (60), and 1·49 Å (60), the figures in parentheses being visual relative intensities. The full pattern does not include either of the carbide phases described above, and does not appear to resemble that of uranium dicarbide.[7, 8] It has not yet been indexed.

The new *substance* melted at about 2200°, which is appreciably higher than the m. p. of plutonium sesquicarbide. It was much less stable in moist air than the known carbides, was more stable to oxidation, and formed a higher proportion of solid and liquid hydrocarbons on hydrolysis. The carbon content varied from 8·5 to 9·5% (PuC_2 requires C 9·1%). Some samples seemed to be less homogeneous than usual and gave poor duplicate analyses.

The temperature dependence of the formation of the higher carbide was demonstrated in two preparations in which a mixture of plutonium hydride and excess of graphite was used. In the first, at 1650°, the product contained a mixture of monocarbide and sesquicarbide, but in the second, at 2200°, the same reactants produced a mixture of the sesquicarbide and the higher carbide.

Comparison with Other Carbides.—The properties of all the plutonium carbides investigated are similar; chemically, they all belong to a class of reactive, heavy-metal carbides which includes UC_2, ThC_2, CeC_2, etc. For example, they are readily hydrolysed by dilute acid or hot water to form mixed hydrocarbons. Plutonium monocarbide, however, has the face-centred cubic structure and the metallic appearance of the interstitial monocarbides TiC, ZrC, HfC, and ThC, without their refractory nature and chemical inertness. Thence, although Wells[9] separates the thorium and uranium monocarbides into a separate class (interstitial) from their higher carbides (salt-like), this is not possible with plutonium carbides.

[9] Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1950, pp. 550, 704.

Plutonium monocarbide is much more reactive than uranium monocarbide, which is not attacked even by hydrochloric acid.[7] This difference also occurs between the mono-nitrides of plutonium and uranium.[10] Plutonium sesquicarbide also is more reactive than the uranium analogue which is not decomposed by water.[5]

Plutonium reacts with carbon at a lower temperature than does uranium and consequently the molten metal should not be handled in graphite containers.

EXPERIMENTAL

X-Ray Crystallography.—Specimens were bound with Canada balsam and photographed in a 19 cm. camera. Even semiquantitative interpretation was made difficult by the complex nature of the patterns, most of which contained several phases, some of them unidentified, and by the variation in particle size of the different phases. Further, the very hard products were often not homogeneous even when crushed. However, the general change in composition of the products with variation of reaction mixture was deduced from the *X*-ray analysis and the carbon content.

Carbon Determination.—To determine total carbon, 10 mg. samples were ignited at 900° in pure oxygen and the carbon dioxide formed was absorbed in 0·1N-barium hydroxide. The excess of alkali was back-titrated with standard acid. 95—100% recovery was obtained from 1 mg. standard graphite samples. In the free carbon determination, 20 mg. samples were hydrolysed with 2M-hydrochloric acid. The insoluble residue was centrifuged out, was washed successively with acid, water, acetone, and ether to remove solid or liquid hydrocarbons, and was then ignited as above.

FIG. 1. *High-temperature furnace.*

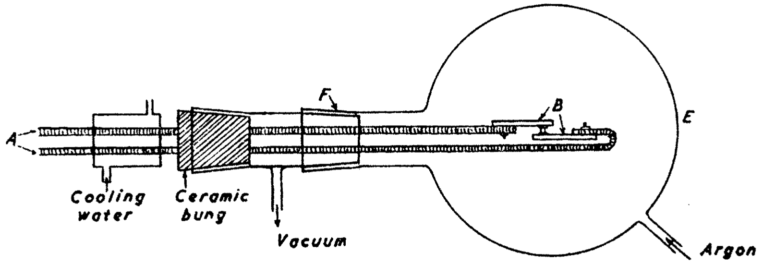
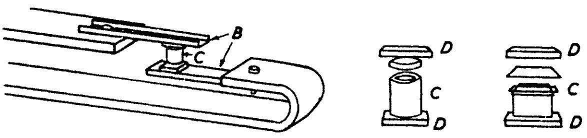


FIG. 2. *Electrode and crucible assembly.*



The difference between the two results was the chemically combined carbon, which is the result reported here in all cases.

Preparations at 800—1000°.—The apparatus was that used previously for the preparation of plutonium hydride [11] and nitride [10] by Brown, Ockenden, and Welch. The sample of about 100 mg. of plutonium metal or plutonium hydride, mixed with pure powdered graphite in a small silica boat, was heated for several hours in a silica tube resistance furnace. The tube was continuously purged with dry argon, which was freed from oxygen and nitrogen by scrubbing with uranium turnings at 800°. Samples were cooled in the argon before removal.

Preparations at 1600—2200°.—A high-temperature microfurnace (Fig. 1), suitable for use in a glove box, was designed to heat a 100 mg. sample to 2200° for 10 min. periods. It operated on a variable A.C. supply of 0—6 v and 0—100 A. One-inch copper strip connectors *A* led into the glove box and were bolted to two small tantalum contacts *B*. A small tantalum or graphite crucible *C* and lid (Fig. 2) were sandwiched between thin graphite discs *D* and wedged between

---

[10] Brown, Ockenden, and Welch, *J.*, 1955, 4196.
[11] *Idem, ibid.*, p. 3932.

the tantalum contacts. Most of the heat was developed at the relatively high resistance of the crucible " sandwich," which was held in position by the resilience of the copper strip even at high temperatures. The furnace jacket *E* was a 1 l. Pyrex flask which was connected to the apparatus with a B.45 standard joint *F*. The apparatus was flushed with argon at 1—2 mm. pressure during operation of the furnace. After reaction the sample cooled to room temperature in a few minutes.

Crucible temperatures were measured with an optical pyrometer calibrated at 1770° by noting the apparent m. p. of platinum. Subsequent measurements were probably accurate to within 100°.

Thanks are offered to K. R. Melhuish for mass-spectrometric analyses of the hydrolysis gases; acknowledgment is made to the Managing Director of the Industrial Group of the U.K. Atomic Energy Authority for permission to publish this paper.

U.K. ATOMIC ENERGY AUTHORITY (INDUSTRIAL GROUP),
WINDSCALE WORKS, CUMBERLAND.

[*Received, April* 15*th*, 1957.]