The Preparation and Some Properties of Plutonium Fluorides.

By J. K. Dawson, (Miss) R. M. Elliott, R. Hurst, and A. E. Truswell.

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The milligram-scale preparation of plutonium trifluoride, tetrafluoride, and possibly two hydroxyfluorides by the reaction of hydrogen fluoride with plutonium dioxide or oxalate is described.

Precipitation of plutonium tetrafluoride from dilute aqueous solution gives a hydrate with the molecular weight of $2PuF_4,5H_2O$; vacuum dehydration of the precipitate at 300° gives plutonium trifluoride. When plutonium trifluoride is precipitated, sufficient water is trapped in the lattice to give material of composition $4PuF_3,3H_2O$. Thermogravimetric curves are described for the anhydrous fluorides and the precipitated fluorides.

The reaction of plutonium trifluoride with very dry oxygen has been studied, and by measurement of the oxygen pressure developed by the reverse reaction the free energy of formation of plutonium tetrafluoride has been deduced as 400 kcal./mole at 298° K.

Plutonium tetrafluoride undergoes disproportionation in vacuum at *ca.* 900° to give the trifluoride and probably the more volatile pentafluoride.

The main contribution to the dry chemistry of plutonium fluorides available in the literature is a paper by Fried and Davidson, who describe investigations into the reaction of plutonium trifluoride with very dry oxygen and into the vacuum decomposition of plutonium tetrafluoride ("The Transuranium Elements," McGraw-Hill Co., 1949, N.N.E.S. **14**, *B*, paper 6.11). The present communication describes more extensive investigations into these systems together with observations on the preparation of the fluorides and their reactions with water vapour.

Experimental

1. *The Thermo-balance.*—The thermogravimetric curves described below were obtained on a silica spring balance of sensitivity 1·30 mm./mg. using 5—30 mg. of material. The samples were supported in a platinum boat on the end of a long extension fibre so that the silica spring was well above the heated zone around the sample. Weight changes were observed by following the movement of an index fibre with a cathetometer which could be read to 0·01 mm. A curve was plotted for the change of apparent weight of the empty platinum boat with increasing temperature and this was applied as a correction to the experiments with the plutonium compounds present.

When change of weight with temperature was being observed, the rate of rise of temperature was kept to about 3°/min.

2. *Preparation of Plutonium Fluorides by Hydrofluorination.*—Hydrated plutonium tetraoxalate, $Pu(C_2O_4)_2,6H_2O$, was precipitated from an aqueous solution of the tetranitrate by addition of oxalic acid crystals. After being centrifuged and washed with very dilute nitric acid, the precipitate was slurried into platinum boats for conversion into oxide or for direct fluorination in a nickel tube.

Conversion of the oxalate into oxide was performed by heating it in a stream of air to about 300°. A stream of anhydrous hydrogen fluoride from a cylinder could be passed through the tube, and oxygen could be added to the hydrogen fluoride either pure or as air. The amount normally added was about 5—10%, although this could be varied over wide limits without affecting the product. The preparations were performed up to the 10 mg. scale and the results are shown in Table 1; *X*-ray powder diffraction photographs were used to determine the product by comparison with Zachariasen's data (*op. cit.*, paper 20.5).

3. *Reduction of* PuF_4 *with Hydrogen or Sulphur Dioxide.*—The tetrafluoride (1—5 mg.) was heated for 1 hr. in a platinum boat inside a Pyrex tube, which was swept out by the reducing gas before heating was commenced. The nature of the product was determined from *X*-ray diffraction photographs and the results are quoted in Table 2.

4. *Precipitation of Plutonium Tetrafluoride from Aqueous Solution.*—(*a*) Aqueous hydrofluoric acid was added to a dilute solution of quadrivalent plutonium in 3N-nitric acid in a plastic

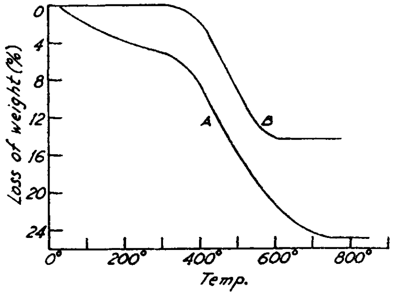
centrifuge tube. The pale pink precipitate was centrifuged, transferred to a glass tube, washed with ethanol, and dried at room temperature in a high vacuum.

TABLE 1. *The preparation of* PuF_3 *and* PuF_4.

Conditions	Temp.	Colour of product	Product	Conditions	Temp.	Colour of product	Product
Oxalate or	25°	Stone	Hydroxyfluoride (?)	Oxalate +	230°	Blue-purple	PuF_3
oxide +	100	,,	,,	HF	530	,,	PuF_3
HF	150	,,	,,		640	,,	PuF_3
					715	,,	PuF_3
Oxide +	450	V. pale pink	PuF_4		780	,,	PuF_3
HF +	530	Light brown	PuF_4				
oxygen	600	,,	PuF_4	Oxalate +	200	Cream	PuF_4
	640	,,	PuF_4	HF +	300	V. light brown	PuF_4
				oxygen	400	,,	PuF_4
PuF_3 +	450	Pink-brown	PuF_4		530	Light brown	PuF_4
HF +	530	Brown	PuF_4		600	,,	PuF_4
oxygen	630	,,	PuF_4				

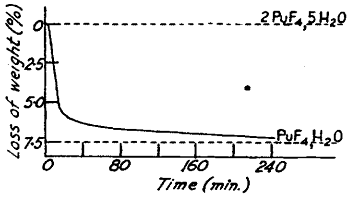
A 17·78 mg. sample was heated in air, and the thermogravimetric curve is shown in Fig. 1, where it is compared with a similar curve on a 12·71-mg. sample of anhydrous plutonium tetrafluoride prepared by hydrofluorination. The total weight change on the precipitated fluoride from room temperature to the final plateau (PuO_2 according to the *X*-ray diffraction pattern) was 24·9% (Calc. for $2PuF_4,5H_2O \longrightarrow 2PuO_2$: 24·75%).

FIG. 1.



A, Precipitated plutonium tetrafluoride.
B, Anhydrous plutonium tetrafluoride prepared by hydrofluorination of the dioxide.

FIG. 2.



(*b*) Small portions of the same fluoride precipitate (~200 μg.) were heated *in vacuo* and the composition of the product was determined from *X*-ray powder photographs (Table 3).

TABLE 2. *Reaction of* PuF_4 *with hydrogen and sulphur dioxide.*

$PuF_4 + H_2$				$PuF_4 + SO_2$			
Temp.	Product	Temp.	Product	Temp.	Product	Temp.	Product
100°	No reaction	230°	PuF_3	270°	No reaction	385°	$PuF_3 + PuF_4$
200	,,	300	PuF_3	300	$PuF_3 + PuF_4$	500	$PuF_3 + PuO_2$
220	,,						

TABLE 3. *The effect of vacuum heating on* $2PuF_4,5H_2O$.

Temp.	Pressure (mm. Hg)	Product
100°	10^{-4}	No change
200	10^{-4}	No *X*-ray diffraction pattern
300	10^{-5}	~90% PuF_3, ~10% PuO_2

(*c*) A sample of the fluoride precipitate (~30 mg.) was heated as in (*a*) at a uniform rate to 900° in a vacuum of 10^{-4} mm. Hg. No distinct plateaux were observed, but above 700° the slope of the weight–temperature curve increased considerably, and this was later seen to be due to sublimation of some material from the boat on to the surrounding silica tube. An *X*-ray diffraction photograph of the product showed it to be a mixture, PuF_3 ~80% + PuO_2 ~20%.

(*d*) A run similar to (*c*) was stopped at 550°, and the product found to be a PuF_3–PuF_4 mixture by *X*-ray diffraction photographs.

(*e*) The hydrated plutonium fluoride (22·62 mg.) was heated at 200° in a platinum boat suspended from the silica spiral, the system being pumped to 10^{-4} mm. Hg. The weight–time curve is shown in Fig. 2; after 200 min. the weight was still decreasing very slowly, the loss observed being 7·1% [Calc. for $2PuF_4,5H_2O \longrightarrow 2(PuF_4,H_2O)$: loss, 7·5%].

5. *Precipitation of Plutonium Trifluoride from Aqueous Solution.*—(*a*) Plutonium(IV) in dilute nitric acid solution was reduced to plutonium(III) by addition of hydroxylamine hydrochloride, and a precipitate was obtained on addition of aqueous hydrofluoric acid. The precipitate was centrifuged, washed twice with water, slurried from the plastic tube in which precipitation had taken place into a glass tube, washed with acetone, and dried at room temperature/10^{-5} mm.

On ignition in air, a 15·95 mg. sample of the dried precipitate gave the thermogravimetric curve shown in Fig. 3; the total weight loss from room temperature to the final PuO_2 plateau (confirmed as PuO_2 by *X*-ray diffraction and shown to have zero fluorine content by analysis) was 12·3%. Theoretical weight changes could be :

$PuF_3,H_2O \longrightarrow PuO_2$, 13·69%
$4PuF_3,3H_2O \longrightarrow 4PuO_2$, 12·44%
$2PuF_3,H_2O \longrightarrow 2PuO_2$, 11·15%
$PuF_3 \longrightarrow PuO_2$, 8·44%

The precipitate gave a very diffuse *X*-ray diffraction pattern, closely related to that of anhydrous plutonium trifluoride. Small samples which were ignited to temperatures of 250°, 275°, and 320° showed the gradual fading of the *X*-ray diffraction lines without the appearance of any other pattern; at 400° the diffraction pattern was that of plutonium dioxide.

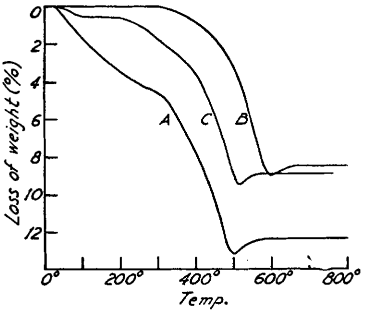


FIG. 3. *A, Precipitated plutonium trifluoride.*
B, Anhydrous plutonium trifluoride freshly prepared by hydrofluorination of the dioxide.
C, Anhydrous plutonium trifluoride after 12 days in air.

(*b*) Further thermogravimetric curves on other samples of precipitated plutonium trifluoride gave 12·25, 12·6, and 12·4% weight changes from room temperature to the PuO_2 plateau.

(*c*) For comparison, the thermogravimetric curve on a sample of anhydrous plutonium trifluoride (29·63 mg.) freshly prepared by hydrofluorination is shown also in Fig. 3. There was no detectable weight change below 300°; the total weight loss between this plateau and the final one beginning at *ca.* 700° (PuO_2) was 8·4% (Calc. for $PuF_3 \longrightarrow PuO_2$: 8·44%).

(*d*) A sample of anhydrous plutonium trifluoride (10·7 mg.), prepared in the same way as sample (*c*), was exposed to laboratory air for 12 days. The thermogravimetric curve then obtained is shown in Fig. 3. The weight change from the plateau at 100—200° to the final plateau was 8·32%, and the curve shows that the trifluoride adsorbed 0·6% of moisture from the atmosphere.

(*e*) A sample of anhydrous plutonium trifluoride prepared by dry hydrofluorination of PuO_2 was kept under dilute aqueous hydrofluoric acid for 3 days. After being washed with acetone and dried in high vacuum at room temperature, the compound gave a thermogravimetric curve very similar to that of the original trifluoride and had not taken up any water.

(*f*) Plutonium trifluoride was precipitated as in (*a*) except that the temperature of precipitation was 80°. The thermogravimetric curve on a 12·10 mg. sample then gave 10·1% loss of weight between room temperature and the plutonium dioxide plateau, *i.e.*, less water had been trapped in the trifluoride lattice than when precipitation was performed at a lower temperature.

6. (*a*) *Reaction of* PuF_3 *with Oxygen.*—As a result of initial experiments at 400—600° it was found necessary to perform a triple condensation of cylinder oxygen at liquid-nitrogen temperature in glass-bead-filled traps, followed by evaporation at liquid-oxygen temperature, in order to dry the gas sufficiently to prevent the formation of 100% PuO_2 as the reaction

product. The third trap, reaction tube, and trifluoride were pumped down to a vacuum of about 10^{-5} mm. Hg, and the trifluoride was degassed at 100° for several hours before admission of oxygen. The apparatus is shown in Fig. 4 together with the additions necessary for a study of the reverse reaction. The forward reactions were carried out for 30 min., and Table 4 gives a summary of the results obtained, the approximate proportions of the plutonium compounds in the products having been determined from *X*-ray powder diffraction photographs. An alternative method of estimating the relative amounts of PuF_4 and PuO_2 is shown in Table 5.

TABLE 4. *Reaction of* PuF_3 *with dry oxygen.*

Temp.	PuF_3 (mg.)	Product, % PuF_3	Product, % PuF_4	Product, % PuO_2
400°	45	60	40	
500	50	—	60	40
600°	48	—	60	40

6. (*b*) *Reverse reaction.*—Initial experiments to measure the oxygen pressure developed by the reverse reaction failed owing to the production of pure PuO_2 instead of PuF_3. This was probably due to the absorption of water vapour during the removal of the reaction mixture (PuF_4 + PuO_2) from the apparatus in order to extract samples for analysis. Only a trace of water vapour would be required to set off a chain reaction at higher temperatures involving the walls of the reaction tube, similar to the well-known decomposition of UF_6, *i.e.*, $PuF_4 + 2H_2O \longrightarrow PuO_2 + 4HF$; $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$. The only way in which this could be avoided was by performing both reactions in the same tube, and not taking out samples; as soon as the forward reaction was complete, the apparatus was re-evacuated overnight. The pressure was measured on a U-manometer (Fig. 4) containing a low vapour-pressure silicone oil of *d* 1·09. The oil was thoroughly degassed by warming during the preliminary evacuation of the apparatus, and pumping was continued on the vacuum-line side of the manometer during the actual pressure measurements. The results are given in Table 6.

FIG. 4.

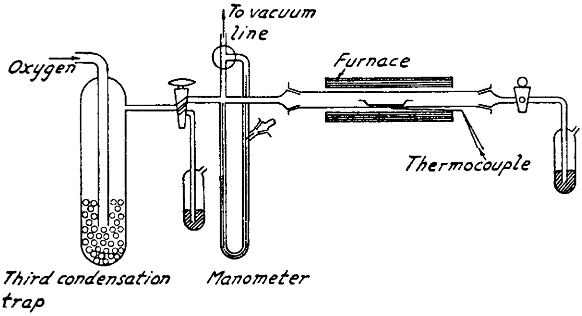
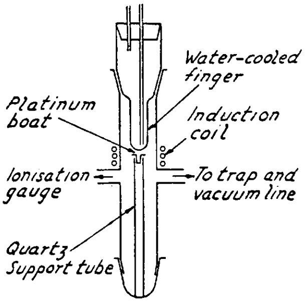


FIG. 5.



7. *Disproportionation of Plutonium Tetrafluoride.*—The apparatus is shown in Fig. 5; PuF_4 was placed in the platinum boat and the apparatus was pumped down to 10^{-5} mm. Hg,

TABLE 5. *Magnetic susceptibilities at* 300° K *of the reaction product.*

Compound	$\chi_g \times 10^6$	Deduced composition of reaction product (%): PuF_4	Deduced composition of reaction product (%): PuO_2
Pure PuF_4	5·59	—	—
Pure PuO_2	2·69	—	—
Product of reaction at 600°	4·20	52	48
Product of reaction at 700°	4·54	64	36

TABLE 6. *The pressure of oxygen developed over a mixture of* PuF_4 *and* PuO_2.

Approx. composition of reaction mixture (%)		Temp.	Pressure developed	Approx. composition of reaction product (%)	
PuF_4	60	510°	Increased slowly for 7 hr., then remained constant for $1\frac{1}{2}$ hr. at 7·2 mm.	PuF_3	70—80
PuO_2	40			PuO_2	30—20
PuF_4	60	800	Increased slowly for 3 hr., then remained constant for 2 hr. at 7·5 cm.	PuF_3	70—80
PuO_2	40			PuO_2	30—20

the tetrafluoride being degassed by warming to about 200°. An isolation tap was then closed, and heating to reaction temperature was commenced; the pressure measured by the ionisation gauge increased to $\sim 10^{-3}$ mm. Hg, but returned to its original value on cooling. The reaction conditions are given in Table 7. The residue in the boat was purple and was shown to be PuF_3 by its *X*-ray diffraction pattern. About 2 mg. of light brown sublimate were scraped off the condensation finger; this material gave no *X*-ray diffraction pattern, but duplicate analyses on the 300—500-μg. scale, performed by air ignition to plutonium dioxide, gave 19·2 and 19·4% decrease in weight (theoretical values are: $PuF_3 \longrightarrow PuO_2$, 8·5%; $PuF_4 \longrightarrow PuO_2$, 14·0%; $PuF_5 \longrightarrow PuO_2$, 18·9%).

TABLE 7. *Disproportionation of plutonium tetrafluoride.*

PuF_4 (mg.)	Heating time, min.	Temp.	Residue in boat	Deposit on finger
50	5	970°	PuF_3	Grey-brown
30	10	920	PuF_3	„ (~2 mg.)

DISCUSSION

Dry Preparation of PuF_3 *and* PuF_4.—A suitable starting material for the preparation of the plutonium fluorides is the dioxide. The latter is obtained in various states of subdivision by the air ignition of many plutonium compounds; at one end of the scale is plutonium hydroxide, which gives a dense, rather unreactive oxide, and at the other end is the oxalate, $Pu(C_2O_4)_2,6H_2O$, which may be precipitated from aqueous solution and gives a very fluffy oxide more suitable for subsequent conversion into halides (Westrum, *op. cit.*, paper 6.57). The present study shows that the oxalate can be fluorinated directly with gaseous hydrogen fluoride without forming the oxide as an intermediate compound.

On the milligram scale, the hydrofluorination of plutonium dioxide does not follow the course (1):

$$PuO_2 + 4HF \longrightarrow PuF_4 + 2H_2O \quad \quad (1)$$

The product of the reaction of excess of high-quality cylinder hydrogen fluoride with either plutonium dioxide or oxalate is actually plutonium trifluoride over the temperature range 250—750°; the tetrafluoride is produced only if oxygen is added to the hydrogen fluoride stream.

A possible explanation of these facts is that the hydrogen fluoride contains traces of a reducing impurity such as sulphur dioxide or hydrogen produced by reaction of the hydrogen fluoride with the metallic walls of the cylinder and the reaction vessel. Qualitative experiments to determine whether plutonium tetrafluoride is easily reduced by sulphur dioxide or by hydrogen were performed and the results are shown in Table 2. It appears that sulphur dioxide is not a good reducing agent for plutonium tetrafluoride and that the production of plutonium trifluoride from the dioxide is probably explained according to (2).

$$PuO_2 + 3HF + \tfrac{1}{2}H_2 \longrightarrow PuF_3 + 2H_2O \quad \quad (2)$$

It is possible to write an expression (3) for the production of plutonium trifluoride without postulating the presence of hydrogen, and the thermodynamic data given by Brewer (Brewer *et al.*, *op. cit.*, paper 6.40; Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," McGraw-Hill Co., 1949, N.N.E.S., **19**, *B*, paper 5) (Table 9) show that the free-energy change of this reaction is —5 kcal./mole at 298° K and +2·5 kcal./mole at 500° K. The reaction is thus thermodynamically possible, and in this respect is similar to reaction (1) which has a free-energy change of —1 kcal./mole at 500° K.

$$2PuO_2 + 6HF \longrightarrow 2PuF_3 + 3H_2O + \tfrac{1}{2}O_2 \quad \quad (3)$$

Since the hydrogen will certainly be present owing to the reasons given above, reaction (2) seems the most probable one to represent the experimental conditions.

Between room temperature and 150° reactions (1), (2), and (3) do not apply. We have obtained two distinct compounds other than the simple fluorides in this temperature range; possibly they are hydroxyfluorides of the type $Pu(OH)_2F_2$ or $Pu(OH)F_3$ which might be expected to be intermediates in the formation of PuF_4 from PuO_2. It is hoped to investigate further the composition and reactions of these low temperature products; they are readily converted into plutonium trifluoride in a stream of hydrogen fluoride and hydrogen, or into the tetrafluoride in a stream of hydrogen fluoride and oxygen by raising the temperature above 200°.

Precipitation of the Fluorides from Aqueous Solution.—It is reported that uranium tetrafluoride, precipitated from aqueous solution by the addition of aqueous hydrofluoric acid, takes the form of a hydrate, $2UF_4,5H_2O$, and that the main part of the water of crystallisation is removed in vacuum at 200° (Grosse, quoted in " The Chemistry of Uranium," McGraw-Hill Co., 1949, N.N.E.S., 5, 360). The present experiments show that a similar hydrate is obtained with plutonium, and since anhydrous plutonium tetrafluoride is stable to moisture up to 300° (Fig. 1), it was supposed that heating the hydrate in vacuum to 200° might give the anhydrous tetrafluoride by analogy with uranium. According to Fig. 2, the precipitated hydrate under these conditions affords a compound having the molecular weight of PuF_4,H_2O (in such a condition that it gave a blank X-ray diffraction photograph). At higher temperatures the product of the vacuum dehydration is plutonium trifluoride. This rather surprising result might be accounted for by assuming that some of the water liberated from the crystals reacts with the tetrafluoride to produce plutonium dioxide and this dioxide reacts with more tetrafluoride according to (4) :

$$\begin{array}{l}
PuF_4 + 2H_2O \longrightarrow PuO_2 + 4HF \\
3PuF_4 + PuO_2 \longrightarrow 4PuF_3 + O_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4) \\
\hline
4PuF_4 + 2H_2O \longrightarrow 4PuF_3 + 4HF + O_2 \quad . \ . \ . \ . \ . \ . \quad (5)
\end{array}$$

By using the free energies of formation taken from Table 9, reaction (5) may be calculated to have a free-energy change of +14 kcal. at 500° K and —17 kcal. at 1000° K. At the temperature of the experiments, the equilibrium pressure developed by the reaction may be calculated to be $\sim 10^{-3}$ mm. Hg, and pumping the system to 10^{-4} mm. Hg would help the attainment of the right-hand side of equation (5). The product was found to be contaminated with a small percentage of plutonium dioxide.

The thermogravimetric curves obtained on samples of the trifluoride precipitated at room temperature from aqueous solution and dried at room temperature in a high vacuum are different from those obtained by using trifluoride prepared by high-temperature hydrofluorination (Fig. 3, curves A and B). According to the weight change observed on ignition to plutonium dioxide, the precipitate contained three-quarters of a molecule of water of crystallisation per plutonium atom. Heating this material in vacuum to about 300° produces the anhydrous fluoride but the change is not reversible. This is shown by the fact that trifluoride prepared in the dry way and kept in contact with dilute aqueous hydrofluoric acid for several days still gave the thermogravimetric curve for the anhydrous salt ; also from an experiment in which the precipitated trifluoride was heated in a sealed tube, one end being cooled so that drops of water condensed there, and on standing at room temperature there was no evidence of the water's recombining with the plutonium trifluoride.

The X-ray diffraction pattern of the precipitated plutonium trifluoride was very diffuse but the spacings appeared to be the same as in the anhydrous salt. It is difficult to see how the water could be accommodated in the trifluoride lattice unless it were to be trapped between layers of fluorine atoms, giving rise to X-ray line intensity variations which we would not have observed owing to the diffuse nature of the films (for the structure of anhydrous plutonium trifluoride, see Zachariasen, *op. cit.*). The precipitate is probably not a definite complex since it begins to lose weight as soon as the temperature is raised, and the amount of water it contains varies with the temperature of precipitation.

These results may mean that a small correction will be necessary to Westrum and Eyring's calorimetric measurement of the heat of formation of plutonium trifluoride ("The Transuranium Elements," McGraw-Hill Co., 1949, N.N.E.S. **14**, *B*, paper 6.52). This was obtained by observation of the heat of precipitation from aqueous solution on the assumption that the precipitate is the anhydrous compound.

The troughs obtained on the plutonium trifluoride thermogravimetric curves at 500—600° were not observed with other plutonium compounds. The weight increases from the troughs to the plutonium dioxide plateaux were somewhat variable, the maximum observed corresponding to the possible existence of $PuO_{1\cdot75}$. Attempts to isolate this phase were not successful, probably owing to rapid conversion into the dioxide as the sample temperature was being lowered.

Reaction of PuF_3 *with Oxygen.*—Fried and Davidson (*loc. cit.*) found that the reaction of very dry oxygen with PuF_3 at 600° did not produce PuO_2 (as had been reported previously) but rather a mixture of PuF_4 (~60%) and PuO_2 (~40%). Since they obtained PuF_3 by heating this mixture in vacuum, they postulated the reversible reaction :

$$4PuF_3 + O_2 \underset{\text{Vacuum}}{\overset{600^\circ}{\rightleftharpoons}} 3PuF_4 + PuO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Confirmation of the relative proportions of PuF_4 and PuO_2 formed in the forward reaction was obtained by the present authors from *X*-ray diffraction data (Table 4). The magnetic susceptibilities of pure PuF_4 and pure PuO_2 have been measured recently (Dawson, *J.*, 1952, 1882) and this suggested an alternative means of analysing this reaction product, the magnetic susceptibility of a mixture being directly dependent on the ratio of its components. The deduced composition of the reaction product (Table 5) was in agreement with that obtained from the *X*-ray photographs; both methods show rather more PuO_2 than the 25% to be expected from reaction (6), but this could easily be accounted for by residual water vapour in the apparatus.

From the data of Table 6 and by the use of the relation $\Delta F = RT \ln p(O_2)$, the free-energy change for the reverse of equation (6) was calculated to give the values shown in Table 8, which also gives values at other useful temperatures obtained by extrapolation and interpolation.

TABLE 8. *The free-energy change for the reverse of reaction* (6).

Temp. (° K)	298	500	783	1000	1073
ΔF, kcal.	14·8	12·2	11·3	10·6 *	10·4

* This value was interpolated; the others were extrapolated.

The free energies of formation of PuF_3 and PuO_2, taken from tables of $(\Delta F - H_{298})/T$ by Brewer (*op. cit.*), are given in Table 9, together with values for HF and H_2O required in other sections of this paper. These values being used in conjunction with the data of Table 8, the free energy of formation of PuF_4 was calculated to have the values given in the last column of Table 9.

TABLE 9. *Free energies of formation,* ΔF (*in kcal./mole*).

Temp. (° K)	PuF_3	PuO_2	HF	H_2O	PuF_4	Temp. (° K)	PuF_3	PuO_2	HF	H_2O	PuF_4
298°	356	238·2	64·9	54·6	400	1000°	315	210	65·8	46·0	353·5
500	344·5	230	65·2	52·4	387						

Disproportionation of Plutonium Tetrafluoride.—It was reported by Fried and Davidson (*loc. cit.*) that if plutonium tetrafluoride was heated in vacuum to about 900°, a residue of plutonium trifluoride was formed and a sublimate of trifluoride could be collected on a cold finger. There are two possible mechanisms by which these facts might be explained; either by the direct reaction (7) or by the successive reactions (8) and (9). They suggested that reaction (9) took place on the cold finger :

$$PuF_4 \longrightarrow PuF_3 + \tfrac{1}{2}F_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$2PuF_4 \longrightarrow PuF_3 + PuF_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$PuF_5 \longrightarrow PuF_3 + F_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We have confirmed that plutonium trifluoride is in fact formed as a residue, but our sublimate was certainly not trifluoride. The colour was rather like that of the tetrafluoride, but evidence against its being PuF_4 was that it was readily soluble in 6N-nitric acid (the original PuF_4 was not), and ignition to PuO_2 in air gave a weight change corresponding to PuF_5. The sublimate appeared to be stable in air although by analogy with UF_5 it would easily be hydrolysed.

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