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THE FLUORINATION OF PLUTONIUM TETRAFLUORIDE

by

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ABSTRACT

The fluorination of plutonium tetrafluoride by elemental fluorine to form plutonium hexafluoride was studied in a flow system at temperatures between 100 C and 600 C. Partial pressures of fluorine from 0.25 to 1.0 atmosphere were used. The plutonium tetrafluoride was obtained from several sources, including the dissolution of uranium-plutonium alloys in bromine trifluoride. Activation energies between 10 and 12 kcal/mole were obtained. Details are included on the techniques and precautions employed in handling powdered plutonium compounds and plutonium hexafluoride.

I. INTRODUCTION

One of the objectives of separation processes is the isolation, decontamination and purification of unused fissionable or fertile material present in the irradiated fuel. Separation processes applied to reactor fuels containing appreciable quantities of U^{238} prior to irradiation are designed to recover the plutonium formed during irradiation. One type of process applicable to plutonium-containing* fuels is based on the advantageous physical and chemical properties of certain fluorides. Briefly,** a fluorinating agent such as bromine trifluoride is allowed to react with irradiated uranium containing plutonium and fission products. The reaction produces uranium hexafluoride, plutonium tetrafluoride, fission product fluorides and bromine. Subsequent distillation of the solution present in the dissolution vessel removes uranium hexafluoride, certain volatile fission product fluorides, bromine and unreacted bromine trifluoride. The residue remaining in the dissolution vessel consists of a mixture of plutonium tetrafluoride and the non-volatile fission product fluorides.

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*No distinction is made here between fuels into which plutonium has been incorporated prior to irradiation and those in which plutonium has been formed by nuclear transformations.

**Considerable literature has been published on the fluoride volatility method of processing reactor fuels. See for example TID-7534, page 498.

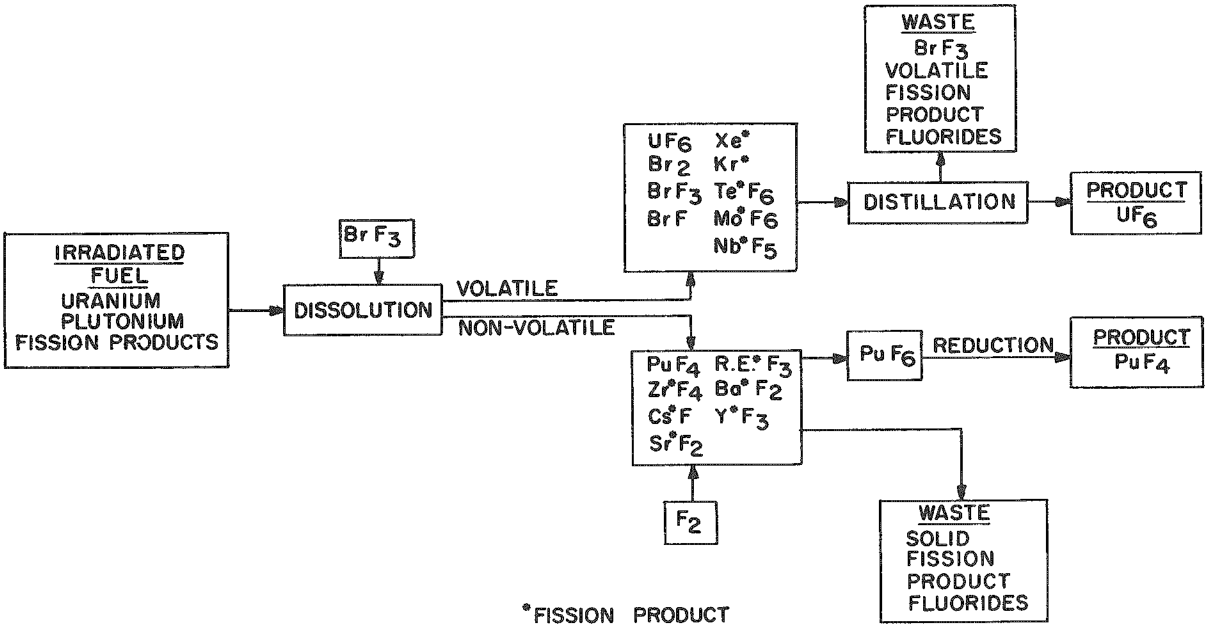
At least two methods have been proposed for the separation and purification of plutonium present in the dissolver after removal of the volatile materials. The mixture of fluorides may be dissolved in an aqueous solution of nitric acid containing a suitable complexing agent for the large quantity of fluoride associated with the residue. On the other hand, direct fluorination of the dissolver residue at elevated temperatures produces plutonium hexafluoride which may be distilled from the dissolver and thus separated from the non-volatile fission product fluorides. The aqueous method for the separation and isolation of plutonium has the advantage of utilizing conventional solvent-extraction techniques and equipment. Much of the technology of the solvent-extraction method has been developed and these processes are presently in use. On the other hand, severe corrosion problems coupled with the hazards of interhalogen-aqueous mixtures which may arise in this operation make the aqueous method unattractive. Finally, the necessity of employing the lengthy conversion chemistry of plutonium nitrate to the metal adds to the disadvantage of the aqueous approach.

Direct fluorination of the plutonium tetrafluoride in the dissolver with subsequent distillation and purification of plutonium hexafluoride has a number of attractive features. Plutonium tetrafluoride is readily fluorinated to the hexafluoride at modest temperatures. The physical properties of plutonium hexafluoride have been investigated by several groups. Since the volatility of plutonium hexafluoride is comparable to that of its uranium analogue, the distillation of plutonium hexafluoride may be a potential method of separating it from the non-volatile fission product fluorides. It is expected that considerable decontamination would be effected during the first distillation. Additional purification of plutonium may be possible by repeated decomposition of the hexafluoride and subsequent refluorination of the decomposition product. Finally, conversion of plutonium hexafluoride to the metal entails a smaller number of steps than the conversion applicable to the solvent extraction product. A schematic outline of the fluoride volatility process employing the fluorination of plutonium is illustrated in Figure 1.

A study of the fluorination of plutonium tetrafluoride was undertaken as part of a program designed to study the basic chemistry of plutonium fluorides as related to this separations process.

FIGURE I

SCHEMATIC OUTLINE OF THE BROMINE TRIFLUORIDE PROCESS
APPLIED TO REACTOR FUELS CONTAINING PLUTONIUM



II. EXPERIMENTAL DETAILS

A. Apparatus. The simple tube furnace assembly used in these investigations is illustrated in Figures 2, 3, 4, 5 and 6. Fluorine was supplied to the four-liter nickel ballast tank from a distribution system external to the laboratory hood. Small cylinders containing one-half pound of high-purity fluorine at 400 psi were purchased from the Pennsylvania Salt Manufacturing Company. Prior to use, the fluorine was passed through a sodium fluoride bed. Tank-grade helium was used directly after passing it through a coil of nickel tubing cooled by liquid nitrogen. The average water and oxygen contents of tank grade helium were between 20 and 40 parts per million.

Packless valves were used throughout the system. Hoke No. 413 diaphragm-type valves, which are made entirely of nickel and Monel, were used in the gas supply system. No. 1103 Hoke bellows valves, which are made of Monel except for a phosphor-bronze bellows, were used with the cold traps. All other metal parts exposed to the fluorine were fabricated from either nickel or Monel.

FIGURE 2

APPARATUS FOR FLUORINATION OF PLUTONIUM FLUORIDES

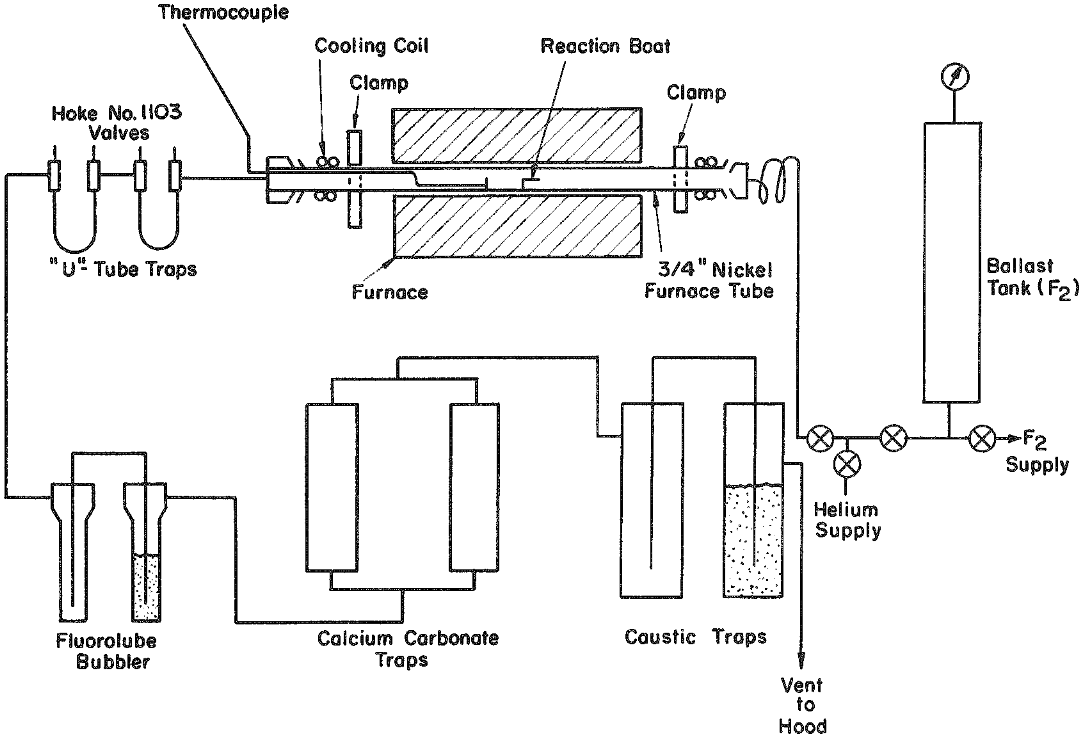
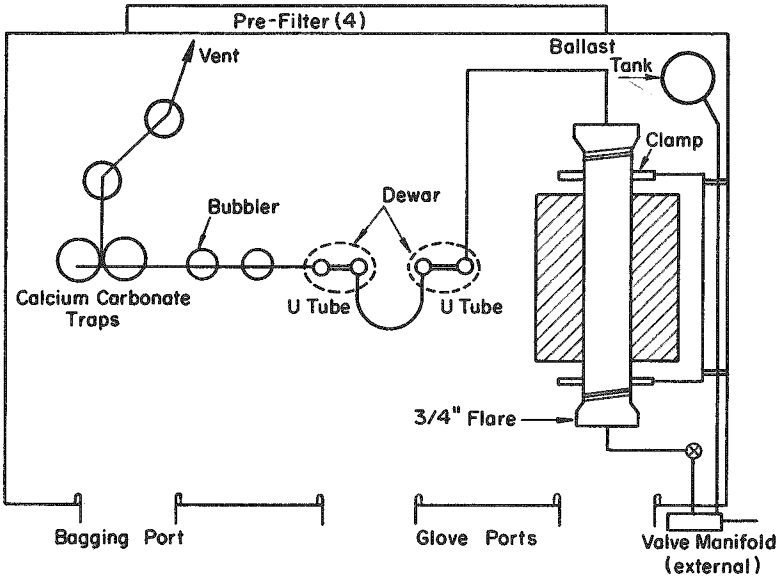


FIGURE 3

APPARATUS FOR FLUORINATION OF PLUTONIUM FLUORIDES

TOP VIEW, IN STANDARD HOOD WITH MODIFIED FRONT



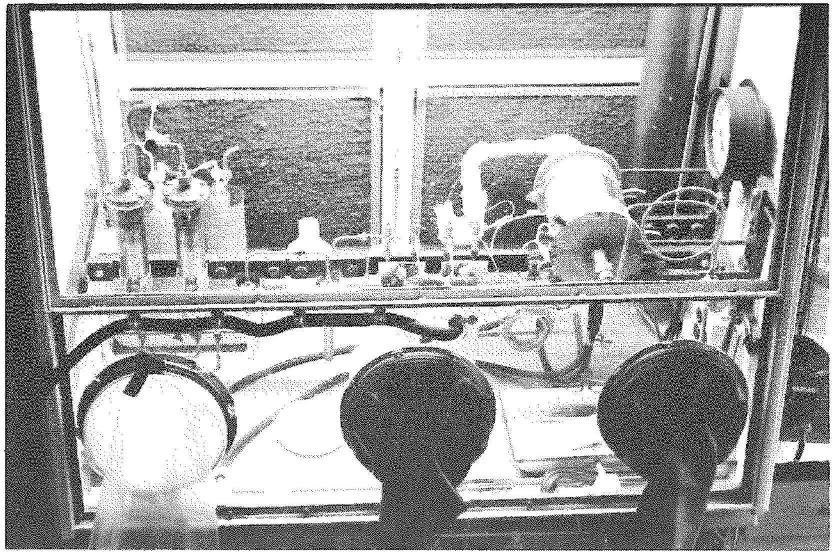


FIGURE 4
APPARATUS FOR THE FLUORINATION OF PLUTONIUM TETRAFLUORIDE

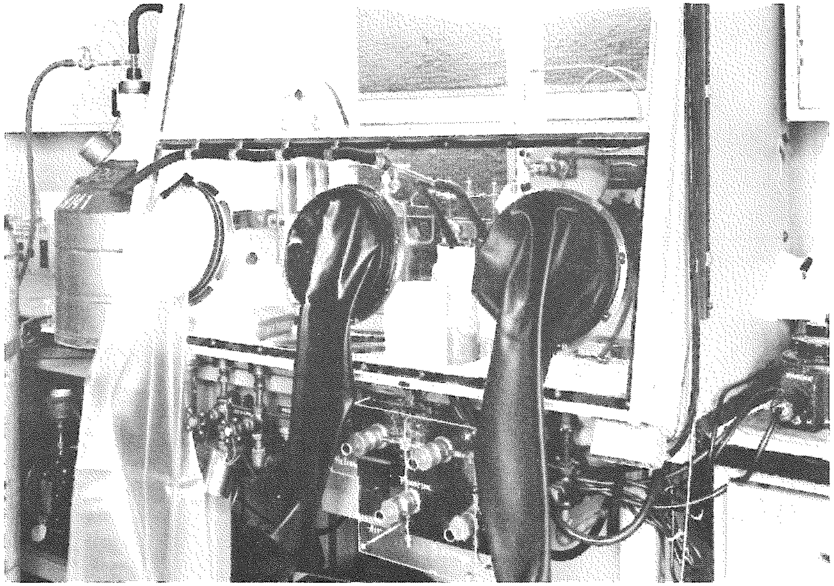


FIGURE 5
APPARATUS FOR THE FLUORINATION OF PLUTONIUM TETRAFLUORIDE

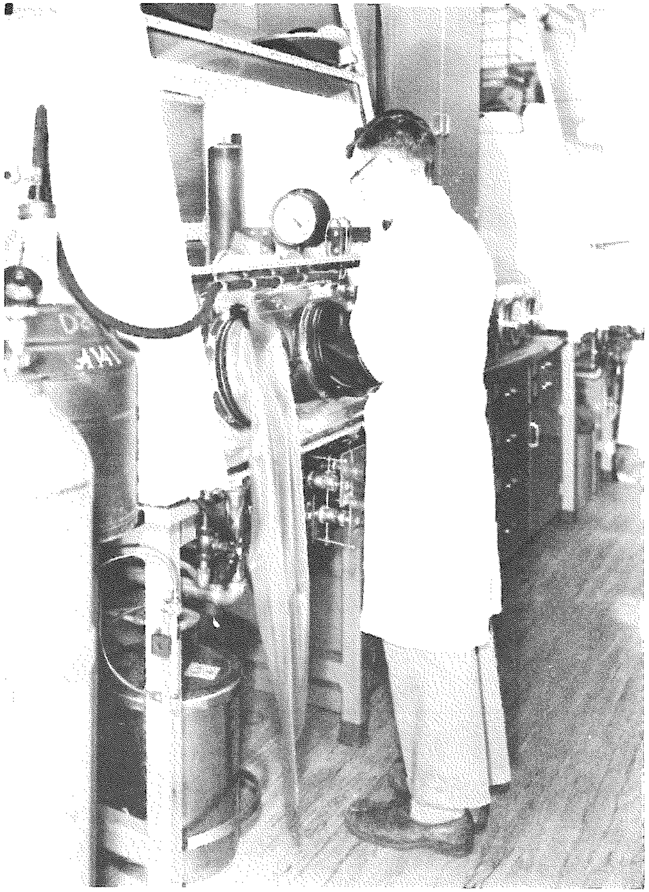


FIGURE 6
APPARATUS FOR THE FLUORINATION OF PLUTONIUM TETRAFLUORIDE

The furnace tube was constructed from 3/4-inch OD, 5/8-inch ID nickel tubing, flared on both ends. The cooling coils, made from 1/8-inch OD copper tubing, were soldered to the ends of the furnace tube. The clamp supports which held the furnace tube consisted of steel sections bolted together. It was found that this arrangement prevented movement of the furnace tube even while the flare connection at the end was tightened. The downstream coupling was drilled to receive the 1/4-inch OD internal nickel thermocouple well which was silver-soldered in place. Teflon flare gaskets were used throughout the equipment.

The hemicylindrical reaction boats were made from 6-mil nickel foil, spot welded together at the ends. A typical boat had an external radius to match the inside dimension of the furnace tube and was 1.25 inches long.

The exit line leading from the furnace tube to the first U-trap and all other connecting lines were made from 1/4-inch OD nickel tubing. The lines leading to the first U-trap were heated to approximately 75 C. Small flare couplings were used to connect the U-traps to other equipment. The U-traps were constructed from 3/8-inch OD nickel tubing, bent sufficiently sharply to fit into a standard small Dewar flask. The traps down stream from the U-traps were standard 3/4-inch flare traps, the final one using a Fluorothene* test tube filled with Fluorolube* oil and serving as a bubbler.

The fluorine-disposal section consisted of two brass cans connected in parallel and filled with crushed limestone supported on a nickel screen. The remaining traps were glass, the final one being filled with an aqueous solution of sodium hydroxide. All gases were ultimately vented to the interior of the hood. The equipment was tested with a helium leak detector prior to use.

B. Handling of Plutonium Compounds - The manipulations required for experimental work with plutonium compounds are complicated by the combined radioactivity and high toxicity of plutonium. The permissible total body burden of plutonium is extremely low (1.7×10^{-7} g) and efficient procedures are necessary to avoid the spread of contamination. Furthermore, plutonium tetrafluoride is a finely divided solid and the hexafluoride is a gas under the conditions of the experiments. Finally, the uncontrolled reaction of plutonium hexafluoride with laboratory air has been known to lead to ignition.

Considerable experience is available in the field of protective enclosures for use with plutonium. In the present case, however, it was not feasible to construct elaborate trains of boxes, a practice usually followed. Nevertheless, it was possible to arrange equipment in existing

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*Polymers of chlorotrifluoroethylene.

facilities, to modify them slightly for use with plutonium and to carry out all operations without exposure of personnel or contamination of the laboratory. Owing to these facts, a more detailed description of the facilities is given in the following paragraphs.

The apparatus was contained in a Blickman type K hood which was slightly modified for this purpose. The interior of the hood was covered with adhesive tape and painted prior to use. That portion of the front of the hood normally equipped with horizontally sliding windows was removed and a panel of Lucite was attached on a gasketed surface. Three holes cut into the panel received rolled stainless steel glove rings, $8\frac{7}{8}$ inches in diameter, which were clamped in place from the outside of the hood by small screws. An interior O-ring sealed the edges of the glove ring against the plastic panel. Figure 5 illustrates the mounting of the front panel. The equipment was arranged so that it could be operated from one side of the hood, utilizing two of the three glove ports. Neoprene gloves attached to the glove rings were held in place by two O-rings and were changed without opening the hood interior to the laboratory air. This technique is diagrammed in detail in Figure 19, ANL-5509.(1)

The third glove port was covered with a vinyl pouch, also held in place by two O-rings. This pouch served as a transfer port for both incoming and outgoing materials. A dielectric sealing device was used to seal across the plastic pouch. Three separate one-quarter-inch wide seals were made on the vinyl pouch when materials were bagged out of the hood. The sealed portion of the pouch was separated from the remaining stub by cutting along the center of the middle seal. No contamination was observed along this cut at any time. All equipment in the hood was of such size as to permit removal through the glove port covered by the vinyl pouch. Transfers of this type have been described by Shuck and Mayfield in ANL-5499, page 123.(2)

The vertically movable front of the hood remained closed after the equipment had been found operative. All openings along the bottom were sealed with wide adhesive tape. Air flow was restricted to narrow openings at the top of the hood and small openings not covered by tape.

All control valves necessary for the operation of the apparatus were located on the outside of the hood. One-quarter-inch nickel lines leading to and from the valves, as well as electrical and thermocouple connections, were passed through a hole in the bottom edge of the hood. This hole was sealed with non-hardening putty. All services to the hood were sealed except the cold-water line used in cooling coils, the output of which was discharged into the retention tanks of the building. Liquid nitrogen was transferred into the Dewars, under nitrogen pressure, through a rubber hose connection visible in Figure 5.

In the course of experimentation, the usual precautions accorded powdered plutonium were exercised. Workers were required to wear laboratory coats, the wrists of which were taped with masking tape. Surgical rubber gloves were worn during the handling of equipment containing plutonium. The aid and advice of the Radiation Safety personnel were sought frequently.

The success of the experimental arrangement is evidenced by the complete lack of contamination external to the hood. The ease and economy with which a standard hood was transformed into one suitable for plutonium work of this kind indicate that in certain instances, at least, extensive glove box systems are not mandatory for plutonium manipulations.

C. Experimental Procedure - The thermocouple extending into the furnace was calibrated against one attached to the bottom of a reaction boat filled with calcium fluoride. In addition, an auxiliary thermocouple was located near the top of the same boat. Suitable temperature corrections were made prior to carrying out experiments. Thermocouples clamped to the bottom of the U-tubes were calibrated, using the boiling point of nitrogen as a reference point. The U-tubes were cooled by boiling nitrogen in the bottom of the Dewar flask, using a small heater to effect and control the boiling. During an experiment, the temperatures of the traps were held at approximately -120 C to avoid condensation of the fluorine. All parts of the system were prefluorinated and the reaction boats were brought to constant weight in a stream of fluorine. The temperature of the furnace was recorded and controlled by a Speedomax multipoint recorder.

A typical experiment was carried out as follows: Plutonium tetrafluoride was weighed into the boat, using a standard analytical balance located in an adjacent glove box facility. The nickel boat was placed in a plastic carrier which, in turn, was placed in an ice cream carton. The latter operation was carried out without contaminating the outside of the carton. The carton and its contents were introduced into the hood through the bagging port. The boat was positioned reproducibly in the furnace by sliding it against the thermocouple well. The apparatus was closed and flushed with helium during the heating of the furnace tube to the desired temperature. The U-traps were cooled before the helium flow was started. When temperature equilibrium was reached, fluorine was substituted for helium and the flow rate was adjusted by inspection of the bubbling rate in the terminal trap. At the conclusion of the experiment helium was substituted for fluorine and the furnace was allowed to cool before removing the boat. Prior to removal of the boat, the contents of the U-traps were isolated by closing of the valves. The cooled boat was returned to the plastic carrier, bagged out of the hood and weighed on the analytical balance in the glove box facility. In this fashion the weight change in the time interval of the experiment was determined. The fluorine flow rate was determined from the pressure drop in the four-liter ballast tank. The temperature was recorded by the Speedomax recorder. Samples submitted for X-ray analysis were prepared in a separate plutonium-handling facility. All other data were derived from the weight changes mentioned above.

III. RESULTS

A. Experimental Data - Plutonium tetrafluoride was obtained from three sources. The Los Alamos and Rocky Flats samples had been prepared at elevated temperatures by the use of anhydrous hydrogen fluoride. Although small differences in the rates of fluorination of these two materials were observed, insufficient information is available to permit a complete evaluation of the pertinent parameters. The third source of plutonium tetrafluoride was the residue from the dissolution of dilute plutonium-uranium alloys in liquid bromine trifluoride. The latter reactions were carried out in closed nickel tubes at room temperature. The resulting solution of bromine, uranium hexafluoride and unreacted bromine trifluoride was removed from the plutonium tetrafluoride by vacuum distillation. The solid residue was heated to approximately 100 C in vacuum prior to weighing for fluorination experiments. X-ray patterns* obtained from this material indicated only the lower hydrate of plutonium tetrafluoride. The hydration is believed to result from exposure of the material to air during transfer to the X-ray capillary. It had been thought previously that the product of the dissolution reaction was plutonium trifluoride. Recent experiments performed in the absence of uranium have confirmed the fact that bromine trifluoride converts plutonium trifluoride to the tetrafluoride.

Plutonium tetrafluoride from all three sources was analyzed chemically.** In addition, determinations of bulk density were carried out in such a manner as to represent the type of handling normally encountered in manipulating the reaction boat. It is recognized that this bulk density is primarily a parameter dependent upon the particular experimental conditions employed. A summary of the analytical data is presented in Table 1.

Table 1

ANALYTICAL DATA AND BULK DENSITIES OF PLUTONIUM TETRAFLUORIDE FROM VARIOUS SOURCES

	Fluorine (Wt Per Cent)	Plutonium (Wt Per Cent)	Bulk Density (g/cc)
Los Alamos PuF_4	24.0, 24.1	75.6, 74.8	1.3[a]
Rocky Flats PuF_4	24.2	75.8	1.29
BrF_3 Dissolution Residue[b]	24.2	75.8	0.885
Theoretical Value	24.13	75.87	-

[a] Bulk density assumed to be similar to that of Rocky Flats material.

[b] Corrected for H_2O and NiF_2 in sample; PuF_4: H_2O = 1:0.85

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*X-ray data obtained and interpreted by D. S. Flikkema and R. V. Schablaske

**Analyses performed by D. P. Krause, W. Sovereign, C. Seils and R. Clark.

It was further necessary to be able to estimate the average surface areas of the samples which were fluorinated. This area was determined from the relation of area to volume derived for a hemicylindrical reaction vessel. The volume was determined by using the average sample weight over the period of the experiment together with the experimental bulk density. Finally, examination of residues left in the reaction boat after fluorination showed plutonium tetrafluoride to be the only species.

Tables 2 through 5 present the observed data on the rates of fluorination of the three types of plutonium tetrafluoride, using one atmosphere of fluorine pressure.

Table 2

FLUORINATION OF LOS ALAMOS PLUTONIUM TETRAFLUORIDE AT ONE ATMOSPHERE FLUORINE PRESSURE

Experiment	Temperature (C)	Time (min)	F_2 Flow Rate (cc/min)	Initial Weight (mg)	Final Weight (mg)
6	200	75	131	44.3	39.3
5	250	120	850	52.1	26.3
4	300	45	96	54.0	27.9
1	375	10	67	49.6	31.8
2	375	20	105	52.1	14.9
7	450	5	95	50.0	24.4
3	500	5	53	46.7	21.0
8	600	1.5	280	51.8	25.3

Table 3

FLUORINATION OF ROCKY FLATS PLUTONIUM TETRAFLUORIDE AT ONE ATMOSPHERE FLUORINE PRESSURE

Experiment	Temperature (C)	Time (min)	F_2 Flow Rate (cc/min)	Initial Weight (mg)	Final Weight (mg)
31	200	60	95	54.1	50.5
22	250	45	105	54.1	51.0
33	250	45	94	49.1	45.3
11	300	45	70	52.3	37.2
10	385	20	98	57.2	24.9
13	500	5	158	57.1	26.3
17	600	1.5	105	47.7	28.9
59	600	2	158	77.2	46.3

Table 4

FLUORINATION OF PLUTONIUM TETRAFLUORIDE FROM THE REACTION OF BROMINE TRIFLUORIDE AND URANIUM-PLUTONIUM ALLOYS. FLUORINE PRESSURE - ONE ATMOSPHERE

Experiment	Temperature (C)	Time (min)	F_2 Flow Rate (cc/min)	Alloy[a] (Wt. % Pu)	Initial Weight (mg)	Final Weight (mg)
49	100	110	51	10	57.8	54.7
50	100	120	51	10	31.4	28.7
48	150	60	57	10	48.2	23.6
30	200	30	112	5	38.5	15.2
18	250	20	95	5	41.2	16.4
45	250	20	97	10	24.0	3.6
36	300	6	246	5	49.5	16.9
32	300	6	220	5	48.2	20.5
15	375	6	175	5	53.1	16.7
23	375	5	100	5	42.0	19.9
26	375	6	122	5	45.7	18.9
29	375	6	140	5	87.3	39.6
42	375	10	163	5	95.8	38.0
41	375	6	149	10	175.3	118.8
44	375	6	88	10	48.4	26.2
20	500	1	105	5	39.0	24.3

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[a] Concentration of plutonium in uranium-plutonium alloy which was dissolved in bromine trifluoride to prepare the plutonium tetrafluoride.

Table 5

FLUORINATION OF ROCKY FLATS PLUTONIUM TETRAFLUORIDE BY REPEATED EXPOSURE TO ONE ATMOSPHERE FLUORINE

Experiment	Temperature (C)	Time (min)	F_2 Flow Rate (cc/min)	Initial Weight (mg)	Final Weight (mg)
47a	200	60	45	52.3	47.0
b	200	60	47	47.0	44.4
c	200	60	44	44.4	42.8
d	200	60	41	42.8	40.0
e	200	60	50	40.0	38.3
f	200	120	48	38.3	33.7
g	200	120	47	33.7	31.1
h	200	120	52	31.1	26.3
i	200	120	48	26.3	22.5
j	200	120	50	22.5	19.4
l	200	120	47	19.4	17.1
m	200	120	52	17.1	14.2
n	200	120	52	14.2	11.3
o	200	120	52	11.3	8.8
p	200	120	53	8.8	6.4
q	200	120	52	6.4	5.3
r	200	120	50	5.3	3.6
35a	250	15	100	173.5	169.0
b	250	15	116	169.0	164.6
c	250	15	140	164.6	159.1
d	250	15	248	159.1	153.5
39a	300	20	132	215.7	205.1
b	300	20	84	205.1	195.8
c	300	20	74	195.8	185.5
d	300	20	140	185.5	174.0
e	300	50	55	174.0	148.6
f	300	70	81	148.6	110.4
g	300	57	60	110.4	82.7
34a	375	5	35	144.6	132.5
b	375	5	46	132.5	122.4
c	375	5	250	122.4	112.0
d	375	5	147	112.0	102.8
40a	400	2	105	245.7	234.7
b	400	2	105	234.7	229.1
c	400	2	300	229.1	220.3
d	400	2	210	220.3	213.5
e	400	10	97	213.5	179.7
f	400	15	102	179.7	134.8
g	400	20	97	134.8	83.7
h	400	27	58	83.7	31.9
46a	500	5	147	260.3	204.6
b	500	3	79	204.6	177.9
c	500	3	96	177.9	152.4
d	500	3	70	152.4	128.0
e	500	3	88	128.0	105.0
f	500	3	114	105.0	80.1
g	500	3	70	80.1	61.7
h	500	3	114	61.7	39.6
i	500	3	105	39.6	22.4
j	500	3	88	22.4	11.0
k	500	3	105	11.0	3.1
l	500	3	88	3.1	1.3

In addition to experiments in which the integrated rate of reaction was measured, experiments were carried out in an attempt to determine the details of the kinetics of the fluorination reaction. In the latter type of experiments, samples of plutonium tetrafluoride from Rocky Flats were exposed repeatedly to a fluorine stream at elevated temperatures. The weight losses of the samples were determined for each exposure. Table 5 summarizes the observed data.

A number of experiments were performed at partial pressures of fluorine of less than one atmosphere. In these experiments helium and fluorine were introduced into the ballast tank and allowed to mix for 15 to 48 hours. The resulting mixture was used as a fluorinating agent on Rocky Flats plutonium tetrafluoride. The data obtained in these experiments are tabulated in Table 6.

A number of additional experiments were carried out to investigate the extent of dust and the effect of changing the geometry of the reaction boat. The results are tabulated with suitable comments in Table 7.

B. Derived Data - In order to interpret the experimental data on the rate of fluorination of plutonium tetrafluoride, it is necessary to define a concentration parameter for the solid reactant. The use of a reaction boat in which a thick bed of solid material is contacted with a gas precludes the meaningful application of a surface area of the particles as normally obtained by the BET method or by microscopic observation of the particle size. Consequently, all the data were converted to rate of weight loss per unit time per square centimeter of top exposed surface area of the sample. The latter was obtained from a graphical representation of the relation between the volume of solid in a hemicylindrical boat and the surface area of such a solid, assuming an even distribution of solid along the bottom of the boat. The average sample weight was calculated from the initial and final sample weights, realizing that simple arithmetical averaging is probably not completely valid in this case. It was felt that the error thus introduced is relatively small. The data thus treated are tabulated in Tables 8, 9, and 10, and shown graphically in Figures 7, 8, and 9.

Data derived from repeated fluorination of samples of Rocky Flats plutonium tetrafluoride could be fit into a linear plot of amount reacted per unit area against time. In order to normalize the data with respect to the solid concentration, it is necessary to determine the incremental amount of material reacted per unit area. Consequently, data shown in Table 11 have been arranged to show the variation of the amount reacted, expressed in milligrams per square centimeter of top exposed surface area, with increasing time. These data are also shown in Figures 10 and 11.

Table 6

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

Source: Rocky Flats
Fluorine Pressure: As indicated
Total Pressure: One Atmosphere

Experiment	Temperature (C)	Time (min)	Gas Flow (cc/min)	Pressure of F_2 (atm)	Initial Weight (mg)	Final Weight (mg)
71a	300	30	183	0.25	38.5	34.6
b	300	20	168	0.25	34.6	32.0
c	300	60	171	0.25	32.0	21.6
d	300	15	165	0.25	21.6	19.9
e	300	60	151	0.25	19.9	11.3
f	300	45	171	0.25	11.3	7.3
g	300	30	173	0.25	7.3	3.2
70a	375	5	211	0.25	65.3	62.1
b	375	5	243	0.25	62.1	57.5
c	375	10	168	0.25	57.5	48.3
d	375	10	200	0.25	48.3	39.3
e	375	10	184	0.25	39.3	31.8
f	375	10	205	0.25	31.8	24.1
g	375	10	200	0.25	24.1	16.9
h	375	10	211	0.25	16.9	10.4
i	375	10	232	0.25	10.4	5.6
75a	200	120	197	0.33	57.5	53.3
b	200	120	193	0.33	53.3	49.5
76a	300	30	191	0.33	44.8	36.1
b	300	30	188	0.33	36.1	29.2
77a	375	10	200	0.33	54.7	45.4
b	375	10	195	0.33	45.4	35.2
69a	200	30	117	0.50	33.8	31.9
b	200	30	86	0.50	31.9	31.0
c	200	30	91	0.50	31.0	29.6
d	200	30	85	0.50	29.6	28.2
e	200	60	99	0.50	28.2	25.5
f	200	60	96	0.50	25.5	23.0
g	200	60	91	0.50	23.0	20.8
h	200	90	97	0.50	20.8	17.8
i	200	90	99	0.50	17.8	15.1
j	200	120	94	0.50	15.1	11.8
k	200	60	90	0.50	11.8	10.5
l	200	60	105	0.50	10.5	9.0
m	200	60	100	0.50	9.0	7.9
n	200	60	95	0.50	7.9	7.3
68a	375	5	105	0.50	77.6	67.7
b	375	5	105	0.50	67.7	59.7
d	375	5	107	0.50	59.7	50.8
e	375	5	104	0.50	50.8	42.1
f	375	10	142	0.50	42.1	29.4
g	375	10	147	0.50	29.4	17.0
h	375	10	105	0.50	17.0	5.9
62a	200	120	131	0.75	47.4	37.8
b	200	120	132	0.75	37.8	29.9
73a	300	30	128	0.75	58.3	38.2
b	300	30	132	0.75	38.2	23.4
74a	375	10	121	0.75	58.1	41.2
b	375	5	127	0.75	41.2	33.4

Table 7

FLUORINATION OF PLUTONIUM TETRAFLUORIDE AT ONE ATMOSPHERE FLUORINE PRESSURE

Experiment	Temperature (C)	Time (min)	F_2 Flow (cc/min)	Initial Weight (mg)	Final Weight (mg)	Comments
28	RT	30	93	77.4	77.4	Dusting experiment[a]
14	375	20	210	102.5	24.2	Boat 2x long[b]
37	300	20	136	321.5	302.4	Low wall boat[c]
38	300	20	171	632.4	612.9	High wall boat[c]
24	375	20	140	318.1	253.5	Low wall boat[c]
25	375	20	84	629.7	573.4	High wall boat[c]

---

[a] Reaction at room temperature (35 C) was too slow to measure. No mechanical loss of solids from reaction boat was observed here and in experiments using helium as the sweep gas.

[b] Special reaction boat having the same radius but twice the normal length; hence both twice the normal sample size and twice the area.

[c] Special boat, having the normal radius and length but having vertical walls. Low-walled boat approximately half the capacity as the high-walled boat. The top surface areas of the samples were identical.

Table 8

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

Source: Los Alamos plutonium tetrafluoride
Fluorine Pressure: One atmosphere

Experiment	Average Weight (mg)	Area (sq cm)	Temperature (C)	Rate (mg cm^{-2} hr^{-1})[a]
6	41.8	1.318	200	3.0
5	39.2	1.291	250	9.9
4	41.0	1.308	300	26.6
1	40.7	1.307	375	81.7
2	33.5	1.227	375	90.9
7	37.2	1.268	450	242.3
3	28.8	1.168	500	366.8
8	38.5	1.283	600	826.2

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[a] $\log_{10}$ Rate (mg cm^{-2} hr^{-1}) = 5.857 - 2545/T (K)

Table 9

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

Source: Rocky Flats plutonium tetrafluoride
Fluorine Pressure: One atmosphere

Experiment	Average Weight (mg)	Area (sq cm)	Temperature (C)	Rate ($mg\ cm^{-2}\ hr^{-1}$)[a]
31	52.3	1.42	200	2.5
22	52.6	1.43	250	2.9
33	47.2	1.371	250	4.2
11	44.7	1.347	300	15.4
10	41.1	1.310	375	73.9
13	41.7	1.317	500	280.6
17	38.4	1.262	600	595.9
59	61.75	1.50	600	618

---

[a] Log_{10} Rate ($mg\ cm^{-2}\ hr^{-1}$) = 5.917 - 2719/T (K)

Table 10

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

Source: Reaction product of plutonium-uranium alloys and bromine trifluoride
Fluorine Pressure: One atmosphere

Experiment	Average Weight (mg)	Area (sq cm)	Temperature (C)	Rate ($mg\ cm^{-2}\ hr^{-1}$)[a]
49 (10%)[b]	56.2	1.64	100	1.04
50 (10%)	30.0	1.342	100	1.01
48 (10%)	35.9	1.42	150	17.3
30 (5%)	26.8	1.294	200	36.0
18 (5%)	28.8	1.322	250	56.3
45 (10%)	13.8	1.040	250	58.8
36 (5%)	33.2	1.386	300	163.1
32 (5%)	34.3	1.402	300	197.6
15 (5%)	34.9	1.408	375	258.5
23 (5%)	30.9	1.354	375	195.9
26 (5%)	32.3	1.373	375	195.2
29 (5%)	63.4	1.72	375	277.3
42 (5%)	66.9	1.75	375	198.3
41 (10%)	147.0	2.24	375	252.2
44 (10%)	37.3	1.43	375	155.2
20 (5%)	31.6	1.363	500	647.1

---

[a] Log_{10} Rate ($mg\ cm^{-2}\ hr^{-1}$) = 5.986 - 2253/T (K)

[b] Concentration of plutonium in alloy shown in parentheses

FIGURE 7

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

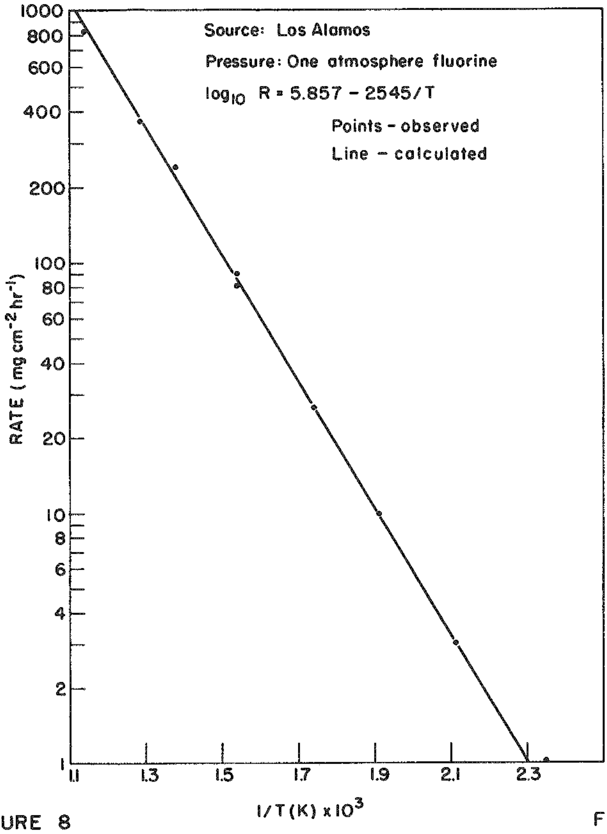


FIGURE 8

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

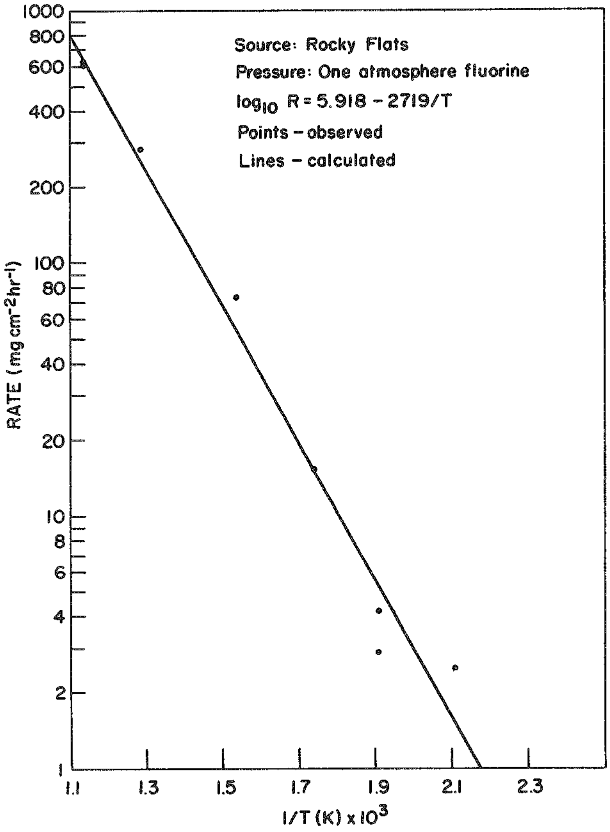


FIGURE 9

FLUORINATION OF PLUTONIUM TETRAFLUORIDE

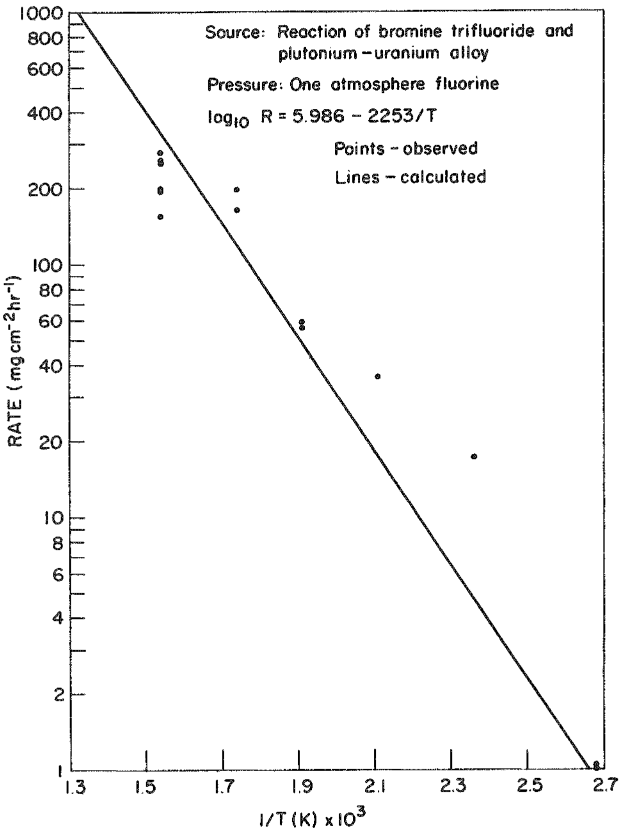


Table 11

FLUORINATION OF ROCKY FLATS PLUTONIUM TETRAFLUORIDE AT ONE ATMOSPHERE FLUORINE PRESSURE: KINETIC STUDY

Experiment	Average Weight (mg)	Area (sq cm)	Temperature (C)	Total Amount Reacted (mg/sq cm)	Total Time (min)
47a	49.7	1.40	200	3.79	60
b	45.7	1.36	200	5.70	120
c	43.6	1.34	200	6.89	180
d	41.4	1.32	200	9.01	240
e	39.2	1.30	200	10.32	300
f	36.0	1.26	200	13.97	420
g	32.4	1.22	200	16.10	540
h	28.7	1.18	200	20.0	660
i	24.4	1.07	200	23.55	780
j	20.9	1.06	200	26.47	900
l	18.3	1.01	200	28.75	1020
m	15.7	0.96	200	31.77	1140
n	12.8	0.90	200	34.99	1260
o	10.1	0.83	200	38.01	1380
p	7.6	0.74	200	41.25	1500
q	5.9	0.68	200	42.87	1620
r	4.5	0.63	200	45.57	1740
35a	171.3	2.08	250	2.16	15
b	166.8	2.06	250	4.29	30
c	161.9	2.04	250	6.99	45
d	156.3	2.02	250	9.76	60
39a	210.4	2.22	300	4.77	20
b	200.5	2.18	300	9.04	40
c	190.7	2.13	300	13.87	60
d	179.8	2.10	300	19.35	80
e	161.3	2.03	300	31.86	130
f	129.5	1.90	300	51.97	200
g	96.6	1.73	300	67.98	257
34a	138.6	1.94	375	6.24	5
b	127.5	1.90	375	11.56	10
c	117.2	1.85	375	17.18	15
d	107.4	1.80	375	22.29	20
40a	240.2	2.31	400	4.76	2
b	230.9	2.28	400	8.09	4
c	223.5	2.26	400	11.32	6
d	216.7	2.23	400	14.14	8
e	196.6	2.17	400	29.72	18
f	157.3	2.02	400	51.94	33
g	109.3	1.81	400	80.17	53
h	67.8	1.54	400	113.8	80
46a	232.5	2.28	500	24.43	5
b	191.3	2.13	500	36.96	8
c	165.3	2.06	500	49.34	11
d	140.2	1.95	500	61.85	14
e	117.0	1.85	500	74.28	17
f	92.6	1.71	500	88.84	20
g	70.9	1.57	500	100.56	23
h	50.7	1.40	500	116.34	26
i	31.0	1.20	500	130.67	29
j	16.7	0.98	500	142.30	32
k	7.1	0.33	500	166.24	35
l	2.2	0.22	500	174.42	38

FIGURE 10
FLUORINATION OF PLUTONIUM TETRAFLUORIDE; KINETIC STUDY

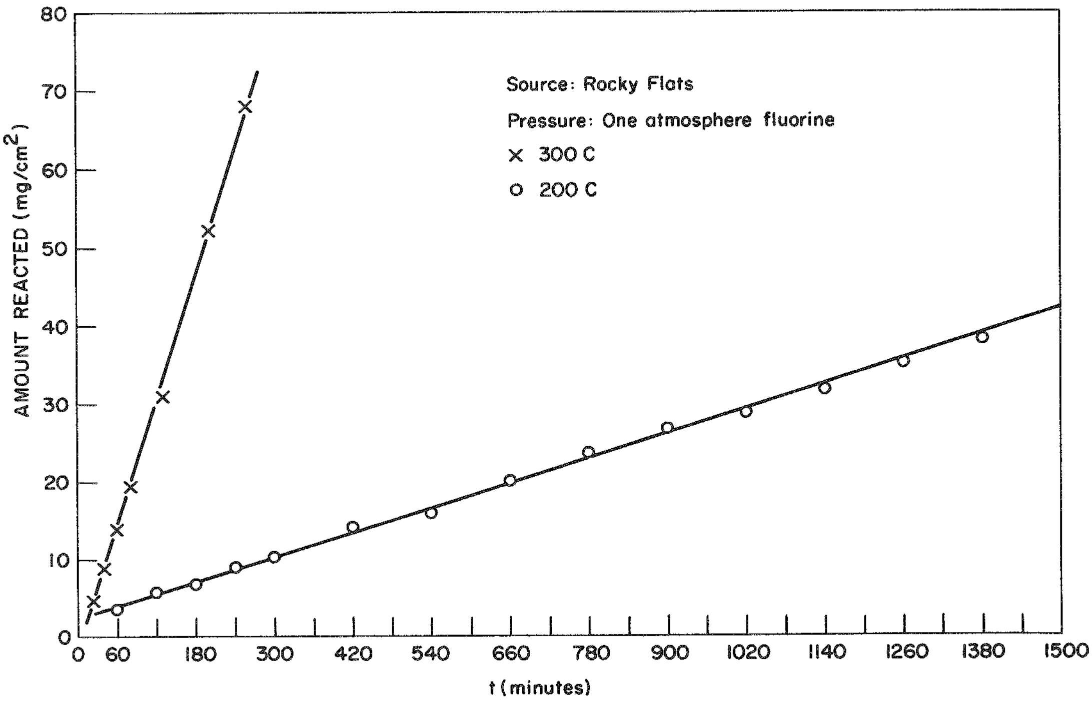
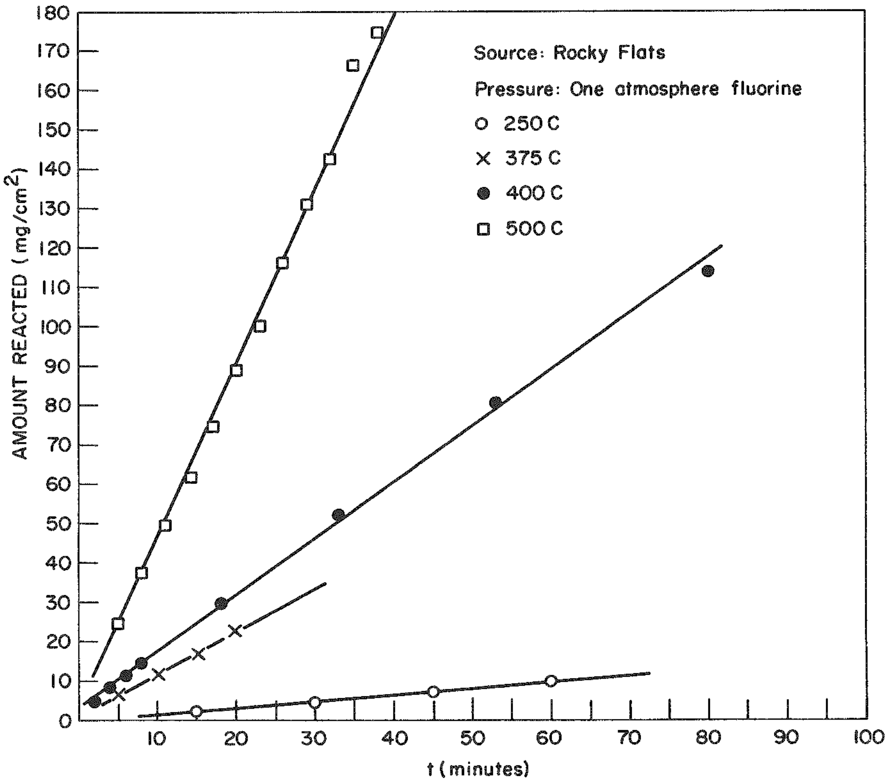


FIGURE 11
FLUORINATION OF PLUTONIUM TETRAFLUORIDE; KINETIC STUDY



Data from experiments with fluorine at partial pressures less than one atmosphere were treated similarly. In Table 12 are the average rates of fluorination of Rocky Flats plutonium tetrafluoride at several partial pressures of fluorine and temperatures. The rates, expressed in units of mg $cm^{-2}hr^{-1}$, were obtained by arithmetic averaging of incremental rates derived from the weight loss, time, and temperature together with the calculated surface areas of the samples. Figure 12 illustrates the relation between the rate of fluorination and the partial pressure of fluorine. Data from Table 12 for the reaction rate at one atmosphere fluorine pressure have been included for comparison.

IV. DISCUSSION

A. Present Study

1. Factors Affecting Kinetics of the Reaction

The reaction rate of a solid with a gas is affected by a number of factors which may be interrelated in a complex manner. The detailed mechanism of the fluorination reaction has not been established. Therefore, the effects of the various rate-controlling parameters are considered separately and empirically. It is recognized that this procedure does not permit a complete theoretical interpretation of the factors affecting the rate and their influence upon one another. It does, however, supply information which should be useful in considering this reaction for process application.

a. Fluorine flow rate: The fluorine flow rate, or the local fluorine concentration, enters into the equilibrium of plutonium tetra- and hexafluorides and probably into the processes involved in removal of the hexafluoride and the diffusion of fluorine into the solid. The latter process has been postulated as the rate-limiting step in the reaction, but no evidence has been presented to support this view.(3) In order to avoid the involvement of an equilibrium-limited observed rate, flow rates of fluorine greater than that required by the equilibrium constant were employed. The rate of weight loss in milligrams of plutonium tetrafluoride per hour for fluorine flow rates of 100 cc/min at one atmosphere fluorine pressure was calculated from the equilibrium constants given by Florin,(4) assuming instantaneous saturation. These data are shown in Table 13.

The data in the present study show rates of weight loss lower than those calculated in Table 13 at all temperatures investigated. In experiments carried out at partial pressures of fluorine of less than one atmosphere, the total gas flow rates were adjusted in such a manner that the fluorine flow rates were comparable to those in experiments in which the fluorine pressure was one atmosphere.

Table 12

FLUORINATION OF ROCKY FLATS PLUTONIUM TETRAFLUORIDE AT SEVERAL TEMPERATURES AND PARTIAL PRESSURES OF FLUORINE

Total Pressure: One atmosphere: partial pressure of fluorine as indicated; remainder helium.

Experiment	F_2 Pressure (atm)	Temperature (C)	Rate (mg cm^{-2} hr^{-1})
71	0.25	300	8.03
70	0.25	375	37.6
75	0.33	200	1.40
76	0.33	300	12.2
77	0.33	375	43.3
69	0.50	200	1.93
68	0.50	375	70.4
72	0.75	200	3.40
73	0.75	300	26.4
74	0.75	375	72.8

FIGURE 12
FLUORINATION OF PLUTONIUM TETRAFLUORIDE

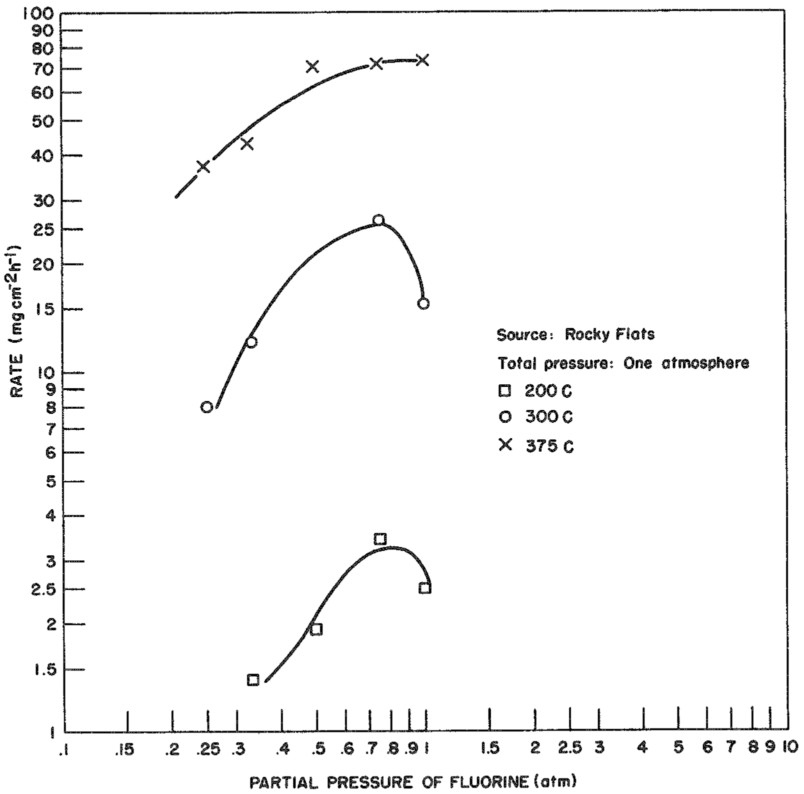


Table 13

CALCULATED RATES OF WEIGHT LOSS OF PLUTONIUM TETRAFLUORIDE EXPOSED TO A FLUORINE FLOW RATE OF 100 cc/min, ASSUMING INSTANTANEOUS EQUILIBRIUM

Temperature (C)	K_{equiv} $\left(\frac{P_{atm}\ PuF_6}{P_{atm}\ F_2}\right)$	Rate (mg/hr)
200	8.3×10^{-4}	70
250	1.6×10^{-3}	135
300	3.0×10^{-3}	252
350	4.7×10^{-3}	380
375	5.9×10^{-3}	498
400	7.1×10^{-3}	570
500	1.4×10^{-2}	1140
600	2.3×10^{-2}	1950

b. Plutonium tetrafluoride: The surface area of the solid influences the reaction rate (see Table 7), but the effect is not easily evaluated on a quantitative basis. No attempt was made to obtain data on the surface area of the tetrafluoride or the thickness of the reaction zone. X-ray line broadening indicates that the plutonium tetrafluoride obtained by reaction of plutonium-uranium alloys and bromine trifluoride has particles sizes much smaller than the tetrafluoride obtained from Los Alamos or Rocky Flats.

In order to normalize the rates observed from experiments in which the sample sizes and hence surface areas were widely varying, the surface area of the solid rather than the mass of the sample was chosen as the pertinent parameter. Experiments 24, 25, 37, and 38 indicate qualitatively that this procedure was sound. It is recognized that for small samples, where the depth of the solid may be less than the thickness of the reaction zone, this approximation is no longer valid.

c. Partial pressure of fluorine: As indicated in Figure 12, the variation of reaction rate with partial pressure of fluorine is complex. It is believed that the maxima in the rates appearing at a fluorine pressure of about 0.75 atmosphere are significant. The extents of the maxima seem to be dependent on temperature and it can be inferred that at temperatures above 375 C the maximum may disappear completely. It is possible that two effects, one being diffusion, are responsible for this phenomenon.

2. Discussion of the Kinetics

An experimental activation energy can be calculated from the integrated reaction rate data for the three types of plutonium tetrafluoride if an order is assumed for the reaction. A reasonable assumption that the rate is first-order with respect to the plutonium tetrafluoride surface area appears to be borne out by detailed differential rate data for the Rocky Flats material. The effect of fluorine concentration is not considered, as it remained constant at 1 atm in these experiments. The activation energies calculated in this manner and constants for the following temperature dependence equation are listed in Table 14.

$$\mathrm{Log}_{10}R(\mathrm{mg\ cm^{-2}hr^{-1}}) = A - (B/T) \quad .$$

Table 14

ACTIVATION ENERGIES FOR THE FLUORINATION OF PLUTONIUM TETRAFLUORIDE FROM SEVERAL SOURCES

$$\mathrm{Log}_{10}\ R\ (\mathrm{mg\ cm^{-2}\ hr^{-1}}) = A - B/T\ (K)$$

Source of PuF_4	A	B	ΔE^* kcal/mole
Los Alamos	5.857	2545	11.7 ± 0.1
Rocky Flats	5.918	2719	12.5 ± 0.4
Dissolution Residue	5.986	2253	10.4 ± 0.6

*Limits for ΔE^* are $\pm\ \sigma$

Differential data obtained from experiments with Rocky Flats plutonium tetrafluoride in which the reaction rate was studied as a function of time were fitted to a general rate equation of the type

$$\mathrm{mg\ PuF_4\ reacted} = k\ f(P)\ S\ t\ \exp\left(-\Delta E^*/RT\right).$$

In this equation k is a constant; f(P) is a function of the fluorine pressure; S is the top exposed surface area of the sample in square centimeters as calculated from the weight of the sample, the bulk density and the geometry of the apparatus; t is the time in hours; ΔE^* is the activation energy as shown in Table 14; R is the gas constant; T is the absolute temperature. The function f(P) could not be evaluated in terms of a simple exponential relationship of the fluorine pressure. If a value of unity is assumed for the function at a fluorine pressure of one atmosphere, values of k for the three types of plutonium tetrafluoride samples were calculated, as shown in Table 15.

Table 15

VALUES OF THE RATE CONSTANT k FOR SAMPLES OF PLUTONIUM TETRAFLUORIDE AT ONE ATMOSPHERE FLUORINE PRESSURE

Source	Rate Constant, k
Los Alamos	7.06×10^5
Rocky Flats	9.17×10^5
Dissolution Residues	11.7×10^5

B. Literature - The reaction of plutonium tetrafluoride with fluorine has been utilized previously for the preparation of plutonium hexafluoride.(4-6) Since the reaction was conducted primarily as a preparative procedure for the hexafluoride, it was usually carried out at high temperatures and no particular attempts were made to measure the rate. In order to achieve optimum yields, the reaction zone was generally heated to about 600 C by induction with a very cold wall in the immediate vicinity to collect the product.

Mandelberg and co-workers(5) carried out a study of the variables affecting the preparation of plutonium hexafluoride, using equipment similar to that employed in the present study. Although insufficient information is available to carry out a detailed comparison of the kinetic data, it is nevertheless profitable to examine their data in more detail. Experiments using comparable sample weights and reaction times yielded the data shown in Table 16.

Table 16

FLUORINATION OF PLUTONIUM TETRAFLUORIDE BY ELEMENTAL FLUORINE

(Data from Mandelberg, et al.,(5) Table 1)

Initial Weight (g)	Temperature (C)	Rate (mg PuF_4/hr)
3.00	320	0
3.02	370	125
3.04	420	230
3.15	470	348
3.18	520	490
2.92	570	600
3.03	620	635
3.00	620	533
2.96	620	612
3.06	620	588
2.96	620	545

All experiments quoted in Table 16 were carried out in the same apparatus. A plot of the logarithm of the rate against the reciprocal of absolute temperature shows a marked deviation from linearity at the highest temperatures. The slope of the linear portion of such a curve yields an activation energy of between 9 and 10 kcal per mole, in reasonable agreement with that observed in the present study. The absolute reaction rates observed by the British workers are roughly comparable to those observed in the present study. In order to account for the deviation from linearity of the plot of the logarithm of the rate against the reciprocal of the absolute temperature, Mandelberg suggests the possibility of a change in mechanism of the reaction or a change in the nature of the surface of the plutonium tetrafluoride. However, on the basis of the equilibrium for the reaction

$$PuF_4 + F_2 \rightleftharpoons PuF_6$$

presented by Florin,(4) a fluorine flow rate of one millimole per minute as used by Mandelberg and co-workers is expected to yield a rate of only about 500 mg/hr at 600 C. Consequently, it appears likely that the diminishing rate of reaction observed at the highest temperatures is due to insufficient fluorine rather than the reasons stated by Mandelberg et al.*

The present work shows no such drastic change in the rate of reaction at the highest temperatures. The vanishing rate of reaction observed at temperatures of 320 C by Mandelberg and co-workers was not observed in the present study. In addition, Adams(7) has also shown that plutonium fluorides can be fluorinated at temperatures as low as 100 C.

A study of the analogous reaction of uranium tetrafluoride and fluorine to form uranium hexafluoride has been reported by Labaton.(8) Labaton presented the results of the kinetic study in terms of a diminishing sphere model for the gas-solid reaction. Labaton's data in these terms, are difficult to compare with those of Mandelberg and those of this study. The data from the present work have on occasion been reported in terms of the diminishing sphere approximation and found to fit this approximation. The validity of the assumptions used in the derivation of the diminishing sphere model equations are open to serious question for reactions which are carried close to completion or for samples in which the particle size distribution is not normal. Consequently, in this report, the data have not been treated by assuming reaction rates proportional to the surface area of a diminishing sphere.

C. Possible Process Applications - On the basis of the rate data presented in this study it appears that the fluorination of plutonium tetrafluoride is sufficiently rapid to justify its consideration as a possible chemical processing step. Some of the variables which affect the rate,

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*The authors are indebted to Dr. A. Florin for a helpful discussion on this point.

such as temperature, surface area, and pressure, have been investigated in enough detail to permit at least a semi-quantitative estimate of their effect under process conditions. Others, such as particle size, the dept of the solid layer, purity, and geometrical factors, need further investigation before the laboratory rate data can be applied with confidence to a chemical process.

V. SUMMARY

The reaction of elemental fluorine and plutonium tetrafluoride was investigated at several temperatures and partial pressures of fluorine. Plutonium tetrafluoride was obtained from both the high-temperature conversion of plutonium compounds to the tetrafluoride by hydrogen fluoride and the dissolution of uranium-plutonium alloys in bromine trifluoride. In the latter case the reaction product was identified as the tetrafluoride.

The course of the reaction was followed by measuring the change of weight of the tetrafluoride. No intermediate fluoride formation was observed in these experiments. The rate of weight change of samples of plutonium tetrafluoride per unit of top exposed surface area was found to be constant with time. Graphical representations of the logarithm of the rate per unit surface area against the reciprocal of the absolute temperature gave activation energies for the reaction ranging from 10.4 to 12.5 kcal per mole. The reaction was fitted to a general rate equation of the type

$$\text{mg reacted} = kSt\, f(P) \exp\left(-\Delta E^*/RT\right),$$

where

k = constant
S = top exposed surface area, sq cm
t = time, hours
$f(P)$ = a function of fluorine pressure
ΔE^* = activation energy
T = Temperature, K

The variation of the rate of reaction with the partial pressure of fluorine was found to be complex, with a maximum in the rate observed at 0.75 atmosphere. The extent of the maximum diminishes with increasing temperature and at temperatures above 375 C it is believed to vanish.

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BIBLIOGRAPHY

1. Kelman, L. R., et al., "The Safe Handling of Radioactive-Pyrophoric Materials," ANL-5509 (December, 1955).
2. Shuck, A. B. and Mayfield, R. M., "The Process Equipment and Protective Enclosures Designed for the Fuel Fabrication Facility," ANL-5499 (January, 1956).
3. Hurst, R., et al., "Plutonium Hexafluoride, Part II, Preparation and Some Chemical Properties," AERE-C/R-1312 (January, 1953).
4. Florin, A. E., et al., "Preparation and Properties of Plutonium Hexafluoride," J. Nucl. Inorg. Chem. 2, 368 (1956).
5. Mandelberg, C. J., "Plutonium Hexafluoride," J. Inorg. Nucl. Chem. 2, 358 (1956).
6. Weinstock, B. and Malm, J. G., "The Properties of Plutonium Hexafluoride," J. Nucl. Inorg. Chem. 2, 380 (1956).
7. Adams, M. D., et al., "The Transfer of Plutonium Hexafluoride in the Vapor Phase,"ANL-5796 (October, 1957).
8. Labaton, V. Y., "A Kinetic Study of the Fluorination of Uranium Tetrafluoride by Fluorine," RDB(Cap)R-8120, (January, 1955).