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AEC Research and
Development Report

# Low-Temperature Refluorination of $PuF_6$ Decomposition Products

*W. L. Robb, R. J. Brandon*
*R. L. Myers, H. N. Galpern*

*March 30, 1957*

Operated for the
United States Atomic
Energy Commission by
GENERAL ELECTRIC

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UC-4, Chemistry - General
(TID-4500, 13th ed, Rev.)

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## ILLUSTRATIONS

# ABSTRACT

The use of direct refluorination to recover plutonium deposited in equipment by consumption and decomposition of $PuF_6$ gas has been the subject of a brief experimental program. Measurable rates of refluorination were obtained at temperatures as low as 170°C and by means of a statistically designed experiment, the approximate significance of the three variables, temperature, fluorine pressure, and fluorine flow rate, was determined. Temperature was found to be the most significant variable, and the heat of reaction based on removal rates measured from 170 to 350°C compared favorably with reported values obtained by equilibrating $PuF_6$ and $F_2$ gas mixtures. At plutonium surface concentrations below $\sim 3\ \mu gm/cm^2$, the rate of refluorination was found to be proportional to the plutonium surface concentration. In no case was the surface concentration decreased below $0.08\ \mu gm/cm^2$.

# LOW-TEMPERATURE REFLUORINATION OF $PuF_6$ DECOMPOSITION PRODUCTS

W.L. Robb, R.J. Brandon, R.L. Myers, H.N. Galpern

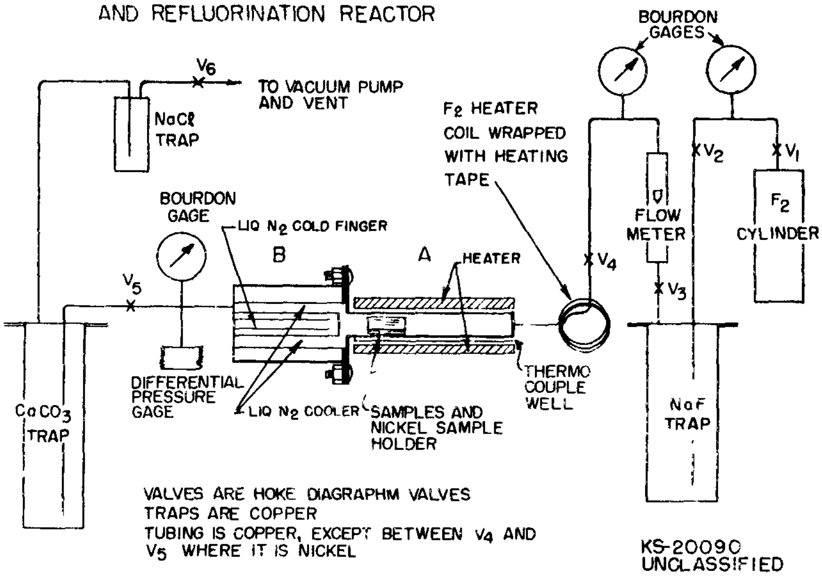
## INTRODUCTION

In any equipment containing $PuF_6$ gas, some decomposition of the $PuF_6$ gas and deposition of a nonvolatile plutonium fluoride must be expected. This deposition can be due to radiation- or thermal-decomposition or due to consumption on the walls of the equipment. Although the rate of this deposition will be affected by the temperature, the gas pressure, the material and surface area of the equipment, and the presence of other constituents in the gas phase, a value of 0.3%/day gives an indication of this deposition rate.[1,2]

Periodically these decomposition products (presumed to be $PuF_4$ in this study) must be removed from the equipment, and to date it is usually assumed that dissolution in an aqueous or organic medium will accomplish this clean-up. However, some construction materials are not corrosion resistant to liquids which will dissolve $PuF_4$, and in other cases it is difficult or impossible to handle liquids in the equipment. In these cases, it would be desirable if the $PuF_4$ could be refluorinated to $PuF_6$ gas, which could then be pumped from the equipment.

Before 1954, it was not believed possible to form $PuF_6$ below 350°C. In 1954, however, Vogel[3] showed that bulk $PuF_4$ could be transported as a vapor

FIGURE I SCHEMATIC DRAWING OF FLUORINE FLOW SYSTEM AND AND REFLUORINATION REACTOR

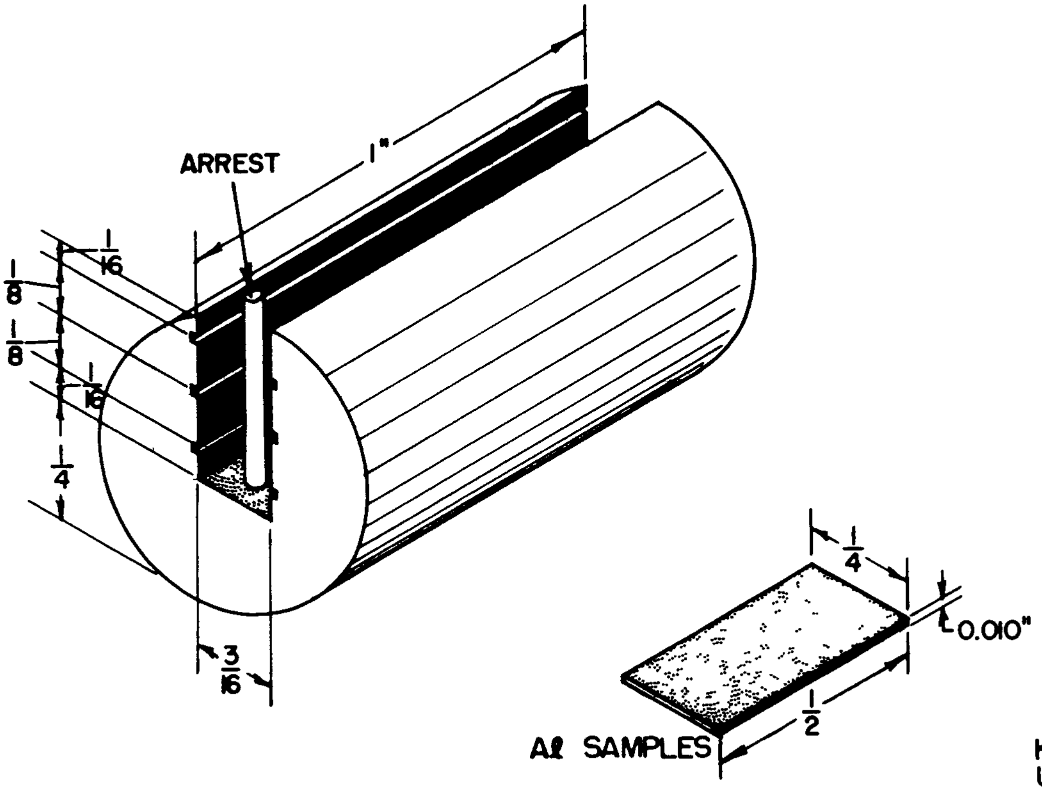


in a fluorine stream at much lower temperatures, which gave promise to the use of direct refluorination as a means of decontamination. To extend his work, an experimental program was begun at the Knolls Atomic Power Laboratory to investigate the refluorination rate of contaminated metal specimens. Preliminary results showed that the $PuF_4$ could be reflourinated and removed at least as low as 200°C. With this encouragement a statistical experiment was performed in an attempt to determine the mechanisms which control the reflourination rate.

## DESCRIPTION OF EXPERIMENTAL EQUIPMENT

The measurement of refluorination rates of $PuF_6$ decomposition products was accomplished in a simple nickel apparatus, mounted in a stainless steel hood and operated manually. The entire flow system is shown in Figure 1, and the details of the sample holder which held the metal samples to be decontaminated are shown in Figure 2. The refluorination reactor was a 16-in.

FIGURE 2 NICKEL SAMPLE HOLDER



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length of nickel tubing with a 1/2-in. ID, wound with insulated resistance wire, asbestos tape, and glass wool. A 1/8-in. stainless steel tube attached to the outside of the nickel tube served as a thermowell, which permitted temperatures to be measured along the tubing by adjusting the depth of the thermocouple in the well. In a preliminary test the sample temperatures were calibrated against a thermocouple in this well. A liquid nitrogen cold trap was attached to the 1/2-in. reactor tube by means of a Teflon gasket between two nickel flanges. The cold trap was intended as a collection surface for any $PuF_6$ produced. In most of the experiments this trap was not kept cold, since there was no need to recover the $PuF_6$ formed. A $CaCO_3$ (finely divided oalitic limestone) trap was used to decompose and collect any $PuF_6$ that was volatilized.

The fluorine flow rate was measured by a gas rotameter. The fluorine pressure was measured by Bourdon pressure gages with Monel bellows placed downstream and upstream of the reactor and by a Taylor differential pressure transmitter downstream from the reactor. The fluorine flow rate and reactor pressure were maintained by manually controlling Hoke diaphragm valves, marked 3 and 5 in Figure 1. A coil of nickel tubing wound with insulated resistance wire was used to preheat the fluorine.

All tests were started with the reactor at temperature and evacuated. Ten to thirty seconds were usually required to fill it to the desired fluorine pressure, and timing of the tests began as soon as the reactor was filled with $F_2$ and the desired flow rate had been obtained. At the end of the intended running time, the reactor was rapidly evacuated and kept this way until it had cooled. Fortunately, tests with zero running time demonstrated that this filling and evacuating procedure did not produce significant $PuF_4$ decontamination compared with that obtained during the timed flow period.

The metal samples to be decontaminated were prepared from highly polished 10-mil-thick sheets of ALCOA 75ST6 aluminum alloy cut into samples 1/4 by 1/2 in. One end of each sample was reserved for handling, and only a circle of 0.131 $cm^2$ on each side was counted by an alpha proportional counter. The samples were first prefluorinated at 75°C for 26 hr and then were exposed to $PuF_6$ for the various times, temperatures, and pressures given in Table 1. After the $PuF_6$ gas had been pumped out of the sample container, the samples were carefully removed, counted on both sides for plutonium activity, and sorted according to the amount of contamination.

TABLE 1. Exposure Conditions for Contaminating Aluminum Samples

| Exposure | Temperature, °C | Exposure Time, hr | Initial $PuF_6$ Pressure, mm Hg | Range of Plutonium Concentrations on Samples |
|---|---|---|---|---|
| 1 | 75 | 22 | 5.2 | 0.6 to 1.5 |
| 2 | 90 | 22 | 19.0 | 5.1 to 8.2 |
| 3 | 90 | 24 | 17.3 | 8.2 to 12.5 |

Alpha counting was done before and after the decontamination tests with a thin mica shield which could be placed in the same position on the samples. Several counts were taken on each surface with the shield repositioned before each count. Checks within 2% were usually obtained.

Control of the initial $PuF_4$ surface concentrations in the tests was accomplished by assigning each sample to one of seven classes (numbered 1, 2, . . ., 7) according to the initial concentration on one side of each sample strip. In this manner only one of the two sides of each sample could be controlled, but, in general, little difference was found in the initial concentrations measured on the two sides of the samples. The controlled side of each sample is referred to as the "prime" side to contrast it with the noncontrolled "reverse" side.

The six contaminated sides of the three samples were classified according to slot position in the sample holder (i.e., top, middle, or bottom) and side (up or down). The prime side of the three sample strips was assigned, respectively, to the upper top, upper middle, and lower bottom positions in the holder. All the specimens assigned to the top position came from the median concentration class. The initial concentrations on the other two controlled positions were varied among the remaining six concentration classes, with the restriction that the sum of the class numbers of the three controlled concentration classes equal 12 for each test. For example, one possible combination would be that of three sample strips from the fourth (the median), seventh, and first concentration classes (i.e., 4 + 7 + 1 = 12).

In addition to the tests required for the statistical experiment, tests were also performed to prove that the removal of plutonium was due to refluorination and to determine the amount of transfer of plutonium from one sample to another. That the decontamination was due to refluorination was confirmed by performing a test in the usual manner, except with helium gas replacing the fluorine. Within the alpha counting accuracy, no plutonium was removed from the sample. The amount of material transferred between samples was measured by placing an uncontaminated metal sample in the reactor along with two contaminated samples. A decontamination test was then performed in the normal manner. Counting of the initially clean sample in two tests showed that 0.009 and 0.03 $\mu$gm Pu/cm$^2$ had been deposited on the specimens. These are lower plutonium concentrations than were obtained on even the most completely decontaminated samples.

No attempts to recover and identify $PuF_6$ gas from the refluorination were undertaken, although this is something that was planned had time been available.

## RESULTS

### $PuF_4$ Refluorination Rates

In an attempt to determine the variables which control the rate in the refluorination of $PuF_6$ decomposition products, twenty-two separate tests were made at five different levels of fluorine flow rate, $W_{F_2}$, and fluorine pressure, $p_{F_2}$ and at six different sample temperatures, T. The conditions of each test and the $PuF_4$ concentrations on the samples before and after each test are given in Tables 2 and 3, respectively. The term $C_o$ refers to the initial $PuF_4$ concentration, and $C_t$ refers to the concentration after refluorination for t minutes. The $PuF_4$ concentrations are given in terms of alpha counts per minute per 0.131 cm$^2$ equal to $\sim 10^{-4}$ $\mu$gm Pu/cm$^2$.

In Table 2 the intended values of the three controlled variables for the designed experiment are given along with the actual values of the variables in the tests. Usually good agreement between planned and actual conditions was obtained. The largest disagreement was found in the fluorine flow rate in Test No. 2. For this reason this test was rerun as Test No. 2R.

## TABLE 2. Comparison of Planned Variables and Actual Experimental Variables

| | | | | | | Sample Group Number | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Flow | Top | Middle | Bottom |
| Run Number | | Run Time, min | Temperature, °C | Pressure, mm Hg | Rate, millimoles/min | Prime Side Up | Prime Side Up | Prime Side Down |
| 1 | Pl | 5 | 250 | 245 | 4.5 | 4 | 6 | 2 |
| | Exp | | 249 | 249 | 4.5 | 4 | 6 | 2 |
| 1R | Pl | 5 | 250 | 245 | 4.5 | 4 | 6 | 2 |
| | Exp | | 249 | 245 | 4.5 | 4 | Clean Al[1] | 2 |
| 2 | Pl | 5 | 200 | 130 | 2.02 | 4 | 6 | 2 |
| | Exp | | 199 | 123 | 4.3 | 4 | 6 | 2 |
| 2R | Pl | 5 | 200 | 130 | 2.02 | 4 | 6 | 2 |
| | Exp | | 199 | 131 | 1.95 | 4 | Rerun[2] | Rerun[3] |
| 3 | Pl | 5 | 312 | 130 | 10.06 | 4 | 2 | 6 |
| | Exp | | 313 | 132 | 9.9 | 4 | 2 | 6 |
| 4 | Pl | 5 | 312 | 461.6 | 2.02 | 4 | 2 | 6 |
| | Exp | | 313 | 458 | 1.9 | 4 | 2 | 6 |
| 5 | Pl | 5 | 200 | 461.6 | 10.06 | 4 | 6 | 2 |
| | Exp | | 200 | 464 | 9.6 | 4 | 6 | 2 |
| 6 | Pl | 5 | 250 | 245 | 4.5 | 4 | 2 | 6 |
| | Exp | | 249 | 244 | 4.0 | 4 | 2 | 6 |
| 7 | Pl | 5 | 200 | 130 | 10.06 | 4 | 1 | 7 |
| | Exp | | 200 | 130 | 10.5 | 4 | 1 | 7 |
| 8 | Pl | 5 | 200 | 461.6 | 2.02 | 4 | 1 | 7 |
| | Exp | | 200 | 462 | 2.0 | 4 | 1 | 7 |
| 9 | Pl | 2.5 | 312 | 130 | 2.02 | 4 | 7 | 1 |
| | Exp | | 313 | 130 | 3.0 | 4 | 7 | 1 |
| 9R | Pl | 5 | 312 | 130 | 2.02 | 4 | 7 | 1 |
| | Exp | | 311 | 131 | 2.1 | 4 | Rerun[4] | Rerun[5] |

[1] Clean aluminum.

[2] Rerun of top sample in Run 5.

[3] Rerun of bottom sample in Run 2.

[4] Rerun of top sample in Run 2.

[5] Rerun of bottom sample in Run 9.

TABLE 2. Comparison of Planned Variables and Actual Experimental Variables (Continued)

| | | | | | | Sample Group Number | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Top | Middle | Bottom |
| Run Number | | Run Time, min | Temperature, °C | Pressure, mm Hg | Flow Rate millimoles/min | Prime Side Up | Prime Side Up | Prime Side Down |
| 10 | Pl | 2.5 | 312 | 461.6 | 10.06 | 4 | 7 | 1 |
| | Exp | | 311 | 461 | 9.8 | 4 | 7 | 1 |
| 10R | Pl | 5 | 312 | 461.6 | 10.06 | 4 | 7 | 1 |
| | Exp | | 310 | 463 | 9.4 | 4 | Rerun[6] | Rerun[7] |
| 11 | Pl | 4 | 250 | 245 | 4.5 | 4 | 7 | 1 |
| | Exp | | 251 | 243 | 4.3 | 4 | 7 | 1 |
| 12 | Pl | 4 | 182 | 245 | 4.5 | 4 | 3 | 5 |
| | Exp | | 181 | 246 | 4.6 | 4 | 3 | 5 |
| 13 | Pl | 1 | 342 | 245 | 4.5 | 4 | 5 | 3 |
| | Exp | | 343 | 247 | 4.65 | 4 | 5 | 3 |
| 14 | Pl | 4 | 250 | 245 | 1.442 | 4 | 5 | 3 |
| | Exp | | 251 | 244 | 1.44 | 4 | 5 | 3 |
| 15 | Pl | 4 | 250 | 245 | 14 | 4 | 3 | 5 |
| | Exp | | 250 | 243 | 13.6 | 4 | 3 | 5 |
| 16 | Pl | 4 | 250 | 100 | 4.5 | 4 | 3 | 5 |
| | Exp | | 249 | 99 | 4.5 | 4 | 3 | Rerun[9] |
| 17 | Pl | 4 | 250 | 600 | 4.5 | 4 | 5 | 3 |
| | Exp | | 250 | 595 | 4.3 | 4 | 5 | Rerun[10] |
| 18 | Pl | 4 | 250 | 245 | 4.5 | 4 | 1 | 7 |
| | Exp | | 248 | 245 | 4.7 | 4 | 1 | Re-re-run[11] |
| 19 (Modified 12R) | Pl | 30 | 170 | 245 | 4.5 | 4 | 3 | 5 |
| | Exp | | 171 | 245 | 4.5 | 4 | Clean Al[1] | Rerun[8] |

[6] Rerun of top sample in Run 7.

[7] Rerun of bottom sample in Run 10.

[8] Rerun of middle sample in Run 12.

[9] Rerun of middle sample in Run 1.

[10] Rerun of top sample in Run 1.

[11] Second rerun of middle sample in Run 1.

## TABLE 3. Initial and Final Concentrations
(ct/min/0.131 cm$^2$)

| Run | Side | Top | | Middle | | Bottom | |
|---|---|---|---|---|---|---|---|
| | | $C_o$ | $C_t$ | $C_o$ | $C_t$ | $C_o$ | $C_t$ |
| 1 | Prime | 50,286 | 13,426 | 7,549 | 2,330 | 94,007 | 19,178 |
| | Reverse | 75,928 | 37,707 | 9,521 | 2,283 | 77,179 | 15,454 |
| 1R | Prime | 69,004 | 6,638 | 0 | 280 | 91,388 | 10,695 |
| | Reverse | 75,945 | 6,499 | 0 | 268 | 91,530 | 30,638 |
| 2 | Prime | 55,340 | 7,976 | 6,850 | 2,765 | 88,193 | 66,089 |
| | Reverse | 53,847 | 21,885 | 8,289 | 3,913 | 88,483 | 69,451 |
| 2R | Prime | 67,794 | 35,560 | 4,276 | 4,519 | 66,089 | 54,465 |
| | Reverse | 77,806 | 68,648 | 10,507 | 10,449 | 69,451 | 60,120 |
| 3 | Prime | 52,281 | 3,386 | 90,235 | 3,137 | 7,243 | 1,320 |
| | Reverse | 48,495 | 1,930 | 81,864 | 4,003 | 8,261 | 1,744 |
| 4 | Prime | 49,928 | 1,698 | 93,504 | 1,632 | 8,051 | 1,875 |
| | Reverse | 60,703 | 1,784 | 71,984 | 2,369 | 8,130 | 1,553 |
| 5 | Prime | 49,984 | 4,276 | 7,099 | 1,297 | 83,180 | 21,773 |
| | Reverse | 61,328 | 10,507 | 7,908 | 763 | 81,339 | 23,591 |
| 6 | Prime | 50,495 | 1,729 | 85,458 | 2,910 | 7,667 | 1,005 |
| | Reverse | 69,640 | 3,301 | 79,053 | 1,684 | 6,567 | 888 |
| 7 | Prime | 49,841 | 6,969 | 100,063 | 43,050 | 6,086 | 1,394 |
| | Reverse | 69,210 | 22,996 | 85,448 | 37,414 | 7,528 | 1,755 |
| 8 | Prime | 61,827 | 10,700 | 100,557 | 80,824 | 6,549 | 1,607 |
| | Reverse | 46,315 | 25,867 | 84,793 | 36,484 | 9,262 | 2,863 |
| 9 | Prime | 48,944 | 7,850 | 5,718 | 752 | 95,970 | 13,821 |
| | Reverse | 70,628 | 14,599 | 4,923 | 1,430 | 95,494 | 19,030 |
| 9R | Prime | 61,643 | 8,880 | 7,976 | 2,660 | 13,821 | 6,246 |
| | Reverse | 41,172 | 4,352 | 21,885 | 4,756 | 19,030 | 7,458 |
| 10 | Prime | 51,632 | 3,547 | 6,413 | 1,328 | 98,588 | 9,758 |
| | Reverse | 48,479 | 4,106 | 5,109 | 1,505 | 90,068 | 6,158 |
| 10R | Prime | 48,250 | 4,876 | 6,969 | 1,764 | 9,758 | 8,895 |
| | Reverse | 69,491 | 8,551 | 22,996 | 2,158 | 6,158 | 3,986 |

## TABLE 3. Initial and Final Concentrations (Continued)
(ct/min/0.131 $cm^2$)

| Run | Side | Top $C_o$ | Top $C_t$ | Middle $C_o$ | Middle $C_t$ | Bottom $C_o$ | Bottom $C_t$ |
|---|---|---|---|---|---|---|---|
| 11 | Prime | 60,290 | 2,116 | 6,143 | 1,112 | 112,875 | 4,684 |
| | Reverse | 75,143 | 2,895 | 7,177 | 1,093 | 95,475 | 3,060 |
| 12 | Prime | 54,330 | 42,351 | 82,883 | 76,035 | 12,934 | 6,052 |
| | Reverse | 47,512 | 40,417 | 108,266 | 94,084 | 7,026 | 3,501 |
| 13 | Prime | 52,562 | 4,667 | 9,932 | 1,849 | 87,844 | 2,066 |
| | Reverse | 47,517 | 2,903 | 9,135 | 1,873 | 87,792 | 1,894 |
| 14 | Prime | 53,055 | 1,687 | 7,822 | 1,184 | 80,248 | 2,955 |
| | Reverse | 58,849 | 1,698 | 6,066 | 1,091 | 83,974 | 3,278 |
| 15 | Prime | 50,105 | 5,268 | 83,205 | 15,268 | 8,455 | 1,958 |
| | Reverse | 70,552 | 17,366 | 56,980 | 6,447 | 6,314 | 1,307 |
| 16 | Prime | 59,265 | 9,639 | 84,159 | 17,359 | 2,330 | 1,707 |
| | Reverse | 47,779 | 22,268 | 83,995 | 6,098 | 2,283 | 1,751 |
| 17 | Prime | 46,112 | 3,943 | 9,526 | 1,030 | 13,426 | 7,326 |
| | Reverse | 71,748 | 34,074 | 8,584 | 944 | 37,707 | 23,242 |
| 18 | Prime | 49,249 | 8,260 | 86,921 | 3,379 | 1,707 | 1,471 |
| | Reverse | 47,061 | 4,381 | 89,281 | 7,729 | 1,751 | 1,548 |
| 19 | Prime | 74,800 | 24,499 | 0 | 238 | 76,035 | 4,320 |
| | Reverse | 86,213 | 41,411 | 0 | 81 | 94,084 | 6,476 |

## TABLE 4. Data on Refluorination of $PuF_4$ from the High $C_o$ Samples in Five Tests at the Mean Temperature, Pressure, and Flowrate

| Test Number | Time of Run, min | $C_o$ | $C_t$ | $\frac{C_o - C_t}{t}$ |
|---|---|---|---|---|
| 1 | 5 | 94,007 | 19,178 | 14,950 |
| 1R* | 5 | 91,530 | 30,638 | 12,180 |
| 6 | 5 | 85,458 | 2,910 | 16,510 |
| 11 | 4 | 112,875 | 4,684 | 27,050 |
| 18 | 4 | 89,281 | 7,729 | 20,390 |

* Test 1R was run after the 18 planned tests were completed and could just as well be called 6R, 11R, or 18R.

Based on several supplementary experiments which were made prior to the statistical experiment, a reaction time of 5 min was chosen for all the tests with the expectation that the samples would all be decontaminated to the extent of removing 20 to 80% of the $PuF_4$ on the most highly contaminated samples. However, after eight tests had been completed, it was found that higher removal rates were being attained than were expected, and in some cases decontamination may have been nearly complete before the test was finished. To avoid this undesirable condition as much as possible, the length of the fluorine exposure in subsequent experiments was varied; the length of the exposure depended on the temperature of the test. This is the reason for the variation in the times of the tests, and the reason that Tests 9 and 10 were made for both 5 and 2.5 min.

An extra test, No. 19, was added to the tests specified in the designed experiment, in order to extend the temperature range of the experiments. It was made at 171°C and represents the lowest temperature at which measurable rates of refluorination of $PuF_6$ decomposition products have been determined.

A high level of reproducibility unfortunately was not attained in the tests. This can be illustrated by two examples.

Runs 1, 1R, 6, 11, and 18 were all made at the same level of temperature, pressure, and flow rate: namely, 250°C, 245 mm Hg, and 45 millimoles $F_2$/min., and in each test the most highly contaminated sample, called High $C_o$ sample, had been given the same pretreatment to deposit the $PuF_4$. Yet, the removal rates for these High $C_o$ samples varied by greater than a factor of two, as is shown in Table 4.on page 11.

Abnormal behavior between the six samples in a single experiment was also noticed. For example, in Test No. 2, which was run for 5 min. at 199°C, 123-mm Hg pressure, and 4.3 millimoles $F_2$/min, the following results were obtained.

TABLE 5 Data on Refluorination of $PuF_4$ in Test No. 2

| Sample | Side | $C_o$ | $C_t$ | $\frac{C_o - C_t}{t}$ |
|---|---|---|---|---|
| Top | Prime | 55 340 | 7 976 | 9,473 |
| | Reverse | 53,847 | 21.885 | 6,392 |
| Middle | Prime | 6,850 | 2 765 | 817 |
| | Reverse | 8,289 | 3 913 | 875 |
| Bottom | Prime | 88,193 | 66,089 | 4,421 |
| | Reverse | 88,483 | 69,451 | 3,806 |

There was not only considerable variation in the removal rates on the different samples, but the direction of this variation was partly contrary to expectation. Ordinarily, the High $C_o$ samples showed the higher rates of removal, as one might logically expect, but in Test 2 and also in Test 8 the results were contrary to expected behavior.

It is not known whether the scattering of the data was caused by some uncontrolled variable (perhaps the microscopic surface roughness of the samples), by poor experimental techniques, or just by the nature of the experiments. Nevertheless, the results of the tests, with and without the additional data obtained in five added tests, were handled statistically to allow the significance of results to be determined.

## Effect of $PuF_4$ Surface Concentration

Although surface concentration was not one of the primary variables in the designed experiment, the effect of concentration was studied by performing each test with specimens initially at several levels of $PuF_4$ concentration. Sample concentrations varied from 0.6 to 12.5 gm/cm$^2$, and the samples were chosen from three of several groups as described previously.

Qualitatively it was found that if one assumed that the removal rate from various samples in any one test was proportional to the surface concentration of $PuF_4$, much better agreement in rate coefficients between samples of widely different initial concentrations was obtained than if one compared rates calculated on the assumption that there was no dependence on surface concentration. These variable rate coefficients are expressed as $\theta = \frac{\ln \frac{C_o}{C_t}}{t}$ and are given for all the samples in Table 6.

Since it was suspected that at some sufficiently high surface concentration the rate would not be dependent on concentration, the decontamination rates for the samples were also calculated in terms of

$$R = \frac{C_o - C_t}{t} \quad .$$

Values of R for all six surfaces in each test are also given in Table 6. More will be said later about the surface concentration, $C_f$, above which the removal rate is constant and below which the rate varies with concentration.

## TABLE 6. Calculated Rates of Refluorination

Basis: Rate is independent of concentration.

$$\frac{C_o - C_t}{t}, \quad \frac{\mu gm}{min\text{-}cm^2}$$

| Test | Top | | Middle | | Bottom | |
|---|---|---|---|---|---|---|
| Number | Prime | Reverse | Prime | Reverse | Prime | Reverse |
| 1 | 0.804 | 0.834 | 0.114 | 0.158 | 1.632 | 1.346 |
| 1R | 1.360 | 1.515 | -- | -- | 1.763 | 1.328 |
| 2 | 1.033 | 0.697 | 0.089 | 0.095 | 0.482 | 0.415 |
| 2R | 0.703 | 0.200 | -0.005 | 0.001 | 0.254 | 0.204 |
| 3 | 1.066 | 1.016 | 1.900 | 1.698 | 0.129 | 0.142 |
| 4 | 1.052 | 1.285 | 2.004 | 1.518 | 0.135 | 0.143 |
| 5 | 0.997 | 1.108 | 0.126 | 0.156 | 1.339 | 1.259 |
| 6 | 1.064 | 1.447 | 1.800 | 1.687 | 0.145 | 0.124 |
| 7 | 0.935 | 1.008 | 1.243 | 1.048 | 0.123 | 0.126 |
| 8 | 1.115 | 0.446 | 0.430 | 1.054 | 0.108 | 0.139 |
| 9 | 1.792 | 2.444 | 0.217 | 0.152 | 3.583 | 3.335 |
| 9R | 1.151 | 0.803 | 0.116 | 0.374 | 0.165 | 0.252 |
| 10 | 2.097 | 1.935 | 0.222 | 0.157 | 3.874 | 3.660 |
| 10R | 0.946 | 1.329 | 0.114 | 0.454 | 0.019 | 0.047 |
| 11 | 1.586 | 1.970 | 0.137 | 0.166 | 2.724 | 2.519 |
| 12 | 0.327 | 0.193 | 0.187 | 0.387 | 0.187 | 0.096 |
| 13 | 5.223 | 4.865 | 0.881 | 0.792 | 9.354 | 9.367 |
| 14 | 1.400 | 1.558 | 0.181 | 0.136 | 2.104 | 2.200 |
| 15 | 1.222 | 1.450 | 1.852 | 1.378 | 0.177 | 0.137 |
| 16 | 1.352 | 0.696 | 1.821 | 2.124 | 0.016 | 0.014 |
| 17 | 1.150 | 1.027 | 0.232 | 0.208 | 0.166 | 0.394 |
| 18 | 1.117 | 1.164 | 2.278 | 2.223 | 0.006 | 0.006 |
| 19 | 0.183 | 0.163 | -- | -- | 0.261 | 0.307 |

## TABLE 6 (continued)

Basis: Rate is proportional to surface concentration.

$$\theta,\ \frac{1}{\text{min}}$$

| Test Number | Top |  | Middle |  | Bottom |  |
|---|---|---|---|---|---|---|
|  | Prime | Reverse | Prime | Reverse | Prime | Reverse |
| 1 | 0.264 | 0.140 | 0.236 | 0.286 | 0.318 | 0.322 |
| 1R | 0.470 | 0.491 | -- | -- | 0.430 | 0.219 |
| 2 | 0.388 | 0.180 | 0.182 | 0.150 | 0.056 | 0.048 |
| 2R | 0.013 | 0.024 | 0 | 0 | 0.038 | 0.028 |
| 3 | 0.546 | 0.644 | 0.672 | 0.604 | 0.340 | 0.312 |
| 4 | 0.675 | 0.706 | 0.811 | 0.684 | 0.292 | 0.330 |
| 5 | 0.492 | 0.352 | 0.340 | 0.468 | 0.268 | 0.250 |
| 6 | 0.665 | 0.610 | 0.676 | 0.777 | 0.400 | 0.407 |
| 7 | 0.398 | 0.220 | 0.168 | 0.165 | 0.294 | 0.292 |
| 8 | 0.350 | 0.116 | 0.043 | 0.168 | 0.281 | 0.235 |
| 9 | 0.732 | 0.630 | 0.812 | 0.492 | 0.775 | 0.645 |
| 9R | 0.388 | 0.450 | 0.220 | 0.305 | 0.159 | 0.187 |
| 10 | 1.070 | 0.988 | 0.630 | 0.490 | 1.071 | 0.924 |
| 10R | 0.459 | 0.450 | 0.275 | 0.474 | 0.016 | 0.088 |
| 11 | 0.840 | 0.815 | 0.427 | 0.470 | 0.797 | 0.860 |
| 12 | 0.062 | 0.041 | 0.021 | 0.035 | 0.190 | 0.173 |
| 13 | 2.42 | 2.89 | 1.68 | 1.58 | 3.75 | 3.84 |
| 14 | 0.864 | 0.885 | 0.472 | 0.428 | 0.825 | 0.812 |
| 15 | 0.563 | 0.351 | 0.424 | 0.545 | 0.366 | 0.394 |
| 16 | 0.455 | 0.190 | 0.396 | 0.656 | 0.078 | 0.066 |
| 17 | 0.615 | 0.186 | 0.556 | 0.552 | 0.151 | 0.121 |
| 18 | 0.446 | 0.594 | 0.811 | 0.610 | 0.036 | 0.031 |
| 19 | 0.037 | 0.024 | -- | -- | 0.096 | 0.089 |

From the results of these tests, as well as from several preliminary tests, it became apparent that the surface concentration asymptotically approached a minimum other than zero. For example, evidence of this is shown by the Low $C_0$ sample of Test 1, which was refluorinated in Test Nos. 16 and 18. Although the surface was still being decontaminated in the third test, the rate of cleanup on this rerun sample was only one-sixteenth of the $PuF_4$ removal rate on the other two samples in that test. Another sample, first decontaminated in Test 5 and then rerun in Test 2R, showed no further decontamination the second time. This behavior was also observed in tests in which only one sample was treated at a time to eliminate the possibility that samples were being contaminated by other more highly contaminated samples in the same test. This residual concentration is identified as $C_\infty$ and is assumed to have a value between 0 and 0.3 μgm Pu/cm$^2$. A plutonium concentration of 0.3 μgm/cm$^2$ corresponds very roughly to a monomolecular layer on the metal, which suggests that the plutonium is in the form of a double salt or in some other complex which can not be refluorinated to $PuF_6$ as easily as the bulk of the deposited $PuF_4$.

In determining $C_f$, the surface concentration below which the removal rate is dependent upon surface concentration, it is possible to calculate an approximate value by assuming a value of $C_\infty$ and assuming that the maximum plutonium removal rate independent of surface concentration can be calculated from the data for the High $C_o$ sample. By combining this information with the data for the Low $C_o$ sample, the following equation should give approximate values of $C_f$:

$$\left(\frac{C_t - C_\infty}{C_o - C_\infty}\right)_{\text{Low } C_o} = e^{-\frac{R_{\text{High } C_o} t}{C_f - C_\infty}} .$$

This calculation was made for a number of tests in which the fraction of decontamination of the samples was relatively small. The results are given in Table 7 and indicate a value of $C_f$ of about 3 to 5 μgm Pu/cm$^2$. Since this represents a $PuF_4$ surface concentration perhaps as thin as 10 molecules thick, it is not too surprising that below this concentration the rate of removal is decreased as the surface becomes less and less covered with $PuF_4$ molecules.

## Result of the Statistical Experiment

As planned in the design of the experiment, the results of the tests were fitted by a method of least squares to the following regression equation:

$$y = b_o + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2$$

$$+ b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

where $y$ = log θ or log R

$x_1$ = log pressure

$x_2$ = log flow, and

$x_3 = \frac{1}{°K}$ .

In order to facilitate the calculations and to yield constants which could be evaluated independently, the independent variables were expressed as a number of standard deviations from the mean, and in Table 8 the regression coefficients, β, obtained for the standardized form of the regression equation are presented. Also given are the standard errors, σ, of each coefficient from which one can determine the statistical significance of the regression coefficients. Whether the coefficients were calculated by machine or by hand is important since the machine calculations used the true test values of the variables, temperature, fluorine pressure, and flow rate, while calculations made by hand were based on the assumption that the variables were at the intended conditions for each test.

In Table 9 the regression equation obtained from the High $C_o$ samples for all 22 experiments has been transposed to a nonstandardized form, and a comparison between the observed and predicted value of θ for the High $C_o$

## TABLE 7. Calculated $PuF_4$ Concentrations Where Removal Rate Becomes Dependent on Concentration, $C_f$

Assumptions:

1. At any condition of temperature, T, $F_2$ pressure, p, and $F_2$ flow rate, W, the maximum removal rate independent of concentration can be calculated from the data for the High $C_o$ sample.
2. The $C_\infty$ and $C_f$ could be related to each other by the Low $C_o$ data in the equation

$$\left(\frac{C_t - C_\infty}{C_o - C}\right)_{Low\ C_o} = e^{-\frac{R_{High\ C_o} t}{C_F - C_\infty}}$$

| Test Number | $R_{High\ C_o,\ avg}$ | Assumed $C_\infty$ | Calculated $C_f$<br>Low $C_o$ Prime Side | <br>Low $C_o$ Reverse Side |
|---|---|---|---|---|
| 1 | 13,650 | 0 | 58,000 | 47,900 |
| | | 500 | 46,000 | 41,550 |
| | | 1000 | 41,500 | 35,000 |
| | | 1500 | 33,000 | 27,700 |
| 3 | 10,500 | 0 | - | - |
| | | 500 | 38,600 | 45,500 |
| | | 1000 | 26,800 | 35,200 |
| | | 1500 | - | - |
| 9 | 31,650 | 1000 | 177,000 | 153,500 |
| | | 3000 | 131,000 | 124,000 |
| 10 | 34,500 | 1000 | 30,800 | 41,000 |

## TABLE 8. STANDARDIZED REGRESSION COEFFICIENTS AND THEIR STANDARD ERRORS CALCULATED FROM EXPERIMENTAL RATE DATA

| y = | $\log \theta_{T_{prime}}$ | | $\log \theta_{High\ C_o}$ | | $\log \theta_{Low\ C_o}$ | | $\log \theta_{T_{prime}}$ | | $\log \theta_{High\ C_o}$ | | $\log \theta_{Low\ C_o}$ | | $\log R_{High\ C_o}$ | | $\log R_{2\ High\ C_o\text{'s}}$ | | $\log \frac{R_{2\ High\ C_o\text{'s}}}{\sqrt{T}}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Variable** | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ | $\beta$ | $\sigma$ |
| $x_1$ | .0369 | .060 | .0353 | .058 | .0597 | .050 | .0221 | .069 | .007 | .063 | .070 | .064 | .006 | .057 | .007 | .067 | .007 | .138 |
| $x_2$ | .0311 | .060 | .0915 | .058 | .0304 | .050 | .008 | .070 | .054 | .065 | .039 | .065 | .099 | .057 | .039 | .067 | .039 | .138 |
| $x_3$ | -.2604 | .061 | -.4772 | .059 | -.2025 | .050 | -.297 | .066 | -.505 | .061 | -.222 | .062 | -.379 | .057 | -.340 | .067 | -.322 | .138 |
| $x_1^2$ | .0140 | .062 | -.1184 | .059 | -.0319 | .051 | .018 | .063 | -.101 | .059 | -.047 | .059 | -.120 | .069 | -.058 | .083 | -.057 | .168 |
| $x_2^2$ | .0164 | .054 | -.0044 | .053 | -.0099 | .045 | .031 | .058 | .025 | .054 | -.026 | .054 | -.035 | .069 | -.017 | .083 | -.015 | .168 |
| $x_3^2$ | -.1150 | .062 | -.1082 | .060 | -.0761 | .051 | -.112 | .066 | -.093 | .061 | -.093 | .062 | -.043 | .069 | -.034 | .083 | -.034 | .168 |
| $x_1x_2$ | -.0333 | .059 | -.0249 | .057 | .0018 | .049 | .036 | .074 | .060 | .069 | -.003 | .069 | .032 | .069 | .052 | .083 | .052 | .168 |
| $x_1x_3$ | -.0061 | .062 | .0183 | .060 | .0306 | .051 | .019 | .073 | .020 | .067 | .033 | .068 | -.038 | .069 | -.034 | .083 | -.034 | .168 |
| $x_2x_3$ | -.0357 | .064 | .1204 | .062 | .0285 | .053 | .025 | .077 | .123 | .071 | .035 | .071 | -.160 | .069 | -.073 | .083 | -.073 | .168 |
| $x_0$ | -.2765 | -- | -.3095 | -- | -.3657 | -- | -.257 | -- | -.336 | -- | -.310 | -- | 0.199 | -- | 0.206 | -- | -1.197 | -- |
| Variation accounted for by regression equation | 65% | | 86% | | 64% | | -- | | -- | | -- | | 87% | | 45% | | 77% | |
| Experiments used | All 22 | | | | | | All but 1, 2R, 9R, and 10R | | | | | | All 22 | | | | | |
| Method of calculation | Machine | | | | | | Machine | | | | | | Hand | | | | | |
| Definition of standardized dependent variables | $x_1 = \frac{\log p - 2.376}{0.2226}$<br>$x_2 = \frac{\log W - 0.6540}{0.2633}$<br>$x_3 = \frac{\frac{1}{T} - 0.001919}{0.0001789}$ | | | | | | $x_1 = \frac{\log p - 2.387}{0.2199}$<br>$x_2 = \frac{\log W - 0.6737}{0.2557}$<br>$x_3 = \frac{\frac{1}{T} - 0.00193}{0.000179}$ | | | | | | $x_1 = \frac{\log p - 2.389}{0.275}$<br>$x_2 = \frac{\log W - 0.653}{0.348}$<br>$x_3 = \frac{\frac{1}{T} - 0.00191}{0.000203}$ | | | | | |

## TABLE 9. Nonstandardized Form of Regression Equation for Log $\theta_{\text{High } C_o}$

$x_1$ = log pressure, mm Hg

$x_2$ = log flow, millimoles/min

$$x_3 = \frac{1}{{}^\circ K}$$

$$\begin{aligned}
\text{Log } \theta = {} & -16.6136 + 10.9192x_1 - 0.53523x_2 \\
& + 6004.94x_3 - 2.3909x_1^2 - 0.06305x_2^2 \\
& - (2.7191x_3^2 \times 10^6) - 0.42493x_1x_2 \\
& + 459.04x_1x_3 + 1029.05x_2x_3
\end{aligned}$$

| Test Number | Log $\theta_{\text{High } C_o}$ Observed | Log $\theta_{\text{High } C_o}$ Predicted | Test Number | Log $\theta_{\text{High } C_o}$ Observed | Log $\theta_{\text{High } C_o}$ Predicted |
|---|---|---|---|---|---|
| 1 | -0.4976 | -0.2992 | 10 | -0.03386 | -0.1907 |
| 1R | -0.6596 | -0.2997 | 10R | -0.3778 | -0.1882 |
| 2 | -1.3188 | -1.2658 | 11 | -0.0985 | -0.2854 |
| 2R | -1.6198 | -1.5639 | 12 | -1.4559 | -1.3262 |
| 3 | -0.1726 | -0.1046 | 13 | 0.5740 | 0.1782 |
| 4 | -0.09098 | 0.03803 | 14 | -0.09044 | -0.4499 |
| 5 | -0.5719 | -0.8567 | 15 | -0.3726 | -0.1479 |
| 6 | -0.1701 | -0.3172 | 16 | -0.4023 | -0.7080 |
| 7 | -0.7747 | -0.8447 | 17 | -0.7305 | -0.6109 |
| 8 | -1.3665 | -1.3478 | 18 | -0.2145 | -0.3012 |
| 9 | -0.1107 | -0.06362 | 19 | -1.6198 | -1.5695 |
| 9R | -0.4112 | -0.06192 | | | |

samples shows the extent of the agreement between the regression equation and the actual data from which the regression equation was calculated.

Regression coefficients and their standard deviations for the independent variables were calculated from the values of $\theta$ for the High $C_O$, the Middel $C_O$, and the Low $C_O$ samples and from values of R for the High $C_O$ samples. No data from rerum samples were used. The coefficients were calculated by using the basic 18 experiments of the experimental Box design and also the basic 18 experiments plus 4 additional tests which repeated some of the planned tests. In every case the exponential temperature effect was found significant. The highest significance level for the temperature variable was obtained in the calculation with the High $C_O$ samples. The least significant results came from the Low $C_O$ samples by using $\theta$'s calculated on the assumption that $C_\infty = 0$. With $\theta$'s calculated at $C_\infty = 500$, the Low $C_O$ data gave slightly better correlation but certainly not enough better to justify the accuracy of the assumed value of $C_\infty$.

A comparison of the regression coefficients calculated for the High $C_O$ sample data with first the rate expressed in $\theta$ and then in R shows too little difference to be significant. The only difference is in the value of the temperature coefficient; i.e., using the rate coefficient, $\theta$, one obtains for the heat of reaction, $\Delta H = 12,900$ ($\sigma = 1,600$), and using the linear removal rate, R, one obtains $\Delta H = 7,650$ ($\sigma = 1,510$).

As was expected, the presence or absence of a square root of temperature term in the rate equation was masked by the exponential temperature effect. This is shown by a comparison of the regression coefficients calculated for $y = \log R_2 \text{ High } C_o\text{'s}$ and $y = \log \frac{R_2 \text{ High } C_o\text{'s}}{\sqrt{T}}$ . The difference between the two sets of coefficients is negligible.

The regression coefficients for the linear effect of fluorine pressure and flow rate were also calculated on several bases, but in no case showed the significance which the temperature variable displayed. By translating the normalized variables to more understandable form, one obtains from the High $C_o$ data:

$$\theta_{\text{High } C_o} \propto P_{F_2}^{0.158 \ (\sigma = 0.26)} \qquad \theta_{\text{High } C_o} \propto W_{F_2}^{0.347 \ (\sigma = 0.22)} .$$

The data from other than the High $C_o$ samples show comparable results for the pressure effect but do not show this large a linear flow rate effect: i.e.,

$$\theta_{T_{\text{prime}}} \propto W_{F_2}^{0.118 \ (\sigma = 0.228)} \qquad R_{\text{High } C_o} \propto W_{F_2}^{-0.112 \ (\sigma = 0.193)} .$$

$$\theta^{*}_{\text{High } C_o} \propto W_{F_2}^{0.211 \ (\sigma = 0.254)}$$

In the same manner the quadratic terms of pressure and flow rate and the interaction terms of all three variables give regression coefficients generally less in value than the standard deviation. In one case where the regression coefficients are based on $\theta_{\text{High } C_o}$, the quadratic pressure term is twice the standard deviation, but this effect does not show this same significance consistently.

Because of the wide variation in results depending upon which samples were used and how the data were handled, it is difficult to place significant figures on the exponent of the pressure or flow rate term. Nevertheless, the following conclusions can be made.

1. With 90% confidence the removal rate is proportional to less than the one-half power of the fluorine pressure.

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*Eighteen experiments only.

2. With 75% confidence the removal rate is proportional to less than the one-half power of the flow rate.
3. With over 99% confidence the removal rate is proportional to less than the first power of the fluorine flow rate.

It is difficult to apply theoretical arguments to justify that the quantities $e^{2 \log P}$ or $e^{2 \log W}$ have any effect on the removal rate, and, in general, one can only assume that the quadratic effects are not significant.

If one tentatively assumes that temperature is the only significant variable of the three tested variables, T, $p_{F_2}$, and $W_{F_2}$, it is simple to calculate a single-factor regression coefficient for the test data. The results of this type of calculation are given in Table 10. If one does this for the High $C_o$ samples, either in terms of $\theta$, R, or $R/\sqrt{T}$, the results compare closely with the regression coefficient calculated by the analysis of the full model equation. Again the $\Delta H$ calculated on the basis of the rate changing with concentration is 65% higher than the $\Delta H$ calculated on the basis of a constant removal rate.

It is of interest to compare the values of $\Delta H$ measured in these tests with the values of $\Delta H$ reported by Florin, Tannenbaum, and Lemons[1] for the reaction

$$PuF_6 \rightleftarrows PuF_4 + F_2.$$

They found that $\Delta H$ equals $+ 6,770$ cal above 308°C and $+ 11,500$ cal below 308°C, while Weinstock and Malin[2] reported a $\Delta H$ of $+ 8,300$ at 25°C, with no break in the $\Delta F$ versus T curve. Hence, the values of $\Delta H$ calculated from these tests are in the range of values previously reported.

TABLE 10. CALCULATED SINGLE-FACTOR REGRESSION COEFFICIENTS

| | | | | | | |
|---|---|---|---|---|---|---|
| y | $\ell n\ \theta_2$ High $C_o$'s | $\ell n\ R_2$ High $C_o$'s | $\ell n \frac{R_2 \text{ High } C_o\text{'s}}{\sqrt{T}}$ † | $\ell n\ \theta - \frac{-6050}{T}$ † | $\ell n\ R - \ell n\ 1000 - \frac{-3780}{T}$ | $\ell n\ \theta - \frac{-6050}{T}$ † |
| x | $\frac{10^3}{T}$ | $\frac{10^3}{T}$ | $\frac{10^3}{T}$ | $\frac{n\ p - 5.5}{0.634}$ | $n\ R - n\ 1000 - \frac{-3780}{T}$ | $\frac{n\ W - 1.503}{0.80}$ |
| Independent variables assumed not significant | $p_{F_2}$, $W_{F_2}$ | $p_{F_2}$, $W_{F_2}$ | $p_{F_2}$, $W_{F_2}$ | $W_{F_2}$ | $W_{F_2}$ | $p_{F_2}$ |
| Sum of squares | | | | | | |
| Regression | 54 | 20.4 | 18.5 | 2.45 | 0.06 | 2.6 |
| Residual | 253 | 16.0 | 15.1 | 23.09 | 14.98 | 22.9 |
| Degrees of freedom | | | | | | |
| Regression | 1 | 1 | 1 | 1 | 1 | 1 |
| Residual | 44 | 44 | 44 | 42 | 42 | 42 |
| F ratio | 94 | 56 | 53.7 | 4.45 | 0.17 | 4.77 |
| $b_{yx}$ | -6.05 | -3.78 | -3.55 | 0.42 | 0.066 | 0.43 |
| Standard deviation, $s_b$ | 0.625 | 0.495 | 0.483 | 0.1985 | 0.159 | 0.198 |
| 5% limits on $b_{yx}$ | -4.79 to -7.31 | -2.78 to -4.78 | -2.58 to -4.52 | -- | -- | -- |
| ΔH | 12,000 ± 1,250 | 7,520 ± 985 | 7,060 ± 963 | -- | -- | -- |
| 5% limits on ΔH | 9,520 to 14,570 | 5,540 to 9,500 | 5,140 to 9,000 | -- | -- | -- |
| Exponents of p or W | -- | -- | -- | 0.664 | 0.100 | 0.537 |
| 5% limits on the exponent | -- | -- | -- | 0.032 to 1.295 | -0.402 to 0.610 | 0.0375 to 1.04 |

NOTE: The results from each side of the High $C_o$ sample are treated as independent data.

† Test 9 was eliminated to simplify the computations.

## Significance of the Statistical Experiment

Because of the large variation in the calculated pressure and flow rate exponents, it is not possible to determine from the statistical analysis what the rate-controlling step is. However, from the absolute rates of removal it is known that the fluorine gas does not leave the reactor saturated in $PuF_6$, so the rate of fluorine flow is certainly not the controlling factor. Also, the fact that the temperature coefficient gives a heat of reaction which agrees very well with previous values for $\Delta H$ indicates there is little likelihood of the process being reaction rate controlling, although this could be possible if the $\Delta H$ of activation were approximately equal to the $\Delta H$ of reaction. Of the three proposed controlling mechanisms, this leaves only the proposition that the process is controlled by diffusion, in which case the temperature effect would approximate the observed behavior. However, for gas diffusion to control, it had been stated that fluorine pressure and flow rate would have no effect on the removal rate. The data suggest there is at least some dependence on these variables, and this dependence is predominately in the direction that one would expect if the process were controlled by a diffusion of $PuF_6$ through a solid film or layer, not through a fluorine gas film. If one assumes a diffusion coefficient of $10^{-8}$ $cm^2/sec$ for the rate of diffusion of $PuF_6$ through an unknown solid film, a solid thickness of about $10^{-6}$cm is obtained. Based on the large variances obtained in these tests, solid diffusion as the controlling step can only be suggested. There can be no question but that certain other possibilities of a more complex nature, such as would depend on the formation of an intermediate $PuF_5$ molecule, may exist as the controlling mechanism. In order to determine the controlling refluorination mechanism, it is hoped that experiments of this type can be extended over a greater range of variables, with the plutonium concentration on the samples measured at shorter time intervals and at several positions on a sample in the direction of the gas flow.

## Practical Significance of the Tests

The practical significance of low-temperature refluorination as a means of recovering decontaminated $PuF_6$ can best be illustrated by a typical problem. Consider a $PuF_6$ container in the form of a tube 4 ft long and 3 in. in diameter. If this pipe were filled with $PuF_6$ gas at room temperature and 25-mm Hg pressure (with an assumed decomposition rate of 0.3%/day), in 3 months 24% of the $PuF_6$, equivalent to 0.432 gm of plutonium, would be deposited on the walls of the tube. If this plutonium were evenly distributed, the surface density would be 297 $\mu gm/cm^2$. Now the better removal rates on the small samples measured at 200°C averaged about 70 $\mu gm$ Pu/hr-cm$^2$, and in one case the decontamination rate was over 80 $\mu gm/hr\text{-}cm^2$. If it is assumed that sufficient $F_2$ can be pumped through the tube so that a removal rate of 70 $\mu gm$ Pu/hr-cm$^2$ could be attained throughout the tube, then it can be calculated that the tube could be 95% decontaminated in $<$ 4 hr at 200°C.

This time would be much less than the time required for a liquid wash followed by rinsing, drying, and refluorination, and in addition, direct refluorination would probably recover the plutonium as usable $PuF_6$ rather than as a plutonium ion solution requiring concentration and fluorination. In a direct refluorination process recycle of the $F_2$ would be necessary but should introduce no unusual problems.

## CONCLUSION

Direct refluorination of $PuF_6$ decomposition products deposited on an aluminum alloy surface has been measured over a range of $F_2$ pressures and flow rates and at temperatures from 1[illegible] to 343°C. Rates of refluorination were measured even at the lowest temperatures, and at 200°C plutonium removal rates of about 70 $\mu$gm/hr-cm$^2$ were obtained. A statistically designed experiment showed temperature to be the most significant variable, and the rate of removal was found to be proportional to the term $e^{-\frac{\Delta H}{RT}}$ where $\Delta H$ varied between 7,000 and 12,000 cal/mole. A reaction controlled by diffusion through a solid film was suggested by the results, but the experimental variation was too large to give much credence to this conclusion. At plutonium surface concentrations below 3 to 6 $\mu$gm Pu/ m$^2$, the rate of refluorination was found to vary linearly with surface contamination.

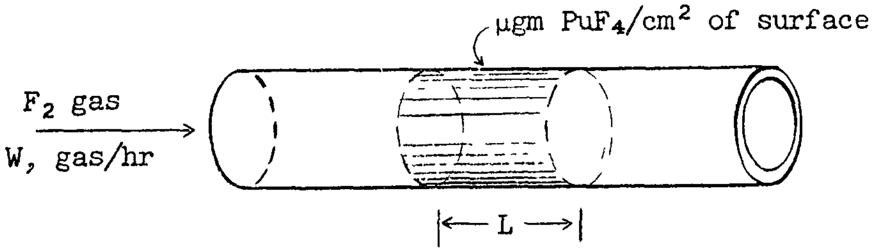
## REFERENCES

1. Florin, A. E., Tannenbaum, I. R., and Lemons, J. F., "Preparation and Properties of Plutonium Hexafluoride and Identification of Plutonium(VI) Oxyfluoride," J. Inorg. Nucl. Chem. 2 (1956), p. 368.
2. Weinstock, B. and Malm, J. G., "The Properties of Plutonium Hexafluoride," J. Inorg. Nucl. Chem. 2 (1956), p. 380.
3. Vogel, R. C. "Chemical Engineering Division Quarterly Report, April, May, June, 1956," ANL-5602, p. 32.

# APPENDIX A

## THEORETICAL CONSIDERATIONS

In order to determine the mechanism which controls the rate in the refluorination process, a statistically designed experiment was performed to study the three variables, temperature, T, fluorine pressure, $p_{F_2}$, and flow rate, $W_{F_2}$. The form of these three variables which would most likely occur in the proper regression equation for the process was determined from the following considerations. Consider $PuF_4$ deposited evenly on the wall of a pipe through which fluorine is flowing. Although this does not correspond physically to the experimental setup, as long as the term $DL\rho/W$ is small and $p_{PuF_6}$ is small compared with $p_{F_2}$, the actual and hypothetical arrangements should be comparable. In the above expression, D is the diffusion coefficient of $PuF_6$ and $F_2$, L is the length of the coated tube, ρ is the fluorine density, and W is the flow rate of fluorine through the tube in mass per unit time.



If the process is controlled by the reaction rate and is a simple one-step process, the rate of removal of $PuF_4$ will be

$$Q \propto k a_{PuF_4} f_{F_2} \cong k p_{F_2} \cong e^{-\frac{\Delta F^*}{RT}} p_{F_2}$$

where $Q$ = the rate of $PuF_4$ removal

$k$ = a forward reaction rate constant

$a$ = activity

$f$ = fugacity, and

$\Delta F^*$ = free energy of activation for the refluorination step.

If the process is controlled by the reaction rate but is not a single-step process, the power of the fluorine pressure in the rate equation may be different from unity but is not likely to be less than one-half.

If the process is controlled by the rate of diffusion, the rate of removal will depend on the rate of diffusion of $PuF_6$ from the surface into the bulk of the gas, and the pressure of $PuF_6$ on the surface will be given simply by

$$p_{PuF_6} = Kp_{F_2} = e^{-\frac{\Delta F}{RT}} p_{F_2}$$

where $K$ = the equilibrium constant for $PuF_{4(s)} + F_{2(g)} \rightarrow PuF_{6(g)}$, and

$\Delta F$ = the free energy of refluorination.

The rate of mass diffusion of $PuF_6$ into the gas stream will be analogous to the transport of heat from a hot wall to a cooler gas stream, and for viscous flow this has been shown to follow an equation derived by Gaertz.* In the limit, as L becomes small, W becomes large, and $p_{PuF_{6(surface)}}$ becomes small, the amount of diffusion will become approximately proportional to DL,

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* Drew, T. B. "Mathematical Attacks on Forced Convection Problems: A Review," Trans. Am. Inst. Chem. Engrs. 26 (1931), 26.

and the amount diffused per unit volume of gas will be $DL\rho/W$.* Then the $PuF_6$ pressure in the exit gas will be proportional to $\left(\frac{DL\rho}{W}\right)\left(p_{PuF_{6(surface)}}\right)$ and the amount of $PuF_6$ removed in the gas stream will be equal to

$$\left(\frac{DL\rho}{W}\right)\left(p_{PuF_{6(surface)}}\right)\left(\frac{W}{\rho RT}\right) = \frac{DLp_{F_2}e^{-\frac{\Delta F}{RT}}}{RT} .$$

If $D \propto \frac{T^{\frac{3}{2}}}{p_{F_2}}$, then the rate of $PuF_6$ removal as a function of the three variables studied will be

$$Q \propto T^{\frac{1}{2}} e^{-\frac{\Delta F}{RT}} ,$$

and it is seen that the rate of removal will not vary with $p_{F_2}$ or W. Furthermore, the exponential effect of the temperature will outweigh the power effect.

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*For liquid diffusion from a flatplate where $DL\rho/W$ is also small, W. H. Linton has derived the following expression for viscous flow

$$\frac{C - C_o}{C_s - C_c} = 5.5\left(\frac{DL\rho}{W}\right)^{-\frac{2}{3}}.$$

(See Linton, W. H. Jr., and Sherwood, T. K., "Mass Transfer from Solid Shapes to Water in Streamline and Turbulent Flow", Chem. Eng. Progr. 46 (1950, 258.) Here $C_s$ is the concentration of the diffusing material at the surface of the plate, $C_c$ is the initial concentration in the liquid, and C is the concentration in the liquid after flow L distance across a flatplate. One would expect some similarity between this equation and the limit equation for the gas diffusion. The difference between $DL\rho/W$ to the first or two-third power would probably not be detectable in these experiments.

A third possibility is that neither reaction rate nor diffusion is rate controlling, but that the gas leaves the tube containing the equilibrium amount of $PuF_6$. In this case, the rate of removal will be proportional to

$$W\left(\frac{p_{PuF_6}}{p_{F_2}}\right) = WK = We^{-\frac{\Delta F}{RT}} .$$

Then the rate will be independent of fluorine pressure but dependent on flow rate and temperature.

To distinguish between these three possibilities, the statistical experiment was designed based on the expression:

$$Q \propto p_{F_2}^{a} W^{b} e^{\frac{c}{T}} .$$

A central composite (Box) design to conform to the empirical model was chosen for the experimental design. The center point of the box was to be tested four times to give a measure of replication. Since three two-sided samples could be run in each test, it was possible to study as secondary variables the position of the six sample surfaces in the holder and the concentration on the six surfaces.

# APPENDIX B

## CALCULATION OF FILM THICKNESSES

In Test 1 the six sides of the three samples had the following absolute plutonium removal rates.

| Sample | Side | $\mu$gm Pu/min-cm$^2$ |
|---|---|---|
| Top | Prime | 0.804 |
| | Reverse | 0.834 |
| Middle | Prime | 0.114 |
| | Reverse | 0.158 |
| Bottom | Prime | 1.632 |
| | Reverse | 1.346 |
| | | 4.888 |

Although this rate was measured only for a small circle on each face, it can be assumed to apply to the entire exposed face area, 1/2-in. long and 3/16-in. wide. During the 5-min run, then, the moles of $PuF_4$ refluorinated to $PuF_6$ are:

$$\left(\frac{4.888 \times 10^{-6}}{239}\right)\left(\frac{1}{2}\right)\left(\frac{3}{16}\right)(2.54)^2 (5) = 6.2 \times 10^{-8} \text{ moles.}$$

During this time $2.25 \times 10^{-2}$ moles of $F_2$ flowed by the samples. Thus, the ratio of $p_{PuF_6}$ to $p_{F_2}$ at the reactor exit was

$$\frac{p_{PuF_6}}{p_{F_2}} = \frac{6.2 \times 10^{-8}}{2.25 \times 10^{-2}} = 2.75 \times 10^{-6}$$

compared with the equilibrium value at 250°C of $1.2 \times 10^{-3}$. The fluorine gas is, therefore, a long way from being saturated in $PuF_6$ upon leaving the reactor; this supports the assumption that the removal rate did not vary along the 1/2-in. length of the sample.

If one assumes that on the High $C_o$ samples the rate of plutonium removal is limited by a diffusion process, it is of interest to determine the diffusion resistance of the limiting film. Since $F_2$ will diffuse or migrate through a film much more rapidly than a $PuF_6$ molecule, assume that the $PuF_6$ pressure in contact with $PuF_4$ is in equilibrium with the fluorine pressure in the tube. Then at 250°C the $PuF_6$ pressure gradient across the film will essentially equal $Kp_{F_2}$, or 0.293 mm Hg for the conditions of Test 1.

Then, we find

$$\frac{D}{X} = \frac{NRT}{A\Delta p} = \frac{\left[\frac{1.5 \times 10^{-6}}{(239)(60)}\right](62{,}300)(523)}{0.293}$$

where $D$ = diffusion coefficient, $cm^2/sec$

$X$ = film thickness, cm

$A$ = area, $cm^2$

$N$ = moles diffused/sec-$cm^2$ averaged for 2 High $C_o$ samples

$R$ = gas constant, $\frac{\text{cc-mm Hg}}{\text{mole-}^{\circ}\text{K}}$, and

$T$ = °K.

Now the diffusion coefficient of $PuF_6$ in $F_2$ under the conditions of Test 1 is about 0.7 $cm^2/sec$, which gives a film thickness of 63 cm. This is obviously much too thick to be reasonable. If the $PuF_6$ must diffuse through a solid film, a diffusion coefficient of $10^{-8}$ $cm^2/sec$ seems possible. This would give a film thickness of about $10^{-6}$ cm, a more reasonable value.

# APPENDIX C

## RESULTS OF SOME PRELIMINARY REFLUORINATION TESTS

Test Conditions

Reaction temperature = 200°C

Reaction pressure = 280 mm Hg

Fluorine flow = 4 millimoles/min

| | Prefluorination | | | $PuF_6$ Exposure | | |
|---|---|---|---|---|---|---|
| Sample | Time, hr | Temperature, °C | Pressure, mm Hg | Time, hr | Temperature, °C | Pressure, mm Hg |
| 1 | 1 | 75 | 25 | 1 | 75 | 10 |
| 2 | 1 | 75 | 25 | 1 | 75 | 10 |
| 3 | 1 | 175 | 25 | 1 | 75 | 10 |
| 4 | unknown | | | unknown | | |

| Test | Sample | Side | Reaction Time, min | Initial Activity, ct/min/0.131 $cm^2$ | Final Activity, ct/min/0.131 $cm^2$ |
|---|---|---|---|---|---|
| A | 1 | Prime | 30 | 28,300 | 5,500 |
| | | Reverse | | 44,500 | 30,000 |
| B | 2 | Prime | 40 | 36,200 | 13,950 |
| | | Reverse | | 19,100 | 3,970 |
| C | 3 | Prime | 10 | 15,100 | 9,600 |
| | | Reverse | | 11,250 | 5,250 |
| D | 1 | Prime | 30 | 5,300 | 4,200 |
| | | Reverse | | 30,600 | 29,130 |
| E | 3 | Prime | 30 | 10,250 | 9,530 |
| | | Reverse | | 5,300 | 4,390 |
| F | 4 | Prime | 5 | 6,200 | 4,498 |
| | | Reverse | | 6,450 | 4,845 |