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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XVII. Fluorination of Neptunium(IV) Fluoride and Neptunium(IV) Oxide

by

L. E. Trevorrow, T. J. Gerding,
and M. J. Steindler

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AEC Research and
Development Report

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Chemical Engineering Division

April 1968

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Part XVI. The Fluorination of UO_2-PuO_2-Fission-product Oxide Pellets with Fluorine in a 2-inch-diameter Fluid-bed Reactor (ANL-7372).

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

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ABSTRACT

Rates of formation of NpF_6 by the reactions of NpF_4 with BrF_3 (6-13 m/o in nitrogen) or BrF_5 (33-35 m/o in nitrogen) or fluorine (100 m/o) were studied at 250-400°C and were interpreted in terms of a rate law which assumes that reaction occurs at a continuously diminishing spherical interface. The relative rates of reaction of NpF_4 with the fluorinating agents at the given concentrations and at 350°C were in the following order: fluorine $>$ BrF_3 $>$ BrF_5. Correlation of the derived rate constants by the Arrhenius equation yielded activation energies of 20 kcal/mole for the reaction of NpF_4 with fluorine and 26 kcal/mole for the reaction of NpF_4 with BrF_5.

Examination of the solid residues from the reactions of NpF_4 with BrF_5 or fluorine by chemical and X-ray-diffraction powder analyses indicated the presence of no species other than NpF_4.

The fluorination of NpO_2 by either BrF_5 or fluorine proceeds through the intermediate compound NpF_4. Thus, the fluorination of NpO_2 is analogous to that of PuO_2 (which proceeds through the intermediate compound PuF_4), but is not analogous to the fluorination of UO_2 (which procceds through the intermediate compound UO_2F_2).

I. INTRODUCTION

Because ^{237}Np can be converted to ^{238}Pu, a valuable source of isotopic power, the separation of neptunium, as well as uranium and plutonium, from spent nuclear fuel by the Fluid-bed Fluoride Volatility Process, is under study. The process flowsheet[1] involves the fluorination of declad, oxidized nuclear fuel, first by BrF_5 to remove uranium by formation and volatilization of UF_6, and then by fluorine to remove plutonium by formation and volatilization of PuF_6.

To plan for the separation and recovery of neptunium, we must establish its behavior in the fluorination steps. Other workers have shown that NpF_4 reacts with fluorine to form NpF_6, a stable compound with volatility similar to that of UF_6 and PuF_6.[2-4] The present work was undertaken to measure the rate of reaction of NpF_4 with fluorine, to establish whether NpF_4 is fluorinated by BrF_5 or BrF_3, and to measure the rates of these reactions.

II. EXPERIMENTAL DETAILS

A. Materials

1. NpF_4

Neptunium tetrafluoride was prepared from $^{237}NpO_2$ obtained from Oak Ridge National Laboratory. Chemical analysis of the NpO_2 showed that it contained 0.13 w/o plutonium and 0.04 w/o uranium. Spectrographic analysis of the NpO_2 showed that it contained only minor amounts of other metallic impurities. To prepare NpF_4, the NpO_2 was treated at 500°C with a gaseous mixture of HF (75 v/o) and oxygen (25 v/o) at a total pressure of about 1 atm. The weight change during a typical preparation indicated that the conversion of NpO_2 to NpF_4 was >99% of the theoretical value. Chemical analysis of the NpF_4 (batch 1) yielded the following results:

	Results, w/o	
	Fluorine	Neptunium
Calculated for NpF_4	24.3	75.7
Observed	24.3	77.2

A gas-adsorption analysis showed that the NpF_4, as prepared, had a specific surface area of 0.3 m^2/g. The bulk density of the NpF_4 was 3.11 g/cm^3.

2. BrF_5 and BrF_3

Both BrF_5 and BrF_3 were obtained from a commercial supplier. The BrF_3 sample contained some BrF_5 as an impurity that was removed by partially freezing the BrF_3 sample and pumping on it. Infrared spectra of gas samples of the BrF_3 taken before and after this procedure showed that it was effective in purifying small (1- to 5-g) samples. The BrF_5 sample contained some bromine as an impurity that was removed by treatment with fluorine.

3. Fluorine

Fluorine, obtained from a commercial source, was passed through a bed of sodium fluoride pellets at 100°C to remove HF.

B. Apparatus

1. Containment of Alpha Active Materials

Operations involving finely divided neptunium compounds were performed in a glovebox[5] to contain the alpha hazard of the ^{237}Np isotope. Operations involving the volatile neptunium compound NpF_6 were confined to a manifold constructed of nickel tubing, Monel diaphragm valves, and fluorothene traps. The reactor (described in B.5 below) and manifold were both contained in the glovebox.

2. Measurement of Specific Surface Area of NpF_4

Specific surface areas of samples of powdered NpF_4 were measured by gaseous adsorption using a Perkin-Elmer Sorptometer.*

3. Measurement of Bulk Density

The bulk densities of samples of NpF_4 powder were measured by tapping weighed quantities of solids into a calibrated glass cylinder.

4. Measurement of Absorption Spectra of Gas Phases

The absorption spectra of gas phases in the visible and near-infrared regions were obtained by expanding the gases into a cylindrical nickel cell with quartz windows[6] and performing measurements with a Cary Model 14 spectrophotometer.** Absorption spectra of gas phases were obtained in the infrared region using the same type of cell with silver chloride windows and performing measurements with a Beckman IR-4 spectrophotometer.†

5. Fluorination

The fluorination reactor, connected to a vacuum manifold, was constructed from a 1-in.-OD nickel tube, closed at both ends by flanges sealed with Teflon gaskets. A nickel thermocouple well, extending through one flange, housed a thermocouple to measure the temperature of a hemi-cylindrical nickel bar on which the boat containing the solid neptunium(IV)

---

*Model 212, Perkin-Elmer Corp., Norwalk, Connecticut.

**Applied Physics Corp., Monrovia, California.

†Beckman Instruments, Inc., Fullerton, California.

compound rested during fluorination. The temperature of the bar was monitored by the signal of an Inconel-clad, Chromel-Alumel thermocouple, read with an automatic potentiometer.[*] The reactor was heated by a 720-W cylindrical furnace.[**] A controlling pyrometer[†] regulated the temperature of the furnace. Figure 1 is a schematic diagram of the fluorination apparatus.

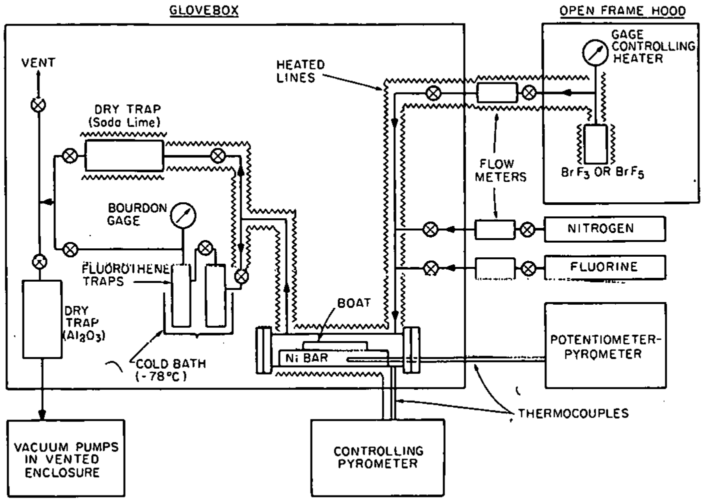

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Fig. 1. Schematic Diagram of Apparatus Used in Fluorination of Neptunium(IV) Compounds

6. Manipulation of Gas Streams

Gaseous fluorine was supplied to the fluorination reactor by expansion from a ballast tank through a thermal flowmeter.[7] The expansion was controlled by throttling through Monel diaphragm valves.

Gaseous interhalogens were supplied to the reactor by heating their containers, located in an open-frame hood, and expanding the vapors at a pressure of about 1000 mm Hg through heated nickel tubing to the fluorination reactor in the glovebox. The interhalogen container vessels, heated by 200-W stainless steel band heaters,[††] were buried in a bed of granulated alumina. The power input to the heaters was controlled by a variable ac transformer. The gas-supply line incorporated a controlling Bourdon gage with auxiliary switches and relays, set to open the heater circuit when the pressure reached 5 psig and to start an audio signal when the pressure reached 8 psig. Interhalogen vapors were mixed with nitrogen gas at a junction inside the glovebox. The compositions of the interhalogen-nitrogen mixtures were determined from the flow rates of the individual components. The flow rate of BrF_5 was measured with a Kel-F flowmeter with a nickel float.[‡] The flow rate of BrF_3 was measured by collecting and weighing the condensible materials from the reactor effluent with a correction for the amount of NpF_6 as indicated by the weight loss of NpF_4.

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[*] Brown Multipoint Potentiometer-Pyrometer, Minneapolis-Honeywell Regulator Co., Philadelphia, Pennsylvania.

[**] Hevi-Duty Electric Co., Milwaukee, Wisconsin.

[†] Guardsman Model, West Instrument Corp., Schiller Park, Illinois.

[††] Acrawatt Electric Corp., Franklin Park, Illinois.

[‡] Brooks Instrument Co., Hatfield, Pennsylvania.

C. Fluorination Procedure

Fluorination rates were measured by determining weight losses of solid NpF_4 during exposure to a gaseous stream of the fluorinating agent for a measured time period. The procedure in a typical determination of reaction rate was as follows: A sample of NpF_4 (1-3 g) was weighed into the nickel boat on a 200-g-capacity analytical balance located in the glovebox. The boat was placed in the reactor at room temperature, a stream of nitrogen gas was started through the reactor, and the furnace temperature was then raised to the chosen reaction temperature. The flow of fluorinating agent and an interval timer were started simultaneously. At the end of a given period, the reaction was stopped either by purging the reactor with nitrogen gas, or by evacuating the reactor. After the reactor had cooled down, the boat was removed from the reactor and reweighed to determine the loss of NpF_4.

III. RESULTS AND DISCUSSION

A. Volatilization of Neptunium by Fluorinating Agents

Weight-loss determinations clearly showed that neptunium was volatilized from the boat containing NpF_4 when any of the fluorinating agents (fluorine, BrF_5, or BrF_3) was passed over the boat containing powdered NpF_4 at 200-500°C. In a blank test, in which gaseous nitrogen was passed over NpF_4, the weight-loss error caused by mechanical removal of dust was negligible.

Table I lists the observed data for the reaction of pure fluorine gas with NpF_4 at 250-400°C. Table II lists the observed weights before and after the reaction of NpF_4 with BrF_5 (33-35 m/o in nitrogen) at 300-400°C. Table III lists the observed weights before and after the reaction of NpF_4 with BrF_3 (6-13 m/o in nitrogen) at 350°C.

TABLE I. Observed Data for Reaction of NpF_4 with Gaseous Fluorine

Fluorine pressure: 1.0 atm
Fluorine flow rate: 200 cc/min

Exp No.	Temp, °C	Reaction Time, min	Weight of NpF_4 before Reaction, g	Weight of NpF_4 after Reaction, g	Exp No.	Temp, °C	Reaction Time, min	Weight of NpF_4 before Reaction, g	Weight of NpF_4 after Reaction, g
1521-F-57L	250	30	3.6891^a	3.3200	1521-F-71R_1	300	10	1.0515^b	0.9958
1521-F-57R	250	30	3.3117^a	3.0412	1521-F-71R_{11}	300	15	0.9958^b	0.9030
1521-F-61	250	15	3.0302^a	2.9218	1521-F-72L	300	20	0.9030^b	0.7814
1521-F-68R	275	10	1.0631^b	1.0298	1521-F-72R	325	5	0.7801^b	0.7201
1521-F-69L	275	20	1.0298^b	0.9615	1521-F-72R_1	325	10	0.7201^b	0.5996
1521-F-69R	275	30	0.9615^b	0.8422	1521-F-72R_{11}	325	10	0.5996^b	0.4869
1521-F-69R_1	275	30	0.8422^b	0.7061	1521-F-72R_{111}	325	10	0.4869^b	0.3716
1521-F-62L	300	5	1.2562^a	1.1429	1521-F-64R	350	5	1.4437^a	1.1789
1521-F-62R	300	5	1.1282^a	0.9776	1521-F-65L	350	5	1.1724^a	0.9475
1521-F-63L	300	5	0.9534^a	0.8214	1521-F-65R	350	10	1.1325^a	0.3966
1521-F-63R	300	10	0.8214^a	0.6589	1521-F-66	350	5	0.3966^a	0.2268
1521-F-64L	300	15	0.6589^a	0.4605	1521-F-67	400	5	2.5062^b	1.5752
1521-F-71R	300	5	1.0712^b	1.0515	1521-F-68L	400	5	1.5752^b	0.5039

[a] Batch No. 1 of NpF_4.
[b] Batch No. 2 of NpF_4.

TABLE II. Observed Data for Reaction of NpF_4 with Gaseous BrF_5-Nitrogen Mixtures

Gas composition: 33-35 m/o BrF_5, 67-65 m/o N_2
Total gas pressure: 1.0 atm
Gas flow rate: 180 cc/min

Exp No.	Temp, °C	Reaction Time, min	Weight of NpF_4 before Reaction, g	Weight of NpF_4 after Reaction, g
1810-F-21	300	60	0.4721[a]	0.4587
1810-F-22	300	60	0.4587[a]	0.4420
1810-F-23	300	60	0.4420[a]	0.4293
1810-F-24	300	60	0.4293[a]	0.4160
1810-F-25	300	60	0.4160[a]	0.4007
1521-F-99L	325	30	0.4780[a]	0.4595
1521-F-99R	325	30	0.4595[a]	0.4424
1521-F-100	325	15	0.4424[a]	0.4328
1492-F-27	325	30	0.4328[a]	0.4149
1810-F-12	350	15	0.4952[a]	0.4761
1810-F-13	350	30	0.4761[a]	0.4413
1810-F-14	350	30	0.4413[a]	0.4049
1810-F-15	350	60	0.4049[a]	0.3114
1810-F-67	350	30	0.3369[b]	0.2974
1810-F-68	350	30	0.2974[b]	0.2644
1810-F-69	350	30	0.2644[b]	0.2318
1810-F-70	350	30	0.2318[b]	0.2008
1810-F-71	350	24	0.2008[b]	0.1781
1810-F-5	400	15	0.7997[a]	0.6892
1810-F-6	400	30	0.6892[a]	0.4173
1810-F-7	400	15	0.4173[a]	0.2821
1810-F-8	400	15	0.2821[a]	0.1518
1810-F-9	400	15	0.1473[a]	0.0746
1810-F-17	400	15	0.7990[a]	0.6741
1810-F-18	400	30	0.6741[a]	0.3665
1810-F-19	400	15	0.3665[a]	0.1957
1810-F-20	400	10	0.1957[a]	0.1324

[a] Batch No. 2 of NpF_4.
[b] Batch No. 3 of NpF_4.

TABLE III. Observed Data for Reaction of NpF_4 with Gaseous BrF_3-Nitrogen Mixtures

Gas composition: 10-13 m/o BrF_3, 90-87 m/o N_2
Total gas pressure: 1.0 atm
Gas flow rate: 180 cc/min
Batch No. 3 of NpF_4

Exp No.	Temp, °C	Reaction Time, min	Weight of NpF_4 before Reaction, g	Weight of NpF_4 after Reaction, g
1810-F-58	350	15	0.6284	0.5357
1810-F-60	350	15	0.5357	0.4533
1810-F-62	350	15	0.4533	0.3230
1810-F-63	350	15	0.3230	0.2497
1810-F-64	350	15	0.2497	0.1762
1810-F-65	350	15	0.1762	0.1192

B. Correlation of Observed Results

The observed weight-loss data have been correlated by the rate law derived by Anderson.[8] This rate law is frequently used to express the kinetics of a reaction between a gas and a solid with the assumption that the reaction takes place at a continuously diminishing spherical interface. The rate law has the form

$$(1 - F)^{1/3} = 1 - k't, \qquad (1)$$

where

F = fraction of solid reacted,

t = reaction time,

k' = apparent rate constant,

and

$$k' = \frac{k}{r_0 \rho}, \qquad (2)$$

where

k = true rate constant,

r_0 = initial radius of solid particle,

and

ρ = bulk density of solid.

Thus, from the measurements of weight loss of solid samples and from Eq. 1, a rate constant at a given temperature can be readily obtained either analytically or graphically from the linear relation between $(1 - F)^{1/3}$ and t.

Figure 2 is a graphical representation, according to Eq. 1, of the data obtained in the reaction of NpF_4 with fluorine.

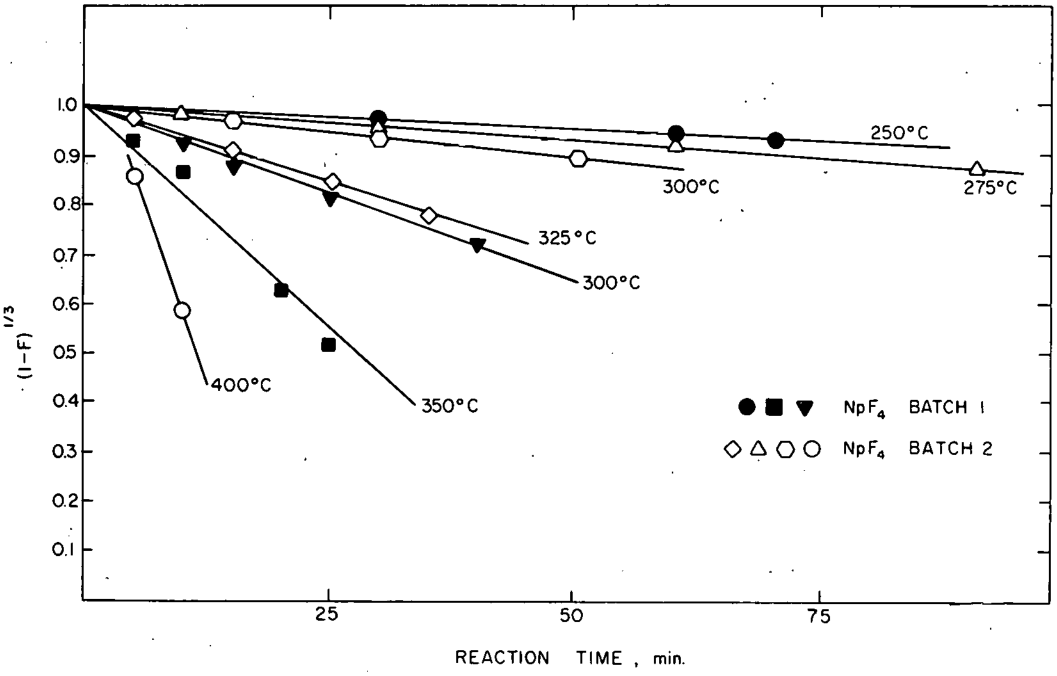

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Fig. 2. Graphical Representation by Eq. 1 of the Rate of Reaction of NpF_4 with Fluorine

The linearity of the graphs in Fig. 3 shows that Eq. 1 can be used to represent the rate of reaction of NpF_4 with BrF_5 at 300, 325, and 350°C, but that the results obtained at 400°C would be expressed better by some other rate law.

Figure 4 shows that Eq. 1 represents the rate of reaction of NpF_4 with BrF_3 at 350°C. The results of the reaction of BrF_5 with a sample of the same batch of NpF_4 are included in Fig. 4 for comparison of rates at 350°C.

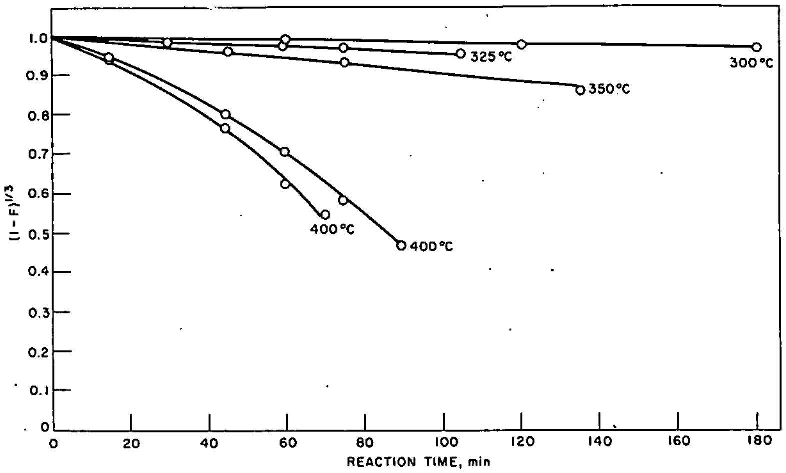

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Fig. 3. Graphical Representation by Eq. 1 of the Rate of Reaction of NpF_4 with BrF_5 (33-35 v/o)

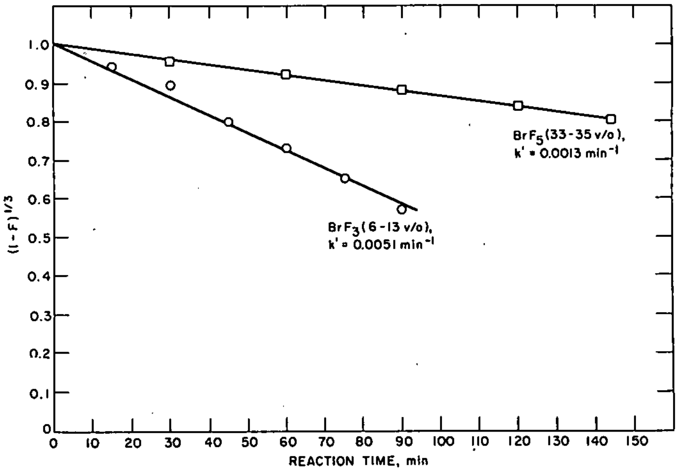

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Fig. 4. Graphical Representation by Eq. 1 of the Rates of Reaction at 350°C of NpF_4 with BrF_3 and with BrF_5

C. Identity of Solid Residues

The solid residues were analyzed to determine whether the rate measurements were being carried out on the same species throughout a reaction. The solids were examined with special attention to any evidence of neptunium fluoride species analogous to the intermediate fluorides of uranium (U_4F_{17}, U_2F_9, and UF_5). No evidence for the existence of such compounds of neptunium has ever been presented.

The formation of intermediate fluorides in the fluorination of UF_4 has been widely observed. Labaton and Johnson[9] found that intermediate fluorides of uranium were produced in the reaction of fluorine with UF_4 in tray reactors. Steindler and Steidl[10] also observed the formation of intermediate fluorides in the reaction of fluorine with UF_4. Jarry and Stockbar[11] found that intermediate fluorides were formed in the reaction of BrF_5 with UF_4.

Although plutonium fluoride species analogous to the intermediate fluorides of uranium have never been isolated and characterized, several investigators have presented evidence of their existence. Mandleberg et al.[12] interpreted the results of chemical analyses and X-ray-diffraction powder analyses as proof of the existence of Pu_4F_{17} in solid residues of the reaction of PuF_4 with fluorine. In other work,[13,14] a break in the temperature dependence of the rate constant for reaction of PuF_4 with fluorine has been attributed to a transformation of the solid phase from PuF_4 to an intermediate fluoride. On the other hand, the formation of intermediate fluorides of plutonium in residues of the reaction of PuF_4 with fluorine was not observed by either Steindler et al.[15] or Vandenbussche.[16]

1. Chemical and X-ray-diffraction Powder Analyses of Solid Residues

At various stages of the reaction of NpF_4 with fluorine, small samples of the solid residues were removed for X-ray-diffraction powder analyses. The results indicated the presence of no species other than NpF_4.

The capability of X-ray-diffraction powder analysis to distinguish between NpF_4 and the possible compound, Np_4F_{17}, is limited by the expected similarity of the two structures. The X-ray pattern of U_4F_{17} is described[17] as that of a "distorted UF_4 lattice." The evidence presented for the existence of Pu_4F_{17} is based partly on minor lines in X-ray-diffraction photographs of a solid with a lattice similar to the distorted UF_4 lattice.

TABLE IV. Comparison of Analyses of Solid Residues from Reaction of NpF_4 with Gaseous BrF_5-Nitrogen Mixtures and Theoretical Compositions of Neptunium Fluorides

Reaction Conditions and Chemical Analyses of Solids Produced

Exp No.	Reaction Temp, °C	Fraction of NpF_4 Reacted	Chemical Analysis Np, w/o	 F, w/o	 Atom Ratio F/Np
1521-F-93	400	0.89	73.6	20.7	3.51
1521-F-98	325	0.76	73.3	22.6	3.85
1810-F-20	400	0.84	72.6	23.4	4.02
1810-F-25	300	0.15	71.2	23.2	4.06
1521-F-93	400	0.89	74.5	24.5	4.11
1810-F-17	400	0.16	72.7	24.0	4.12
1521-F-98	325	0.76	73.8	24.6	4.16

Theoretical Compositions of Solids

Compound	Np, w/o	F, w/o	F/Np
NpF_4	75.7	24.3	4.00
Np_4F_{17}	74.6	25.4	4.25
Np_2F_9	73.5	26.5	4.50
NpF_5	71.4	28.6	5.00

Solid residues of the reaction of NpF_4 with BrF_5 were removed for chemical analyses for neptunium and fluoride and for X-ray-diffraction powder analyses. The X-ray-diffraction photographs showed only lines attributed to NpF_4. The results of chemical analyses of the solid residues (Table IV) show that, although the observed values of w/o for neptunium and fluoride are lower than those calculated for NpF_4, the atom ratio, F/Np, found in the solid is essentially 4, without discernible dependence on reaction temperature or the fraction of NpF_4 reacted.

2. Bulk Densities of Solid Residues

Equation 2 shows that the bulk density of the solid must remain unchanged in the reaction with the fluorinating agent if k' is to be a constant. The bulk densities of the NpF_4 were therefore measured before and after reaction with BrF_5 to determine whether the reaction changed the bulk density of the solid.

Table V lists the bulk densities of the solid obtained at various stages of the reaction of NpF_4 with BrF_5. Although the number of data is insufficient to permit a detailed correlation of bulk density with experimental conditions, it is apparent that, regardless of reaction temperature or fraction reacted, the bulk density of solid residues of the reaction of NpF_4 with BrF_5 is less than that of initial solid NpF_4.

TABLE V. Change of Bulk Density of Solid Phase in Reaction of NpF_4 with Gaseous BrF_5

Gas composition: 33-35 m/o BrF_5 in nitrogen
Batch No. 2 of NpF_4

Exp No.	Reaction Temp, °C	Fraction of NpF_4 Reacted	Bulk Density, g/cc
NpF_4 (initial)	-	-	3.11_8
1810-F-25	300	0.15	2.35_5
1492-F-29	325	0.13	2.33_8
1810-F-17	350	0.60	1.06_1
1810-F-20	400	0.84	0.57_3

The curvature of the lines representing the reaction of NpF_4 with BrF_5 at 400°C (shown in Fig. 3), corresponding to a progressive increase of k', might therefore be the result of a progressive decrease in bulk density of the solid and the inverse dependence of k' on bulk density shown by Eq. 2.

3. Specific Surface Area of Solid Residues

Surface areas of the solid NpF_4 were measured before and after reaction with BrF_5 to characterize the physical nature of the solid and to provide a measure of any changes in the physical nature of the solid caused by exposure to the fluorinating agent. Although the number of data was insufficent to permit a detailed correlation of surface area with experimental conditions, the results listed in Table VI show that specific surface areas of solid residues from the reaction of BrF_5 with NpF_4 were always greater than the specific surface area of the initial solid, NpF_4.

TABLE VI. Surface Areas of Solid Residues from Reaction of NpF_4 with Gaseous BrF_5

Fraction of Solid Reacted	BrF_5 Concentration in Nitrogen, m/o	Reaction Temp, °C	Specific Surface Area, m^2/g
0	-	-	0.30
0.13	33	325	0.42
0.76	33	400	3.1
0.77	33	325-450	1.9
0.89	23	325-450	1.0

If it is assumed that the reaction rate should increase with an increase in the total available surface area of the solid, the curvature of the graph representing reaction of NpF_4 with BrF_5 at 400°C (Fig. 3), corresponding to a progressive increase of k', might be attributed to a progressive increase in surface area of the solid. Note, however, that Labaton and Johnson[9] were unable to obtain a direct correlation between the rate of fluorination of UF_4 and the specific surface area of the UF_4 measured by gas adsorption. They explained this lack of correlation by suggesting that the area measured by gas adsorption includes the areas of pores and channels which do not participate effectively in the various processes of the fluorination reaction such as diffusion of reactant to the reaction site or diffusion of product away from the reaction site.

D. Chemical Species Produced in the Fluorination Reactions

The rate of a reaction may be expressed by the rate law of Eq. 1 without knowledge of the stoichiometry of the reaction. Nevertheless, because of their importance to planning the separation of NpF_6, the identities of the species produced in the fluorination reactions deserve some discussion.

The reaction of fluorine with NpF_4 results simply in the formation of NpF_6,

$$NpF_4 + F_2 \rightarrow NpF_6, \tag{3}$$

according to published information.[2-4]

The reaction of BrF_5 with NpF_4, carried out in the present work, produces NpF_6 and bromine. The condensible constituents of the reaction mixture were initially condensed into a fluorothene trap at -78°C, and then partially vaporized at room temperature into a spectrometer cell. The presence of NpF_6 was proved by comparison of the absorption spectrum in the near-infrared region with previous measurements[18] on pure NpF_6, and the presence of bromine was proved by its absorption spectrum in the visible region. The identification of NpF_6 as a product of the reaction of NpF_4 with BrF_5 was rendered difficult by a back-reaction between the products in the collection traps as they warmed from -78°C to room temperature. In a different type of experiment, bromine and pure NpF_6 were condensed together at -78°C, then warmed to room temperature; a reaction occurred before the mixture reached room temperature. Chemical analysis showed that the solid produced in this experiment was NpF_4. The infrared spectrum of the vapor phase over the reaction mixture indicated that BrF_3 was produced in the reaction. Therefore, it was assumed that the reaction occurring in the collection traps at temperatures of $\leq 30°C$ can be represented by the equation

$$3NpF_6 + Br_2 \rightarrow 3NpF_4 + 2BrF_3. \tag{4}$$

The reaction of BrF_3 with NpF_4, carried out in the present work, produced bromine, readily identified from its absorption spectrum in the visible region. The volatile neptunium compound produced in this reaction was not identified by analysis, but was assumed to be NpF_6.

E. Derivation of Activation Energies

Activation energies have been derived from the apparent rate constants, $k' = k/r_0\rho$, and the Arrhenius equation,

$$k = Ae^{-E_a/RT}, \tag{5}$$

where

k = true rate constant,

A = a constant,

E_a = activation energy,

R = gas constant,

and

T = Kelvin temperature.

Figure 5 shows the temperature dependence of the apparent rate constants k' for both the NpF_4-fluorine reaction and the NpF_4-BrF_5 reaction. The slopes of the curves in Fig. 5 are $-E_a/R$, and the intercepts (not shown) are $A/r_0\rho$.

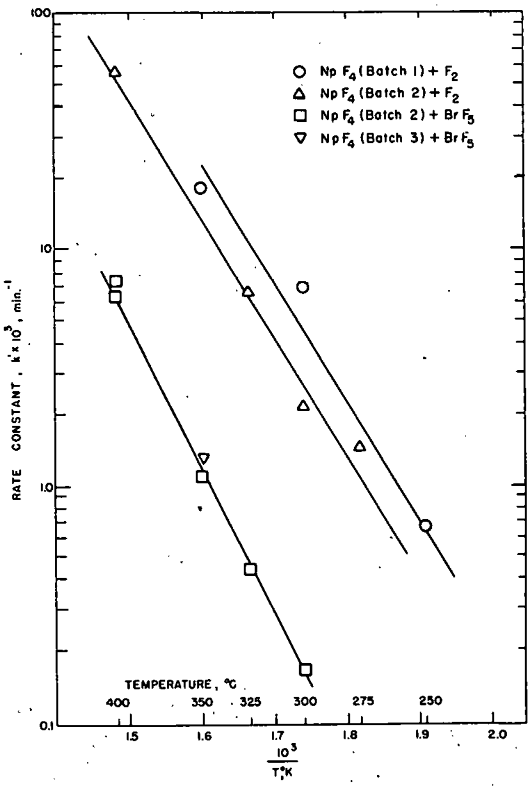

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Fig. 5. Temperature Dependence of Rate Constants for the Fluorination of NpF_4

F. Comparisons of Reaction Rates and Activation Energies

1. Limitations of Comparisons

Comparison of rates of reaction of different fluorinating agents with representative samples of a given solid, using rate constants obtained from Eq. 1 and experimental data, is considered fitting. However, comparison of rates of reaction of different compounds (or even different batches of the same compound) with a fluorinating agent, using rate constants obtained from Eq. 1 and experimental data, is subject to reservation.

Gomes[19] has pointed out that rate constants and activation energies obtained for reactions involving solids may differ from the usual concepts of rate constant and activation energy.

In the usual sense of the term, the rate constant is the proportionality factor between the reaction velocity and concentration or pressure of reactant. The specification of concentration or partial pressure and temperature is sufficient to fix the reactivity or reaction velocity of a homogeneous, fluid system, since it can be assumed that the rate depends on an equilibrium between activated and unactivated molecules expressed by the Boltzmann law. It is more difficult, however, to specify the reactivity of a solid, and this difficulty is recognized in comparisons made in this report of apparent rate constants and activation energies for reactions between gases and solids.

2. Comparison of Rates of Fluorination of Actinide(IV) Fluorides

Rate constants for reaction of actinide tetrafluorides at 350°C for given concentrations of fluorination agents can be compared (as shown in Table VII) using the results presented for neptunium and the results presented in the literature for uranium and plutonium. The rates of reaction of NpF_4 with the fluorinating agents are in the following order: fluorine (100 m/o) $>$ BrF_3 (6-13 m/o) $>$ BrF_5 (33-35 m/o). The rates of reaction of the actinide tetrafluorides with pure fluorine are in the following order: $UF_4 > NpF_4 > PuF_4$. The rate of reaction of BrF_5 with UF_4 is higher than the rate of reaction of BrF_5 with NpF_4.

TABLE VII. Comparison of Rate Constants for Reaction of Actinide Tetrafluorides with Gaseous Fluorinating Agents at 350°C

	Rate Constant, k', min^{-1}		
Compound	Reaction with Fluorine (100 m/o)	Reaction with BrF_3 (6-13 m/o)	Reaction with BrF_5 (33-35 m/o)
UF_4	0.05-0.13[a]	Data unavailable	0.19[b]
NpF_4	0.014-0.023[c]	0.0051[c]	0.0013[c]
PuF_4	0.0062[a] 0.0032[d]	No reaction	No reaction

[a] Vandenbussche.[16]
[b] Jarry and Stockbar.[11]
[c] Obtained from experimental data and Eq. 1.
[d] Estimated from data presented by Steindler and Steidl.[20]

Since the rate of reaction of BrF_3 with NpF_4 is higher than the rate of reaction of BrF_5 with NpF_4, fluorination with BrF_3 might offer higher rates of removal of uranium from nuclear fuel. The use of BrF_3 would provide selective volatilization of uranium as UF_6, leaving plutonium in the bed as PuF_4, which is desirable for the fluid-bed fluoride-volatility process.

With respect to the relative rates of reaction with BrF_3 and with BrF_5, NpF_4 behavior is similar to the behavior of UF_4. Jarry and Stockbar[11] found that the rate of reaction of BrF_3 with UF_4 is higher than the rate of reaction of BrF_5 with UF_4.

The relative rates of reaction of NpF_4 with BrF_3 and BrF_5 may also be an indication of the rate-determining step in the reaction of BrF_5 with NpF_4. Since the reduction of BrF_5 involves breaking several bonds per molecule, it is assumed that the reaction of BrF_5 with NpF_4 occurs in a series of steps, each involving the reduction of a lower bromine fluoride. The only bromine species stable enough to be observed under the experimental conditions employed, however, are BrF_5, BrF_3, and possibly BrF. The reaction of NpF_4 with BrF_3 has been shown to proceed faster than the reaction of NpF_4 with BrF_5. Therefore, if the mechanism of the reaction of NpF_4 with BrF_5 involves the successive steps

$$NpF_4 + BrF_5 \rightarrow NpF_6 + BrF_3, \tag{6}$$

and

$$3NpF_4 + 2BrF_3 \rightarrow 3NpF_6 + Br_2, \tag{7}$$

the first step (Eq. 6) must be the rate-determining one.

3. Comparisons of Activation Energies

The activation energies for the reactions of three actinide tetrafluorides can be compared with fluorine by using the present work on neptunium and literature values for uranium and plutonium as shown in Table VIII.

TABLE VIII. Activation Energies for Reaction of Actinide Tetrafluorides with Gaseous Fluorinating Agents

Compound	E_a, Reaction with BrF_5 (33-35 m/o), kcal/mole	E_a, Reaction with Pure Fluorine, kcal/mole
UF_4	16.9[a]	18.1-18.7[b]
NpF_4	26	20
PuF_4	No reaction[c]	15.5[b] (200-460°C) 10.4[d] (170-500°C) 9.97-10.36[e] (200-370°C) 8.70-8.83[e] (>370°C)

[a] Jarry and Stockbar.[11]
[b] Vandenbussche.[16]
[c] Jarry and Stockbar.[21]
[d] Steindler and Steidl.[20]
[e] Gendre.[13]

The reactivity of a solid commonly varies with the preparation or batch. Labaton and Johnson[9] found that the activation energy for the reaction of various samples of UF_4 with fluorine varied from about 15.5 to 19.9 kcal/mole. Steindler and Steidl[15] found that the activation energy for reaction of PuF_4 with fluorine varied from about 10.4 to 12.5 kcal/mole, depending on the history of the sample of PuF_4. In the reaction of NpF_4 with fluorine, two batches of

NpF_4 exhibited different rates of reaction at a given temperature (as is evident from Fig. 5), but the change of reaction rate with temperature, and therefore the activation energy (20 kcal/mole), was about the same for both batches.

G. Mechanism of Fluorination of NpO_2

The intermediate solid species formed in the fluorination of NpO_2 was studied briefly to compare the fluorination mechanism of NpO_2 with literature reports of the fluorination mechanisms of UO_2 and PuO_2. The reaction of PuO_2 with fluorine proceeds with the formation of PuF_4, which subsequently reacts with fluorine to form PuF_6.[15,16] In contrast, the reaction of UO_2 with fluorine proceeds with the formation of UO_2F_2, which subsequently reacts with fluorine to form UF_6. Also, Jarry and Stockbar[21] found that, in the reaction of UO_2 with BrF_5, UO_2F_2 and UF_4 are present in the partially reacted solid residue. Since Rampy[22] has shown that UF_6 reacts with UO_2 to produce UO_2F_2 and UF_4, this secondary reaction could be responsible for the formation of UO_2F_2 in the fluorination of UO_2. It is also possible that UO_2 is converted to UF_6 in simple steps, and that UO_2F_2 is the intermediate species in the stepwise conversion of UO_2 to UF_6, as suggested by Vandenbussche[16] and by Steindler and Steidl.[23]

For a study of the fluorination behavior of NpO_2, a sample of the powdered solid in a tube reactor was exposed to a flowing stream of pure fluorine at 1 atm and 310°C. In a similar experiment, a sample of NpO_2 was exposed to a flowing stream of BrF_5 (33 m/o in nitrogen) at a total pressure of 1 atm and 350°C.

The solids resulting from both fluorination treatments were similar. In each case, a small amount of dark-brown underlayer resembling the initial NpO_2 remained, but the major portion had been converted to a green solid. Both layers were sampled and identified by X-ray-diffraction powder analysis. In both experiments, the green layer was NpF_4 containing a trace of NpO_2, and the brown layer was NpO_2 containing a trace of NpF_4. In both experiments, X-ray-diffraction analysis showed no evidence of a compound with a pattern analogous to that of UO_2F_2 (Ref. 24). Since NpO_2F_2 and UO_2F_2 would have the same structure and similar unit-cell dimensions,[25] it was concluded that NpO_2F_2 was not present in the solid reaction residues.

Table IX compares the stable species observed in the fluorination of NpO_2 and the stable species observed in the fluorination of UO_2 and PuO_2 (described in the chemical literature). It is concluded that the mechanism of the fluorination of the Np(IV) oxide is analogous to that of Pu(IV) oxide, but is not analogous to that of U(IV) oxide.

TABLE IX. Stable Species Formed in Fluorination of Actinide(IV) Oxides

Fluorinating Agent	Initial Species	Intermediate Species	Final Species
Fluorine	UO_2	UO_2F_2	UF_6
Fluorine	NpO_2	NpF_4	NpF_6
Fluorine	PuO_2	PuF_4	PuF_6
BrF_5	UO_2	UO_2F_2	UF_6
BrF_5	NpO_2	NpF_4	NpF_6
BrF_5	PuO_2	PuF_4	PuF_4

IV. SUMMARY

Although the primary aim of the fluid-bed fluoride-volatility process is the recovery of uranium and plutonium from irradiated nuclear fuel, the recovery of neptunium also is desirable because ^{237}Np is a nuclear parent of ^{238}Pu, a valuable isotopic power source.

Experimental work was performed to determine the behavior of neptunium in two operations of the process flowsheet: treatment of oxidized nuclear fuel with gaseous BrF_5 at 350°C, and treatment of the resulting residue with gaseous fluorine at 350-500°C. Other workers had shown that NpF_6 was formed by the reaction of NpF_4 with fluorine. The present work demonstrated that NpF_6 and bromine are formed by the reactions of NpF_4 at 300-400°C with BrF_3 and with BrF_5. The reverse reaction between NpF_6 and bromine occurs at lower temperatures, $\leq 30°C$.

Reaction rates were obtained from measurements of weight losses of powdered NpF_4 during exposure to gaseous fluorinating agents for a measured time period. Apparent rate constants, obtained from correlation of the experimental data by the rate law which assumes reaction to take place at a continuously diminishing spherical interface, were in the following order: fluorine (100 m/o) $>$ BrF_3 (6-13 m/o in nitrogen) $>$ BrF_5 (33-35 m/o in nitrogen). The apparent rate constants were correlated by the Arrhenius equation to yield activation energies of 20 kcal/mole for the reaction of NpF_4 with pure fluorine, and 26 kcal/mole for the reaction of NpF_4 with BrF_5 (33-35 m/o in nitrogen).

The fluorination of NpO_2 by either fluorine or BrF_5 proceeds through the formation of the intermediate NpF_4. The mechanism of fluorination of NpO_2, therefore, parallels that of PuO_2 (which proceeds through the intermediate PuF_4), but differs from the fluorination of UO_2, which proceeds through the intermediate UO_2F_2.

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