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THE TRANSFER OF PLUTONIUM HEXAFLUORIDE
IN THE VAPOR PHASE

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ABSTRACT

Plutonium hexafluoride is decomposed by heat, by its alpha radiation and by reactions with most materials of construction. Laboratory experiments were performed to investigate means by which plutonium losses due to these reactions can be minimized during vapor-phase transfers of the compound.

The experiments showed that plutonium hexafluoride vapor could be transferred satisfactorily through well-fluorinated nickel equipment in a stream of fluorine or helium. The decomposition product of plutonium hexafluoride was refluorinated at 250 C by fluorine.

I. INTRODUCTION

A series of small-scale laboratory experiments have been conducted in an effort to determine whether or not plutonium hexafluoride can be handled satisfactorily under conditions typical of a chemical process step. In order to form plutonium hexafluoride from the tetrafluoride and fluorine, temperatures above 350 C are required for adequate reaction rates. Once formed, the compound is decomposed by heat, by radiation, and by reactions with most container materials.

To a certain extent the radiation decomposition is unavoidable.¹ Losses from this cause can be minimized, however, by keeping the plutonium hexafluoride in the gaseous state, diluted when possible with fluorine or an inert gas. The result is that a larger proportion of the alpha radiation from the plutonium is absorbed by the container walls and by the diluent gas. The radiation decomposition may also be limited by not storing the compound for longer periods of time than necessary.

¹Weinstock, B., and Malm, J. G., "The Properties of Plutonium Hexafluoride," International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, New York: United Nations, 1956, pp. 377-381.

The decomposition due to reduction by container materials and thermal decomposition is also difficult to avoid completely, but losses from these causes can be kept very small if the proper handling precautions are exercised. In a group of experiments designed to study these effects, plutonium hexafluoride was passed through heated sections of nickel tubing packed with nickel wool. The experiments were of three types:

(1) Plutonium hexafluoride was condensed on nickel surfaces which had been subjected to various prefluorination treatments in order to determine those conditions favoring minimum decomposition

(2) The deposition of plutonium activity on nickel surfaces was measured as a function of temperature and prefluorination conditions. Both helium and fluorine were employed as carrier gases.

(3) Plutonium hexafluoride was decomposed on nickel surfaces in a fluorine atmosphere and refluorinated at temperatures around 200 C.

II. EXPERIMENTAL

A. Apparatus - The apparatus as a whole is represented by the diagram in Figure 1. With the exception of a few experiments in which Trap 1 was not present, the equipment remained unchanged throughout the work.

A more detailed sketch of the decomposition zone and preparation furnace is presented in Figure 2. When a fluorine atmosphere was used in the decomposition zone, the equipment consisted of a single piece of 3/4-inch OD nickel tubing. The plutonium hexafluoride was prepared in the first few inches of the tube, the remainder being packed with nickel wool and serving as the decomposition zone.

The packed section which served as the decomposition zone was prepared by wrapping coarse nickel wool in 100-mesh nickel screen and rolling it to a tight fit in a 0.625-inch ID nickel tube. It was then cut into 2.5-inch sections, and four of these were inserted in the decomposition zone. After use they were removed with long forceps and dissolved individually in nitric acid solution for plutonium analysis. A 10-inch packed section of this type contained about 32 grams of nickel wool and had an estimated surface of 1500 sq cm.

B. Preparation of Plutonium Hexafluoride - The plutonium tetrafluoride was weighed into a hemicylindrical nickel boat which was shaped to fit the inside of the 3/4-inch nickel furnace tube. The weighing was performed on an analytical balance enclosed in a glove box. The boat was placed in a closed Lucite carrier and transferred in a clean plastic bag to the Blickman Type K hood in which the work was done.

FIGURE 1

APPARATUS USED FOR DECOMPOSITION STUDIES ON PLUTONIUM HEXAFLUORIDE

FIGURE 2

APPARATUS IN WHICH PREFLUORINATION STUDIES WERE CARRIED OUT

The boat, which contained about 20 mg of plutonium tetrafluoride, was placed in the furnace tube. All the joints of the apparatus were then tightened and helium was passed through the equipment at a rate of about 200 cc/min. The helium was dried and purified from traces of oxygen by passing it through an activated charcoal trap which was immersed in liquid nitrogen.

While the helium was flowing through the system the furnace temperature was raised to about 500 C. Fluorine from a ballast tank was then substituted for the helium stream. The fluorine flow rate was calculated from the pressure drop in the ballast tank which was of a known volume.

The plutonium hexafluoride for all the experiments was prepared in this manner. The procedures following the preparation varied, however, and they are described under the various types of experiments.

C. Analyses - At the completion of each experiment the equipment was completely disassembled. The packing sections were removed and dissolved individually. The furnace tube and traps were washed with a nitric acid-aluminum nitrate solution and care was taken to dissolve any solid residues. The resulting solutions were analyzed for plutonium activity by direct-plate alpha counting. If the solutions contained a sufficiently high concentration of dissolved solids to absorb an appreciable part of the alpha radiation, the plutonium was removed before counting by a lanthanum fluoride coprecipitation procedure.²

III. RESULTS AND DISCUSSION

A Prefluorination of a Nickel Trap for Plutonium Hexafluoride - A nickel trap was pretreated with fluorine gas, using a variety of combinations of time and temperature. An attempt was made to define a set of prefluorination conditions that would pretreat the surface of the trap so that plutonium hexafluoride condensed in it would not be decomposed by reaction with the nickel. The criterion for the effectiveness of these treatments was the amount of plutonium hexafluoride which could be revolatilized from the trap.

In these experiments plutonium tetrafluoride was first placed in the furnace tube for the preparation of the hexafluoride. Instead of heating the furnace immediately, however, Trap 1 was heated by means of resistance windings to the desired prefluorination temperature. Fluorine was then substituted for the helium stream which had been flowing through the system during the heating. After the desired prefluorination time of

²"Summary Report, Development of Radiochemical Analytical Procedures for Plutonium," CN 2040 (Sept. 23, 1944).

30 to 90 minutes the fluorine was swept out of the system with helium. Trap 1 was cooled while the furnace tube was being heated for the plutonium hexafluoride preparation.

During the prefluorination of Trap 1 the temperature in the furnace tube at the position of the boat containing the plutonium tetrafluoride did not exceed 120 C. At this temperature plutonium losses resulting from formation of the hexafluoride and those from dusting of the solid tetrafluoride were negligible. In one experiment the boat was removed from the furnace tube after the prefluorination of Trap 1 and weighed. The loss amounted to 0.7 mg.

When the furnace tube had reached 500 C, Trap 1 was immersed in a Dewar flask containing liquid nitrogen. Fluorine was again passed through the system. The plutonium hexafluoride formed in the furnace tube was condensed in Trap 1. After 15 minutes at 500 C all the plutonium tetrafluoride in the boat was fluorinated. The excess fluorine was then flushed from the system with helium at a flow rate of 100 cc/min.

The Dewar flask containing liquid nitrogen was removed from Trap 1 and placed around Trap 2. Trap 1 was warmed gradually to a temperature between 70 and 90 C by means of a small current in the heater windings. A period of one hour was allowed for the plutonium hexafluoride to be vaporized from Trap 1 and condensed in Trap 2.

The apparatus was disassembled and the amounts of plutonium deposited in the various sections were obtained by analyses of the nitric acid-aluminum nitrate wash solutions.

The data from these experiments are presented in Table 1. Prefluorinations at higher temperatures and for longer periods of time resulted in less decomposition of the plutonium hexafluoride. When the trap had been prefluorinated for 90 minutes at 560 C, revolatilization of the plutonium hexafluoride was nearly quantitative.

The somewhat erratic results from these experiments and also from later ones is probably a consequence of the small quantities of plutonium used. The largest quantity used in any one experiment was 20 mg (as plutonium). Due to the high atomic weight of plutonium this represents only 8.3×10^{-5} mole. This small amount of material is very susceptible to losses arising from traces of moisture in the helium or from reaction with the nickel if a crack in the protective fluoride coating should be present.

B. The Decomposition of Plutonium Hexafluoride on Nickel Surfaces as a Function of Temperature and Prefluorination Conditions in Fluorine and Helium Atmospheres - The first group of experiments were performed with a fluorine atmosphere and with packing which was not

Table 1

RELATIONSHIP OF PREFLUORINATION CONDITIONS
TO VAPORIZATION OF PLUTONIUM HEXAFLUORIDE
FROM A NICKEL TRAP

Plutonium hexafluoride condensed in a nickel cold trap, then revolatilized into a helium stream by warming the trap to 70-90 C for one hour.

<u>Cold Trap</u> <u>Prefluorination</u> <u>Conditions</u>	<u>Per Cent PuF₆ Decomposed</u> <u>(i.e., amount remaining in trap)</u>			
<u>Time (min)</u>	<u>15</u>	<u>30</u>	<u>60</u>	<u>90</u>
<u>Temp (C)</u>				
280	100			
300		71		
330			70	
420		(47)		
450		70		8.7
490		(28)		
560		(69)		4.4
		22.2		

prefluorinated. The apparatus consisted of a length of 3/4-inch nickel tubing running through the preparation furnace directly to Trap 2 (see Figures 1 and 2). The plutonium hexafluoride was prepared in the first few inches and passed immediately through the 10-inch decomposition zone in the same tube. The packing sections in the 10-inch decomposition zone were 2½ inches long and were made of nickel wool rolled in 100 mesh nickel screen.

The boat containing plutonium tetrafluoride was placed in the preparation zone and the apparatus was assembled. Helium was passed through the system while the tube furnace and decomposition system were being heated. When the furnace temperature had reached 500 C and the decomposition zone temperature had become constant at 120, 180 or 240 C, fluorine was substituted for helium in the system.

After a half-hour period the heaters were disconnected and the fluorine was flushed from the system with helium. The equipment was disassembled and the amount of plutonium hexafluoride which had decomposed in the various sections was determined. The experimental results are summarized in Table 2.

Table 2

TEMPERATURE DEPENDENCE OF RATE OF DECOMPOSITION
OF PLUTONIUM HEXAFLUORIDE

$$\text{Definitions: Residence Time} = \frac{\text{Volume of Packed Tube}}{\text{Flow Rate of Carrier Gas}}$$

$$\% \text{ PuF}_6 \text{ Decomposed/sec} = \frac{(\text{PuF}_6 \text{ Decomposed})(100)}{(\text{PuF}_6 \text{ used})(\text{Residence time})}$$

Prefluorination Conditions		Per Cent PuF ₆ Decomposed per Second									
Temperature (C)	- ^a	210	250	350	350	450	450	450	560	560	
Time (minutes)	-	75	30	30	90	30	60	90	30	90	
Decomposition Temperature (C)											
120	1.8 ^b	0.09 ^b		0.01 ^c 0.18 0.13							
180	0.9 ^b		0.05 ^b	0.12		0.51 0.30 0.04 ^c	0.63	0.12 0.07	0.17	0.11	
240	0.3 ^b			0.94 0.01 ^b	0.82	0.38					

^a Not prefluorinated.

^b Fluorine used as carrier gas instead of helium.

^c Doubtful values.

A similar series of experiments were performed in the same manner as those just described, except that the packing was prefluorinated. The apparatus was loaded and assembled as before. The decomposition zone was heated by the nichrome resistance windings to a temperature approximately 100 C above the decomposition temperature selected for the particular experiment. Fluorine was then admitted to the system at a rate of 30 to 100 cc/min.

After the prefluorination treatment, the system was flushed with helium, and both the preparation furnace and the decomposition zone were heated to their operating temperatures. From this point on the procedure was identical to that used in the experiments with the packing which had not been prefluorinated. The conditions used in these experiments and data from them are also presented in Table 2.

Figure 3

trap experiments (Section III, A) and condensed in Trap 1. When fluorine had been flushed from the system and the decomposition zone temperature had been stabilized at the required temperature (120, 180, 240 C), Trap 1 was warmed to a temperature of 70 to 90 C. The plutonium hexafluoride in the trap was then sublimed into the helium stream and was carried through the packed zone into Trap 2.

The amounts of plutonium hexafluoride decomposed in the various portions of the apparatus were determined as before. The data from these experiments are presented in Table 2 along with those data from the fluorine atmosphere experiments.

In Figure 4 the decomposition rates obtained with the helium atmosphere are plotted against the temperature of the decomposition zone. These rates are considered to be divided into the two groups indicated by the lines. It appeared that the prefluorination treatment was less effective in that group with the higher decomposition rates. This is not dependent upon the prefluorination temperature alone; it is also influenced by the duration of exposure to the fluorine.

As might be expected, in the helium atmosphere the stability decreased with increasing temperature. With adequate prefluorination of the apparatus, however, the rates of decomposition were low. A quantitative determination of the stability changes with temperature or of decomposition rates was not attempted due to the large number of variables involved, the limitations in equipment, and the fact that only small quantities of material could be handled in the available facilities.

The decomposition rates are compared graphically in Figure 3. In a fluorine atmosphere the plutonium hexafluoride is more stable at higher temperatures. If the equipment was prefluorinated, the decomposition was slight at 240 C.

The decomposition studies in helium atmospheres were performed only with prefluorinated nickel packing. In each experiment the apparatus illustrated in Figure 2 was used, and the packing was prefluorinated in the manner described previously.

Plutonium hexafluoride was prepared as for the prefluorinated

FIGURE 4
EFFECT OF INCREASING TEMPERATURE ON RATE OF
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE
(prefluorinated nickel wool, helium carrier gas)

The results of two experiments in which copper turnings were substituted for the nickel wool packing are presented in Table 3. In these experiments the decomposition rates were significantly higher than those obtained with nickel packing. Virtually all the plutonium hexafluoride was decomposed by the copper.

Table 3

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE ON
UNPREFLUORINATED COPPER TURNINGS

<u>Atmosphere</u>	<u>Decomposition Temperature (C)</u>	<u>Plutonium Used (mg)</u>	<u>Plutonium Deposited (mg)</u>	<u>Per Cent PuF₆ Decomposed Per Second</u>
Fluorine	200 - 300	16.2	13.29	4.91
Helium	180	4.94	4.92	1.27

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C. Refluorination of the Plutonium Hexafluoride Decomposition Product - Apparently the non-volatile decomposition product of plutonium hexafluoride can be refluorinated in a current of fluorine at temperatures below 250 C. This effect was noted in the variation of the amount of plutonium hexafluoride as related to position in the packed section. In the short experiments the plutonium was deposited largely in the first section of packing. In the longer ones larger amounts of plutonium were found in those sections farther downstream.

This phenomenon is illustrated by the two graphs in Figure 5. The amount of plutonium found by analysis is shown as a function of the position at which it was deposited. The approximate temperature at each position is also indicated.

FIGURE 5
INFLUENCE OF TIME AND TEMPERATURE
ON LOCATION OF PLUTONIUM DEPOSITION

The apparatus used for these experiments differed from that shown in Figure 2 in that no trap was used between the preparation and decomposition zones. The decomposition zone, which was $7\frac{1}{2}$ inches long, was divided into four sections. The first was 3 inches long and it was followed by three $1\frac{1}{2}$ -inch sections. The decomposition zone in this case was heated by a small tube furnace. The temperature was not uniform over the length of packing, but varied from 325 to 350 C at the beginning to about 100 C at the end.

After the plutonium tetrafluoride had been placed in the furnace tube, both heaters were turned on as helium was passed through the system. When the proper temperature was reached, fluorine was substituted for the helium. The plutonium hexafluoride passed directly into the packing as it was formed.

In some of the experiments the fluorine was permitted to flow through the heated packing for 15 minutes, while in others the time was increased to 60 minutes. At the end of the allotted time period the system was flushed with helium as the furnace cooled. The apparatus was disassembled and each section of the packing was dissolved separately for plutonium analyses. The data from several of these experiments are presented in Table 4.

Table 4

REFLUORINATION OF THE DECOMPOSITION PRODUCT
OF PLUTONIUM HEXAFLUORIDE

<u>Time of</u> <u>Fluori-</u> <u>nation</u> <u>(min)</u>	<u>Plutonium</u> <u>Used</u> <u>(mg)</u>	<u>Fluorine</u> <u>Flow Rate</u> <u>(cc/min)</u>	<u>Site of</u> <u>Deposition</u> <u>of Plutonium</u> <u>(See Figure 2)</u>	<u>Estimated</u> <u>Temperature</u> <u>of Packing</u> <u>Section (C)</u>	<u>Amount of</u> <u>Plutonium</u> <u>Deposited</u> <u>(mg)</u>
60	17.0	40	1	350	0.50
			2	300	0.54
			3	200	2.60
			4	100	1.74
60	15.2	50	1	325	0.58
			2	200	0.95
			3	140	1.16
			4	100	1.13
15	19.3	77.5	1	350	1.04
			2	220	0.81
			3	125	0.67
			4	100	0.64
15	12.5	29	1	290	2.31
			2	250	0.58
			3	160	0.49
			4	100	0.95

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IV. CONCLUSIONS

The results of these experiments indicate that plutonium hexafluoride vapor can be transferred and manipulated satisfactorily provided the proper precautions are exercised. The following conclusions were reached regarding the handling of gaseous plutonium hexafluoride.

Plutonium hexafluoride can be moved through nickel equipment of a simple nature if the equipment has been well prefluorinated and is held at a temperature above 200 C with a fluorine atmosphere.

Decomposed plutonium hexafluoride can be refluorinated at 250 C in a current of fluorine.

Plutonium hexafluoride vapor can be transferred short distances in a current of helium if the nickel equipment is well prefluorinated.

Prefluorination conditions of 500 to 550 C for a 90-minute period are adequate for the handling of plutonium hexafluoride in nickel if the lines are kept short and temperatures around 100 C are employed.

Copper is to be avoided as a material for equipment in contact with plutonium hexafluoride vapor.