

*The Hydrated Tetrafluorides of Uranium and Plutonium.*

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The tetrafluorides of uranium and plutonium form two hydrates, the higher one having 2.5 molecules of water per metal atom and the lower one 2.0 molecules of water or less. Methods for their formation have been investigated.

The lower hydrate is pseudo-cubic,  $a = 5.69 \text{ kX}$  for the uranium and  $5.63 \text{ kX}$  for the plutonium compound, and the proposed structure is similar to that of uranium dioxide, the water molecules occupying vacant uranium sites and being hydrogen-bonded to the fluorine. Very little change of cell dimension was observed over the range  $\text{UF}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{UF}_4 \cdot 0.75\text{H}_2\text{O}$ .

The fluorination, at temperatures below  $100^\circ$ , of the dioxides with gaseous hydrogen fluoride gives the lower fluoride hydrate and a second product which may be  $\text{M}(\text{OH})\text{F}_3 \cdot \text{HF}$ .

A PREVIOUS communication described the preparation of anhydrous plutonium trifluoride and tetrafluoride by the reaction of gaseous hydrogen fluoride on plutonium dioxide at temperatures above  $200^\circ$  (Dawson, Elliott, Hurst, and Truswell, *J.*, 1954, 558). The same reactants at room temperature were found to give two new products, however, and the identification of these is given below.

During this investigation, it was shown that one of the products of the low-temperature fluorination was a hydrate of plutonium tetrafluoride, identical with a hydrate which could be precipitated from aqueous solution and isomorphous with a uranium tetrafluoride hydrate obtained by adding aqueous hydrofluoric acid to uranium tetrachloride solution. The uranium precipitation was then investigated in more detail, the products were analysed and their properties observed. X-Ray diffraction photographs showed that the uranium

fluoride hydrate could be indexed on the basis of a pseudo-cubic unit cell and it will be referred to below as the "pseudo-cubic hydrate."

Some of the experiments on the fluorination of uranium and plutonium dioxides gave an additional product with a more complex X-ray diffraction photograph. The analytical and X-ray data on this phase are given below and a possible formula is assigned; it will be referred to as "product A."

Several hydrates of uranium tetrafluoride have been reported. The highest hydrate definitely to be established is  $UF_4 \cdot 2.5H_2O$ ; this was prepared by von Grosse by suspending ordinary precipitated uranium tetrafluoride in dilute aqueous hydrofluoric acid overnight ("The Chemistry of Uranium," Katz and Rabinowitch, National Nuclear Energy Series, VIII-5, McGraw-Hill Co. Inc., New York, 1951, p. 360). Khlopin and Gerling (*Zhur. Obschey Chim.*, 1936, 6, 1701) and Khlopin and Yashenko (*Isvest. Akad. Nauk, U.S.S.R., Otdel. Khim. Nauk*, 1942, 87) claim to have isolated three hydrates,  $UF_4 \cdot 2H_2O$ ,  $UF_4 \cdot 1.5H_2O$ , and  $UF_4 \cdot 0.5H_2O$ , by electrolytic reduction of uranyl fluoride in aqueous hydrofluoric acid. Bolton (*Bull. Soc. chim.*, 1866, 2, 450) found that addition of aqueous hydrofluoric acid to aqueous uranous chloride solution gave a precipitate which had the composition  $UF_4 \cdot H_2O$  after vacuum-drying or air-drying at  $100^\circ$ . It is now shown that the hydrates below the limit of  $UF_4 \cdot 2.0H_2O$  all have the same structure.

#### EXPERIMENTAL

*Analytical Procedures.*—(a) *Uranium analysis.* A thermogravimetric curve for the air-ignition of a sample from precipitation No. 8 (Table 1) is shown in Fig. 1, curve A. It will be

TABLE 1. *Precipitation of uranous fluoride from hydrochloric acid solution by the addition of 40% aqueous hydrofluoric acid.*

No.	Temp.	Concentrations		Standing time	Final wash liquid	Found, %			Mole ratio $H_2O/UF_4$
		U (mg./ml.)	HCl (M)			U	F	$H_2O$	
1	20°	50	3.7	—	COMe <sub>2</sub>	70.3	22.4	9.34	1.76
2	20	14	1.0	—	"	69.6	—	9.85	1.87
3	20	7	0.52	—	"	68.9	—	9.61	1.85
4	20	6	0.54	—	"	69.0	—	9.96	1.91
5	20	5	0.37	—	"	68.2	—	10.24	1.99
6	20	5	3.7	—	"	68.8	—	9.45	1.82
7	20	4	0.30	—	"	68.1	—	10.34	2.01
8	20	3.5	0.28	—	"	68.2	21.8	10.67	2.06
9	20	2	0.15	—	"	68.1	—	10.57	2.05
10	20	1.4	0.10	—	"	68.1	—	10.84	2.10
11	20	1.25	0.09	—	"	66.8	—	12.30	2.44
12	20	1.0	0.07	—	"	66.95	—	12.08	2.38
13	20	0.70	0.05	30 Min.	"	66.9	21.4	12.67	2.50
14	20	0.55	0.04	30 Min.	"	67.0	—	13.15	2.59
15	20	0.28	0.02	2.5 Days	"	66.9	—	12.87	2.52
16	20	0.14	0.01	—	—	No ppt. after 3 days			—
17	20	0.5	3.0	—	—	No ppt. except with very large excess of HF			—
18	11	20	1.4	—	COMe <sub>2</sub>	69.1	—	8.37	1.60
19	6	20	1.4	—	EtOH	69.8	22.2	9.20	1.74
20	20	20	1.4	—	"	69.8	22.1	9.27	1.76
21	20	20	1.4	2 Days	"	70.1	—	9.46	1.79
22	80	80	4	—	"	70.9	22.9	7.67	1.43
23	20	8.5	14	—	COMe <sub>2</sub>	70.3	—	8.24	1.55
24	20	8.5	14	—	EtOH	69.6	—	7.89	1.50
25	20	8.5	0.4	—	"	69.2	22.5	9.26	1.77

seen that constant weight was attained at temperatures above  $800^\circ$  and the product was found to be  $U_3O_8$  by X-ray diffraction analysis. Part of the thermogravimetric curve on sample 4 (Table 2), *i.e.*,  $UF_4 \cdot 2.5H_2O$ , is shown in Fig. 1, curve B, and this likewise gave a constant weight of  $U_3O_8$  above  $800^\circ$ . These facts were used as the basis for uranium analysis, other samples being heated to constant weight at about  $850^\circ$ . This was found to be not completely reliable when anhydrous uranium tetrafluoride was used, since some of the sample was oxidised only as far as  $UO_2F_2$  unless the sample was in the form of a very thin layer. This could be overcome, if it was known to have occurred, by adding a drop of sulphuric acid to the residue and re-igniting it. The hydrates were more easily converted into  $U_3O_8$  than was the anhydrous fluoride.

(b) *Plutonium analysis.* Thermogravimetric curves indicated that the product of the ignition of plutonium fluoride hydrates in air at 700° was plutonium dioxide and this was used as the basis for plutonium analysis.

(c) *Water analysis.* It was evident from the thermogravimetric curves that at 300° the product of heating the hydrates in air was mainly anhydrous uranium tetrafluoride and this was confirmed by X-ray diffraction photographs. For the actual analyses, in order to prevent partial oxidation, the samples were heated to 300° in nitrogen which had been dried by passing through a bead trap immersed in liquid oxygen. The heating time was reduced to a minimum: preliminary tests indicated that 20 min. was sufficient. As a check against excessive oxidation, a sample of  $\text{UF}_4 \cdot 1.6\text{H}_2\text{O}$  was heated to 300° for 20 min; the residue was then shaken with oxygen-free water to dissolve uranyl fluoride. Analysis of the solution for uranyl ion indicated that the extent of oxidation had been 0.5%.

Some of the first analyses were made by passing the nitrogen over the heated sample and then through Karl Fischer reagent. Back-titration of the excess of reagent with methanol of known water content and correction for an apparatus blank gave the amount of water in the sample. Preliminary trials of the method gave an  $\text{H}_2\text{O}/\text{Ca}$  ratio of 1.97 in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and an  $\text{H}_2\text{O}/\text{Ba}$  ratio of 2.06 in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Since the result obtained from the titration was found to agree with the weight loss of the sample to within 0.1 mole of  $\text{H}_2\text{O}$  per mole of  $\text{UF}_4$ , subsequent analyses were made by using the weight-change measurement only.

FIG. 1. Thermogravimetric curves for two uranium fluoride hydrates.

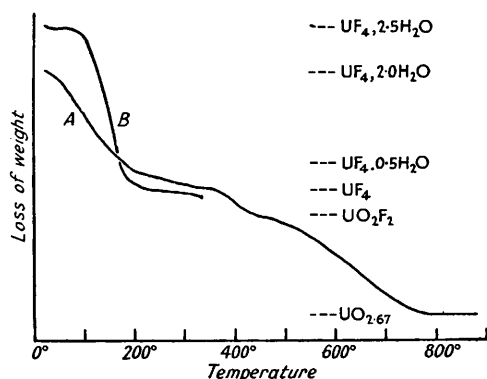
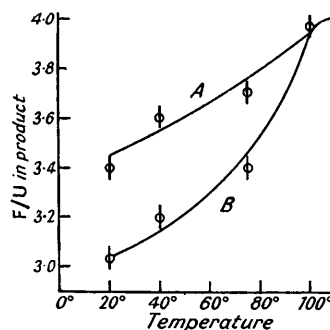
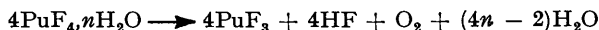


FIG. 2. Fluorination of uranium dioxide with gaseous hydrogen fluoride and hydrogen: A, brown  $\text{UO}_2$ ; B, black  $\text{UO}_2$ .



Heating of plutonium fluoride hydrates in dry nitrogen to 300° produced the trifluoride. This is similar to the behaviour in a vacuum previously observed (Dawson *et al.*, *loc. cit.*) and is probably explained according to the equation



Consequently, a direct determination of the water content of the plutonium samples was not possible, and it was obtained by analogy with the uranium compounds and by difference after analysis for plutonium and fluorine.

(d) *Fluorine analysis.* The fluorine in the samples was estimated by the pyro-hydrolytic removal of hydrogen fluoride with steam at temperatures up to 1000°, condensation of the steam-hydrogen fluoride mixture, and titration with standard alkali. Duplicates agreed usually to  $\pm 0.5\%$  of the total fluorine content.

(e) *X-Ray diffraction analysis.* X-Ray diffraction photographs of the powdered specimens were taken, filtered copper-K $\alpha$  radiation and 11.4-cm. and 19-cm. Debye-Scherrer type cameras being used. Samples of the pseudo-cubic hydrates usually gave only low-angle lines, and the film lengths on the 11.4-cm. camera were calibrated by exposing silver-wire diffraction lines on the same films.

*Uranium Fluoride System.*—(a) *Precipitation of uranium tetrafluoride from aqueous solution.* A stock solution of quadrivalent uranium was made by dissolving uranium metal in concentrated hydrochloric acid and centrifuging off any precipitate which was formed. To obtain various concentrations the stock solution was diluted as indicated in Table 1. Precipitation of the fluoride hydrate was usually carried out in a plastic tube by the addition of about 10% calculated excess

of 40% aqueous hydrofluoric acid dropwise with stirring. The effects of some variations on this technique are noted in Table 1 and, except where a definite standing time is quoted, the precipitate was centrifuged off as soon as possible, washed once with water, sludged with water into a glass tube, and washed with acetone (a few samples were washed with absolute methanol, see Table 1). The samples were dried by being kept in laboratory air at room temperature.

(b) *Reactions of UF<sub>4</sub> and UO<sub>2</sub> with aqueous hydrofluoric acid.* Anhydrous uranium tetrafluoride and the dioxide both reacted slowly with aqueous hydrofluoric acid; if the dioxide was prepared by heating uranous oxalate in hydrogen at 350°, it reacted vigorously with the hydrofluoric acid. The results are summarised in Table 2. A sample from Expt. 4 gave the thermogravimetric curve shown in Fig. 1(B).

TABLE 2. *Reactions with aqueous hydrofluoric acid at 20°.*

	Reactant	HF concn. (% w/w)	Standing time (days)	Product (X-ray)	Analysis of product
1	UF <sub>4</sub>	40	4	UF <sub>4</sub>	75.1% U
2	UF <sub>4</sub>	40	28	UF <sub>4</sub>	—
3	UF <sub>4</sub>	10	2.5	UF <sub>4</sub> ·2.5H <sub>2</sub> O	—
4	UF <sub>4</sub>	2	2	UF <sub>4</sub> ·2.5H <sub>2</sub> O	{ 66.6% U 12.4% H <sub>2</sub> O 21.8% F
5	UO <sub>2</sub>	40	6	UF <sub>4</sub> ·H <sub>2</sub> O	{ 69.8% U 8.4% H <sub>2</sub> O
6	UO <sub>2</sub>	10	2.5	UF <sub>4</sub> ·2.5H <sub>2</sub> O	—
7	UF <sub>4</sub> ·2.5H <sub>2</sub> O	10	2.5	UF <sub>4</sub> ·2.5H <sub>2</sub> O	—
8	UF <sub>4</sub> ·1.6H <sub>2</sub> O	10	2.5	UF <sub>4</sub> ·2.5H <sub>2</sub> O	—
9	UF <sub>4</sub> ·1.6H <sub>2</sub> O	2	2.5	UF <sub>4</sub> ·2.5H <sub>2</sub> O	—

(c) *Fluorination of uranium dioxide by gaseous hydrogen fluoride.* This was investigated in order to determine whether the pseudo-cubic hydrate was formed at temperatures below 100°. This complex was, in fact, identified but was usually mixed with a second product still not characterised and called complex "A" below. The results are summarised in Fig. 2. The uranium dioxide obtained by heating uranous oxalate in hydrogen at 350° was sometimes brown and sometimes black (indicating excess of oxygen over the ideal composition UO<sub>2</sub>). The products of hydrofluorination were dried in a high vacuum at room temperature before analysis. Trial experiments indicated a plateau (stable complex) on the thermogravimetric curve at 300°; heating fresh samples to this temperature to provide material for analysis gave the results shown in Table 3. The composition of the product with F/U = 3.0 is close to that of U(OH)F<sub>3</sub> [Calc.: U, 76.3; F, 18.3; (OH), 5.46%]. The products of fluorination at 75° evidently lose both hydrofluoric acid and water on heating. Complex "A" was converted into UF<sub>4</sub>·2.5H<sub>2</sub>O by reaction with 10% aqueous hydrofluoric acid for three days.

TABLE 3.

Hydrofluorination conditions	Original mixture				Complex formed at 300°			
	U, %	F, %	(O + H), %	F/U	U, %	F, %	(O + H), %	F/U
From black UO <sub>2</sub> at 20°	74.5	18.1	7.4	3.04	75.6	18.7	5.7	3.0
„ brown UO <sub>2</sub> at 75°	70.8	20.9	8.3	3.7	76.3	19.2	4.5	3.1
„ black UO <sub>2</sub> at 75°	73.7	19.1	7.2	3.4	76.3	19.7	4.0	3.2

*Plutonium Fluoride System.*—(a) *Fluorination of PuO<sub>2</sub> with gaseous hydrogen fluoride at 25°.* Two products were obtained, isomorphous with the uranium compounds UF<sub>4</sub>·H<sub>2</sub>O and complex "A" described above. Usually the product was the pure pseudo-cubic compound in reactions performed on the 10–100-mg. scale, occasionally a mixture was obtained, and occasionally the complex "A" was the major phase (on the 1–10-mg. scale). Several quantitative fluorinations of plutonium dioxide were performed with gaseous hydrogen fluoride to produce the pure pseudo-cubic compound (according to the X-ray diffraction analysis) and the results are given in Table 4.

A fluorination of about 150 mg. of plutonium dioxide obtained by igniting the oxalate in air at 350° gave a vacuum-dried product with the pseudo-cubic X-ray pattern and having the analysis: Pu, 71.6; F, 23.2%. A sample of this was used to obtain a thermogravimetric curve which showed that water was lost continuously as the temperature was raised to about 300°; above this temperature there was a gradual formation of plutonium dioxide.

Complex "A" was obtained by reaction of gaseous hydrogen fluoride with plutonium dioxide at temperatures between 20° and 100°, but the amounts obtained were insufficient for

TABLE 4.

	Starting material	Drying conditions	Wt. increase (%)	Product formula
1.	15.74 Mg. PuO <sub>2</sub> (350°) *	Vacuum, 20°	22.8	PuF <sub>4</sub> ·1.0H <sub>2</sub> O
2.	15.48 Mg. PuO <sub>2</sub> (350°) .....	Air, 105°	20.1	PuF <sub>4</sub> ·0.6H <sub>2</sub> O
3.	15.90 Mg. PuO <sub>2</sub> (660°) .....	Air, 105°	21.3	PuF <sub>4</sub> ·0.8H <sub>2</sub> O

\* The number in parentheses indicates that the dioxide was obtained by ignition of the oxalate to that temperature.

analysis apart from X-ray diffraction photography. The same product was obtained irrespective of whether or not hydrogen was added to the hydrogen fluoride.

(b) *Precipitation from aqueous solution.* Stock solutions of quadrivalent plutonium in hydrochloric acid and nitric acid were found to contain negligible impurities by spectrographic analysis. After dilution of the solutions to the required concentrations (with 0.1M-acids), sufficient 40% aqueous hydrofluoric acid was added to make the solution about 10% in aqueous hydrofluoric acid and to precipitate the plutonium. The results are given in Table 5. After precipitation, the hydrate was centrifuged off, washed with acetone, and dried in air at room temperature. With the exception of sample 1, Table 5, the precipitations were done on the

TABLE 5.

	Plutonium, mg./ml.	Acid	Standing time	Product (X-ray)
1	18	HCl	30 min.	Pseudo-cubic hydrate
2	12	"	15 "	" "
3	3.2	"	3 hr.	" "
4	42	HNO <sub>3</sub>	5 min.	} Pseudo-cubic hydrate + additional phase
5	10	"	1 hr.	
6	5	"	16 hr.	} PuF <sub>4</sub> ·2.5H <sub>2</sub> O
7	1.25	"	"	
8	0.5	"	3 days	No precipitate

1—10-mg. scale and a water-wash of the precipitates was omitted since the solubilities in the plutonium system were higher than in the uranium system. Sample 1 was prepared on a scale such that after a water-wash of the precipitate there was still sufficient for duplicate plutonium and fluorine analyses: Pu, 69.3; F, 21.5%; Pu : F, 1 : 3.9 (Calc. for PuF<sub>4</sub>·1.6H<sub>2</sub>O : Pu, 69.5; F, 22.1%).

(c) *Reaction of PuF<sub>4</sub> and PuO<sub>2</sub> with aqueous hydrofluoric acid.* These experiments were performed at 20° on the 5-mg. scale in HF-resistant plastic tubes. After standing for 2 days in the aqueous hydrofluoric acid, the residues were washed with a small quantity of water, then with acetone, and were dried in air at room temperature. Both plutonium tetrafluoride and the dioxide reacted with 2, 10, and 40% aqueous hydrofluoric acid to give PuF<sub>4</sub>·2.5H<sub>2</sub>O.

## DISCUSSION

(a) *Chemical.*—The tetrafluorides of uranium and plutonium have two hydrates; the higher one, MF<sub>4</sub>·2.5H<sub>2</sub>O, has been reported previously (von Grosse, *loc. cit.*; Zachariasen, reported in Katz and Rabinowitch, *op. cit.*, p. 367). The lower hydrate MF<sub>4</sub>·*n*H<sub>2</sub>O, where 0.5 < *n* < 2, shows a simple cubic pattern on the X-ray diffraction photographs (see below).

In colour, the pseudo-cubic hydrate of uranium tetrafluoride is a somewhat darker green than UF<sub>4</sub>·2.5H<sub>2</sub>O although sometimes bluish-green samples were obtained. This variable colour was also noted by Khlopin and Yashenko (*loc. cit.*), who indicated that the effect was one of particle size since the chemical composition of the two forms was identical. There is a similar slight variation of colour in the plutonium system: the pseudo-cubic hydrate is a somewhat darker brown than PuF<sub>4</sub>·2.5H<sub>2</sub>O (in tungsten light the plutonium hydrates are pale green).

The higher hydrate, UF<sub>4</sub>·2.5H<sub>2</sub>O, is stable in a vacuum at 25° and in air up to 100°

(Fig. 1); above this temperature it rapidly loses water to form  $\text{UF}_4$ . The lower hydrates of uranium and plutonium tetrafluorides are much less stable, however; Fig. 1 shows that as soon as the temperature is raised above room temperature water is lost until the composition is  $\text{MF}_4 \cdot 0.5\text{H}_2\text{O}$ . The conversion of  $\text{MF}_4 \cdot 0.5\text{H}_2\text{O}$  into  $\text{MF}_4$  is considerably slower than the original loss of water to  $\text{MF}_4 \cdot 0.5\text{H}_2\text{O}$ .

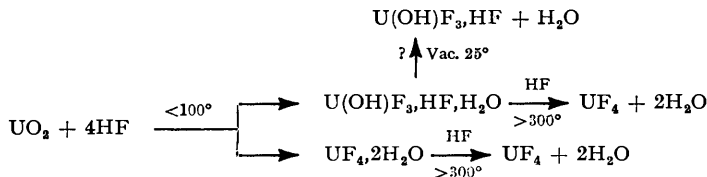
Some of the water is removed from the pseudo-cubic hydrate by shaking with dry methanol, whereas only adsorbed water appears to be removed from  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ . The higher hydrate,  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ , is formed from the lower one by suspending the latter in 2–10% aqueous hydrofluoric acid, but the process is not reversible; thus  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$  remained unchanged after standing in 40% aqueous hydrofluoric acid even though the latter produces the lower hydrate by reaction with uranium dioxide. The pseudo-cubic hydrate is probably only metastable. In the plutonium system,  $\text{MF}_4 \cdot 2.5\text{H}_2\text{O}$  is more easily formed than in the uranium system.

During attempts to make hydrates of varying composition, the precipitation of uranous fluoride from aqueous hydrochloric acid was investigated in some detail. Table 1 shows that the temperature of the solution at the time of precipitation had no marked effect on the water content of the hydrate. The hydrochloric acid concentration had only a small effect on the water content (precipitations Nos. 5, 6, 24, 25). The largest effect was due to the concentration of the uranous ion: at concentrations less than 2 mg./ml. of U(IV) there was an increase of the water content of the precipitated hydrate from  $\text{UF}_4 \cdot 2.0\text{H}_2\text{O}$  to  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ . A sample which was obtained intermediate between these values (precipitation No. 12;  $\text{UF}_4 \cdot 2.38\text{H}_2\text{O}$ ) was shown by X-ray diffraction to be a mixture. This apparent concentration effect may include an effect due to the time of standing; at low uranium concentrations the precipitation rate was so low that it was necessary to leave some of the precipitate in the supernatant liquid much longer than for the higher uranium concentrations, and it was shown in other experiments (Table 2) that the lower hydrate is converted into the higher on contact with dilute aqueous hydrofluoric acid. It was shown by X-ray diffraction that precipitations from plutonium nitrate yielded a phase additional to the hydrates observed when using chloride solutions but this was not investigated in detail.

The hydrofluorination of plutonium dioxide below  $100^\circ$  gave two products. One was the pseudo-cubic  $\text{PuF}_4 \cdot \text{H}_2\text{O}$ , and the other had an X-ray diffraction pattern isomorphous with that of the uranium complex "A" obtained by hydrofluorination of uranium dioxide at room temperature. We failed to make the plutonium complex "A" phase on a scale greater than 10 mg. and so analytical data are not available. In the uranium system, however, fluorination of uranium dioxide prepared by heating the oxalate in hydrogen at  $350^\circ$  usually gave a mixture of product "A" and the pseudo-cubic phase with an average F/U ratio of less than 4. The X-ray diffraction patterns obtained from the vacuum-dried material were very poor, but both the pseudo-cubic and the complex "A" products were detected. Thermogravimetric curves indicated that heating the products in air to  $300^\circ$  gave a stable material after some loss of weight, and the F/U ratio became closer to 3.0. Also, at  $300^\circ$  some hydrogen fluoride was distilled off during the pyrohydrolytic determination of fluorine, whereas if the product had been previously heated to  $300^\circ$  in air no appreciable amount of fluorine was removed by pyrohydrolysis below  $450^\circ$ . This indicates that some of the fluorine in complex "A" is more loosely bound than the rest.

It seems probable that the hydrofluorination products are mixtures of  $\text{UF}_4 \cdot n\text{H}_2\text{O}$  and  $\text{U}(\text{OH})\text{F}_3 \cdot m\text{HF}$ , where  $0.5 < n < 2$  and  $m < 1$ ; because of the possible variability of  $m$  it is difficult to assess the relative amounts of the complexes in any particular product. At temperatures above about  $300^\circ$ , the product of the hydrofluorination is known to be anhydrous  $\text{UF}_4$  which is produced according to the reaction  $\text{UO}_2 + 4\text{HF} \rightarrow \text{UF}_4 + 2\text{H}_2\text{O}$ , the water being carried away in the hydrogen fluoride gas stream. Below  $100^\circ$ , however, the water produced in the reaction can be accommodated in the lattice structure of the product with the formation of the pseudo-cubic lower hydrate, this structure being very similar to that of the original uranium oxide (see below). Insufficient water is produced by the reaction for the formation of the more stable  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$ . Both complex "A" and the pseudo-cubic hydrate are converted into anhydrous tetrafluoride in a stream of

hydrogen fluoride at elevated temperatures. Possibly, then, the hydrofluorination of  $\text{UO}_2$  (or  $\text{PuO}_2$ ) may follow either of the paths:



Finally, it is noteworthy that a complex,  $\text{UF}_4, \text{HF}$ , has been reported, although no X-ray data were quoted, from the reaction of  $\text{UCl}_4$  with liquid anhydrous hydrogen fluoride (Kraus, quoted by Katz and Rabinowitch, *op. cit.*, p. 365). We have not, however, observed a F/U ratio greater than 4 on samples of the pseudo-cubic complex prepared by the methods described above. Presumably, there is not an easy exchange between  $\text{H}_2\text{O}$  and HF in the lattice once the complex has been formed. In the case of thorium, we observed a fluorine-to-metal ratio greater than 4 by heating  $\text{ThF}_4, \text{H}_2\text{O}$  in hydrogen fluoride at  $400^\circ$ .

(b) *Crystallographic.*—(i)  $\text{UF}_4, n\text{H}_2\text{O}$ . The diffraction patterns of samples in the composition range  $\text{UF}_4, 0.75\text{H}_2\text{O}$  to  $\text{UF}_4, 2.0\text{H}_2\text{O}$  were identical. The pattern could be indexed, from a consideration of the  $\sin^2 \theta$  values, as simple cubic with a cell edge  $a = 2.84 \text{ kX}$  and a volume  $23 \text{ kX}^3$ . This cell is too small to contain a molecular unit  $\text{UF}_4, n\text{H}_2\text{O}$  which has a calculated volume of  $95 \text{ kX}^3$  on the basis of Zachariasen's values of 18–19  $\text{kX}^3$  for the volume of an oxygen or fluorine atom in a uranium fluoride (*Acta Cryst.*, 1951, 4, 231).

If the unit cell is enlarged to  $a\sqrt{2}$  with a volume of  $64 \text{ kX}^3$ , it is still too small to contain the  $\text{UF}_4, n\text{H}_2\text{O}$ . A further enlargement of the cell to  $a\sqrt{3}$  is not possible, as the reflection with  $\sin^2 \theta = 0.3654$  cannot be indexed. However, a unit cell of edge  $2a$ , giving a volume of  $184 \text{ kX}^3$ , will index the diffraction pattern and would also be compatible with two molecular units of  $\text{UF}_4, n\text{H}_2\text{O}$  per cell. The characteristic absences in the observed indices of the reflections are  $h, k, l \neq 2n$ .

Any distribution of the two uranium atoms on two-fold positions, irrespective of space-group, gave insufficient extinctions. So, similarly, did any distribution on one-fold positions.

A random distribution of the two U atoms over the 8 (c) special position of space-group  $\text{O}_h^5 - Fm/m$  with the eight fluorine atoms on special positions 4 (a) and 4 (b) does give the requisite number of extinctions. The reflections with  $h + k, k + l, l + h = 2n$ , where  $h, k, l = 2n + 1$ , are necessarily absent even though permitted by the space-group because the U contribution to these phases is zero and the fluorine atoms on the 4 (a) position scatter completely out of phase with those on the 4 (b) position. Intensities calculated on this basis show good agreement with the observed intensities as can be seen from Table 6.

TABLE 6.  $\text{UF}_4, 1.5\text{H}_2\text{O}$ .

$\theta$	$\sin^2 \theta$	$I_0$	$I_c^*$	$hkl$	$\theta$	$\sin^2 \theta$	$I_0$	$I_0^*$	$hk$
15.71	0.0733	m	31	200	32.75	0.2927	w	15	400
22.49	0.1463	s	100	220	37.19	0.3654	w	15	420
27.93	0.2194	w	10	222	41.45	0.4382	w+	29	224

$$* I_c \propto (1 + \cos^2 2\theta) F^2 p / \sin^2 \theta \cos \theta.$$

It appears therefore that the observed data are compatible with  $\text{UF}_4, n\text{H}_2\text{O}$ , having a cubic structure with  $a = 5.69 \pm 0.01 \text{ kX}$ , space-group  $\text{O}_h^5 - Fm\bar{3}m$ , with the two uranium atoms statistically distributed over the 8 (c) position and the eight fluorine atoms on the 4 (a) and 4 (b) positions. There would be two molecular units per unit cell, giving a coordination number of eight for the uranium. This suggested unit cell might well be a pseudo-cell, with the true cell being of lower symmetry. Attempts to index the pattern with a symmetry other than cubic failed, as did also attempts to detect lines which could be attributed to a "true" cell.

The water molecules in this structure would presumably be accommodated on the

8 (c) positions at points not occupied by the uranium atoms. Thus the unit cell could contain six water molecules, giving a formula  $\text{UF}_4 \cdot 3\text{H}_2\text{O}$ .

On volume considerations, the number of molecules of water per unit cell would be unlikely to exceed four, *i.e.*,  $\text{UF}_4 \cdot 2\text{H}_2\text{O}$ , and this is confirmed by the experimental evidence. Densities calculated on the basis  $\text{UF}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{UF}_4 \cdot \text{H}_2\text{O}$  are respectively 6.32 and 5.98. For comparison, the densities of anhydrous  $\text{UF}_4$  (Burbank, U.S. Atomic Energy Commission AEC D 3216) and  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$  (Zachariasen, *loc. cit.*) are respectively 6.63 and 4.74.

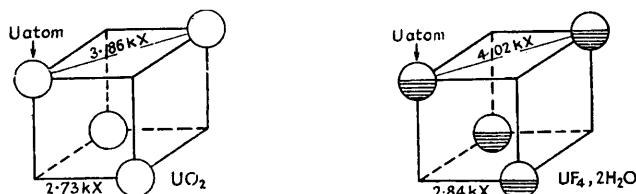
The interatomic distances for the proposed structure can be calculated as 2.46 and 2.84  $kX$  for U-F and F-F distances respectively, which are in fair agreement with the distances in other uranium fluorides. For example, in anhydrous  $\text{UF}_4$  (Burbank, *loc. cit.*) the U-F and F-F distances are respectively 2.3 and 2.8  $kX$ .

The O-F distance of 2.46 is rather small compared with the accepted radius sum of 2.76 for the oxide and fluoride ions. This seems to imply that this distance is really an O-H-F distance with the water hydrogen-bonded to the fluorine atoms.

TABLE 7.

$n$ in $\text{UF}_4 \cdot n\text{H}_2\text{O}$ .....	1.5	1.3	1.2	0.7
$a$ , $kX$ , $\pm 0.01$ .....	5.69	5.67	5.67	5.65

Removal of part of the water, which would necessarily involve rupture of some O-H-F bonds, might be thought to cause some variation in cell volume. Some indication of cell shrinkage has been observed (Table 7) on removal of some of the water in these hydrates.

FIG. 3. Comparison of the structures of  $\text{UO}_2$  and  $\text{UF}_4 \cdot 2\text{H}_2\text{O}$ .

It is of interest to compare the proposed structure with that of  $\text{UO}_2$  which is face-centred cubic. The oxygen atoms form a simple cubic array with a spacing of 2.73  $kX$ , which is directly comparable to the simple cubic array of fluorine atoms with a spacing 2.84  $kX$  in the proposed structure. The uranium atoms in  $\text{UO}_2$  can be considered as being at four corners of a cube of spacing 2.73  $kX$  with a closest-approach distance of 3.86  $kX$ . In the case of the hydrate the two uranium atoms are randomly distributed over the eight corners of a cube of spacing 2.84  $kX$ . However, as the closest-approach distance in this case is 4.02, one can consider 2 uranium atoms distributed over four corners of a cube similar to the arrangement in  $\text{UO}_2$ . The two structures are compared in Fig. 3. Apparently the structure of  $\text{UF}_4 \cdot n\text{H}_2\text{O}$  bears a closer resemblance to  $\text{UO}_2$  than to either  $\text{UF}_4$  (Burbank, *loc. cit.*) or  $\text{UF}_4 \cdot 2.5\text{H}_2\text{O}$  (Zachariasen, *loc. cit.*).

(ii)  $\text{PuF}_4 \cdot n\text{H}_2\text{O}$ . Photographs of  $\text{PuF}_4 \cdot n\text{H}_2\text{O}$ , where  $n < 2.0$ , were identical with those of  $\text{UF}_4 \cdot n\text{H}_2\text{O}$ . In the following Table the  $\sin^2 \theta$  values are given from which a cell constant  $a = 5.63 \pm 0.01$   $kX$  has been calculated.  $\text{PuF}_4 \cdot n\text{H}_2\text{O}$  thus appears to be isostructural with  $\text{UF}_4 \cdot n\text{H}_2\text{O}$  with a cubic cell slightly smaller owing to the difference in size of the heavy cations.

The calculated interatomic distances for Pu-F, F-F, and O-H-F have the values 2.43, 2.81, and 2.43  $kX$ , respectively.

$I_0$ .....	m	s	w	w	w	w	vw*	vw*	vw*
$\sin^2 \theta$ .....	0.0742	0.1494	0.2251	0.3000	0.3747	0.4493	0.5976	0.6724	0.7478

\* Lines are very diffuse.

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