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Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XV. Estimation of Rates of Thermal Decomposition of Plutonium Hexafluoride in Process Streams

by

L. E. Trevorrow and M. J. Steindler

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ABSTRACT

The need to predict rates of thermal decomposition of PuF_6 to PuF_4 and fluorine in fluoride volatility process streams has prompted a review of results of several types of experiments in which PuF_6 was thermally decomposed.

The "initial rate" of thermal decomposition of PuF_6 was previously correlated by the combination of a heterogeneous rate equation with zero-order dependence on partial pressure of PuF_6 and a homogeneous rate equation with first-order dependence on partial pressure of PuF_6 ,

$$-dp/dt = k_0 + k_1p.$$

This equation neglects the effects of a back reaction and does not justify calculation of rates at surface-to-volume ratios different from those existing in the experiments from which the equation was developed.

In this report, the results of experiments with varying fluorine pressures and surface-to-volume ratios are correlated by a rate equation that expresses the dependence on those variables,

$$\ln \frac{R_t - K_{eq}}{R_0 - K_{eq}} = k't(s/v),$$

in which R_0 , R_t , and K_{eq} are the mole ratios of PuF_6 to F_2 , initially, after a reaction period of t minutes, and at equilibrium, respectively. The dimensions of the surface-to-volume ratio (s/v) are expressed in cm^{-1} . The dimensions of the rate constant are expressed in cm min^{-1} , and the variation of the rate constant with temperature is expressed by the equation,

$$\log k' = \frac{-3169}{T(^{\circ}\text{K})} + 5.364.$$

The latter two equations are recommended for prediction of the rate of thermal decomposition of PuF_6 in process streams in which the partial pressure of fluorine is significantly high.

I. INTRODUCTION

In the fluid-bed fluoride volatility process, plutonium would be separated from nuclear fuels by fluorination of the fuel to produce volatile PuF_6 . The design of equipment to cool the gas flowing from the fluorination reactor and the attendant problem of thermal decomposition of PuF_6 in the cooler have prompted a re-examination of information available on the rate of thermal decomposition of PuF_6 . In the operation for plutonium recovery, spent nuclear fuel will be treated with fluorine gas in a fluid-bed reactor at 350 to 550°C. The gaseous mixture flowing from the reactor will have a PuF_6/F_2 ratio with an upper limit determined by the equilibrium constant of the reaction

The mixture will flow from the reactor through a gas cooler section before it reaches a section of apparatus containing metallic filters.

The equilibrium constant, $* p_{\text{PuF}_6}/p_{\text{F}_2}$, decreases with decreasing temperature.^{1,2} At some point in the cooling section, the PuF_6/F_2 ratio in the gaseous effluent is expected to exceed the equilibrium constant, and PuF_6 will decompose to PuF_4 and fluorine. The rate of decomposition of PuF_6 also decreases with decreasing temperature, however, so that although the PuF_6 becomes less stable thermodynamically as the gas mixture cools, the rate of approach to equilibrium (rate of decomposition) also becomes lower.

This review has been prepared to make conveniently available all information obtained in the ANL Chemical Engineering Division on the rate of thermal decomposition of PuF_6 so that these data could be used to predict the amount of decomposition that would occur during plant operations.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Preparation of PuF_6

The PuF_6 used in the decomposition-rate studies was prepared by the reaction of fluorine, at 400 to 550°C, with PuO_2 or PuF_4 . Figure 1

*Table XII in the appendix lists the pressure of PuF_6 in equilibrium with PuF_4 and 760 mm F_2 for the range 25-600°C.

Fig. 1. Apparatus for Preparation of PuF_6

is a schematic diagram of the fluorination system. All parts of the equipment exposed to fluorine and plutonium compounds were constructed of nickel or Monel, and all the equipment was pretreated with fluorine before use. Pure fluorine gas was circulated over the plutonium (IV) compounds contained in a boat located in a tube reactor. The PuF_6 produced was removed from the gas stream by condensation in the cold traps at -78°C . The PuF_6 was purified from low-boiling impurities by the method described by Weinstock and Malm.³

B. Decomposition of PuF_6 under Static Conditions⁴

In the most extensive series of experiments, the decomposition of PuF_6 was observed under static conditions; samples of pure PuF_6 vapor were heated in a closed vessel, and after a given reaction period the amounts of PuF_4 deposited in the vessel were determined.

1. Apparatus and Procedure

The rate of thermal decomposition of PuF_6 vapor was studied by the static method at initial pressures of PuF_6 of 14 to 110 cm Hg and at 140, 161, and 173°C . A few similar experiments were subsequently carried out at 150 and 80°C .

Since there is no change in the number of gas molecules during the thermal decomposition of PuF_6 vapor as shown by Eq. 1, the rate of decomposition of the vapor cannot be followed by pressure measurements in a static system. Since the deposition of solid PuF_4 would interfere with measurement of the partial pressure of PuF_6 , many common physical methods that might be used to follow the reaction continuously are inapplicable.

Rates of decomposition were obtained from initial and final compositions after a sample of PuF_6 was heated for a measured period of time. Before each experiment, the storage vessel containing PuF_6 was evacuated to remove fluorine accumulated from radiation decomposition. The decomposition vessel was preheated to the experimental temperature in a thermostated ($\pm 0.2^\circ$) aluminum block wound with Nichrome heating wire. An experiment was initiated by opening the valve to the evacuated decomposition vessel and allowing PuF_6 to expand into it. At the end of a reaction period, the furnace was lowered, and the decomposition vessel was quenched in liquid nitrogen. After quenching, the decomposition vessel was warmed to room temperature and weighed to determine the starting amount of PuF_6 .

The vessel was then evacuated at 25°C to remove residual PuF_6 and the fluorine formed during the reaction. The vessel was weighed again to determine the weight of PuF_4 formed. The weights were used to calculate the amount of PuF_6 that had decomposed. Partial pressures of PuF_6 were calculated from the weights by the ideal gas law. A single reaction vessel was used for several consecutive experiments. Therefore, each experiment was carried out in the vessel containing PuF_4 which had accumulated from previous experiments. A small correction was made to the volume of the vessel to account for the accumulation of PuF_4 .

The rate of decomposition of PuF_6 was studied by the static method in two types of vessels at 161°C. The volumes of the vessels were almost equal, but the surface/volume ratios were different. In one case, the vessel was packed with nickel wool to increase the internal surface area. For the nonpacked vessel, the surface/volume ratio was 1.8 cm^{-1} and the volume was 52 cc. For the packed vessel, the surface/volume ratio was 14 cm^{-1} and the volume was 51 cc. These surface/volume ratios were based on geometric measurements.

2. Results in Nonpacked Vessel

The first experiment yielded atypical, low decomposition rates. The rates increased as PuF_4 accumulated in the first few experiments for the nonpacked vessel, and then remained almost constant in subsequent experiments.

After several experiments, the nonpacked reaction vessel was cut open; the PuF_4 was found as a coating on the walls of the vessel and as a pile of thin, flat pieces on the bottom of the vessel. The distribution of the PuF_4 was not uniform.

After the deposition of a small quantity ($\leq 3 \text{ g}$) of PuF_4 in the nonpacked vessel, the rates appeared to be independent of the quantity of PuF_4 in the vessel. Perhaps because the PuF_4 accumulated in the vessel as a pile of solid pieces, the active surface area of PuF_4 did not continue to increase with the weight of PuF_4 . For this reason, it is assumed that the active solid surface area did not increase significantly throughout the set of experiments in the nonpacked vessel, making it possible to obtain a consistent set of results. The results of the rate experiments at 140.1, 160.6, and 173.1°C in the nonpacked vessel are shown in Table I. A later set of experiments, summarized in Table II, was carried out at 150.3°C.

Additional static experiments on the rate of decomposition of PuF_6 vapor were carried out at 80°C. In contrast to the previous work, the nickel vessel was not treated with fluorine prior to use with PuF_6 . The conditioning of the vessel consisted only of exposure to PuF_6 vapor at 25°C for 3 hr, during which time about 7 mg of PuF_4 deposited in the vessel. The results⁵ of four experiments at 80°C are listed in Table III.

TABLE I. Thermal Decomposition of PuF_6 Vapor in Nonpacked Vessel at Various Temperatures; Static Conditions^a

Volume of reaction vessel: 52 cc

Temp, °C	Reaction Time, min	Observed Initial Pressure PuF_6 , cm Hg	Observed Final Pressure PuF_6 , cm Hg	Observed Integral Rate, cm Hg/hr	Calculated ^b Final Pressure PuF_6 , cm Hg	Deviation, cm Hg
140.1	120	101.8	86.8	7.5	86.9	+0.1
140.1	120	99.5	85.6	7.0	84.8	-0.8
140.1	120	86.7	73.6	6.6	73.1	-0.5
140.1	120	76.3	62.2	7.1	63.6	+1.4
140.1	120	70.0	56.1	7.0	55.9	-0.2
140.1	120	64.0	52.2	5.9	52.3	+0.1
140.1	120	56.4	45.7	5.4	45.3	-0.4
140.1	120	48.5	37.4	5.6	38.1	+0.7
140.1	120	41.1	30.9	5.1	31.3	+0.4
140.1	120	14.0	7.1	3.4	6.4	-0.7
					Av Dev	±0.4
160.6	90	98.1	70.4	18.5	69.2	-1.2
160.6	90	59.6	37.9	14.5	38.6	+0.7
160.6	90	51.2	31.5	13.1	31.9	+0.4
160.6	90	32.6	16.5	10.7	17.1	+0.6
160.6	90	16.8	5.9	7.3	4.5	-1.4
					Av Dev	±0.9
173.1	60	108.7	74.2	34.5	71.7	-2.5
173.1	60	92.8	59.9	32.9	59.3	-0.6
173.1	60	75.5	43.8	31.7	45.9	+2.1
173.1	60	75.4	46.3	29.1	45.8	-0.5
173.1	60	68.9	39.8	29.1	40.7	+0.9
173.1	60	63.7	35.4	28.3	36.7	+1.3
173.1	60	53.0	27.0	26.0	28.4	+1.4
173.1	60	44.9	20.0	24.9	22.1	+2.1
173.1	60	31.2	13.1	18.1	11.4	-1.7
173.1	60	25.7	8.3	17.4	7.2	-1.1
173.1	60	22.2	6.0	16.2	4.5	-1.5
					Av Dev	+1.4

^aThe weight of PuF_4 in the reaction vessel during these experiments varied from 3 to 6 g; however, the integral rates did not change as the weight of solid increased in this range.^bCalculated from rate constants obtained by fitting Eq. 2 to the data.TABLE II. Thermal Decomposition of PuF_6 Vapor in Nonpacked Vessel at 150.3°C; Static Conditions^a

Volume of reaction vessel: 52 cc

Experiment No.	Reaction Time, min	Initial Pressure PuF_6 , cm Hg	Observed Final Pressure PuF_6 , cm Hg	Calculated ^b Final Pressure PuF_6 , cm Hg	Deviation, cm Hg
88	120	102.5	77.9	78.9	+1.0
89	120	49.8	31.9	33.0	+1.1
90	90	14.3	6.0	5.4	-0.6
92	90	14.0	6.1	5.1	-1.0
				Av Dev	±0.9

^aThe weight of PuF_4 in the reaction vessel varied from 2.8 g at the start of Experiment 88 to 3.2 g at the end of Experiment 92.^bCalculated from rate constants obtained by fitting Eq. 2 to the data.

TABLE III. Thermal Decomposition of PuF_6 Vapor in Nonpacked Vessel at 80°C ; Static Conditions

Volume of reaction vessel: 53 cc
 Initial pressure: ~ 100 cm Hg^a
 Final pressure: ~ 98 cm Hg^a

Reaction Time, hr	PuF_4 Initially in Reaction Vessel, g	PuF_6 Decomposed, g	Integral Rate, %/day	
			Observed ^c	Predicted ^d
25	0.0071 ^b	0.0225	2.4	4.6
46	0.0272	0.0202	1.2	4.5
71	0.0452	0.0319	1.3	4.6
47	0.4050	0.0301	1.8	4.6

^aPressures were not observed directly, but were calculated from weights of PuF_6 , the vessel volume, and the reaction temperature, using the ideal gas law.

^b PuF_4 formed during initial treatment of vessel with PuF_6 at 25°C for 3 hr.

^cTotal rate of decomposition includes radiation decomposition by alpha particles.

^dCalculated from rate constants obtained by fitting Eq. 2 to the data.

3. Results in Packed Vessel

Data on the rate of decomposition of PuF_6 vapor in the vessel packed with nickel wool at 161°C under static conditions are shown in Table IV. In the packed vessel, the rates increased to a value much greater than those in the nonpacked vessel containing about the same amount of PuF_4 . In the packed vessel, the active surface of solid PuF_4 probably was more available than in the nonpacked vessel since the PuF_4 was deposited over a greater area on the surface and in the interstices of the nickel wool. We concluded from these considerations that the rate of decomposition of PuF_6 is dependent upon the surface area of PuF_4 .

TABLE IV. Thermal Decomposition of PuF_6 Vapor in Packed Vessel at 161°C ; Static Conditions

Volume of packed reaction vessel: 51.1 cc
 Geometric surface/volume ratio of reaction vessel: 14 cm^{-1}

Reaction Time, min	Initial Pressure PuF_6 , cm Hg	Final Pressure PuF_6 , cm Hg	Av Wt PuF_4 in Vessel, g	Calculated ^a k_0 , cm Hg/min
360	84.8	0.8	0.26	0.14
90	22.8	0.02	0.58	0.22
90	89.6	43.0	0.79	0.35
120	74.3	4.6	1.13	0.49
30	22.9	6.0	1.39	0.53
180	103.0	0.7	1.74	0.45
30	22.3	2.8	2.10	0.62
90	89.5	3.8	2.41	0.83
30	69.3	31.9	2.78	1.11
30	32.9	6.7	2.96	0.83

^aCalculated by substituting the value of k_1 at 161°C into Eq. 2.

4. Interpretation

The results obtained in the static experiments can be expressed by a rate equation of concurrent first and zero orders with respect to the partial pressure of PuF_6 ,

$$-dp/dt = k_0 + k_1 p, \quad (2)$$

which, in integrated form is

$$p = p_0 e^{-k_1 t} + \frac{k_0}{k_1} e^{-k_1 t} - \frac{k_0}{k_1}, \quad (3)$$

where p_0 is the initial pressure and p the partial pressure after reaction time t . Equation 3 was used to correlate the experimental data.

The fraction of PuF_6 remaining at time t can be expressed by a rearrangement of Eq. 3:

$$\text{Fraction of } \text{PuF}_6 \text{ remaining} = \frac{p}{p_0} = e^{-k_1 t} + \frac{k_0/k_1}{p_0} (e^{-k_1 t} - 1). \quad (4)$$

Also,

$$\begin{aligned} \% \text{PuF}_6 \text{ decomposed after time } t &= \left(1 - \frac{p}{p_0}\right) \times 100 \\ &= \left[1 - e^{-k_1 t} + \frac{k_0 - k_1}{p_0} (e^{-k_1 t} - 1)\right] \\ &\quad \times 100 \end{aligned} \quad (5)$$

Equation 3 shows that p is a linear function of p_0 for a constant reaction time. Therefore, experiments at a given temperature were carried out for the same reaction time but at various initial pressures so that values of k_0 and k_1 could be calculated conveniently by solution of a linear equation. The rate constants obtained in this manner are listed in Table V.

TABLE V. Rate Constants Obtained for Thermal Decomposition of PuF_6 Vapor under Static Conditions

Temp., °C	k_0 , ^{a,b} cm Hg/min	k_1 , ^b min ⁻¹
140.1	$5.58 \pm 0.36 \times 10^{-2}$	$7.25 \pm 0.53 \times 10^{-4}$
160.6	$10.9 \pm 0.94 \times 10^{-2}$	$25.0 \pm 1.8 \times 10^{-4}$
173.1	$24.2 \pm 1.6 \times 10^{-2}$	$41.9 \pm 2.8 \times 10^{-4}$

^aThe reaction surface area of the experimental vessel is implicit in the constant k_0 .

^bThe uncertainty values are calculated probable errors.

The Arrhenius equation was used to obtain the following correlation of the rate constants with temperature:

$$\log k_0 = 7.124 - \frac{3.469 \times 10^3}{T^\circ\text{K}}; \quad (6)$$

$$\log k_1 = 7.260 - \frac{4.292 \times 10^3}{T^\circ\text{K}}. \quad (7)$$

The experimental activation energies were 15.9 ± 1.5 kcal/mole for the zero-order reaction, and 19.6 ± 0.7 kcal/mole for the first-order reaction.

Since the reaction rates are expressed as the rate of change of pressure, the rate constant for the zero-order reaction is assumed to be dependent on the surface/volume ratio; i.e., $k_0 = k'_0(s/v)$. Thus a new rate constant should be defined: $k'_0 = k_0(v/s)$, which does not depend on the surface area and the gas volume. Laidler⁶ points out, however, that the constant k'_0 is rarely used, since accurate values of surface areas are seldom available. Since measurements of absolute surface areas were not obtained in the present work, the values for k_0 derived from the experimental results must be considered to hold true only for the surface/volume ratio used in these experiments. This limitation is important to subsequent discussions.

Attempts to correct k_0 for the effect of geometric surface/volume ratio were not successful since the calculated rates were not in agreement with experimental results. Best agreement was achieved by the use of Eq. 2 without modification.

The rates obtained in the packed vessel at 161°C (Table IV) increased with the weight of PuF_4 in the vessel. The rate constant k_1 for the homogeneous reaction, derived from experiments in the nonpacked vessel at 161°C (Table I), was assumed to hold for the rates in both the packed and nonpacked vessels. The value of k_1 was then used together with the results obtained in the packed vessel and Eq. 2 to calculate values of k_0 for the rates in the packed vessel (see Table IV). The values of k_0 were not constant, but increased in order of the average weight of PuF_4 present during an experiment, as shown by Fig. 2. Assuming that the surface area of PuF_4 generally increases as more solid is deposited in the packed vessel, Fig. 2 demonstrates that the rate of decomposition increases with increase in surface area. If the same amount of PuF_4 were deposited in an unpacked vessel, the rate of increase in k_0 would be less since the total active surface area of PuF_4 is less owing to accumulation of PuF_4 at the bottom of the vessel.

The concurrent zero- and first-order dependence of the rate of reactant pressure is similar to that reported⁷ for the decomposition of

GeH_4 . By analogy, the first-order dependence of the rate can be attributed to the unimolecular, homogeneous decomposition of PuF_6 in the gas phase, and the zero-order dependence can be attributed to the simultaneous, heterogeneous decomposition of PuF_6 on the surface of PuF_4 .

Fig. 2
Dependence of Zero-order Rate Constant
on Weight of PuF_4 in Packed Reaction
Vessel; Static Conditions at 161°C

For static decomposition at 80°C , the first experiment gave a higher reaction rate than any of the others, perhaps owing partly to reaction between PuF_6 and the nickel wall of the vessel. Table III also includes reaction rates for PuF_6 at 80°C predicted by Eq. 2. The observed rates for the last three experiments vary from 1.2 to 1.8% per day, whereas the predicted results are about 4.6% per day. This disagreement between the predicted and observed rates may be caused by the difference in the active surface areas in the reaction vessels.

The decomposition observed in experiments listed in Table III include radiation decomposition caused by alpha particles emitted by plutonium-239. The rate of radiation decomposition by alpha particles may be a significant fraction of the total decomposition rate observed at 80°C . At any rate, the extrapolated rates of decomposition at 80°C calculated from Eq. 2 differ from the observed rates by a factor of about two.

In summary, measurements of the amounts of PuF_4 deposited when samples of pure PuF_6 vapor were heated under static conditions in a closed vessel yielded rates of thermal decomposition of PuF_6 from 140 to 170°C . The observed rates were correlated by a linear combination of two simple rate laws, one of zero order and the other of first order with respect to the partial pressure of PuF_6 . The observations indicated that the rate of decomposition is dependent on the surface area in the reaction vessel, and perhaps especially dependent on the active surface area of PuF_4 in the vessel.

C. Decomposition of PuF_6 in Fluorination Reactor Effluent⁸

Several determinations were made of the rate of decomposition of PuF_6 in the effluent mixture (fluorine, PuF_6) from a laboratory-scale fluorination reactor. The purpose of these experiments was to provide observations of the rate of thermal decomposition of PuF_6 under conditions simulating those to be expected in the effluent of a fluid-bed reactor in which nuclear fuel is fluorinated. The decomposition rate of PuF_6 in the presence of high concentrations of fluorine was of special interest.

1. Conditions

Fluorine gas was passed over solid PuF_4 at 550°C contained in a boat located in a tube reactor. The resulting gas mixture of fluorine and

Fig. 3. Apparatus for Determination of Thermal Decomposition of PuF_6 in Fluorination Reactor Effluent

PuF_6 was passed through a nickel decomposition vessel. The fluorine- PuF_6 mixture flowed from the decomposition vessel through two cold traps (-78°C) to condense the PuF_6 that had not decomposed. The fluorine passed through the traps and was recirculated over the PuF_4 at 550°C . The decomposition vessel was weighed before and after each experiment to determine the amount of PuF_4 deposited in it. Figure 3 is a schematic diagram of the apparatus used in these experiments.

2. Results

Table VI summarizes the conditions and the results for experiments in which the decomposition vessel contained no packing. Table VII summarizes the conditions and results of similar experiments in which the decomposition vessel was packed with nickel wool to increase the surface/volume ratio.

TABLE VI. Thermal Decomposition of PuF_6 in Fluorination Reactor Effluent; Decomposition Vessel Nonpacked

Vessel volume: 446 cc
 Surface/volume ratio of decomposition vessel: 1 cm^{-1}
 Average flow rate of effluent stream: 170 cc/min at 300°K

Decomp. Vessel Temp, $^\circ\text{C}$	Average Total Pressure, mm Hg	Residence Time in Decomp. Vessel, min	Average Mole Ratio PuF_6/F_2 Entering Decomp. Vessel	Equilibrium Constant PuF_6/F_2 at Temp of Decomp. Vessel	PuF_6 Recovered in Cold Trap, g	PuF_6 Decomp., g	Observed Decomp. Rate, %/min of Residence Time
144 ± 25	640	1.9	0.008	0.000341	23.83	0.093	0.2
206 ± 2	670	1.5	0.008	0.000883	19.91	2.32	7.0
244 ± 30	608	1.5	0.008	0.00143	16.19	5.98	18

TABLE VII. Thermal Decomposition of PuF_6 in Fluorination Reactor Effluent; Decomposition Vessel Packed
Average flow rate of effluent stream: 200 cc/min at 300°K

Decomp. Vessel Temp, °C	Volume Decomp. Vessel, cc	Average Total Pressure, mm Hg	Residence Time in Decomp. Vessel, min	Decomp. Vessel Surface/Volume Ratio, cm^{-1}	Average Mole Ratio PuF_6/F_2 Entering Decomp. Vessel	Equilibrium Constant PuF_6/F_2 at Temp of Decomp. Vessel	PuF_6 Recovered in Cold Trap, g	PuF_6 Decomp. g %	PuF_6 Decomp. Rate, %/min of Residence Time
152 ± 1	432	703	1.5	16	0.010	0.00039	30.66	4.70 13	8.7
251 ± 3	116	650	0.33	15	0.012	0.0015	1.89	1.26 40	120
251 ± 2	116	650	0.33	15	0.015	0.0015	0.97	3.20 77	230

The total number of moles of PuF_6 in the effluent of the fluorinator was calculated by summing the moles of PuF_6 in the cold trap and the moles of PuF_4 in the decomposition vessel. The number of moles of fluorine in the effluent stream was calculated from the ideal gas law, with the aid of the average volume flow rate, the total flow time, the average pressure, and the temperature at the flowmeter. These calculated values of total moles of PuF_6 and fluorine were used to calculate the average mole ratio of PuF_6/F_2 in the effluent stream. Data in Tables VI and VII show that in all experiments, the PuF_6/F_2 ratios of the gas mixtures entering the decomposition vessel were higher than the equilibrium ratio at the temperature of the decomposition vessel, thus ensuring that some decomposition would occur in the decomposition vessel.

3. Interpretation

These studies of the rate of decomposition of PuF_6 in a bench-scale fluorination reactor simulated process conditions with respect to the partial pressure of PuF_6 and to the PuF_6/F_2 ratio. It therefore seemed desirable to correlate these data by an equation that could be used to estimate the rate of decomposition under process conditions. Since the results obtained in Section D below also provided observations of the rate of thermal decomposition in the presence of significantly high concentrations of fluorine, they were also used in the derivation of Eqs. 20 and 21 (presented in Section III below).

D. Decomposition of PuF_6 (Ref. 9) at Constant Partial Pressure of PuF_6

The thermal decomposition of PuF_6 vapor was also observed under conditions such that the partial pressure of PuF_6 was maintained constant at 18 mm Hg, but the partial pressure of fluorine was allowed to increase as it formed in the decomposition reaction. These experiments therefore provided some information on the effect of fluorine on the rate of thermal decomposition of PuF_6 .

1. Conditions

The experimental conditions for observation of decomposition of PuF_6 at constant pressure were as follows: The PuF_6 vapor, supplied continuously to the system by vaporization of PuF_6 from a source vessel

at 0°C in series with the vapor circulation path, was circulated by a magnetic piston pump through a heated vessel. We assumed that the rate of vaporization was higher than the rate of decomposition, and therefore that the partial pressure of PuF_6 in the system remained at a constant pressure of 18 mm Hg, the vapor pressure of solid PuF_6 at 0°C. A Taylor pressure transmitter measured the total system pressure continuously during the experiment. The amount of solid PuF_4 deposited in the vessel was determined by weighing the decomposition vessel before and after the experiment. The total gas pressure increased during the experiment as a result of the series of reactions,

Consequently, the change of total pressure with time could be used to measure the rate of decomposition of PuF_6 vapor.

2. Results for Nonpacked Vessel

Table VIII summarizes the experimental conditions and results of thermal decomposition of PuF_6 at a constant PuF_6 pressure of 18 mm Hg. Figure 4 shows the observed total pressures as a function of time.

3. Results for Packed Vessel

A second series of experiments was carried out at conditions similar to those described in Section D-1 above, except that the reaction vessel was packed with nickel wool to increase the surface/volume ratio. Table VIII summarizes the experimental conditions and results. The packed vessel had been prefluorinated with fluorine gas at temperatures ranging

TABLE VIII. Thermal Decomposition of PuF_6 at Constant Partial Pressure of PuF_6 (18 mm Hg)

Experiment No.	Geometric Surface/Volume Ratio, cm^{-1}	Decomp. Temp, °C	Av Wt PuF_4 in Decomp. Vessel, g	PuF_6 Decomposed, g	Total Reaction Time, hr	Residence Time, min	Integral Decomp. Rate, % PuF_6 /min of Residence Time	
21	1.2 ^a	150	15.4	0.60	24	1.6	0.39 ^c	0.018 ^d
22	1.2 ^a	200	17.2	3.41	23.5	1.4	2.6 ^c	2.4 ^d
23	1.2 ^a	256	23.3	10.3	24	1.3	8.1 ^c	8.1 ^d
25	16 ^b	150	0.9	1.96	24	1.5	1.3 ^c	1.2 ^d
25-II	16 ^b	150	2.7	2.12	7.5	1.5	4.5 ^c	5.2 ^d
27	16 ^b	150	15.1	3.65	5.0	1.5	12 ^c	12 ^d
26	16 ^b	200	8.5	10.95	10.0	1.4	19 ^c	19 ^d
30	16 ^b	200	28.2	8.50	8.0	1.4	19 ^c	19 ^d

^aDecomposition vessel not packed.

^bDecomposition vessel packed with nickel wool.

^cCalculated from weight of PuF_4 collected in decomposition vessel.

^dCalculated from total pressure increase with correction for fluorine formed by radiation decomposition, assuming a rate of 2% per day for the rate of radiation decomposition of solid PuF_6 .

Fig. 4. Pressure Changes Indicating Thermal Decomposition of PuF_6 in Nonpacked Vessel

comes reproducible only after the walls of the reaction vessel are coated with the solid product of the reaction.¹⁰ On the other hand, the progressive increase in the rate of fluorine evolution may be the result of insufficient prefluorination. The rate of pressure rise therefore might have been low during the initial stages of Experiment 25 because fluorine was consumed by a corrosion mechanism until the metal surfaces were sufficiently passivated. Figure 6 shows the results of additional experiments on decomposition of PuF_6 at constant partial pressure of PuF_6 in a packed vessel.

E. Decomposition of PuF_6 in Mixtures with UF_6 (Ref. 11)

1. Conditions and Results

The thermal decomposition of PuF_6 in gaseous mixtures with UF_6 was studied with the main objective of demonstrating that UF_6 and PuF_6 could be separated by a selective thermal decomposition. The results of this study are included here because they yield some information on the rate of thermal decomposition of PuF_6 .

from 25 to 400°C, but at the start of Experiment 25 the vessel had not been exposed to PuF_6 , and therefore contained no PuF_4 . The results are given as a graph of the increase of total pressure with time in Fig. 5, which also contains the results of an experiment in the nonpacked vessel for comparison.

The total-pressure curve of Experiment 25 (Fig. 5) indicates an increase in rate of fluorine evolution throughout the experiment. Since the inner surfaces had not been treated with PuF_6 before the experiment but only with fluorine, this increase may indicate that the reaction takes place at a faster rate when solid PuF_4 is present. The reaction rate in the succeeding Experiment (25-II) remained nearly constant and was about equal to the rate finally attained in the latter stages of Experiment 25. This behavior could be similar to that observed in other systems whereby the rate of a unimolecular pyrolysis reaction be-

Fig. 5. Pressure Changes Indicating Thermal Decomposition of PuF_6 ; Effect of Packing the Vessel

Fig. 6. Pressure Changes Indicating Thermal Decomposition of PuF_6 in Packed Vessels

circulated gases through the apparatus. The cylindrical nickel decomposition vessels were 2 in. in diameter and 2 in. long. They were packed with 25 to 28 g of nickel wool to increase their internal geometric surface area to the order of $1.5 \times 10^3 \text{ cm}^2$.

The surface area of the walls of the vessel was calculated from the geometry of the vessel. The surface area of the nickel wool was calculated from the total weight and the surface area per unit weight, which had been determined by micrometer measurements on weighed samples chosen at random from the supply of wool. This procedure yielded a geometric surface area since the roughness factor of the metal surfaces was unknown.

Although the deposition of solid PuF_4 probably increased the interior surface area, the real value was not determined since it was not

Gaseous mixtures of UF_6 and PuF_6 were circulated through heated nickel vessels. In every case, the vessels were packed with nickel wool.

To avoid reaction of either PuF_6 or UF_6 with nickel metal, a protective film of nickel fluoride was produced on the interior of the vessels and on the nickel wool packings by prefluorinating the system with fluorine gas. Since the rate of thermal decomposition of PuF_6 is apparently increased by the presence of PuF_4 , an initial coating of PuF_4 was deposited on the inner surfaces and packing of the vessel to achieve as high a decomposition rate as possible.

Figure 7 is a schematic diagram of the apparatus used in the separation experiments. Nickel and Monel were used to construct the apparatus, which was contained in a glovebox. A pump* with a Monel diaphragm

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Fig. 7. Apparatus Used to Observe Thermal Decomposition of PuF_6 in Mixtures with UF_6

*Lapp Pulsafeeder No. CPS-1, Lapp Insulator Co., Inc., LeRoy, New York.

possible to measure directly the surface area of the PuF_4 deposit in the thermal-decomposition vessels. The specific surface area of a sample of loose crystallites and powder of PuF_4 produced by thermal decomposition of PuF_6 was $0.02 \text{ m}^2/\text{g}$, as determined by a Perkin-Elmer Sorptometer. It was not expected, however, that the specific surface area of the film of PuF_4 on the walls and packing of the thermal decomposition vessels would be equal to that of the sample of crystallites and powder. The specific area of PuF_4 can vary greatly, depending on its method of preparation; for example, the specific surface area of a sample of PuF_4 formed by radiation decomposition of PuF_6 at room temperature was $43 \text{ m}^2/\text{g}$.

Before each experiment, the vessel was exposed to fluorine and plutonium hexafluoride according to the following procedure: (1) Fluorine gas at 1 atm was circulated through the vessel at 300°C for 6 hr. (2) PuF_6 vapor was then circulated through the vessel at 250°C so that several grams of PuF_4 were deposited as a coating on the walls and packing of each vessel. The quantity of PuF_4 deposited in this initial treatment of the vessel was determined by weighing the vessel. The initial ratios of uranium to plutonium were determined by analysis of samples of the gas mixtures obtained after preliminary circulation of the gases through the system, excluding the decomposition vessel.

After the preliminary circulation and the initial sampling for analysis of uranium and plutonium, the mixture was circulated through a closed loop, which included the heated nickel vessel (100-ml volume), the ballast tank (8530-ml volume), and associated lines (670-ml volume). Thus, at any given instant during circulation, only a small fraction of the mixture was in the heated nickel vessel.

In the experiment at 150°C , the gas mixture was sampled for analysis throughout the course of the circulation. In all other experiments, the gas phase was sampled only at the beginning and end of the circulation period. All gas circulations were carried out at a flow rate of 800 ml/min .

Table IX summarizes the experimental results. Since the procedures for sampling the gas mixture yielded samples of varying size, the data were reported in terms of the ratios of uranium to plutonium. The analyses of the solids deposited in the thermal-decomposition vessel showed that only a very small fraction of the uranium deposited during an experiment. Approximately 15 g of UF_6 ($\sim 10 \text{ g}$ of uranium) were used in making up the mixture for a typical experiment. Since only a small quantity of uranium ($\leq 0.005 \text{ g}$) appeared in the PuF_4 deposit, the concentration of UF_6 remained essentially constant throughout an experiment. Thus, the change of the ratio of uranium to plutonium during a given circulation time reflects a change only in concentration of PuF_6 , and the change of the ratio with time is an indication of the rate of removal of PuF_6 from the gas phase.

TABLE IX. Separation of Gaseous Mixtures of UF_6 and PuF_6 by Thermal Decomposition of PuF_6 .
 Mixtures of UF_6 (~90 mm), PuF_6 (~10 mm), and He (~660 mm) were circulated through nickel vessels packed with nickel wool.

Volume of each packed vessel: 100 ml
 Volume of total system: 9300 ml

Temp of Decomp Vessel, °C	Total Internal Geometric Surface, cm ²	Wt of PuF_6 Initially in Vessel, g	Circulation ^a Time, hr	Analysis of Gas Sample			Pu Removed from Gas, % of Initial ^b Pu Content	Analysis of Solids Deposited from Gas Mixture		
				Wt U, mg	Wt Pu, mg	Ratio, U/Pu		Wt U, g	Wt Pu, ^c g	Percent U of Solid ^d
150	1600	3.891	0	34.9	3.3	10.6				
			1-1/4	45.1	3.96	11.4	6			
			5	37.6	2.22	16.9	35			
			10	30.6	0.76	40.0	69			
200	1500	4.225	0	763	62.1	12.3				
			1-1/3	438	10.7	40.9	70.0	0.00092	0.37	0.25
200	1400	4.483	0	474	14.8	32.0				
			2-2/3	405	0.085	4.8×10^3	99.4	0.0055	0.42	1.3
200	1400	4.117	0	429	28.3	15.2				
			4	411	0.164	2.51×10^3	99.4	0.0044	0.66	0.67
200	1600	4.456	0	504	39.5	12.8				
			10	472	0.0243	1.94×10^4	99.9			
300	1600	3.810	0	477	48.3	9.90				
			1-1/3	397	0.114	3.48×10^3	99.7	0.00098	1.08	0.091
300	1600	4.218	0	456	26.4	17.3				
			2-2/3	474	0.0772	6.17×10^3	99.7	0.00172	0.65	0.26
300	1600	4.644	0	445	37.4	11.9				
			4	406	0.147	2.76×10^3	99.5	0.0030	0.84	0.36
300	1500	5.370	0	511	38.6	13.2				
			10	472	0.13	3.63×10^3	99.6	0.0081	0.60	1.3

^aOne hour of circulation time is equivalent to 0.66 min of residence time of the entire sample in the decomposition vessel.

^bPercentage plutonium removed from gas = $\frac{(\text{Pu/U})_{\text{initial}} - (\text{Pu/U})}{(\text{Pu/U})_{\text{initial}}} \times 100$.

^cThis does not include the quantity of plutonium deposited as tetrafluoride in the vessel before each experiment.

^dPercentage uranium in solid = $\frac{(\text{Wt U in solid}) \times 100}{(\text{Wt U in solid}) + (\text{Wt U deposited from mixture})}$.

Since the circulation path in these experiments was a closed loop, the average residence time of the total mixture in the decomposition vessel is dependent only on the total circulation time and the ratio of the volume of the decomposition vessel (100 ml) to the total volume of the system (9300 ml). That is,

$$\frac{\text{Residence time of total sample in vessel}}{\text{Vessel volume}} = \frac{\text{Total volume}}{\text{Total volume}} \times \text{circulation time} \quad (9)$$

$$= 1.1 \times 10^{-2} \times \text{circulation time.} \quad (10)$$

Figure 8 shows the increase of the ratios $(\text{U/Pu})/(\text{U/Pu})_{\text{initial}}$ with the circulation and residence times. A tangent to any curve in Fig. 8 is an indication of the rate of separation obtained by thermal decomposition. Data were not obtained on the kinetic portion of the curve at 300°C.

Since the change in the ratio of uranium to plutonium in the gas stream is caused by the thermal decomposition of plutonium hexafluoride, a theoretical limit for the ratio of uranium to plutonium in a gas mixture

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Fig. 8. Change of Uranium/Plutonium Ratios of UF_6 - PuF_6 Mixtures Resulting from Thermal Decomposition of PuF_6

2. Calculation of Rate of Decomposition of PuF_6 in Mixtures with UF_6 Using Eq. 2

If the uranium concentration in the gas mixture does not change, the ordinate of Fig. 8, $(\text{U}/\text{Pu})/(\text{U}/\text{Pu})_{\text{initial}}$, is equal to the reciprocal of the fraction of PuF_6 remaining. To test the applicability of Eq. 2 to conditions somewhat different from those for which it was derived, values for the fraction of PuF_6 remaining and, therefrom, the values for $(\text{U}/\text{Pu})/(\text{U}/\text{Pu})_{\text{initial}}$ were calculated for various decomposition times for comparison with actual values obtained for decomposition of PuF_6 in mixtures with UF_6 . We assumed that UF_6 and helium do not affect the rate. Figure 9 compares the calculated values of $(\text{U}/\text{Pu})/(\text{U}/\text{Pu})_{\text{initial}}$ with the observed values and shows that the rates can be estimated by the use of Eq. 2. The relative agreement between observed and estimated values may be fortuitous considering the uncertainty of the effect of surface/volume ratios. The geometric surface/volume ratios in the vessel used for experiments from which the constants for Eq. 2 were derived was 1.8 cm^{-1} , whereas in these experiments the ratio was 14 to 16 cm^{-1} .

can be calculated from the initial ratio and the equilibrium constant K_{eq} for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) = \text{PuF}_6(\text{g})$ at the temperature of the decomposition vessel. The theoretical maximum ratio is

$$\frac{(\text{U}/\text{Pu})}{(\text{U}/\text{Pu})_{\text{initial}}} = \frac{K_{\text{eq}} + 1}{K_{\text{eq}}} \quad (11)$$

Figure 8 compares the maximum ratios obtained experimentally and the theoretical maximum ratios. The maximum ratio of uranium to plutonium increases as the decomposition temperature decreases. This is expected since the equilibrium constant, PuF_6/F_2 , for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) = \text{PuF}_6(\text{g})$ increases as temperature increases.

Fig. 9. Comparison of Observed and Calculated Changes of Uranium/Plutonium Ratios Resulting from Thermal Decomposition of PuF_6

The agreement between calculated and observed values is probably promoted by the experimental conditions with respect to fluorine concentration: Each experiment involving decomposition of PuF_6 in UF_6 mixtures was performed with no fluorine initially present, the same condition existing in the experiments from which the constants of Eq. 2 were evaluated.

Although the curves in Fig. 9, calculated from Eq. 2, reasonably represent the initial portion of observed points, the curve for 200°C shows that Eq. 2 does not account for the effect of the back reaction as the system approaches the equilibrium position.

F. Decomposition of PuF_6 during Flow of PuF_6 -Fluorine Mixtures through Thermal Gradient¹²

A series of experiments was performed to demonstrate the recovery of PuF_6 from mixtures of PuF_6 and fluorine that passed through a temperature gradient during flow through nickel pipe and tubing. The objective of this work was to explore on a small scale the extent of decomposition of PuF_6 that occurs under conditions similar to those in the effluent of a fluorination reactor.

Gaseous mixtures of PuF_6 and fluorine were passed through a heated pipe, then through a length of nonheated nickel tubing into a cold trap. The mixture was thus transported from lower temperatures, where the PuF_6/F_2 ratio exceeded the equilibrium constant, to a maximum of 600°C in the pipe, where the PuF_6/F_2 ratio was less than the equilibrium constant, and back to lower temperatures again. Decomposition of PuF_6 was expected to occur at temperatures somewhere between the minima and maxima on both the heating and cooling cycles.

Fig. 10. Apparatus for Observation of Thermal Decomposition of PuF_6 during Passage of PuF_6 -Fluorine Mixtures through a Thermal Gradient

Figure 10 is a schematic flowsheet of the equipment used to determine the behavior of PuF_6 when mixtures of PuF_6 and fluorine were subjected to a thermal gradient. The experimental procedure involved volatilization of PuF_6 into a fluorine gas stream and circulation of the mixture through a pipe (12 in. long, 2 in. in diameter) heated to a maximum of 600°C . The mixture was then passed through a series of two cold traps to condense the PuF_6 . The percentage of PuF_6 recovered was determined from the weighed amounts collected in the cold traps and the weight loss of the supply container.

The results of Experiments 1 through 5, listed in Table X, show that 98 to 100% of

the PuF_6 sublimed into the gas stream was recovered in the cold traps. The ratio of PuF_6 to fluorine in these runs was less than the equilibrium ratio at the temperature (600°C) of the hot pipe, and the residence time in the temperature gradient section was relatively short (1.4 to 5 sec).

TABLE X. Recovery of PuF_6 from a Fluorine Stream after Passage through a Furnace Tube and Thermal Gradient

Expt. No.	Gradient Temperature, $^\circ\text{C}$		Flow Time, hr	Avg Flow Rate, cc/min	Linear Flow Rate in 5/16-in.-ID Tube at 300°K , ft/sec	Avg Mole Ratio, ^a PuF_6/F_2	Avg F_2 Pressure, mm	Weight of PuF_6 Introduced to Stream, g	Weight of PuF_4 Condensed from Stream, g	Recovery, %
	Hot Tube	Cold Exit								
1	551	49	18.33	640	0.71	0.0028	736	26.94 (0.22) ^b	26.94 (0.03) ^b	99.88
2	556	48	18.53	660	0.73	0.0020	780	21.59 (0.17) ^b	21.64 (0.32) ^b	100.25
3	577	46	16.75	430	0.48	0.0038	714	22.36 (0.14) ^b	21.96 (0.05) ^b	98.21
4	599	45	17.00	170	0.19	0.0062	695	14.18 (0.06) ^b	13.95 (0.14) ^b	98.38
5	553	43	25.17	160	0.18	0.0078	723	25.50 (0.10) ^b	25.16 (0.04) ^b	98.67
6	590	44	10.00	160	0.18	0.0210	720	22.20 (0.16) ^b	20.08 (0.01) ^b	90.50

^aMoles PuF_6 calculated from total quantity of PuF_6 vaporized; moles F_2 calculated from total flow time, average pressure, and flow rate measured by thermal flowmeter at about 25°C .

^bNumber in parentheses indicates weight correction (grams) for amount of fluorine lost because of radiation decomposition of PuF_6 .

In Experiment 6, the ratio of PuF_6 to fluorine was higher than the equilibrium ratio at 600°C . As expected, in the heated pipe more of the PuF_6 decomposed than in the other experiments. After this experiment, the thermal-gradient tube was sectioned; only a reddish-brown, adherent film (presumably PuF_4) was found on the walls.

All weighings of PuF_6 in the above experiments were corrected for the amount of fluorine lost because of radiation decomposition ($\sim 2\%$ per day) of the PuF_6 . This minor correction is a function of the residence time and the amount of PuF_6 in the container. The thermal-gradient experiments indicate that mixtures of PuF_6 and fluorine with PuF_6/F_2 ratios approximating those to be encountered in the effluent of a fluorination reactor can be transported through a thermal gradient from 600°C to a cold trap at -78°C with a small percentage decomposition.

G. Decomposition of PuF_6 in a Nickel Filter

In the fluorination of nuclear fuels in a fluid-bed reactor, the effluent gas mixtures are passed through nickel filters to prevent the entrainment of particles of nonvolatile solids. To test the behavior of nickel filters under conditions simulating those at the outlet of a fluid-bed fluorination reactor, R. W. Kessie¹³ performed experiments in which mixtures of PuF_6 and fluorine were circulated through a heated nickel filter. Some information on the rate of thermal decomposition of PuF_6 was also obtained from the results.

A porous nickel filter of the bayonet type* was used in the test. The filter was fabricated by placing particles of 35- to 75-micron diameter

*Grade G (10-micron average pore size), Catalogue No. B-14-6, Pall Corp., Cortland, New York.

on trays in a uniform layer, 1/8 in. thick, in a sintering oven, then welding the sheets obtained into the final form of the filter.

The experimental procedure consisted of passing a gaseous mixture of PuF_6 and fluorine at a total pressure of 500 to 900 mm Hg through the filter at an elevated temperature in a furnace. A vessel containing PuF_6 was kept in an ice bath so that the partial pressure of PuF_6 was maintained at 18 mm Hg in equilibrium with the solid. A diaphragm pump circulated the mixture of PuF_6 and fluorine through the vessel and filter at 800 ml/min.

Figure 11 is a sketch of the filter mounted in its container. The two thermowells were in contact with the surface of the filter. In general, the temperatures of the thermowells differed by less than 20°C .

Fig. 11. Porous Nickel Filter and Container

considerably as more PuF_4 was deposited. The weight increase of the filter and container during the 54-hr run was 11.73 g. Of this amount, 10.1 g of material had accumulated on the filter as determined by separate weighing of the filter.

During the experiment at 203°C , 880 g of PuF_6 should have circulated through the vessel. The weight increase of the container of 11.73 g PuF_4 indicated a total decomposition of 13.2 g PuF_6 , and thus a total of 1.5% decomposition. The total decomposition calculated for a 54-hr period using Eq. 2 was 5.6%.

The filter was prefluorinated at 200°C for 7 hr with 760 mm Hg fluorine pressure (weight gain 42 mg). The filter was then exposed to the PuF_6 and fluorine mixture for 5.7 hr at 144°C . No measurable rise in pressure occurred during the run, indicating a low decomposition rate. The weight gain of the filter during this experiment was 223 mg. The decomposition was then continued for 54 hr at 203°C . The increase in pressure in the loop resulting from decomposition of PuF_6 was constant at 9 mm Hg per hour over the entire 54 hr. These data appeared to indicate that, under these conditions, the decomposition rate of PuF_6 was independent of the quantity of PuF_4 on the filter. Previous kinetic studies performed in a container packed with nickel wool (Section C above) indicated that the decomposition rate increased

With a container volume of about 515 cm³ and a flow rate of 800 cm³/min, the residence time of the circulating gas in the container was 0.41 min; thus the average observed decomposition rate was 3.7%/min. The internal surface area of the filter was high; assuming that the filter was constructed from spherical particles, a surface area of 21,000 cm² was calculated. However, it is surprising that the decomposition rate was comparable to results obtained in similar experiments (Table VIII) in a vessel with a much lower surface-to-volume ratio. Perhaps the surface area of the filter was much less than the 21,000 cm² calculated as outlined above.

The pressure drop in the filter during the decomposition was less than 5 mm Hg. A more sensitive test was made on pressure drop after the filter was removed from the container. This test used metered air flow and a water manometer. Pressure-drop measurements across the test filter and two clean filters showed that the behavior of the test filter was within the range expected for clean filters. In the test filter, 7.4% of the void volume was apparently filled with PuF₄. This result suggests that a large fraction of void volume in the filter media would have to be filled with PuF₄ before the pressure drop became high enough to affect operations involving a fluid bed.

III. DERIVATION OF A RATE EQUATION INCORPORATING THE EFFECTS OF FLUORINE AND SURFACE/VOLUME RATIO

A. Introduction

The decomposition of $\text{PuF}_6(\text{g})$ is complicated by the existence of an equilibrium between PuF_6 , PuF_4 , and fluorine. Hence, data on the decomposition of PuF_6 in the absence of significant pressures of fluorine can be treated by Eq. 2. But such an equation is of limited use under conditions that permit the back reaction to proceed. Further, there are indications that the gas-phase decomposition is influenced (accelerated) by the presence of solid PuF_4 , which, in effect, permits more rapid establishment of equilibrium. Under conditions encountered in the fluoride volatility process, however, PuF_6 will only be exposed to temperatures high enough to cause significant decomposition where fluorine is also present. Hence we must provide equations that will allow the rate of decomposition to be predicted under conditions approaching equilibrium.

B. Assumptions and Derivation of the Rate Equation

The following assumptions are employed:

1. The rate of decomposition is proportional to the difference between the mole ratio of PuF_6/F_2 at equilibrium (i.e., K_{eq}) and the mole ratio of PuF_6/F_2 in the gas phase in any system under study.
2. The rate of decomposition increases as a function of the geometric surface-to-volume ratio of the apparatus.
3. There will be no decomposition if the PuF_6/F_2 ratio is less than K_{eq} (i.e., the system contains PuF_4).
4. Significant elemental fluorine is present in the system.

If

$$\text{Decomposition rate} = f(R_t - K_{\text{eq}}), \quad (12)$$

where R_t is the PuF_6/F_2 ratio at time t , and K_{eq} is the equilibrium ratio at the temperature of the system, we assume

$$R_t = A + (R_0 - K_{\text{eq}}) e^{-kt}, \quad (13)$$

where R_0 is the PuF_6/F_2 ratio at $t = 0$. Considering the boundary condition, i.e., at $t \rightarrow \infty$, $R_t \rightarrow K_{\text{eq}}$, Eq. 13 becomes

$$R_t = K_{\text{eq}} + (R_0 - K_{\text{eq}}) e^{-kt}, \quad (14)$$

or

$$\ln \frac{R_t - K_{eq}}{R_0 - K_{eq}} = -kt. \quad (15)$$

We will assume that the dependence of the rate on the surface/volume ratio (s/v) is of the form

$$k = k'(s/v), \quad (16)$$

where k' is a rate constant that is independent of surface and volume effects.

The fraction of PuF_6 decomposed is defined by

$$F = \frac{\text{PuF}_6 \text{ decomposed}}{\text{PuF}_6 \text{ introduced}}; \quad (17)$$

then

$$R_t = R_0 \frac{1 - F}{1 + R_0 F}, \text{ or } F = \frac{R_0 - R_t}{R_0(1 + R_t)}. \quad (18)$$

C. Evaluation of Rate Constants

Results of measurements of the decomposition of PuF_6 in the presence of fluorine were evaluated to derive both the constants k and k' of the rate equations (Eqs. 15 and 16). We assumed that the rate constant k' obeys the Arrhenius relation; thus the variation of k' with $T(^{\circ}\text{K})$ can be expressed as

$$\log k' = A/T + B. \quad (19)$$

The experimental results in Tables VI and VII and Figs. 4-6 were used in the evaluation of k' . Only Experiment 25-II was used from Fig. 5 to obtain values of k and k' . The thermal-gradient experiments listed in Table X could not be used to evaluate k' since they were all carried out under conditions where $R_0 < K_{eq}$, except Experiment 6, in which the average mole-ratio data were probably erroneously high because of experimental difficulties. Finally, the results of experiments on the decomposition of PuF_6 in filter material could not be applied to the calculation of the rate constants since the estimate of the filter surface area probably involved a high degree of error.

Analysis of the experimental data resulted in the two following equations:

$$\ln \frac{R_t - K_{eq}}{R_0 - K_{eq}} = -k'(s/v) \cdot t. \quad (20)$$

The temperature dependence of the rate constant is

$$\log k' = -\frac{3169}{T} + 5.364. \quad (21)$$

From Eq. 21 we calculated an activation energy of 14.5 kcal/mole.

The quality of the experimental data does not warrant highly precise constants for the above equations. Further, the activation energy falls in the range of the activation energies derived for k_1 (19.6 kcal/mole) and k_0 (15.9 kcal/mole) for decomposition of PuF_6 in the absence of fluorine. Equation 20 therefore should be treated as an empirically derived description of the decomposition of PuF_6 in the presence of fluorine and some PuF_4 .

IV. APPLICATION OF THE RATE EQUATIONS TO CALCULATE DECOMPOSITION OF PuF_6 IN PROCESS STREAMS

A. Decomposition in a Gas Cooler

The gas-stream effluent from a fluid-bed fluorinator will pass through a thermal gradient in a gas-cooling section before contacting the filter section. The rate equations developed above can be used to calculate the percentage of PuF_6 that would decompose in a hypothetical cooler.

The temperature of the gas will decrease along the length of the cooler. If the cooler is considered to consist of a large number of equal segments, each of length dL , having temperatures $T_1, T_2, \dots$, then,

$$\begin{aligned} \text{Total \% PuF}_6 \text{ decomposed} &= (\text{decomposition rate at } T_1)(\text{residence time at } T_1) \\ &+ (\text{decomposition rate at } T_2)(\text{residence time at } T_2) + \dots \quad (22) \end{aligned}$$

$$\begin{aligned} &= \text{decomposition rate } T_1 \left(\frac{dL}{\text{linear flow rate}} \right) \\ &+ \text{decomposition rate } T_2 \left(\frac{dL}{\text{linear flow rate}} \right) + \dots \quad (23) \end{aligned}$$

$$= \frac{1}{\text{linear flow rate}} (\text{decomposition rate } T_1 dL + \text{decomposition rate } T_2 dL + \dots) \quad (24)$$

$$= \frac{1}{\text{linear flow rate}} \int_0^L \text{decomposition rate } T_n dL. \quad (25)$$

The integral in Eq. 25 can be evaluated if temperature can be expressed as a function of length along the cooler,

$$t = f(L). \quad (26)$$

A temperature profile for a typical pilot-scale cooler was estimated by Breton.¹⁴ He assumed that the temperature of the cooler is related to its length by the equation

$$\frac{T_{\text{gas}} - T_{\text{wall}}}{T_{\text{gas inlet}} - T_{\text{wall}}} = e^{-QL}, \quad (27)$$

where Q is a constant, and L is the distance from the gas inlet. A pilot-scale cooler was assumed to have an ID of 8 in., a length of 4.5 ft, and internal fins to give an internal geometric s/v ratio of 0.56 cm^{-1} . The temperature of the gas at the inlet was assumed to be 500°C , and the walls of the cooler were assumed to be maintained at a constant 50°C . The gas flow rate was assumed to be 45 ft/min .

B. Application of Eq. 20

Using the specifications in Section A above the temperature profile shown in Table XI, and Eq. 20, we calculated the total decomposition in the cooler for a series of different ratios of PuF_6/F_2 entering the cooler, as shown in Fig. 12. The ratio of PuF_6/F_2 in the effluent from a fluid-bed

TABLE XI. Temperature Profile
for Hypothetical Pilot-plant
Gas Cooler¹⁴

Fraction of Total Length	Temp, $^\circ\text{C}$
0	500
0.1	411
0.2	340
0.3	283
0.4	237
0.5	200
0.6	170
0.7	147
0.8	128
0.9	112
1.0	100

Fig. 12. Percent PuF_6 Decomposed in a Vessel
As a Function of PuF_6/F_2 Ratio of
Gas Entering Vessel

reactor should be much less than the equilibrium value at the fluorination temperature. For fluorination at 500°C, the ratio of PuF_6/F_2 in the effluent stream may be only 0.001, i.e., about one-tenth the equilibrium value. At these conditions, Fig. 12 predicts that 0.02% of the PuF_6 would decompose in the cooler.

C. Application of Eq. 2

Equation 2 was also used to calculate, by a graphical integration, the total decomposition in the cooler described in Section A above. The percentage of PuF_6 decomposed was calculated over 0.5-ft segments of the cooler, and the total percent decomposition was calculated by summation of the differential values, using a PuF_6/F_2 ratio at the cooler inlet of 0.01. The total fluorine pressure was assumed to be 76 cm, and the initial PuF_6 pressure was assumed to be 0.76 cm. These calculations show that, at a typical flow rate of 45 ft/min, the total percentage of PuF_6 decomposed is greater than 100%. Only by using Eq. 2 with an unrealistic flow rate of 5000 ft/min is it possible to calculate a total decomposition of 4%, a figure in the same range as that obtained using Eq. 20 with a flow rate of 45 ft/min.

We therefore suggest that Eq. 20 is more appropriate than Eq. 2 for this calculation. The constants evaluated for Eq. 2 are based on experiments at much lower temperatures than those in the cooling section and at conditions in which the starting material was pure PuF_6 . The net decomposition of PuF_6 in the stream flowing from the fluorination reactor would be expected to be much less than the values estimated from Eq. 2, which does not take into account the back reaction, important at the low ratios of PuF_6/F_2 expected to exist in the effluent gas issuing from the fluorination reactor. The use of Eq. 20, which takes into account the back reaction, is therefore indicated.

V. SUMMARY AND CONCLUSIONS

A review of the data on the thermal decomposition of PuF_6 indicates the following:

1. In the absence of appreciable "back-reaction," i.e., formation of PuF_6 from PuF_4 and F_2 , the rate of decomposition of PuF_6 may be expressed by the equation

$$-\frac{dp}{dt} = k_0 + k_1 p.$$

The effect of solid PuF_4 on the rate of reaction is only crudely defined, and indications are available to suggest that active surface area rather than mass of PuF_4 is important in defining the rate of decomposition.

2. In the presence of appreciable back-reaction, the equilibrium ratio of PuF_6/F_2 is believed to determine the rate of reaction as shown by the equation

$$\ln \frac{R_t - K_{eq}}{R_0 - K_{eq}} = -k't(s/v).$$

The geometric surface/volume ratio (s/v) is used to represent the accelerating effect of surface on the decomposition. The temperature coefficient of the rate constant has been defined in the equation

$$\log k' = - \frac{3169}{T} + 5.364$$

from data available in several studies cited in this report.

3. Limited experiments on the decomposition of PuF_6 in metallic filters have shown that the rates of decomposition are not increased by the high, calculated, surface area of the filter medium. Instead, the filters appear to behave as though many of the pores are plugged to PuF_6 or as though they present only a modest surface for decomposition.

4. Although the values obtainable for the decomposition of PuF_6 by use of these equations agree with the data from experiments cited in this report (the data used to obtain the constants in the rate equations), the ill-defined effect of the surface/volume ratio requires a great deal of caution in the application of the equations to other situations.

APPENDIX

PuF₄-Fluorine-PuF₆ Equilibrium Data

Table XII lists the pressure of PuF₆ (in mm Hg) in equilibrium with 1 atm of fluorine and some PuF₄ at temperatures between 25 and 600°C.

TABLE XII. PuF₄-Fluorine-PuF₆ Equilibrium Data

Temp, T, °C	Pressure, P, mm Hg ^{a,b}	Log p ^a	10 ³ /T, °K	Temp, T, °C	Pressure, P, mm Hg ^{a,b}	Log p ^a	10 ³ /T, °K
25	0.01	-1.85840	3.354	315	2.20	0.34277	1.700
30	0.02	-1.78477	3.299	320	2.30	0.36185	1.686
35	0.02	-1.71353	3.245	325	2.40	0.38061	1.672
40	0.02	-1.64456	3.193	330	2.51	0.39905	1.658
45	0.03	-1.57776	3.143	335	2.61	0.41720	1.644
50	0.03	-1.51303	3.095	340	2.72	0.43504	1.631
55	0.04	-1.45027	3.047	345	2.84	0.45260	1.618
60	0.04	-1.38940	3.002	350	2.95	0.46988	1.605
65	0.05	-1.33032	2.957	355	3.07	0.48688	1.592
70	0.05	-1.27297	2.914	360	3.19	0.50361	1.579
75	0.06	-1.21726	2.872	365	3.31	0.52008	1.567
80	0.07	-1.16314	2.832	370	3.44	0.53630	1.555
85	0.08	-1.11052	2.792	375	3.57	0.55226	1.543
90	0.09	-1.05935	2.754	380	3.70	0.56798	1.531
95	0.10	-1.00957	2.716	385	3.83	0.58346	1.519
100	0.11	-0.96113	2.680	390	3.97	0.59871	1.508
105	0.12	-0.91397	2.644	395	4.11	0.61373	1.497
110	0.14	-0.86804	2.610	400	4.25	0.62853	1.486
115	0.15	-0.82329	2.576	405	4.40	0.64311	1.475
120	0.17	-0.77968	2.544	410	4.54	0.65747	1.464
125	0.18	-0.73716	2.512	415	4.69	0.67163	1.453
130	0.20	-0.69570	2.480	420	4.85	0.68558	1.443
135	0.22	-0.65526	2.450	425	5.00	0.69933	1.432
140	0.24	-0.61579	2.420	430	5.16	0.71289	1.422
145	0.26	-0.57727	2.391	435	5.32	0.72625	1.412
150	0.29	-0.53966	2.363	440	5.49	0.73943	1.402
155	0.31	-0.50292	2.336	445	5.65	0.75243	1.392
160	0.34	-0.46704	2.309	450	5.82	0.76524	1.383
165	0.37	-0.43197	2.282	455	6.00	0.77788	1.373
170	0.40	-0.39770	2.257	460	6.17	0.79035	1.364
175	0.43	-0.36419	2.231	465	6.35	0.80264	1.355
180	0.47	-0.33142	2.207	470	6.53	0.81478	1.346
185	0.50	-0.29936	2.183	475	6.71	0.82674	1.337
190	0.54	-0.26800	2.159	480	6.90	0.83856	1.328
195	0.58	-0.23731	2.136	485	7.08	0.85021	1.319
200	0.62	-0.20726	2.113	490	7.27	0.86171	1.310
205	0.66	-0.17785	2.091	495	7.47	0.87307	1.302
210	0.71	-0.14904	2.070	500	7.66	0.88427	1.293
215	0.76	-0.12082	2.049	505	7.86	0.89533	1.285
220	0.81	-0.09318	2.028	510	8.06	0.90625	1.277
225	0.86	-0.06609	2.007	515	8.26	0.91704	1.269
230	0.91	-0.03953	1.987	520	8.47	0.92768	1.261
235	0.97	-0.01351	1.968	525	8.67	0.93819	1.253
240	1.03	0.01202	1.949	530	8.88	0.94858	1.245
245	1.09	0.03705	1.930	535	9.10	0.95883	1.237
250	1.15	0.06160	1.911	540	9.31	0.96896	1.230
255	1.22	0.08568	1.893	545	9.53	0.97896	1.222
260	1.29	0.10932	1.876	550	9.75	0.98884	1.215
265	1.36	0.13251	1.858	555	9.97	0.99860	1.208
270	1.43	0.15528	1.841	560	10.19	1.00825	1.200
275	1.51	0.17763	1.824	565	10.42	1.01778	1.193
280	1.58	0.19958	1.808	570	10.65	1.02720	1.186
285	1.66	0.22114	1.792	575	10.86	1.03650	1.179
290	1.75	0.24231	1.776	580	11.11	1.04570	1.172
295	1.83	0.26311	1.760	585	11.34	1.05479	1.165
300	1.92	0.28355	1.745	590	11.58	1.06377	1.159
305	2.01	0.30363	1.730	595	11.82	1.07265	1.152
310	2.11	0.32337	1.715	600	12.06	1.08143	1.145

^aCalculated from equation expressed in Ref. 2.

^bP is pressure of PuF₆ in equilibrium with 1 atm fluorine.

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