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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part VII. The Decomposition of
Gaseous Plutonium Hexafluoride
by Alpha Radiation

by

Raymond P. Wagner, William A. Shinn,
Jack Fischer, and Martin J. Steindler

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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part VII. The Decomposition of Gaseous Plutonium Hexafluoride by Alpha Radiation

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ABSTRACT

Gaseous plutonium hexafluoride (PuF_6) decomposes at temperatures between 26 and 82°C to plutonium tetrafluoride (PuF_4) and fluorine, at least in part due to irradiation by alpha particles from the plutonium. The rate of decomposition is nonlinear, varying from 1.78 to 0.064% per day in the range from 0.5 to 571 days. Experiments with PuF_6 at initial pressures of 50 and 100 showed that at the lower pressure slightly lower decomposition rates are obtained. Decomposition in large vessels proceeds at slightly lower rates than decomposition in small vessels. The presence of initial PuF_4 decreases the rate of decomposition, but this decrease in rate appears to be independent of the quantity of initial PuF_4 . The presence of helium or krypton lowers the rate, but not appreciably. Oxygen or fluorine decreases the PuF_6 decomposition rate. Nitrogen reacts slowly with PuF_6 to form nitrogen trifluoride (NF_3). Higher PuF_6 decomposition rates than those observed in nickel spheres are obtained when quartz or Pyrex spheres are used. Increased nickel surface area gives increased PuF_6 decomposition rates in the absence of initial PuF_4 . At 82°C the PuF_6 decomposition rate is higher than at 26°C. No mechanism for the decomposition is postulated because it is not possible to proportion accurately the contribution of chemical reaction, thermal decomposition, and decomposition due to alpha radiation to the total decomposition observed.

I. INTRODUCTION

Ever since PuF_6 has been produced in gram quantities, all workers have reported the decomposition of PuF_6 during storage.⁽¹⁻⁵⁾ Since PuF_6

is generally stored as a solid, most reported measurements of the decomposition rate are for solid PuF_6 , and range from 0.6 to 2.1% per day. Three measurements reported by Weinstock and Malm⁽³⁾ for the average rate of decomposition of gaseous PuF_6 , 0.35, 0.063, and 0.060% per day, show the gas-phase decomposition to be substantially less than the decomposition in the solid phase. No systematic studies of the decomposition of gaseous PuF_6 up to 80°C are reported in the literature. The PuF_6 decomposition data, for temperatures below 80°C, available from the literature, are summarized in Table 1.

Table 1
DECOMPOSITION OF PuF_6 BY ALPHA RADIATION: SUMMARY OF DATA AVAILABLE FROM LITERATURE

Decomposition Rate (%/day)	Duration of Decomposition	Initial Quantity of PuF_6 (g)	Nature of Vessel Used	Method Used	Reference
<u>Solid PuF_6</u>					
1	6 to 36 days	~1	Nickel-Glass; sample in glass vessel at -70°C	Amount of $\text{PuF}_4 \cdot 1.5 \text{ H}_2\text{O}$ produced after different times; determined by weighing.	1
2	34 days	-	Pyrex	Pressure readings of PuF_6 and F_2 at 0°C.	1
1.3 ± 1	-	-	Nickel	Rate of pressure rise due to F_2 evolution when a known amount of PuF_6 decomposed in a known volume.	2
0.9	9 months	-	Nickel		2
0.6	9 months	-	Nickel		2
1.5	24 hours	0.244	Pyrex	Alpha counting of remaining solid, while determining and correcting for amount of hexavalent Pu present.	3
1.5	6.9 days	0.346	Pyrex	In 6.9-day experiment, amount of F_2 also determined.	3
1.9	-	-	Nickel	Weight of PuF_4 produced.	4
2.1	-	-	Nickel	Weight of PuF_4 produced.	4
1.1	42 days	1.073	Nickel	Weight of F_2 produced.	5
<u>Liquid Phase</u>					
1.8	25.5 hours	38	Nickel vessel at 60°C.	Weight of PuF_4 produced.	6
<u>Gas Phase</u>					
0.35	67 days	-	Nickel	Pressure change, by removing F_2 .	3
0.063	624 days	-	Small quartz cell	Amount of PuF_6 remaining, determined from the vapor pressure and a measurement of the highest temperature at which solid PuF_6 could be condensed.	3
0.060	542 days	-	Large quartz cell		3

Plutonium-239, the most abundant isotope of plutonium, has a specific activity of 2.27×10^9 d/sec-g.⁽⁷⁾ A single α particle produces more than 10^5 ion pairs over its entire path. What fraction of these ion pairs lead to total decomposition of the PuF_6 is not known.

The decomposition of PuF_6 at low temperatures is thought to be due to alpha radiation because the decomposition rate is independent of the temperature, although this has been shown only for the solid. Uranium

hexafluoride (UF_6) was shown to be decomposed by alpha radiation by Shiflett, Bernhardt, and coworkers^(8,9) who used radon-222 as a source of alpha particles and calculated a G value* of about unity for the decomposition in the temperature range from 21 to 87°C.

Some of the complexities present in the UF_6 - Rn^{222} system are absent in the PuF_6 case. The plutonium has a higher specific alpha activity than normal uranium; hence no extraneous source of alpha particles is needed. Further, plutonium as a source of alpha particles has the advantage that the alpha particles are generated in situ and are all of similar energy, whereas radon has a short half-life and has alpha-emitting daughter products of short half-life. Hence, the alpha energy from radon must be averaged. However, because of previous experiences with systems using radon, determination of the alpha dose can be readily made.⁽¹⁰⁾ The chemical reactivity of PuF_6 has thus far prevented direct dosimetry determinations.

In contrast to the many possible products from the decomposition of UF_6 , the only known decomposition product of PuF_6 is PuF_4 .^(11,12) Therefore, except for the problem of dosimetry, PuF_6 offers an opportunity to study the radiation chemistry of a relatively simple inorganic system.

This study of the radiation decomposition of PuF_6 was undertaken to provide information useful to the planning of the Fluoride Volatility Process for the reprocessing of spent nuclear fuels. The data on PuF_6 decomposition will aid in making engineering estimates of the amount of plutonium "hold-up" in the equipment due to the ever-present radiation decomposition of PuF_6 to nonvolatile PuF_4 . A determination of the extent and rate of the decomposition of gaseous PuF_6 by alpha radiation was the prime objective of this work. A brief search was also undertaken for ways to retard or enhance the decomposition, as desired. The effects of such additives as solid PuF_4 , fluorine, oxygen, nitrogen, krypton, or helium were determined.

Some of the methods used by various investigators to follow the PuF_6 decomposition are outlined in Table 1. In gas-phase PuF_6 decomposition there is no change in the total pressure of the system; hence the reaction cannot be followed by manometric methods without the condensation of PuF_6 . The method employed in the present study consisted of the determination of the amount of PuF_4 formed for a given duration of PuF_6 decomposition.

A study of the decomposition of gaseous PuF_6 caused by gamma radiation was reported by Steindler, Steidl, and Fischer.^(13,14) Partial results for the alpha decomposition of PuF_6 were reported earlier.⁽¹⁵⁾

*G = number of molecules decomposed per 100 eV absorbed.

II. EXPERIMENTAL PROCEDURES

All vessels used in this study were spherical. Most were made of nickel, but some experiments were carried out in aluminum, Monel, quartz, or Pyrex vessels. The metal spheres were obtained from the Chicago Float Works and consisted of two hemispheres welded together. The nickel and aluminum spheres had 6.35-cm outside diameter and wall thickness of 0.0635 cm. The Pyrex and quartz vessels had outside diameters of 6.36 and 6.08 cm, respectively. The Monel sphere had an outside diameter of 35.56 cm and its wall thickness was 0.20 cm. One nickel sphere was 22.86 cm OD with 0.185-cm walls.

The Monel vessel and the large nickel vessel were each fitted with two Hoke 413 valves. All the other spheres were fitted with a single, small, phosphor-bronze bellows valve (Hoke number 1479). These valves had Monel downlegs 2.0 to 2.8 cm long and were 0.635 cm in OD. In the case of the nickel vessels, the valve downlegs were silver soldered to the nickel sphere. An aluminum solder was used to join the downleg to the aluminum sphere. The Pyrex and quartz spheres had valves connected to them by means of Kovar graded seals.

Prior to the attachment of the valves, each sphere was washed with 6 N HNO_3 and thoroughly rinsed with distilled water. After assembly, the vessels were degreased with trichloroethylene. The volumes of the spheres and downlegs of the valves were determined by the weight of the distilled water (at ambient temperature) necessary to fill them. The expansion of a gas (nitrogen or helium) at a known pressure and volume to the vessel and an observation of the new pressure provided a further check on the volume of the decomposition vessel. The volumes of the nickel and aluminum spheres ranged from 125 to 129 cc, and will be referred to in this report as 127-cc vessels. The volumes of the two Pyrex spheres used were 137 and 141 cc. The quartz spheres had volumes of 119 and 122 cc. The larger nickel vessel had a volume of 5.96 liters and that of the Monel was 22.55 liters. These volumes were determined by the same methods used to determine the volumes of the small vessels.

All the vessels, except one 127-cc nickel and one 127-cc aluminum vessel, were prefluorinated with fluorine and/or chlorine trifluoride before use.

The PuF_6 used was prepared by the fluorination of PuF_4 or PuO_2 with fluorine. The reaction was carried out by circulating fluorine at 700 to 1000 mm Hg over PuF_4 in a nickel boat which was heated in a tubular furnace to 450-550°C. The recycle of fluorine was achieved by means of a Lapp Pulsafeeder remote-head diaphragm pump. A flow rate of about 800 cc/min was employed. The PuF_4 used was obtained from the radiation decomposition of previous batches of PuF_6 . There was little chance for the presence of

americium in the PuF_6 from this source, since americium does not form any volatile fluorides. Only the residue from PuO_2 in the nickel boat was found to contain americium.

The gases leaving the reaction zone were passed through two or three traps cooled to -80°C to condense the PuF_6 . The vapor pressure of PuF_6 at a temperature in the range from 20 to 25°C was used as a criterion of purity.⁽¹⁶⁾ The material collected at -80°C usually showed, at 20 - 25°C , a pressure greater than that reported for the vapor pressure of pure PuF_6 .⁽¹⁶⁾ Several batches of PuF_6 were purified by trap-to-trap fractional condensation under vacuum. The material collected at -45°C but passing through a trap held at -20°C was found to be of suitable purity. In some instances, continued pumping on a sample held at -80°C proved satisfactory.^(3,11) In most cases the most volatile fraction was removed and a middle fraction was used.

Determination of the vapor density of PuF_6 at room temperature permitted calculation of the molecular weight by use of the perfect gas law. The values for the molecular weight obtained in several volumes indicated PuF_6 to be pure and monomeric in the gas phase under these conditions.

The following experimental sequence was employed in the decomposition experiments. After prefluorination and evacuation, the vessel was weighed shortly before filling. Each vessel was weighed against a tare similar in size, shape, and material of construction to avoid the need for buoyancy corrections. The vessel was attached, by means of flare fittings, to the gas-vacuum manifold, which also led to the PuF_6 supply. After evacuating the air from the connections, the vessel was opened to the manifold, and the PuF_6 was expanded into the vessel and connecting lines until the desired pressure was reached as measured by a Booth-Cromer pressure relay⁽¹⁷⁾ connected to a mercury-in-glass manometer. The PuF_6 in the connecting lines was returned to the source container by condensation. The vessel was removed and weighed within 24 hr after filling. The difference in weight indicated the amount of PuF_6 introduced. In all cases more than one vessel was filled simultaneously from a given source of PuF_6 . The vessels were observed to gain weight slightly and slowly during storage; therefore the vessels were weighed again shortly before removal of the undecomposed PuF_6 and product fluorine at the end of the test. The vessels were reattached to the manifold and after evacuation of the connections, the residual gases in the vessels were transferred through a series of traps cooled to -80°C , an activated alumina trap, and a vacuum pump. The vessel was pumped out until a pressure of 0.1 mm or less was attained. In some cases the vessels were heated with a heat gun to 70 - 100°C during evacuation to facilitate removal of the residual gases. It has been noted that some gas is sorbed on the product PuF_4 . It is not known if the sorbed gas is PuF_6 , fluorine, or both. Weinstock and Malm⁽³⁾ have detected from 1% to 15% hexavalent plutonium in the residue from the decomposition of solid PuF_6 .

These authors believe the difficulty in removing PuF_6 completely is due to its occlusion in the decomposition product. After evacuation, the vessel valves were closed and the vessels were reweighed (within 24 hr) to determine the amount of fluorine and undecomposed PuF_6 removed.

A subtraction of the weight loss from the original amount of PuF_6 in the vessel indicates the weight of the PuF_4 formed. The percent of the initial PuF_6 which decomposed can be calculated from the weight of PuF_4 .

In order to facilitate comparisons of the decomposition under various experimental conditions (e.g., initial PuF_6 pressure or decomposition temperature), the decomposition was expressed as the average rate of decomposition per day.

The larger vessels could not be weighed on the balances available in the glovebox; hence the amount of PuF_6 introduced initially was determined by the loss of weight of the PuF_6 supply vessel. At the end of the storage period the gases were passed through two or three weighable traps cooled to -80°C , then through an activated alumina trap, samples of which were analyzed for plutonium. The percent of PuF_6 decomposed was calculated from the weight of the trapped undecomposed PuF_6 and the initial quantity of PuF_6 .

As a check of the accuracy of the weighing method used for the 127-cc vessels, several spheres were completely dissolved in nitric acid-aluminum nitrate solution after removal of the fluorine and undecomposed PuF_6 and after the final weighing. The valves were removed and the internal portions of the valve were washed thoroughly with the nitric acid solution. These washings were added to the solution containing the dissolved sphere. The final solution was analyzed for plutonium by a hexone extraction and alpha-counting method.⁽¹⁸⁾ The PuF_6 decomposition rates calculated from the weight of PuF_4 agreed well with those calculated from the radiochemical data. When available, data obtained by dissolution and counting were given instead of those obtained by weight, since the standard deviations of the decomposition rates of PuF_6 determined radiochemically were slightly less than those obtained from weight data.

In a few cases the valve was severed from the sphere and dissolved separately. The amount of PuF_6 decomposed in the valve was determined by radiochemical analysis. The results showed that enough PuF_6 was decomposed in the valve to require corrections to be made for the PuF_6 lost in all experiments carried out in vessels with Hoke 1479 valves.

III. RESULTS AND CONCLUSIONS

A. Correction for Valve Corrosion

Table 2 contains a list of results of the analysis for the PuF_6 decomposed within the Hoke 1479 valves. The component having the largest surface area within the valve was the phosphor-bronze bellows. The geometrical surface area of the bellows was about forty times greater than the geometrical surface area of the sphere. The bellows were exposed to PuF_6 only during the filling and emptying of the spheres. The exact exposure times of the bellows to PuF_6 were not recorded, but exposures on filling ranged from 15 min to 2 hr. Exposure of undecomposed PuF_6 to the bellows during the emptying operation was less than a few minutes and was neglected. During storage the bellows were exposed to the atmosphere. The amount of PuF_6 decomposed on the bellows was independent of the amount of PuF_6 decomposed within the sphere. Three reuses of the same sphere resulted in a threefold increase in the amount of PuF_6 decomposed in the valve.

Table 2
DISTRIBUTION OF DECOMPOSED PuF_6 IN 127-cc VESSELS

Experiment(s) for Which Vessel Was Used	Initial PuF_6 Introduced (mg)	mg PuF_6 Decomposed in		
		Sphere ^a	Valve	
75 day--100 mm	218.6	26.6	2.9	Average 2.5 mg experiment
2 day--100 mm	193.7	4.4	2.0	
5.6 day--100 mm	232.9			
176 day--100 mm	229.4			
75.6 day--100 mm	234.9	88.2	6.7 ^b	
571 day--50 mm	118.4	47.9	3.9	Average 4.6 mg/ experiment
571 day--50 mm	115.6 ^c	50.2	5.0	
571 day--50 mm	116.5 ^c	43.3	4.1	
571 day--50 mm	118.2 ^c	45.3	5.2	

^aThese values include the PuF_6 decomposed on the silver solder seal between the valve downleg and the sphere.

^bThis is the total accumulation from three experiments.

^cThese spheres were filled simultaneously from a common PuF_6 source; therefore their phosphor-bronze bellows had been exposed to PuF_6 for nearly equal times.

An average of 2.4 mg PuF_6 /experiment was found to be decomposed in the valve. In one set of experiments in which only 50 mm of PuF_6 was introduced, more PuF_6 was decomposed in the valves than in the spheres. Sufficient data are not available to explain this result nor to explain the apparent inverse dependence of valve corrosion on the PuF_6 pressure. The 2.4-mg (for 100-mm experiments) and 4.6-mg (for 50-mm--571-day experiments) corrections were subtracted from both the initial quantity of PuF_6 and the quantity of PuF_6 decomposed. Plutonium hexafluoride decomposition rates for those experiments listed in Table 2 were calculated directly using the experimentally determined valve corrections.

In view of the above, all data in this report are corrected versions of results reported in ANL summary reports.⁽¹⁹⁾

B. Effect of Time

The rate of decomposition of 100 mm of pure PuF_6 at $26 \pm 2^\circ\text{C}$ in a 127-cc nickel vessel is a nonlinear function of time. As shown in Figure 1,

Figure 1

AVERAGE DECOMPOSITION RATE OF GASEOUS PuF_6 VERSUS TIME (SHORT TERM)

Temperature: $26 \pm 2^\circ\text{C}$

Vessels: Nickel, Spherical

Volume: $127 \pm 2 \text{ cc}$

Initial PuF_6 Pressure: 100 mm

Uncertainty: $\pm\sigma$ (standard
deviation)

the rate decreases rapidly from $1.78 \pm 0.48\%$ * per day for the 0.5-day experiment to $0.29 \pm 0.03\%$ per day for the 12.0-day experiment. The rate decreases further to $0.18 \pm 0.03\%$ per day for a 75-day experiment and to 0.041% per day for 571 days, the longest duration for which data were obtained. These data are summarized in Table 3.

Table 3
DECOMPOSITION OF 100 mm PuF₆ STORED
IN 127-cc NICKEL VESSELS AT $26 \pm 2^\circ\text{C}$

Duration (days)	Rate (%/day)	Number of Experiments	Duration (days)	Rate (%/day)	Number of Experiments
0.5	1.78 ± 0.48	5	16.0	0.074; 0.28*	2
1.0	0.92 ± 0.27	4	75.0 ± 0.3	0.18 ± 0.03	11
2.0	0.82 ± 0.23	5	156.7	0.13	1
5.0	0.46 ± 0.12	5	229	0.15	1
5.6	0.17; 0.12*	2	327	0.081; 0.088*	2
8.0	0.32 ± 0.06	5	386	0.075	1
12.0	0.29 ± 0.03	5	571	0.041	1
12.6	0.21; 0.33*	2			

*Where only two results are available, both are listed and no standard deviation is calculated.

For an initial PuF₆ pressure of 75 mm, decomposition rates of 0.13 and 0.094% per day were found in experiments lasting 386 and 571 days, respectively.

Results obtained with an initial PuF₆ pressure of 50 mm are shown in Table 4.

Table 4
DECOMPOSITION OF 50 mm PuF₆ STORED
IN 127-cc NICKEL VESSELS AT $26 \pm 2^\circ\text{C}$

Duration (days)	Rate (%/day)	Number of Experiments	Duration (days)	Rate (%/day)	Number of Experiments
12.6	0.069	1	229	0.16	1
12.6	0.14	1	571	0.064 ± 0.009	8
157.7	0.12	2			

*Unless noted otherwise all uncertainties are one standard deviation

$$\sigma = \frac{\sum_{n=1}^k (\delta x_n)^2}{k - 1}, \text{ where } \delta x_n \text{ is the deviation and } k \text{ is the total number of values.}$$

C. Effects of Temperature

An experiment in which 94 mm of PuF_6 was stored for 21.0 days in a 127-cc nickel vessel at 82°C indicated a decomposition rate of 0.92% per day. Although there was no experiment of equal duration at 26°C , the rate at 82°C was much higher than 16.0-day (0.074, 0.028% per day) and 75-day rates ($0.18 \pm 0.03\%$ per day) at 26°C , indicating higher PuF_6 decomposition rates at higher temperatures. This conclusion was further substantiated by four experiments in which 100 mm PuF_6 was stored in 127-cc nickel vessels at 82°C for 77 days. An average decomposition rate of $0.64 \pm 0.06\%$ per day was obtained in these tests.

D. Effect of Pressure at 82°C

One experiment was performed at 82°C with 797 mm of PuF_6 decomposing for 21.8 days at an average rate of 1.09% per day. A comparison of this rate with the rate 0.92% per day (21.0 days at 82°C) obtained with an initial PuF_6 pressure of 94 mm indicated a slight increase in rate with an increase in initial PuF_6 pressure. Both experiments were carried out in 127-cc prefluorinated nickel vessels.

E. Effect of Pressure at 26°C

A summary of data indicating the effect of the initial PuF_6 pressure on the PuF_6 decomposition rate is listed in Table 5. For the short-term experiment of 12.6 days, lower rates were observed with lower initial PuF_6 pressure. However, for longer durations, the pressure effect appeared to be less significant. The 386-day results, which suggest an inverse dependence of the rate on initial PuF_6 pressure, cannot be explained at present. The validity of the 571-day--100-mm result is discussed below in Section III.J. The 50- and 75-mm, 571-day results support the direct dependence of rate on initial PuF_6 pressure. It must be noted that since the number of experiments for each set of conditions was small the conclusions are not definitive.

Table 5
THE EFFECT OF INITIAL PuF_6 PRESSURE ON THE DECOMPOSITION RATE

Duration (days)	Initial PuF_6 Pressure (mm Hg)	Number of Experiment	Rate of Decomposition of PuF_6 (%/day)
12.6	50	2	0.069, 0.14
12.6	100	2	0.21, 0.33
157.7	50	1	0.12
156.7	100	1	0.13
229	50	1	0.16
229	100	1	0.15
386	75	1	0.13
386	100	1	0.075
571	50	8	0.064 ± 0.009
571	75	1	0.094
571	100	1	0.041

F. Effect of Surface-to-volume Ratio of the Reaction Vessel

The surface-to-volume ratio was changed in two ways: first, by packing 127-cc vessels with sufficient nickel wool to increase the geometrical surface area tenfold while only slightly decreasing the volume; second, by increasing the volume (e.g., to 5.96 liters and 22.55 liters).

Experiments carried out at 26°C for 75 days in 127-cc nickel vessels with 100 mm PuF_6 resulted in decomposition rates of $0.18 \pm 0.03\%$ per day. However, when the packed spheres were used, the rate increased to $0.29 \pm 0.04\%$ per day under similar conditions. Under the same conditions (75 days, 26°C, 100 mm PuF_6) but in a larger volume (5.96 liters, no nickel wool), and hence a lower surface-to-volume ratio, the rate was 0.11% per day. These data indicated a rate dependence on the initial prefluorinated nickel surface area.

The effect of a lower surface-to-volume ratio was also observed in a 572-day experiment at 26°C with 100 mm of PuF_6 stored in a 22.55-liter Monel vessel. Under these conditions a 0.067% per day PuF_6 decomposition rate was observed. This PuF_6 decomposition rate was less than the 0.094% per day (75 mm, 26°C, 571 days) obtained with the use of a smaller (127-cc nickel) vessel. When 50 mm of PuF_6 decomposed under similar conditions in a 127-cc vessel the decomposition rate was 0.064% per day.

When the 22.55-liter Monel sphere was filled, the initial PuF_6 pressure was 100.2 mm at 27.5°C. After 572 days the total gas pressure (PuF_6 and fluorine) in the sphere was only 95 mm at 27.5°C, indicating that either PuF_6 or fluorine was sorbed on the PuF_4 or that further fluorination of the Monel vessel had taken place.

G. Effect of Container Material

Data which show the effects on the PuF_6 decomposition rate of the nature of the container material are shown in Table 6.

Table 6
DECOMPOSITION OF PuF_6 IN VESSELS OF VARIOUS MATERIALS

Vessel Material	Storage Temp (°C)	Initial PuF_6^a Pressure (mm Hg)	Decomposition (percent per day)	
			21.0-21.9 days	175.9 days
Quartz	26	100	-	0.23
Quartz	26	100	-	0.23
Pyrex	26	100	-	0.35
Pyrex	26	100	-	0.36
Nickel	26	80	1.11	-
Nickel	82	94	0.92	-
Nickel	82	797	1.09	-
Aluminum	26	75	1.15	-
Aluminum	82	87	0.67	-
Aluminum	82	88	0.79	-
Aluminum	82	787	0.80	-
Aluminum ^b	82	805	2.81	-

^aAt storage temperature.

^bVessel was not prefluorinated.

The decomposition of gaseous PuF_6 was greater in quartz (0.23% per day, over 175.9 days) and Pyrex (0.35 and 0.36% per day, for 175.9 days) vessels than in nickel vessels (0.13% per day, for 157 days; 0.15% per day for 229 days). The use of nickel or aluminum vessels resulted in similar PuF_6 decomposition rates at 26°C. The 21-day, 26°C results (nickel, 1.11% per day; aluminum 1.15% per day), however, were very high and did not fit into the decomposition versus time curve. At 82°C, the PuF_6 decomposition within the nickel vessel (1.09% per day, 0.92% per day) was greater than that within the aluminum vessels (0.67, 0.79, and 0.80% per day). It may also be noted that the effect of initial PuF_6 pressure on the rate of decomposition in aluminum vessels is not clear (see Table 6). In nickel vessels however, a greater PuF_6 decomposition was obtained with a higher initial PuF_6 pressure (1.09% per day for 797 mm of PuF_6 versus 0.92% per day with 94 mm PuF_6).

H. Effects of Prefluorination

The need for surface protection provided by prefluorination was indicated by the high rate of PuF_6 decomposition (2.81% per day) obtained within an unprefluorinated aluminum vessel at 82°C. Under similar conditions, (82°C, 787 mm, 127 cc, 21 days) but in a prefluorinated aluminum vessel, the PuF_6 decomposition rate was 0.80% per day.

One experiment was carried out with 100 mm of PuF_6 stored at 26°C in an unprefluorinated 127-cc nickel vessel for 75.0 days. The PuF_6 decomposed at an average rate of 0.21% per day compared to 0.18% per day when carried out in a prefluorinated vessel under similar conditions.

Prefluorination of the decomposition vessels varied in severity with the mildest treatment consisting of a 4-day exposure of the vessel to 400 mm F_2 at ambient temperatures. The most severe conditions consisted of exposure of the vessel to 1200 mm ClF_3 for 1 hr at ambient temperatures, followed by a 13-day exposure to one atmosphere F_2 at ambient temperature with occasional heating of the vessel to 120°C. The data on the rate of decomposition of PuF_6 were not precise enough to detect effects attributable to the differences in prefluorination of the vessels.

I. Effect of PuF_4

The effect of PuF_4 present at the start of an experiment on the rate of decomposition of PuF_6 is shown by data in Table 7. The PuF_4 in the vessels was obtained by decomposition of PuF_6 during previous experiments.

The rate of decomposition of gaseous PuF_6 was lower when the decomposition takes place in vessels which have been previously exposed to PuF_6 . In the 75-day experiments with 100 mm of PuF_6 at 26°C, decomposition proceeded at an average rate of $0.18 \pm 0.03\%$ per day in new prefluorinated vessels and at $0.13 \pm 0.03\%$ per day in reused vessels. As shown in Figure 2, the rate was independent of the quantity of PuF_4 initially

Table 7
EFFECT OF PuF_4 ON PuF_6 DECOMPOSITION

Nickel Vessels: 127 ± 2 cc
Temperature: $26 \pm 2^\circ\text{C}$, except as noted

Initial PuF_6 Pressure (mm Hg)	Weight of Initial PuF_4 (mg)	Average Decomposition (percent per day) (Number of days)				
		75	77	175.9	229	571
50	0	-	-	-	0.16	0.064
75	0	-	-	-	-	0.094
100	0	0.18	-	-	0.15	0.041
100 ^a	0	-	0.64 ^b	-	-	-
50	8.6	-	-	-	0.19 ^c	-
75	1.8	-	-	-	-	0.088
100	1.4	-	-	0.24	-	-
100	1.9	-	-	-	-	0.089
100	2.0	-	-	0.21	-	-
100	5.5	-	-	-	-	0.092
100	9.9 to 347.1	0.13 ^d	-	-	-	-
100 ^a	19.7 to 33.2	-	0.52 ^e	-	-	-

^aAt 82°C .

^b $\pm 0.06\%$ per day; an average for 4 experiments.

^c232 days instead of 229 days.

^d $\pm 0.03\%$ per day; an average for 25 experiments.

^e $\pm 0.12\%$ per day; an average for 6 experiments.

Figure 2

RATE OF DECOMPOSITION OF PuF_6 VERSUS
QUANTITY OF PuF_4 INITIALLY PRESENT

Vessels: Nickel spheres
Volume: 127 ± 2 cc
Decomposition Time: 75.2 ± 0.6 days
Temperature: $26 \pm 2^\circ\text{C}$
Initial PuF_6 Pressure: 100 mm
Uncertainty: $\pm \sigma$ (standard deviation)

present. As little as 1.8 mg PuF_4 , initially present in the 571-day experiment with 100 mm of PuF_6 at 26°C , was sufficient to lower the rate from 0.094 to 0.088% per day. The effect of the initial presence of PuF_4 was also observed at 82°C , the 77-day rates being lowered from 0.64 ± 0.06 to $0.52 \pm 0.12\%$ per day. The 232-day rate (0.19% per day) however, was high when compared to the 229 day rate (0.16% per day) obtained in the absence of initial PuF_4 .

Two of the spheres, packed with nickel wool to increase the surface area, were reused in 77-day experiments (100 mm PuF_6 at 26°C) to determine the effect of the PuF_4 which remained from the first use of these vessels. Rates of decomposition of plutonium hexafluoride of 0.12 to 0.17% per day were found. These rates were substantially lower than the $0.29 \pm 0.04\%$ per day obtained for the first PuF_6 decomposition experiments within these vessels.

J. The 571-day, 100-mm Result

It is not possible at present to discredit the 100-mm, 571-day experiment or to explain the low PuF_6 decomposition rate (0.041% per day). Determination of the amount of PuF_4 formed by weight and by radiochemical analysis gave similar results. The low rate (0.041% per day) when compared to other 571-day results indicated that an increase in the initial PuF_6 pressure results in a decrease in decomposition rate, that the presence of initial PuF_4 increases the PuF_6 decomposition rate, and that an increase in container volume results in higher PuF_6 decomposition rates. All these conclusions are in opposition to the conclusions on the effects of PuF_6 pressure, initial PuF_4 , and container volume drawn from other 571-day experiments (e.g., 75 mm PuF_6 versus 50 mm PuF_6) and 75-day experiments. In view of this, the 100-mm, 571-day experiment must be deemed suspect.

K. Effects of Gaseous Additives

All experiments with gaseous additives employed 100 mm of PuF_6 and were carried out at $26 \pm 2^\circ\text{C}$. The two decomposition times employed were 74.7 to 76.6 days and 229 to 232 days. Either fluorine, oxygen, nitrogen, krypton, or helium was added to the filled decomposition vessel usually within 11 days after the introduction of PuF_6 . The rates of PuF_6 decomposition in these binary gas mixtures are listed on Table 8.

The presence of fluorine decreased the PuF_6 decomposition rate. When fluorine was added to the 100 mm of PuF_6 in spheres containing no PuF_4 initially, the PuF_6 decomposition rates for periods of 74.7 days and 230 ± 1 days were less than those found for the same periods when only PuF_6 was present at the start of the decomposition. For a decomposition period of 74.7 days, the average rates of decomposition of PuF_6 in the presence of added fluorine generally decreased with increasing fluorine pressure. When the duration of the experiment was 230 ± 1 days, fluorine reduced the PuF_6 decomposition rate from 0.15% per day for pure PuF_6 to

0.022 (100 mm PuF₆-2280 mm fluorine) and 0.025% per day (100 mm PuF₆-682 mm fluorine) for PuF₆-fluorine mixtures.

Table 8

RATES OF ALPHA DECOMPOSITION OF GASEOUS PuF₆ MIXTURES

Spherical Nickel Vessels: 125 to 129 cc
 Storage Temperature: 26 ± 2°C
 Initial PuF₆ Pressure: 100 mm
 Initial Weight of PuF₆: 215 to 250 mg

Second Gas Component	Pressure of Second Gas Component (mm Hg)	Average Rate of PuF ₆ Decomposition (percent per day)	
		74.7-76.6 days	229-231 days
None	-	0.18	0.15
Fluorine	138	0.068	-
	395	0.11	-
	3610	0.039	-
	682	-	0.025
	2280	-	0.022
Oxygen	148	0.085	-
	430	0.082	-
	2610	0.099 ^a	-
	658	-	0.055
	660	-	0.073
Nitrogen	88	0.44	-
	119	0.46	-
	382	0.54	-
	1080	0.62 ^b	-
	2670	0.70 ^b	-
	649	-	0.40
	653	-	0.42
Krypton	2250	-	0.34 ^c
	673	-	0.078
	695	-	0.069
Helium	3720	-	0.10
	677	-	0.097
	680	-	0.14
	2230	-	0.10

^aNo oxygen-fluorine compounds (e.g., OF₂) were found by an infrared scan of the gases which were not condensable at -80°C.

^bAn infrared scan of the product gases after removal of PuF₆ showed NF₃ to be present.

^cAn infrared scan showed NF₃ to be present. X-ray analysis of the solid suggested it to be amorphous PuF₄.

Addition of oxygen also decreased the PuF₆ decomposition rate appreciably. Average decomposition rates of 0.089 ± 0.009% per day were obtained in 74.7-day experiments. A slight increase in PuF₆ decomposition rate was observed with an increase in oxygen pressure. These rates are to be compared with the decomposition rate of 0.18% per day obtained with PuF₆ alone in the 75-day experiments. Similar reductions in rate were observed in experiments in which PuF₆ was stored for 231 days in the presence of oxygen. X-ray diffraction analysis of the solid remaining after a 231-day decomposition in the presence of oxygen showed the

solid to be amorphous PuF_4 ; no PuO_2F_2 was found. An infrared scan of the gases not condensable at -80°C indicated that no oxygen-fluorine compounds were produced in an experiment in which 100 mm PuF_6 was mixed with 2610 mm oxygen. There appeared to be no evidence of reaction with oxygen.

The presence of helium during long (230 days) experiments resulted in an average decomposition of PuF_6 of $0.11 \pm 0.02\%$ per day which appeared to be unrelated to the pressure of helium. Modest (approximately 680 mm Hg) pressures of krypton produced an average decomposition rate of 0.073% per day. One experiment carried out at high pressures of krypton (3720 mm Hg) produced a slightly greater average rate of decomposition (0.10% per day). This decomposition rate was close to the value obtained with PuF_6 alone (0.15% per day).

The presence of nitrogen greatly increased the extent and rate of PuF_6 decomposition. The 75.9-to-79.6-day decomposition experiments (see Figure 3) showed that the amount of PuF_6 decomposed increased with increasing nitrogen pressure. These results are to be compared with a total decomposition of 13.5% (0.18% per day) in 75-day experiments without nitrogen. Experiments carried out for 231 days showed an average decomposition rate for PuF_6 (initial pressure--100 mm Hg) of 94.7% (0.41% per day) when approximately 650 mm Hg nitrogen was added to PuF_6 . A 3.5-fold increase in nitrogen pressure resulted in a lower decomposition (78.5%). These results were much higher than the 34.6% (0.15% per day decomposition rate) obtained with PuF_6 alone in the 229-day experiment.

Figure 3

DECOMPOSITION OF PuF_6 GAS VERSUS PRESSURE OF NITROGEN GAS

Vessel:	Nickel sphere
Volume:	127 ± 2 cc
Decomposition Time:	76.2 ± 0.4 days
Temperature:	$26 \pm 2^\circ\text{C}$
Initial PuF_6 Pressure:	100 mm
Uncertainty:	Estimated experimental error

The very high PuF_6 decomposition rates found in PuF_6 -nitrogen mixtures were due at least in part to a slow reaction between nitrogen and PuF_6 or nitrogen and the fluorine formed. The reaction products were

NF_3 and PuF_4 . The occurrence of a reaction with nitrogen was confirmed by examination of the gaseous products. In three of the 76.2-day experiments with nitrogen present, the gases remaining at the end of the decomposition period were passed through several traps cooled to -80°C to remove the undecomposed PuF_6 . The gases were then passed through a trap cooled to -196°C to remove any condensable compounds. The fluorine and nitrogen were removed by evacuation. An infrared spectrum of the gas condensed at -196°C showed it to be NF_3 , which is characterized by a strong peak at 1032 cm^{-1} and a very strong peak at 905 cm^{-1} .⁽²⁰⁾ Nitrogen trifluoride was also observed as a product in an experiment carried out for 229 days with 2250 mm Hg nitrogen. An X-ray diffraction pattern was obtained for the solid formed in this experiment and showed only amorphous PuF_4 or PuF_4 of small particle size. Not enough information was available to determine if the nitrogen reacts with the PuF_6 or if the nitrogen reacted with the fluorine formed by the decomposition. The former would remove PuF_6 directly from the mixture, and the latter reaction would remove fluorine and thus reduce the fluorine- PuF_4 recombination.

It is interesting to note that Bernhardt *et al.*^(8,9) have studied the effects of helium, oxygen, and nitrogen on the alpha decomposition of UF_6 in an attempt to define possible electron transfer processes. Their experiments showed that nitrogen increases the rate of the alpha-particle decomposition of UF_6 . While the authors explained this nitrogen effect in terms of a charge transfer process, they indicated that a reaction of fluorine or its ions may have occurred to some extent, but they did not report finding NF_3 .^{*} In the case where oxygen was added, the oxygen was found to be permanently removed from the system. The extent of oxygen reaction appeared to depend on pressure.

^{*}We have exposed a gas mixture of 100 mm UF_6 and 660 mm N_2 in a 127-cc nickel vessel to 2.7×10^9 rads (determined by Fricke dosimetry) of fission product gamma radiation. About 40% of the uranium was found as UF_4 (identified by X-ray diffraction; determined by colorimetric analysis) after irradiation and removal of the volatile vapors. An infrared scan of the vapors, after removal of the undecomposed UF_6 , indicated the presence of NF_3 .

IV. DISCUSSION

In view of the thermal instability of PuF_6 at higher temperatures (150-600°C),^(2,21) the stability of PuF_6 vapor at lower temperatures (26-80°C) in the presence of some fluorine is unexpected.⁽²¹⁾ Weinstock and Malm⁽³⁾ observed 23.5% of their initial PuF_6 to be decomposed in 67 days, while 32.5 and 39.2% decomposed in 542 and 624 days. These authors made calculations of the times required to obtain the observed decompositions. The calculations were based on an estimated range of alpha particles in PuF_6 gas as a function of pressure and the fractional ionization produced. The time calculated to decompose 23.5% of the PuF_6 was 75 days, which was in good agreement with the observed period (67 days). The calculated time to produce 39.2% PuF_6 decomposition was only 193 days instead of the observed 624 days. To explain this discrepancy, Weinstock suggested that at longer times a steady state is reached in which little or no further decomposition of PuF_6 occurs because the fluorine produced by the radiation decomposition permits the ion fragments to recombine.

Steindler⁽²³⁾ calculated the alpha decomposition rates expected for gaseous PuF_6 in 6.35-cm-diameter spheres. It was assumed that the G value of 7 molecules/100 eV obtained for the gamma radiation-induced decomposition of PuF_6 was applicable to the alpha radiation-induced decomposition. It was further assumed that PuF_4 , as an alpha-particle source, behaved like PuF_6 . Any PuF_4 -fluorine recombination was not considered in these calculations. Even with these and other assumptions the calculated results were in satisfactory agreement with the observed values (see Table 9). The agreement was best for short-term experiments. Since the longer-term PuF_6 decomposition rates

Table 9

COMPARISON OF THE CALCULATED AND OBSERVED RATE OF
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY
ALPHA PARTICLES IN A SPHERICAL VESSEL

Energy of Alpha Particles: 5.15 MeV
Radius of Spherical Container: 3.175 cm
 $G(-\text{PuF}_6, \gamma) = 7 \text{ molecules/100 eV}$

Pressure PuF_6 (mm Hg)	Range ^a (cm)	Decomposition (percent per day)		
		Calculated	Observed	Reference
28	24.21	0.23	0.35	3
50	13.52	0.43	0.16 to 0.064	This work, Table 4
100	6.76	0.93	1.78 to 0.064	This work, Table 3
1000	0.67	2.92	2.4 to 1.2	26
solid	0.002	3.21	2.1 to 0.6	This work, Table 1

^aRange of 5.15-MeV alpha particle in PuF_6 at the indicated pressure.

were lower, it appeared that at longer terms other modes of reaction, such as the recombination reaction or the quenching by fluorine of excited intermediate PuF_6 species, became important. The calculated rates predicted a pressure dependence. The experimental results available did show a dependence of the decomposition rate on the initial pressure, but the experiments were not of short enough duration for a good comparison with the calculated pressure dependence.

The decomposition of gaseous PuF_6 by alpha particles can be considered in terms of a gaseous system with several modes of reaction. The source of alpha particles may be considered constant since no plutonium is lost from the system during the reaction time. On the other hand, the alpha particles from PuF_4 do not contribute as much of their energy to the gas phase as do those which originate in gaseous PuF_6 , because some alpha particles from the solid PuF_4 are completely lost to the vessel wall. Owing to the uncertainty of the effective energy deposition in the gaseous system, it is not possible to determine the total energy introduced into the gas phase and, hence, calculation of G values for the decomposition cannot readily be made.

In addition to the uncertainty regarding the amount of energy released into the gas phase by alpha particles, chemical reactions of plutonium fluorides need to be considered. Plutonium hexafluoride is a very reactive compound and, except under certain specific conditions, e.g., with helium, SF_6 , and NF_3 , can be expected to react with most substances. As was pointed out in the previous section, corrosion reactions have been observed. The reactivity of PuF_6 has thus far prevented direct dosimetry measurements. Hence, the separation of the two modes of PuF_6 behavior--loss of PuF_6 due to decomposition and loss due to chemical reaction--is somewhat difficult. Slow reactions of PuF_6 and the container material, even pre-fluorinated metal, are possible, except that general experience has shown that this reaction becomes insignificant after prolonged periods. Prefluorination of metal vessels with fluorine diminishes the loss of PuF_6 to the vessel walls, but it appears that a PuF_6 pretreatment is also necessary.

The PuF_6 decomposition rate is said to be less for the vapor than for the solid because in the solid a greater percentage of the alpha particles complete their paths within PuF_6 whereas in the vapor, where the alpha particle ranges are longer, more of the alpha energy is lost to the walls of the container. The alpha energy lost to the walls can be increased by packing the vessel with nickel wool. When this was done in a vessel not previously exposed to PuF_6 , the decomposition rate of PuF_6 increased. This, however, could be explained by the increased surface available for chemical reaction with PuF_6 . When the experiment was repeated in the same packed vessels, however, the PuF_6 decomposition rate was comparable to rates obtained in reuse of unpacked vessels. Since the decrease in rate which was expected, assuming a gas-phase alpha decomposition, was not observed, it could be

tentatively concluded that even at 75 days (the duration employed in the packed-vessel studies) some chemical reaction may be proceeding. Data contributing to this conclusion are summarized in Table 10.

Table 10
EFFECT OF CHANGE OF SURFACE-TO-VOLUME RATIO
ON THE PuF_6 DECOMPOSITION RATE

Initial PuF_6 Pressure: 100 mm
Duration: 75 days
Temperature: $26 \pm 2^\circ\text{C}$

Decrease in Surface/Volume Ratio	Rates of Decomposition	
	No Initial PuF_4	Initial PuF_4 Present
<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> <div style="height: 100px; border-left: 1px solid black; position: relative;"> <div style="position: absolute; top: 0; left: 5px;">36-fold</div> <div style="position: absolute; bottom: 0; left: 5px;">↓</div> </div> <div style="margin-left: 10px;"> <div style="height: 100px; border-left: 1px solid black; position: relative;"> <div style="position: absolute; top: 0; left: 5px;">10-fold</div> <div style="position: absolute; bottom: 0; left: 5px;">↓</div> </div> </div> </div> </div>	2.29%/day { 127 cc Packed ^a 3 experiments	
	0.18%/day { 127 cc Unpacked 11 experiments	0.17%/day { 127 cc Packed ^a 1 experiment
		0.13%/day { 127 cc-- Unpacked 25 experiments
	0.11%/day { 5.96 l Unpacked 1 experiment	0.12%/day { 127 cc-- Packed ^a 1 experiment

^aVessels used for these experiments were packed with a quantity of nickel wool sufficient to increase the surface/volume ratio by a factor of 10.

The loss of PuF_6 due to decomposition, as distinguished from chemical reaction, may be due to thermal and/or radiation processes. It is difficult to estimate the contribution of each mode. It has been shown that PuF_6 is thermodynamically unstable at ambient temperatures toward the formation of PuF_4 and fluorine. The equilibrium at room temperature extrapolated from the data of Trevorrow, Shinn, and Steunenberg⁽²¹⁾ indicates that the ratio of PuF_6 to F_2 in equilibrium with solid PuF_4 is approximately 1.8×10^{-5} . Although the rate of thermal decomposition of PuF_6 at room temperature is probably very small, a portion of the total gas-phase PuF_6 decomposition may be due to thermal decomposition in experiments carried out for long periods of time.

Finally, the recombination reaction of PuF_4 and F_2 to form PuF_6 has been shown^(13,14) to proceed in the presence of gamma radiation at 60 to 70°C to yield significant quantities of PuF_6 . That such quantities are formed by this route is not particularly surprising since the high energies (or temperature equivalent) accompanying the radiation interactions would lead to products whose thermal decomposition would proceed only at a low rate to thermodynamic equilibrium once the products have reached thermal equilibrium with the surrounding vessel.

In the light of the foregoing, it seems necessary to view the results of this study from several aspects. These are:

1. the source and variations in the amount of energy deposited in the gas phase as decomposition proceeds;
2. the chemical reactions which accompany the decomposition of PuF_6 by other routes;
3. the approach to steady state as a function of time, both by reduction in the gas-phase concentration of PuF_6 as well as the radiation-induced formation of PuF_6 .

Not mentioned previously, but possibly of interest, is the notion that catalytic decomposition of PuF_6 may be possible. Evidence to support this concept is drawn from the experience of workers^(14,24) in this field who observe that even after extensive pretreatment of the surfaces of equipment, measurable quantities of PuF_6 are deposited on these surfaces before the rate of loss of PuF_6 by this means is reduced to immeasurable quantities and rates. On the other hand, this concept is based on the assumption that pretreatment procedures, which are believed to be adequate for the most reactive fluorides known, are, in fact, not adequate for PuF_6 . Since no adequate method of judging the validity of this assumption exists, the existence of a catalytic mechanism for the decomposition of PuF_6 remains undetermined.

The rate of decomposition of gaseous PuF_6 decreases with time, as shown by data presented in a previous section. Figure 4 illustrates this effect. The data obtained in the present work from long-term experiments show satisfactory agreement with data obtained by Weinstock and Malm.⁽³⁾ This agreement lends support to the conclusion that the decrease in decomposition rate of gaseous PuF_6 with increasing exposure time is valid. At least two types of reactions could account for the observed decrease in rate. If the very short-term experiments are ignored for the present discussion, a decrease in rate with time can be obtained if the recombination of the products increases in importance with time. In addition, the reduction in rate could be due to the inhibition of intermediate steps in the decomposition reaction.

may result in the inhibition of one or more of the steps in the decomposition process. One of the more likely ways in which such inhibition could be effected is through the quenching of an excited species important in the decomposition process. It has been shown (see Table 8) that fluorine decreases the rate of decomposition. However, owing to the role of fluorine in the recombination reaction, the effect of fluorine is not unequivocal. It may be pointed out that other gases, which do not take part in the recombination reaction, also depress the rate of decomposition of PuF_6 . Thus, the effect of oxygen and krypton indicate that quenching of an excited state is at least a possible mechanism of action of these "inert" gases.

If the excited state affected by the inert gas is assumed to be of lower energy than the ionization potential of PuF_6 (see Table 11), then it

Table 11
IONIZATION AND
EXCITATION ENERGIES

Process	Energy (eV)	Reference
$\text{O}_2 \rightarrow \text{O}_2^{*a}$	0.998	27
$\text{O}_2 \rightarrow \text{O}_2^+$	12.2	28
$\text{F}_2 \rightarrow 2\text{F}$	~1.5	29
$\text{F} \rightarrow \text{F}^{*a}$	0.05	30
$\text{F}^* \rightarrow \text{F}^{**b}$	12.69	30
$\text{F} \rightarrow \text{F}^+$	17.42	28
$\text{F}_2 \rightarrow \text{F}_2^+$	16.5	28
$\text{He} \rightarrow \text{He}^{*a}$	19.818	31
$\text{He} \rightarrow \text{He}^+$	24.586	31
$\text{Kr} \rightarrow \text{Kr}^{*a}$	9.915	31
$\text{Kr} \rightarrow \text{Kr}^+$	13.999	31
$\text{PuF}_6 \rightarrow \text{PuF}_6^+$	~15 ^c	32

^aLowest excited state.

^bNext lowest excited state.

^cEstimated from the value for UF_6 .

could be expected that the influence of helium on the rate of decomposition should be minor. On the other hand, both oxygen as well as krypton should be able to take part in both energy and charge transfer processes based on the energetics of the processes. Observations recorded in Table 8 indicate that this assumption is borne out by the experiments. These data, together with the tabulated data for energy requirements for processes involving molecular and atomic fluorine, would suggest that the inhibition of decomposition could be due to the interaction of fluorine with an intermediate in the decomposition process.

It has been shown that the decomposition of PuF_6 is independent of the amount of PuF_4 present in the reaction vessel (see Figure 2). It should be noted that this result is not at variance with the above proposal for the mechanism of the reduction in decomposition rate with time. Plutonium tetraflu-

oride deposited by alpha decomposition of PuF_6 has not been found to be uniformly dispersed over the surface of the container. On the contrary,

experience has shown that the solid can usually be found agglomerated at a small number of sites. Under these conditions, only the surface of the bulk PuF_4 would be expected to be available for contact with fluorine, and this surface should remain relatively constant in area as the decomposition proceeds.

It is necessary to consider further the role of PuF_4 in the decomposition process. The decline in the rate of decomposition has been discussed on the basis of an underlying assumption that the energy input to the system has remained constant. If, in fact, the state of agglomeration of PuF_4 is as described above, it can be argued that there may be a significant decrease in the rate of energy input to the gas since alpha particles would, under agglomerated conditions of PuF_4 , lose a significant part of their energy before they escape from the solid into the gas. Further, approximately half of the alpha particles are emitted toward the wall of the container and expend their energy in the wall. If, however, the rates of decomposition at short times and long times are compared, the differences in the observed average rates are significantly greater than could be accounted for solely on the basis of depletion of alpha-emitting materials from the gas phase.

The effect of temperature on the rate of decomposition of PuF_6 (see Section III.C. above) indicates that the rate at 82°C is greater than that observed at 26°C . Since the energies involved in the radiation decomposition of PuF_6 are equivalent to very high temperatures, it can be anticipated that radiation decomposition reactions should be essentially temperature independent. Hence, the increased rate at the higher temperature (82°C) must involve factors other than those which are operative at 26°C , and these factors should not include the influence of the radiation. The decomposition of PuF_6 in the condensed state has been measured at -70°C , room temperature, and slightly above the melting point. Results indicate decomposition rates which were independent of temperature and hence were assumed to be due to alpha-radiation effects. It appears reasonable to conclude that the effects of alpha radiation on the gas phase would also show no temperature dependence. On this basis, the increased decomposition observed at 82°C could only be assigned to thermal decomposition or chemical reaction of PuF_6 . Experiments by Trevorrow and Shinn⁽²⁶⁾ on the thermal decomposition of gaseous PuF_6 at 80°C indicate rates of 2.4 and 1.5% per day for exposures of 1 and 2 days, respectively, using a pressure of 1000 mm Hg PuF_6 in 53-cc vessels. These values may be compared to the short-term room-temperature results shown in Figure 1, which indicate rates lower by a factor of approximately 2. Since the large rates of decomposition at short exposure times have been attributed to chemical (corrosion) reactions, it can be suggested that the results of experiments carried out in the present work at 82°C represent primarily decompositions due to thermal effects, with smaller contributions from chemical reaction and alpha decomposition. It is not possible, however, to clearly delineate the roles of each of the mechanisms in the total decomposition of PuF_6 .

Experiments in which the surface-to-volume ratio of the container was varied indicate a possible increase in the decomposition rate with increasing surface area within the vessel. In the absence of accurate experiments on the thermal decomposition of PuF_6 at low temperatures, this increase in apparent rate cannot be assigned unequivocally to alpha decomposition, since it has been shown by Fischer, Trevorrow, and Shinn⁽²⁴⁾ that the thermal-decomposition kinetics involve both a homogeneous as well as a heterogeneous step. Experiments done in large spheres indicated a decrease in average rate with increasing vessel volumes. Although it would be expected that a larger fraction of the alpha particle energy would be expended in the gas phase in larger vessels, the decrease in apparent rate would indicate an overriding importance of the surface reaction on the container walls. Unfortunately, the data on this point are not sufficiently precise to permit a more definitive conclusion to be drawn.

It has already been pointed out that the high initial rates observed in short-term experiments are probably due to chemical reactions with the walls of the reaction vessel. Since all of the other influences on the rate of decomposition would not produce a high initial decomposition rate, this conclusion seems to be on reasonably firm ground.

V. SUMMARY

The decomposition of plutonium hexafluoride is due, at least in part, to irradiation by alpha particles from the plutonium. The observed rate of decomposition of gaseous PuF_6 was not a linear function of time, but decreased with time from 1.78 to 0.064% of the initial PuF_6 (100 mm) per day in the range from 0.5 to 571 days at 26°C. The initial PuF_6 decomposition rate was rapid (1.78% per day at 0.5 day) and is attributed to chemical reaction with the container, a prefluorinated 127-cc nickel sphere.

The effects of changing the initial PuF_6 pressure from 100 to 50 mm is not great, but a lower rate was observed at lower pressures. For example, in 12.6-day experiments, 100 mm of PuF_6 decomposed at an average of 0.27% per day, whereas 50 mm decomposed at a rate of 0.10% per day.

Some thermal decomposition of PuF_6 at 82°C is indicated by the observed higher PuF_6 decomposition rates at 82°C than at 26°C. After 75 to 77 days of decomposition, PuF_6 decomposition rates were $0.64 \pm 0.06\%$ per day at 82°C and only $0.18 \pm 0.03\%$ per day at 26°C.

Other factors influencing the rate of decomposition were studied. Among these was the nature of the container. Higher PuF_6 decomposition rates were obtained in unprefluorinated aluminum (at 82°C) or nickel (at 26°C) vessels than were obtained within prefluorinated vessels. Plutonium hexafluoride decomposition in Pyrex vessels (0.35% per day) was

greater than in quartz vessels (0.23% per day). Plutonium hexafluoride decomposition rates were higher in vessels packed with nickel wool and prefluorinated than in unpacked prefluorinated vessels of nearly equal volume. An increase, from 127 cc to 5.96 ℓ , in container volume resulted in lower PuF_6 decomposition rates (0.18% versus 0.11% per day).

Another factor influencing the PuF_6 decomposition rate is the presence of PuF_4 at the start of the PuF_6 decomposition. Reuse of nickel vessels (which contained some PuF_4 from previous PuF_6 decomposition) resulted in lower PuF_6 decomposition, both at 26°C (0.13% versus 0.18% per day) and at 82°C (0.52% versus 0.64% per day).

The addition of krypton, oxygen, or helium decreased the PuF_6 decomposition rate slightly. Fluorine greatly depressed the PuF_6 decomposition (0.15% versus 0.02% per day). Nitrogen increased the PuF_6 decomposition by the formation of NF_3 .

No mechanism for the decomposition of PuF_6 is postulated because it is not possible to proportion accurately the contribution to the total decomposition observed of chemical reaction, thermal decomposition, and decomposition due to alpha radiation. It has, however, been shown that handling of PuF_6 can be accomplished with a minimum of loss by storage in the gas phase and at low pressures, by use of large volumes with a minimum of surface area, by use of prefluorinated surfaces exposed to PuF_6 prior to use, and by addition of fluorine to storage vessels. Application of the technique during handling of PuF_6 in a separation process should result in a minimum loss of PuF_6 .

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