

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

LABORATORY INVESTIGATIONS IN SUPPORT OF
FLUID BED FLUORIDE VOLATILITY PROCESSES
PART V.. THE RADIATION CHEMISTRY OF PLUTONIUM HEXAFLUORIDE

by

Martin J. Steindler, David V. Steidl, and Jack Fischer

Chemical Engineering Division

December 1963

Part I of this series is ANL-6742
Part II of this series is ANL-6753
Part III of this series is ANL-6762
Part IV of this series is ANL-6763

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
I. INTRODUCTION.	3
II. EXPERIMENTAL PROCEDURES.	5
III. RESULTS	7
A. Stoichiometry	7
B. Decomposition of Gaseous Plutonium Hexafluoride	8
C. Decomposition of Plutonium Hexafluoride in Mixtures with Helium.	9
D. Decomposition of Plutonium Hexafluoride in Mixtures with Krypton	11
E. Decomposition of Plutonium Hexafluoride by Gamma Radiation in the Presence of Either Fluorine or Oxygen.	15
IV. DISCUSSION	16
V. FORMATION OF PLUTONIUM HEXAFLUORIDE BY IR- RADIATION OF MIXTURES OF PLUTONIUM TETRA- FLUORIDE AND ELEMENTAL FLUORINE BY GAMMA RADIATION.	20
VI. SUMMARY	21
VII. ACKNOWLEDGMENT	22
VIII. BIBLIOGRAPHY.	23

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part V. The Radiation Chemistry of Plutonium Hexafluoride

by

Martin J. Steindler, David V. Steidl, and Jack Fischer

ABSTRACT

Plutonium hexafluoride exposed to fission product gamma radiation decomposes to form plutonium tetrafluoride and elemental fluorine with a G value of 7.5 ± 1.7 . Addition of one atmosphere of helium to plutonium hexafluoride at a pressure of ~ 80 mm Hg does not significantly change the G value for the decomposition compared with that for pure plutonium hexafluoride. Addition of 2 atmos of helium to plutonium hexafluoride at ~ 80 mm Hg results in a G value for the decomposition of 5.8 ± 0.9 .

A study of the effect of krypton on the decomposition of plutonium hexafluoride by gamma radiation revealed a marked enhancement of the decomposition at an electron fraction of krypton of 0.73 and an exposure dose of 1×10^8 rads. No such enhancement was observed at an exposure dose of 2×10^8 rads.

Addition of fluorine or oxygen to plutonium hexafluoride resulted in a G value for the decomposition which was less than that obtained from the irradiation of pure plutonium hexafluoride.

Irradiation of mixtures of plutonium tetrafluoride and elemental fluorine produced plutonium hexafluoride in concentrations greater than that calculated from the thermodynamic equilibrium constant at the temperature of the irradiations.

I. INTRODUCTION

The stability of plutonium hexafluoride toward gamma radiation has become of interest in connection with the Fluoride Volatility Process for the separation of uranium and plutonium from spent reactor fuels. In this process, uranium and plutonium are separated from the fission products by converting the actinides to their volatile hexafluorides and carrying out the separation by distillation. During these and subsequent operations, the hexafluorides are exposed to radiation from fission products. A study of the decomposition of plutonium hexafluoride by fission product gamma radiation was undertaken to evaluate the extent of the decomposition and, if possible, to study the mechanism of the decomposition in the presence of added gases.

Plutonium hexafluoride has been shown to be less stable than the corresponding compounds of uranium and neptunium.^(1,2) This instability is evidenced not only in the case of thermal decomposition, but also in the decomposition by radiation. Plutonium hexafluoride is well known for its instability toward alpha decomposition, and rates up to two percent per day in the solid have been reported.⁽³⁾

The literature contains only scant reference to studies of the decomposition of plutonium hexafluoride by radiation. The decomposition of plutonium hexafluoride by its own alpha radiation has been studied,⁽⁴⁾ but it has not been possible to assign a G value to the decomposition. It has been shown, however, that the decomposition proceeds at a rate which decreases with time. Further, the product of the decomposition of plutonium hexafluoride by alpha radiation has been shown to be plutonium tetrafluoride and elemental fluorine.⁽³⁾ No other studies on the decomposition of plutonium hexafluoride by radiation have been reported.

Some information on the radiation chemistry of uranium hexafluoride is available, and it is instructive to review these results. A study of the decomposition of uranium hexafluoride by alpha radiation from radon has been reported by Bernhardt,⁽⁵⁾ who found that the G for the decomposition is approximately unity. The product of the decomposition could not be identified, probably because of the low-temperature reaction of uranium hexafluoride with the decomposition product. It was concluded by these workers that the back reaction, i.e., the reaction of the product of the decomposition with fluorine to form uranium hexafluoride in the presence of alpha radiation, contributes to the net decomposition at prolonged exposure times.

Two brief reports on the decomposition of liquid uranium hexafluoride by high-energy electrons and deuterons have been issued.⁽⁶⁾ In all experiments, the product of the decomposition of liquid uranium hexafluoride irradiated at 76°C was uranium pentafluoride and gaseous elemental fluorine. In one experiment, the pressure rise in the irradiation vessel was observed on irradiation with 2.7-MeV electrons and a G for the loss of uranium hexafluoride of approximately 2.3 was calculated from the meager data available. It was further found that the decomposition exhibited a definite steady state which was shown to depend on the electron beam current of the accelerator. Interrupted experiments also showed that the back reaction to reform uranium hexafluoride proceeds only slowly in the absence of irradiation.

Kikoin and coworkers⁽⁷⁾ have reported the results of experiments with a nuclear reactor fuelled by gaseous uranium hexafluoride in which the decomposition of uranium hexafluoride by pile radiation was observed. It was concluded that uranium hexafluoride is decomposed primarily by fission fragments to form uranium pentafluoride with a G for the decomposition of uranium hexafluoride of 0.8. Addition of chlorine trifluoride to the gaseous

mixture reduced the decomposition of uranium hexafluoride at the expense of chlorine trifluoride, presumably by refluorination of uranium pentafluoride at the operating temperature of the reactor (93°C).

II. EXPERIMENTAL PROCEDURES

Plutonium hexafluoride was prepared by the reaction of plutonium tetrafluoride and elemental fluorine.⁽⁸⁾ The resulting volatile product was purified by trap-to-trap distillation under vacuum to remove traces of impurities such as hydrogen fluoride, carbon tetrafluoride, and other constituents normally found as contaminants in commercial fluorine. The vapor pressure of plutonium hexafluoride at the ice point⁽⁹⁾ was usually used as a criterion of purity, although the vapor pressure at other temperatures was also used as a supplemental check of the purity of the samples.

The gases used were taken directly from commercial cylinders. Elemental fluorine was passed through a heated bed of sodium fluoride to remove traces of hydrogen fluoride. Other gases were passed through beds of Molecular Sieves to remove traces of moisture. Analyses of the gases by mass spectrometry usually indicated that the total impurity content of the gases was less than 50 ppm.

Standard Blickman Type K hoods were converted for use with large quantities of plutonium.⁽¹⁰⁾ Air circulation was maintained in the hoods by providing suitable inlet and outlet filters, and the hoods were connected to the laboratory ventilation system through several high-efficiency filters. Materials were transferred into and out of the hoods by use of standard bagging techniques, employing PVC bags of 25-mil thickness. These bags were sealed by a dielectric sealing press. Vacuum lines and auxiliary equipment were located within the specially prepared enclosures, and all manipulations with plutonium were carried out within these hoods. Owing to the extreme toxicity of plutonium,⁽¹¹⁾ considerable care was required to prevent contamination exterior to the hoods.

The portion of the apparatus exposed to fluorine and plutonium hexafluoride was constructed of nickel. Standard flare fittings, traps, and other fixtures were used. Hoke No. 411 or 413 valves were used throughout, except where the need for small valves dictated the use of Hoke No. 1479 valves. Teflon flare gaskets were employed in most instances.

Pressure measurements were made with the aid of a Booth-Cromer pressure transmitter and self-balancing relay,⁽¹²⁾ connected to a Heise precision gage or a mercury manometer located outside the hoods.

Vessels used for irradiation were cylindrical, nickel containers with a wall thickness of 0.0625 in. The vessels were equipped with a $\frac{3}{4}$ -in. flare

fitting to which an assembly consisting of a flare plug and a valve was attached. The flare connection was sealed with an annealed copper gasket.

The reaction vessels were treated with approximately one atmosphere fluorine at 100°C for a minimum of 48 hr prior to the introduction of plutonium hexafluoride. The vessels were also pretreated with plutonium hexafluoride at room temperature for 17 hr prior to the introduction of samples for study of the decomposition. Careful treatment of the vessels in this manner resulted in an uptake of plutonium hexafluoride during the conditioning of the nickel vessels, which was generally predictable and reproducible. Suitable corrections were made for the plutonium hexafluoride which was formed during the pretreatment of the vessels.

In addition, the decomposition of plutonium hexafluoride by alpha radiation, yielding plutonium tetrafluoride and fluorine, proceeds at a low rate in the gas phase. Correction for this source of fluorine and plutonium tetrafluoride, based on a decomposition rate of 0.22 percent per day, was also made.

Samples of purified plutonium hexafluoride were introduced into the reaction vessel of known volume, and the pressure and temperature of the system were measured. The valve on the vessel was closed, and the flare fitting by which the vessel was attached to the vacuum line was tightly capped. The reaction vessel was next encased in a plastic bag, which was sealed. The sealed bag was introduced into a container made of several commercial number 2 cans assembled into a vertical array. The container lid was sealed to the array with soft solder. This assembly was then irradiated to a predetermined dose. After removal of the container was bagged into the hood, opened, the plastic bag removed, and the irradiation vessel was attached to the vacuum line.

Fluorine was measured manometrically while a portion of the vessel was cooled to -80°C by a mixture of dry ice and trichlorethylene. The fluorine was removed by evacuation through a trap filled with activated alumina. The quantity of undecomposed plutonium hexafluoride remaining was determined by warming the vessel to room temperature and measuring the pressure in a calibrated volume.

In order to determine the quantity of plutonium tetrafluoride formed, the vessel was opened at the flare connection after evacuation of all plutonium hexafluoride and rinsed several times with a mixture of dilute nitric acid and aluminum nitrate. It was demonstrated that all of the plutonium could be removed from the vessel by this procedure. The aqueous solutions were analyzed for plutonium by extraction of plutonium and alpha counting. In the case of large samples, extraction of plutonium was followed by an amperometric titration.⁽¹³⁾

All irradiations were carried out in the High Level Gamma Irradiation Facility at Argonne National Laboratory.⁽¹⁴⁾ This facility utilized spent reactor fuel elements from the Materials Testing Reactor as the source of gamma radiation. Calculations, based on the irradiation and cooling time of the fuel elements, indicated that the average energy of the gamma radiation was approximately 0.75 MeV. The temperature of the irradiation vessels during irradiation was 60-70°C due to gamma heating.

The dose rates available in the Facility were variable owing to the decay of the fission products; dose rates utilized in the experiments varied from approximately 1×10^4 rads/min to 4×10^4 rads/min. Dosimetry was based on the Fricke dosimeter using a G value of 15.6.⁽¹⁵⁾ Owing to the fact that the irradiation vessels were constructed of nickel, dosimetry was carried out in nickel tubes plated with a thin layer of gold to avoid reaction of the dosimetry solution with nickel.

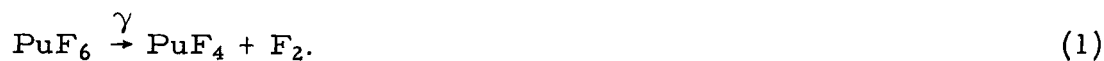
Energy absorption in plutonium hexafluoride was calculated from aqueous dosimetry data and the ratio of the electron densities of liquid water and gaseous plutonium hexafluoride. Energy absorption in gaseous mixtures of plutonium hexafluoride and other gases were calculated by use of the ratio of electron densities of liquid water and the gaseous mixture which was irradiated.

III. RESULTS

A. Stoichiometry

The decomposition of plutonium hexafluorides by heat⁽¹⁾ as well as the product of all known chemical reductions of plutonium hexafluoride yield only plutonium tetrafluoride.⁽³⁾ In order to determine the stoichiometry of the decomposition of plutonium hexafluoride by gamma radiation, a sample of plutonium hexafluoride was exposed to approximately 1×10^8 rads. The solid produced by the irradiation was analyzed by X-ray diffraction and chemical techniques, the results of which established the composition as plutonium tetrafluoride (Anal. Found: F-23.5%, Pu-76.4%; Calc. for PuF₄, F-24.1%, Pu-75.9%).

Further evidence to support the conclusion that the nonvolatile product is plutonium tetrafluoride was obtained directly from the decomposition experiments. The molar ratio of fluorine to nonvolatile plutonium was observed to be unity. In general, the moles of plutonium tetrafluoride formed also corresponded to the amount of plutonium hexafluoride lost, although occasional experiments showed deviations which are believed to be due to experimental difficulties. It can be concluded that the decomposition proceeds according to the equation



Since the determination of fluorine in the products of the decomposition is relatively troublesome, once the stoichiometry for the decomposition was established, no further attempt to obtain accurate values for the fluorine produced during the decomposition were carried out.

B. Decomposition of Gaseous Plutonium Hexafluoride

Irradiation of gaseous plutonium hexafluoride by fission product gamma radiation yielded results shown in Table 1 and Figure 1. The data in Table 1, that indicated the amount of plutonium tetrafluoride formed and the amount of plutonium hexafluoride lost were averaged and plotted against the energy absorbed in plutonium hexafluoride, as shown in Figure 1. The line shown in Figure 1 represents the calculated best fit for the data and results in a G for the decomposition of 7.5 ± 1.7 , where the uncertainty is one sigma. On the basis of the experiments carried out at pressures greater than 80 mm Hg, there appears to be no effect of pressure on the G value for the decomposition.

Table 1

DECOMPOSITION OF GASEOUS PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION

\bar{E}_γ :	~0.75 MeV
Temperature:	60-70°C
Dose Rate:	1×10^4 to 4×10^4 rads/min
Pressure of PuF ₆ :	~80 mm Hg at 25°C, except where indicated

<u>Initial PuF₆</u> (millimoles)	<u>Absorbed Dose^a</u> (eV x 10 ⁻²⁰)	<u>PuF₄ Formed</u> (millimoles)	<u>PuF₆ Lost</u> (millimoles)
0.279	1.48	0.017	0.024
0.323	1.59	0.032	0.028
0.302	4.88	0.031	0.058
0.315	6.34	0.038	0.050
0.976 ^b	14.7	0.230	0.195
1.057	18.8	0.285	0.275
1.113	23.9	0.282	0.270
1.031	28.7	0.405	0.317
2.076 ^c	31.2	0.372	0.333
0.992	35.6	0.490	0.505
0.953	37.3	0.370	0.404

^a Calculated from the average amount of plutonium hexafluoride present, the dose as determined by Fricke dosimetry, and the ratio of electron densities of water and gaseous plutonium hexafluoride.

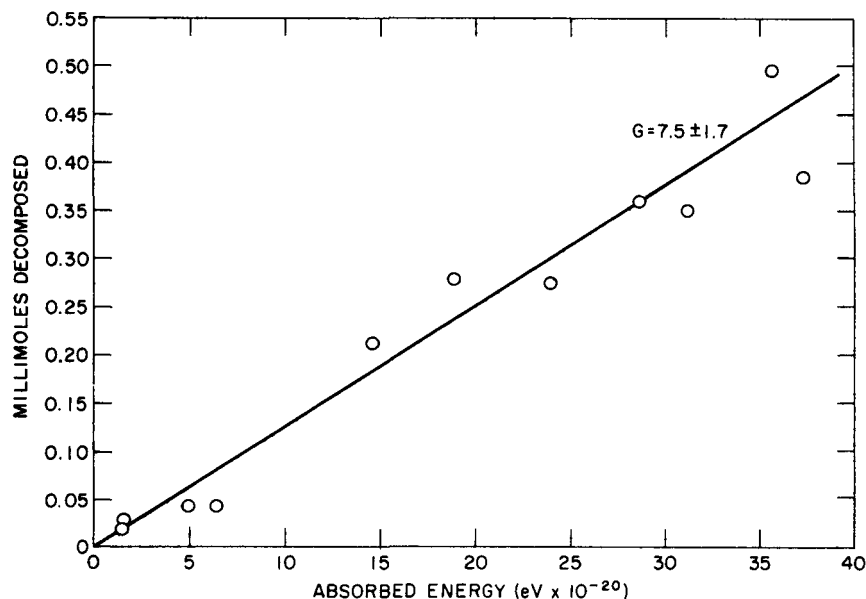
^b Pressure of PuF₆ equivalent to 360 mm Hg at 25°C.

^c Pressure of PuF₆ equivalent to 169 mm Hg at 25°C.

Figure 1

DECOMPOSITION OF PLUTONIUM HEXA-
FLUORIDE BY GAMMA RADIATION

Pressure of PuF_6 : ~80-380 mm Hg
 Temperature: 60-70°C
 Average Gamma Energy: 0.75 MeV
 Dose Rate: 1×10^4 to
 4×10^4 rads/min.



108-6759

C. Decomposition of Plutonium Hexafluoride in Mixtures with Helium

Irradiation of mixtures of helium and plutonium hexafluoride resulted in decomposition of the hexafluoride as shown in Tables 2 and 3 and in Figures 2 and 3. Table 2 and Figure 2 show the results of experiments in which one atmosphere of helium was added to approximately 80 mm Hg of plutonium hexafluoride and subjected to irradiation. The data in Figure 2 were based on the energy absorbed in plutonium hexafluoride only and the average of the plutonium hexafluoride lost and the plutonium tetrafluoride formed. The slope of the resulting line led to a value of G for the decomposition of 7.2 ± 1.3 , where the uncertainty is one sigma.

The data for experiments in which 2 atmos of helium were added to plutonium hexafluoride resulted in a G of 5.8 ± 0.9 . The latter value is significantly different from the data obtained with one atmosphere of helium added to plutonium hexafluoride.⁽¹⁶⁾

Table 2

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES WITH ONE ATMOSPHERE OF HELIUM

\bar{E}_γ : ~0.75 MeV
 Temperature: 60-70°C
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Pressure of PuF₆: ~80 mm Hg at 25°C
 Helium Pressure: ~1 atmos

Initial PuF ₆ (millimoles)	Initial Helium (millimoles)	Absorbed Dose (eV × 10 ⁻²⁰)		PuF ₆ lost (millimoles)	PuF ₄ formed (millimoles)
		In PuF ₆ ^a	In He ^b		
0.996	8.863	8.0	1.0	0.072	0.084
1.010	8.659	8.1	1.0	0.134	0.086
1.026	8.413	8.7	1.0	0.147	0.116
1.043	8.629	14.7	1.8	0.185	0.139
0.982	8.342	15.1	1.9	0.185	0.196
1.016	8.998	15.1	2.0	0.192	0.187
1.073	8.132	15.6	1.8	0.252	0.222
0.964	8.133	26.7	3.7	0.299	0.291
1.015	8.566	38.9	5.5	0.373	0.317
0.935	8.298	40.5	6.2	0.361	0.436

^a Calculated from the average amount of plutonium hexafluoride present, the dose as determined by Fricke dosimetry, and the ratio of electron densities of plutonium hexafluoride and liquid water.

^b Calculated from the initial helium content, the Fricke dose, and the ratio of electron densities of gaseous helium and liquid water.

Table 3

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES WITH TWO ATMOSPHERES OF HELIUM

E_γ : ~0.75 MeV
 Temperature: 60-70°C
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Pressure of PuF₆: ~80 mm Hg at 25°C
 Helium Pressure: ~2 atmos

Initial PuF ₆ (millimoles)	Initial Helium (millimoles)	Absorbed Dose (eV × 10 ⁻²⁰)		PuF ₆ lost (millimoles)	PuF ₄ formed (millimoles)
		In PuF ₆ ^a	In He ^b		
1.035	17.16	15.6	3.7	0.150	0.203
1.097	17.29	16.8	4.0	0.184	0.183
0.967	17.22	25.7	7.5	0.315	0.223
1.045	17.58	28.2	7.6	0.314	0.315
1.010	17.31	28.6	7.6	0.242	0.236
1.022	18.14	30.6	8.3	0.216	0.231
1.005	17.78	40.8	11.8	0.324	0.347
1.018	17.58	40.8	11.9	0.391	0.389

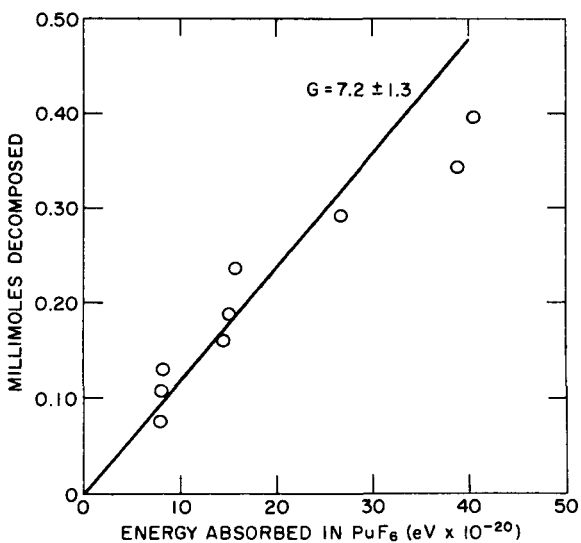
^a Calculated from the average amount of plutonium hexafluoride present, the Fricke dose, and the ratio of electron densities of gaseous plutonium hexafluoride and liquid water.

^b Calculated from the initial helium content, the Fricke dose, and the ratio of electron densities of gaseous helium and liquid water.

Figure 2

DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES
WITH HELIUM

Pressure of PuF₆: ~80 mm Hg
 Pressure of Helium: 1 atmos
 Temperature: 60-70°C
 Dose Rate: 1 x 10⁴ to
 4 x 10⁴ rads/min
 Average Gamma Energy: 0.75 MeV

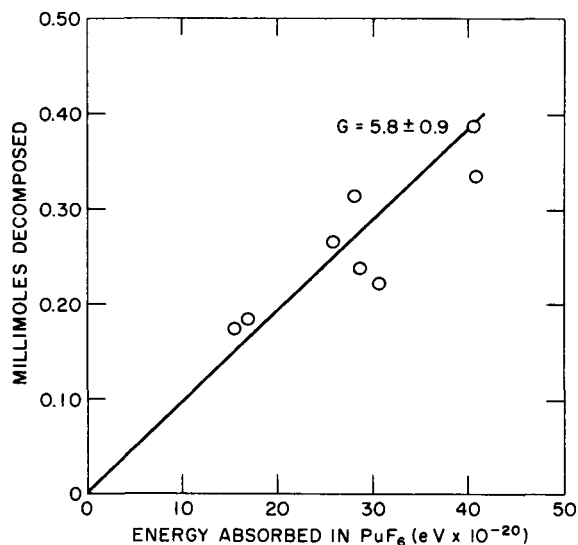


108-6762

Figure 3

DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES
WITH HELIUM

Pressure of PuF₆: ~80 mm Hg
 Pressure of Helium: 2 atmos
 Temperature: 60-70°C
 Dose Rate: 1 x 10⁴ to
 4 x 10⁴ rads/min
 Average Gamma Energy: 0.75 MeV



108-6760

D. Decomposition of Plutonium Hexafluoride in Mixtures with Krypton

Experiments on the decomposition of plutonium hexafluoride in mixtures with krypton resulted in data shown in Tables 4 and 5 and in Figures 4 and 5. In all cases, the pressure of plutonium hexafluoride was approximately 80 mm Hg.

Different values of the electron fraction of krypton were obtained by varying the partial pressure of krypton in the mixtures. The average electron fraction of krypton was obtained by using the average of the concentration of plutonium hexafluoride at the beginning and end of the irradiation.

Table 4 and Figure 4 show the data obtained at an exposure dose of 1 x 10⁸ rads (~15 x 10²⁰ eV absorbed in plutonium hexafluoride). Similar data, obtained at an exposure dose of 2 x 10⁸ rads (~30 x 10²⁰ eV absorbed in plutonium hexafluoride) are shown in Table 5 and Figure 5.

Table 4

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION
IN MIXTURES WITH KRYPTON

Exposure Dose: $\sim 1 \times 10^8$ rads
 Temperature: 60-70°C
 Average Gamma Energy: 0.75 MeV
 PuF₆ Pressure: ~ 80 mm Hg at 25°C

Initial PuF ₆ (millimoles)	Initial Krypton (millimoles)	Absorbed Dose (eV x 10 ⁻²⁰)		PuF ₄ Formed (millimoles)	PuF ₆ Lost (millimoles)	Average Electron Fraction of Krypton ^a	G ^b
		In PuF ₆	In Kr ^c				
0.996	0.295	14.8	1.2	0.149	0.170	0.075	6.5
1.030	1.552	15.2	6.0	0.165	0.149	0.283	6.2
1.000	2.376	15.2	9.5	0.161	0.138	0.385	6.0
1.024	3.304	16.4	14.2	0.191	0.189	0.464	7.0
0.984	4.753	14.8	19.7	0.141	0.195	0.571	6.8
1.042	5.408	15.1	21.1	0.198	0.191	0.583	7.8
1.074	8.146	15.1	32.9	0.332	0.313	0.685	12.9
1.006	9.238	13.8	37.5	0.352	0.346	0.731	15.2
1.005	9.157	14.0	39.5	0.480	0.423	0.738	19.4
0.979	10.05	13.1	38.9	0.337	0.302	0.748	14.7
1.021	14.04	15.5	55.1	0.120	0.109	0.780	4.5
0.998	17.64	15.4	73.1	0.145	0.166	0.826	6.1
0.537	17.79	16.0	154.7	0.148	0.167	0.906	5.9

^a Average of the initial and final electron fractions of krypton. Equivalent to the ratio of energy absorbed in krypton to the total energy absorbed in the mixture.

^b Based on the average of the PuF₆ lost and the PuF₄ formed and calculated on the basis of energy absorbed in PuF₆ only.

^c Calculated as outlined in Table 3, footnote b.

Table 5

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION
IN MIXTURES WITH KRYPTON

Exposure Dose: $\sim 2 \times 10^8$ rads
 Temperature: 60-70°C
 Average Gamma Energy: 0.75 MeV
 PuF₆ Pressure: ~ 80 mm Hg

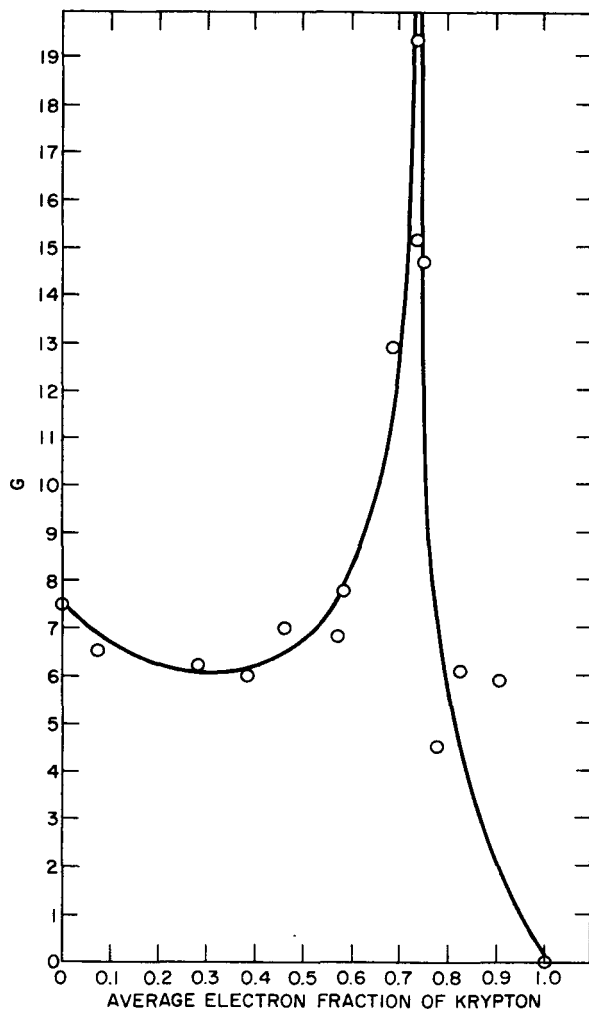
Initial PuF ₆ (millimoles)	Initial Krypton (millimoles)	Absorbed Dose (eV x 10 ⁻²⁰)		PuF ₄ Formed (millimoles)	PuF ₆ Lost (millimoles)	Average Electron Fraction of Krypton ^a	G ^b
		In PuF ₆	In Kr ^d				
0.991	0.446	25.8	3.6	0.295	0.286	0.122	6.8
1.011	0.870	26.3	6.6	0.295	0.270	0.201	6.4
0.999	0.949	25.9	7.0	0.235	0.216	0.213	5.2
1.006	1.327	29.1	11.2	0.312	0.316	0.278	6.5
1.007	1.977	30.3	16.9	0.257	0.269	0.358	5.2
1.035	2.931	29.5	23.8	0.235	0.280	0.447	5.2
1.049	4.877	32.4	41.4	0.208	0.203	0.561	3.8
1.003	7.063	31.6	60.5	0.222	0.223	0.657	4.3
1.023	8.427	32.9	73.6	0.160	0.198	0.691	3.3
1.032	8.575	24.6 ^c	55.1	0.112	0.185	0.691	3.6
1.007	8.575	29.7	70.0	0.185	0.218	0.702	4.1
1.001	18.23	32.1	156.3	0.131	0.160	0.830	2.7

^a Average of the initial and final electron fraction of krypton. Equivalent to the ratio of energy absorbed in krypton to the total energy absorbed in the mixture.

^b Based on the average of PuF₆ lost and PuF₄ formed and using the energy absorbed in PuF₆ only.

^c Exposure dose $\sim 1.5 \times 10^8$ rads.

^d Calculated as outlined in Table 3, footnote b.



108-6758

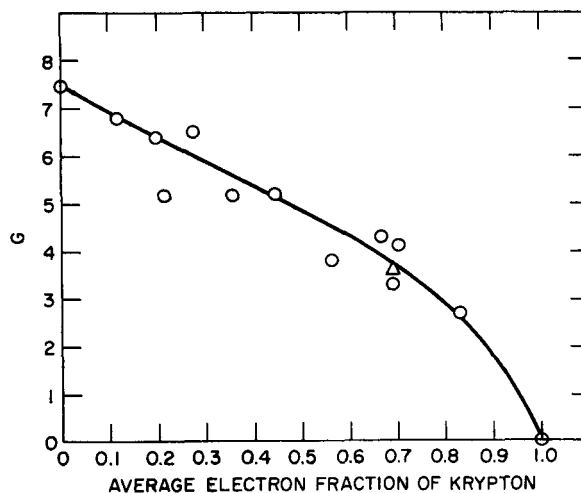
Figure 4

DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES
WITH KRYPTON

Pressure of PuF₆: ~ 80 mm Hg
 Pressure of Krypton: variable
 Total Exposure Dose: 1×10^8 rads ($\sim 15 \times 10^{20}$ eV
 absorbed in PuF₆)
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Temperature: 60-70°C
 Average Gamma
 Energy: 0.75 MeV
 G calculated only from energy absorbed in PuF₆

Figure 5
 DECOMPOSITION OF PLUTONIUM
 HEXAFLUORIDE BY GAMMA
 RADIATION IN MIXTURES
 WITH KRYPTON

Pressure of PuF₆: ~80 mm Hg
 Pressure of Krypton: variable
 Total Exposure Dose: ○ 2×10^8 rads,
 △ 1.5×10^8 rads
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Temperature: 60-70°C
 Average Gamma
 Energy: 0.75 MeV
 G calculated only from energy absorbed in PuF₆.



108-6761

The G values were obtained from individual experiments rather than being determined from the slope of a graph of amount decomposed versus energy absorbed. Further, the G values have been calculated on the basis of only the energy absorbed in plutonium hexafluoride to permit comparison with the data obtained on the decomposition of pure plutonium hexafluoride. As shown in Figure 4, a pronounced increase in the G value for the decomposition is obtained at an exposure dose of 1×10^8 rads and an average electron fraction of krypton of approximately 0.73. Comparison of the data shown in Figures 4 and 5 show that the G value for the decomposition of plutonium hexafluoride obtained at 1×10^8 rads is greater than the corresponding value obtained at 2×10^8 rads at all electron fractions between 0.30 and 0.85.

Figures 6 and 7 show the results of the experiments with krypton except that the G values have been calculated on the basis of the total energy absorbed in the system.

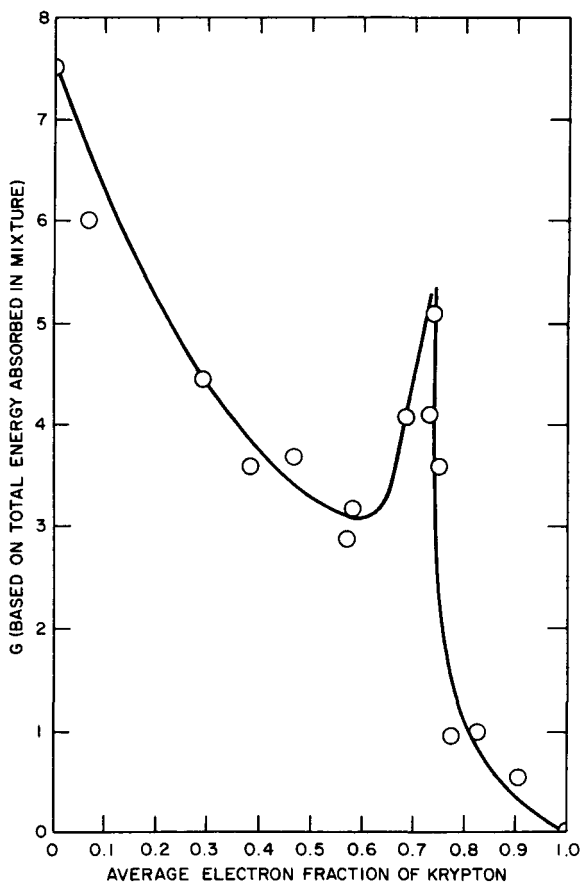


Figure 6
 DECOMPOSITION OF PLUTONIUM
 HEXAFLUORIDE BY GAMMA
 RADIATION IN MIXTURES
 WITH KRYPTON

Pressure of PuF₆: ~80 mm Hg
 Pressure of Krypton: variable
 Total Exposure Dose: 1×10^8 rads
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Temperature: 60-70°C
 Average Gamma Energy: 0.75 MeV
 G calculated on the basis of the total energy absorbed in the mixtures.

108-6822

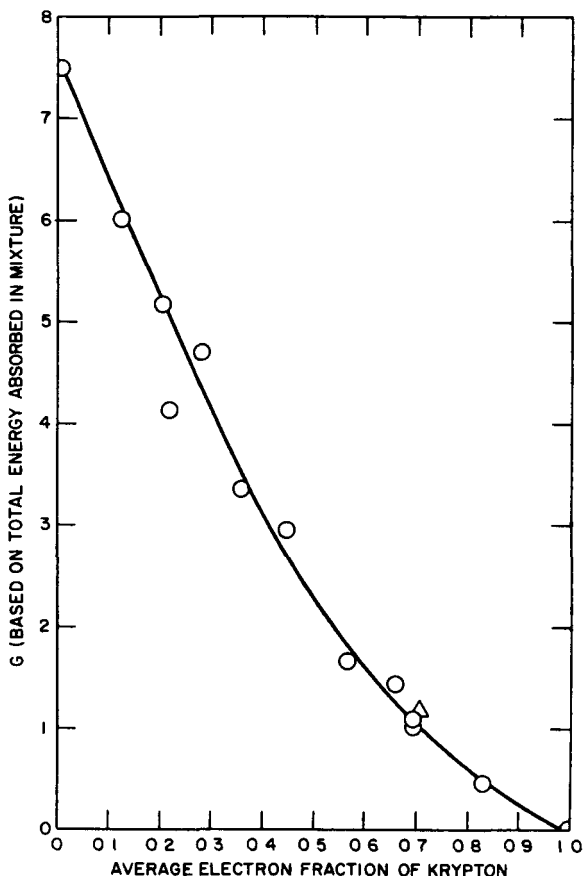


Figure 7

DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY GAMMA
RADIATION IN MIXTURES
WITH KRYPTON

Pressure of PuF_6 : ~ 80 mm Hg
 Pressure of Krypton: variable
 Total Exposure Dose: Δ $1 \times 5 \times 10^8$ rads,
 \circ 2×10^8 rads
 Dose Rate: 1×10^4 to 4×10^4 rads/min
 Temperature: $60-70^\circ\text{C}$
 Average Gamma Energy: 0.75 MeV
 G calculated on the basis of the total energy absorbed in the mixtures.

108-6821

E. Decomposition of Plutonium Hexafluoride by Gamma Radiation in the Presence of Either Fluorine or Oxygen

A small number of experiments were carried out in which either elemental fluorine or oxygen was added to plutonium hexafluoride. The results of these experiments are shown in Table 6. The resulting G values for the decomposition were lower than either the G for decomposition of

Table 6

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION IN THE PRESENCE OF FLUORINE OR OXYGEN

Initial PuF_6 (millimoles)	Initial Gas (M) (millimoles)	Absorbed Dose ($\text{eV} \times 10^{-20}$)		PuF_4 Formed (millimoles)	PuF_6 Lost (millimoles)	Average Electron Fraction of M^a	G^b
		In PuF_6	In M^c				
1.020	7.958 (O_2)	16.1	14.2	0.039	0.075	0.47	2.1
1.112	17.32 (O_2)	33.1	62.2	0.122	0.186	0.65	2.8
1.026	1.039 (F_2)	15.8	2.15	0.072	0.087	0.12	3.0

^aAverage of initial and final electron fraction of the added gas equivalent to the ratio of energy absorbed in the gas M to the total energy absorbed in the mixture

^bBased on energy absorbed in PuF_6 only

^cCalculated as outlined in Table 3 footnote b

plutonium hexafluoride (see Figure 1), the G for the decomposition of plutonium hexafluoride in the presence of helium (see Figures 2 and 3), or the G value for the decomposition of plutonium hexafluoride in the presence of krypton (see Figures 4 and 5) at equivalent electron fractions of the added gas.

IV. DISCUSSION

It is recognized that the calculation of absorbed energy by use of the electron density ratio between liquid water and gaseous plutonium hexafluoride may result in errors in the absorbed dose. There exists insufficient information to resolve this problem. However, the relative values of G for the decomposition under various conditions are not affected, even though the absolute values of G may be in error.

The decomposition of pure, gaseous plutonium hexafluoride shows no dependence on total dose nor, within the limits of the present experiments, on dose rate. Experiments in which one atmosphere of helium was added to plutonium hexafluoride showed no significant difference in the G for the decomposition of plutonium hexafluoride compared with the G obtained from pure plutonium hexafluoride. One atmosphere helium is equivalent to an electron fraction of approximately 0.1, and hence the energy absorbed in helium is relatively small. With 2 atmos helium added to plutonium hexafluoride, the resulting G for the decomposition was significantly lower than that obtained either from pure plutonium hexafluoride or from mixtures of plutonium hexafluoride with one atmosphere of helium. In the absence of other data, it is not possible to formulate a definite conclusion as to the mechanism which is effective in this case. It may be pointed out, however, that a decrease in G for the decomposition can be brought about by either the deactivation of precursors of the decomposition products or an enhancement of the back reaction. The latter may be written as



As shown in Section V of this report, the gamma-radiation-induced back reaction proceeds as written in Equation 2. The back reaction in the absence of radiation can be expected to be insignificant. It may be, therefore, that activated helium reacts with either fluorine or plutonium tetrafluoride which, in turn, may react with the other component to produce plutonium hexafluoride. According to this mechanism, the back reaction should become important only when the energy absorbed in helium becomes appreciable, and this is in agreement with the observations.

The magnitude of the decrease in G for the decomposition in the presence of helium is in qualitative agreement with the data obtained for the effect of krypton on the decomposition of plutonium hexafluoride. Reduction in the G value by deactivation of the precursors of the decomposition products appears to be unlikely in view of the high energy of the lowest excited state of helium (19.818 eV).⁽¹⁷⁾

The effect of krypton on the decomposition of plutonium hexafluoride is unusual. The enhancement of the G for the decomposition has been observed only at an exposure dose of 1×10^8 rads (approximately 15×10^{20} eV absorbed in plutonium hexafluoride), although a single experiment, carried out at $1/2 \times 10^8$ rads and an electron fraction of krypton of 0.31, also resulted in a high G value (14.5) for the decomposition. It appears likely that the shape of the curve shown in Figure 4 can be explained by considering several competing processes, although in the absence of additional data it is not possible to suggest a definitive mechanism.

The initial drop in G for the decomposition, occurring at low concentrations and hence for low electron fractions of krypton, may be due to processes such as shown in Equations 3 and 4:



The lowest excited state of krypton is 9.915 eV above the ground state.⁽¹⁷⁾ No data are available on the energy levels of plutonium hexafluoride. If the first ionization potential of plutonium hexafluoride is the same as that of uranium hexafluoride,⁽¹⁸⁾ a value of approximately 15 eV can be assumed. Thus, excitation energy could be transferred between krypton and plutonium hexafluoride without ionization of either species if the energy available is less than the ionization potential of krypton⁽¹⁸⁾ (13.99 eV). Reaction 4 represents a charge-transfer process which is energetically possible, except that 1 eV of excitation energy must be dissipated, probably in plutonium hexafluoride. The absorption spectrum of plutonium hexafluoride⁽¹⁹⁾ shows several peaks above and below 8100 cm^{-1} (1 eV), indicating that partition of excitation energy is at least possible. Both reactions 3 and 4 result in the deactivation of excited or ionized plutonium hexafluoride which, in turn, should result in a lowering of the G for the decomposition.

A second process may become important as the concentration, and hence the energy absorbed by krypton, increases. This is shown by Equation 5:



In this case, the activated krypton species has been identified as Kr^{*1} to indicate the difference between reactions 3 and 5. Further, the reaction has been written to show complete decomposition, although it is realized that the primary reaction product may be a precursor of the products indicated. As the energy absorbed by krypton increases, reaction 5 should become increasingly important and hence result in an increase in the G for the decomposition.

It is necessary to mention the possible contribution of krypton fluorides to the decomposition of plutonium hexafluoride. This work was begun at a time when the rare gases were believed to be unreactive, but recent data have shown the existence of rare gas fluoride compounds, particularly krypton fluorides.⁽²⁰⁾ No direct evidence for the formation of krypton fluorides has been obtained in the present experiments. On the basis of the few data which are available for the properties and preparation of krypton fluorides,⁽²⁰⁾ it appears unlikely that appreciable quantities of krypton fluorides would remain in the reaction vessels after irradiation, owing to the thermal instability of these fluorides. On the other hand, low concentrations of krypton fluorides could be formed during the irradiation by processes such as those shown by Equations 6 and 7:

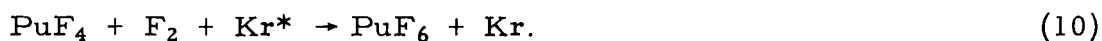


In both instances, the krypton fluorides would be unstable and decompose to elemental fluorine and krypton according to the equation



All reactions leading to the formation of krypton fluorides can be expected to enhance the G value for the decomposition of plutonium hexafluoride and thus may contribute to the rise in G value observed at an exposure dose of 1×10^8 rads. In order to account for the fact that at longer exposures to radiation, no enhancement of the G value of the decomposition is observed, it is necessary to assume that the formation of krypton fluorides proceeds with unactivated molecules or with molecules having a very small amount of excitation energy. In view of the instability of the krypton fluorides, such an assumption is not unreasonable.

At still larger concentrations of krypton, reactions shown by Equations 9 and 10 may become important:



Reaction 9 would represent the deactivation of a highly excited and short-lived species of plutonium hexafluoride. There exists no evidence for this reaction at this time. On the other hand, enhancement of the back reaction by a process such as shown by Equation 10 may well be possible. Although the reaction has been written as a three-body process, it is more likely that either fluorine or plutonium tetrafluoride is first activated by krypton and then reacts with the other species to form plutonium hexafluoride.

Although the series of reactions mentioned above may account for the results obtained at an exposure dose of 1×10^8 rads ($\sim 15 \times 10^{20}$ eV absorbed in plutonium hexafluoride), the same scheme is not easily applied to the data obtained at an exposure dose of 2×10^8 rads. In the latter case, the G value for the decomposition of plutonium hexafluoride decreases with increasing electron fraction of krypton, and no rise in the G value is observed. This complete lack of enhancement of the G value is in contrast with most phenomena observed in the radiation chemistry of gases where the processes generally do not vary abruptly with absorbed dose. A set of processes must be operative at longer exposures* which reduces the net extent of decomposition of plutonium hexafluoride. Thus, at longer exposures, reactions 3, 4, 9, and 10 may be operative. The formation of krypton fluorides, mentioned above in connection with the increasing G for the decomposition must, by inference, not be important at long exposures.

If the mechanism proposed for the decomposition of plutonium hexafluoride is coherent, it can be predicted that the addition of other gases incapable of forming fluorides would inhibit the decomposition of plutonium hexafluoride. Further, if the back reaction is important in reducing the net decomposition of plutonium hexafluoride, a gradual decrease in G with increasing exposure dose would be predicted for pure plutonium hexafluoride. Addition of gases which form fluorides should result in an increase of the G value for decomposition. Experiments carried out with elemental fluorine and elemental oxygen added to plutonium hexafluoride show a significant decrease in G for the decomposition. In the case of added fluorine, it can be anticipated that the net decomposition is decreased because of enhancement of the back reaction (Equation 2). In the case of added oxygen, it is possible that the stoichiometry of the decomposition reaction involves species other than plutonium tetrafluoride, and hence direct comparison of G values may not be proper. Experiments in which nitrogen was added to plutonium hexafluoride showed a marked increase in the decomposition of plutonium hexafluoride by alpha radiation⁽⁴⁾ together with the formation of nitrogen trifluoride.

* Experiments done at differing total exposure doses were carried out in identical fashion and differed only in length of exposure. The dose rates, materials of construction, methods of analysis, methods of calculating results, etc., were the same in both sets of experiments. In addition, experiments were done without attention as to the sequence of either the krypton concentration or the irradiation time.

It was pointed out earlier that over the range of absorbed energy studied, the decomposition of plutonium hexafluoride does not show dependence on total absorbed dose, except possibly in the case of added helium. It is believed that the absence of an observed decrease in G is due only to the limitations of the present experiments. In a long-term study of the decomposition of plutonium hexafluoride by alpha radiation,⁽⁴⁾ it has been shown that the rate of decomposition decreases with increasing time. In view of the fact that in these experiments increasing time is equivalent to increasing exposure, such a decrease in rate serves to confirm the equilibrium nature of the processes which affect the decomposition of plutonium hexafluoride by radiation.

V. FORMATION OF PLUTONIUM HEXAFLUORIDE BY IRRADIATION OF MIXTURES OF PLUTONIUM TETRAFLUORIDE AND ELEMENTAL FLUORINE BY GAMMA RADIATION

Mixtures of plutonium tetrafluoride and elemental fluorine were irradiated with gamma radiation in order to determine if appreciable concentrations of plutonium hexafluoride would be formed. The equilibrium in the system $\text{PuF}_6\text{-PuF}_4\text{-F}_2$ in the absence of radiation other than that from plutonium (alpha particles) has been reported by Trevorrow,⁽²¹⁾ whose data indicate that at room temperature, a very small pressure of plutonium hexafluoride is in equilibrium with one atmosphere of fluorine and solid plutonium tetrafluoride. It was anticipated that the presence of radiation would lead to the formation of more plutonium hexafluoride than what would be predicted from the usual thermodynamic considerations.

In order to demonstrate that the volatile product produced by irradiation of mixtures of plutonium tetrafluoride and elemental fluorine was the hexafluoride, the infrared spectrum of samples of the gaseous product was determined and found to agree completely with the spectrum reported for plutonium hexafluoride.⁽²²⁾ Further, a determination of the vapor pressure of the volatile product at the ice point gave the same value as that reported for plutonium hexafluoride.⁽⁹⁾ On the basis of these data it can be concluded that irradiation of mixtures of plutonium tetrafluoride and elemental fluorine by gamma radiation yields plutonium hexafluoride.

Table 7 shows the results of the experiments on the irradiation of mixtures of plutonium tetrafluoride and fluorine. The data show considerable variation, and it has not been possible to correlate the yield of plutonium hexafluoride with the exposure dose. Since the mechanism of the reaction is unknown, the dose listed in Table 7 is expressed in terms of the exposure dose. It should be noted that in almost all instances, the pressure of plutonium hexafluoride formed is greatly in excess of that predicted from the thermodynamic equilibrium constant at the temperature of the irradiation.

Table 7

FORMATION OF PLUTONIUM HEXAFLUORIDE BY IRRADIATION OF MIXTURES
OF PLUTONIUM TETRAFLUORIDE AND FLUORINE WITH GAMMA RADIATION

$\bar{E}\gamma$: 0.75 MeV
Dose Rate: 1×10^4 to 4×10^4 rads/min
Temperature: 60-70°C

Initial PuF ₄ (millimoles)	Initial F ₂ (mm Hg)	Volume ^c (cm ³)	Dose (H ₂ O) ^a (rads x 10 ⁻⁸)	PuF ₆ Formed	
				millimoles	mm Hg ^{b,d}
2.03	731	18	1.09	0.019	19.7
4.09	728	18	1.98	0.038	39.5
1.73	730	18	2.02	0.006	6.2
9.48	730	18	2.02	0.015	15.6
18.97	735	18	2.03	0.034	35.0
6.39	730	18	2.10	0.007	7.3
5.00	730	18	3.00	0.036	37.4
2.04	745	18	3.08	0.006	6.2
9.93	725	50	0.10	0.011	3.7
9.79	738	50	1.00	0.131	44.5
9.92	717	50	1.00	0.247	84.0
23.27	716	50	1.08	0.046	15.6
26.73	375	230	0.90	0.019	1.5
26.73	743	230	0.94	0.0005	0.04
26.71	740	230	0.95	0.002	0.02
26.71	188	230	1.00	0.002	0.02
35.85	727	230	1.51	0.208	16.7
26.71	204	230	2.01	0.005	0.4
26.75	727	230	2.06	0.014	1.1

^a Obtained by Fricke dosimetry.

^b At 65°C and 760 mm F₂ (g), 0.046 mm Hg PuF₆ is in equilibrium with solid PuF₄ in the absence of radiation. (21)

^c Volume of the reaction vessel.

^d Pressure of plutonium hexafluoride at the temperature of the irradiation.

It is clear that the back reaction to form plutonium hexafluoride proceeds in the presence of gamma radiation and hence may contribute significantly to the observed decomposition on irradiation of plutonium hexafluoride.

VI. SUMMARY

It has been shown that plutonium hexafluoride exposed to gamma radiation from fission products decomposes to form plutonium tetrafluoride and elemental fluorine. Under the conditions of the Fluoride Volatility

Process, it can be anticipated that the extent of decomposition will not represent a serious problem. The G for the decomposition of plutonium hexafluoride in the absence of added gases was determined to be 7.5. Additions of helium produced a lowering of the G value only at high helium pressures, and this result has been interpreted in terms of an enhancement of the back reaction by activated helium. Addition of krypton to plutonium hexafluoride resulted in an enhancement of the G value for the decomposition, particularly at an electron fraction of krypton of 0.73 and an exposure dose of 1×10^8 rads. Similar enhancement was not observed at an exposure dose of 2×10^8 rads. No completely satisfactory mechanisms can be proposed at this time for the results obtained with krypton.

Irradiation of mixtures of plutonium tetrafluoride and elemental fluorine yields plutonium hexafluoride at concentrations greater than that calculated from thermodynamic considerations alone.

VII. ACKNOWLEDGMENT

Irradiations were carried out at the Argonne High Level Gamma Irradiation Facility under the direction of H. G. Swope. Chemical and radiochemical analyses were carried out by C. A. Seils. The authors also wish to acknowledge the contributions made by Dr. L. Dorfman and Dr. M. Sauer in several helpful discussions and W. Gunther for aid in some of the experimental work.

VIII. BIBLIOGRAPHY

1. Fischer, J., Trevorrow, L. E., and Shinn, W. A., J. Phys. Chem., 65, 1843 (1961).
2. Malm, J. G., Weinstock, B., and Weaver, E. E., J. Phys. Chem., 62, 1506 (1958).
3. Steindler, M. J., ANL-6753 (1963).
4. Steindler, M. J., Wagner, R. P., and Fischer, J., Abstracts of Papers Presented at the 144th ACS Meeting, Los Angeles, California (1963), p. 41P.
- 5a. Bernhardt, H. A., Davis, W., and Shiflett, C. H., Proceedings of the Second UN International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 29, 62 (1958).
- 5b. Shiflett, C. H., Steidlitz, M. E., Rosen, F. D., and Davis, W., J. Inorg. Nucl. Chem., 7, 210 (1958).
- 6a. Jenks, G., Burns, W., and Tetenbaum, M., CN-735 (1943).
- 6b. Jenks, G., Livingston, R., Tetenbaum, M., and Burns, W., CN-785 (1943).
7. Kikoin, I. K., et al., Proceedings of the Second UN International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 9, 528 (1958).
8. Steindler, M. J., Steidl, D. V., and Steunenberg, R. K., Nucl. Sci. Eng., 6, 333 (1959).
9. Weinstock, B., Weaver, E. E., and Malm, J. G., J. Inorg. Nucl. Chem., 11, 104 (1959).
10. Steindler, M. J., Steidl, D. V., and Steunenberg, R. K., ANL-5875 (1958).
11. Steindler, M. J., ANL-6021 (1959).
12. Cromer, S., MDDC-803 (1947).
13. Seils, C. A., Jr., Meyer, R. J., and Larsen, R. P., Anal. Chem., 35, 1673 (1963).

14. Swope, H. G., The Argonne High Level Gamma Irradiation Facility, Atompraxis 7/8, 249 (1958).
15. Swope, H. G., ANL-5819 (1958).
16. Davies, O. L., Ed., Statistical Methods in Research and Production, Oliver and Boyd, London (1947).
17. Cook, G. A., Ed., Argon, Helium and the Rare Gases, Interscience Publishers, New York (1961), p. 99.
18. Warren, V. L., and Horton, J. C., K-1429 (1959).
19. Steindler, M. J., unpublished results.
- 20a. Grosse, A. V., et al., Science, 139, 1047 (1963).
- 20b. Turner, J. J., and Pimentel, G. C., Science, 140, 974 (1963).
- 20c. MacKenzie, D. R., and Wiswall, R. H., Jr., J. Inorg. Chem., 2, 1064 (1963).
21. Trevorrow, L. E., Shinn, W. A., and Steunenber, R. K., J. Phys. Chem., 65, 398 (1961).
22. Malm, J. G., Weinstock, B., and Claasen, H. H., J. Chem. Phys., 23, 2192 (1955).