

Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XIX. Reaction of Bromine Pentafluoride with Selected Compounds of Uranium and Plutonium

by

R. L. Jarry, J. J. Stockbar,
and M. J. Steindler

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Chemical Engineering Division

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Other reports in this series are:

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ABSTRACT

The use of BrF_5 to selectively remove uranium from mixtures with plutonium has been studied. The results show that uranium in mixtures with alumina, plutonium dioxide, and fission-product compounds can easily be converted to UF_6 at 350°C or lower using 20% BrF_5 in nitrogen as the fluorinating gas while converting the plutonium only to the non-volatile PuF_4 . The presence of Zircaloy or stainless steel decladding product did not hinder the removal of uranium. Plutonium could be satisfactorily converted to PuF_6 by a second fluorination step at $500\text{-}550^\circ\text{C}$ using elemental fluorine.

The kinetics of the reaction of BrF_5 with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3 were determined; and activation energies of 16.9, 8.3, 9.2, 7.5, and 7.7 kcal/mole, respectively, were derived. Values of the coefficient n for the pressure term in the equation $k' = Ae^{-E/RT}p^n$ of 0.38, 0.71, 0.90, 0.84, and 1.05 were derived for the reactions with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3 , respectively.

I. INTRODUCTION

The fluid-bed fluoride-volatility process (FBFVP) is designed to recover uranium and plutonium from low-enrichment, stainless steel or Zircaloy-clad, uranium dioxide fuels. The ANL reference flowsheet¹ involves the following steps: (1) removal of Zircaloy cladding by reacting it with gaseous HCl to form volatile ZrCl_4 , with subsequent conversion of ZrCl_4 to the solid oxide in a second vessel by reaction with steam, or removal of the stainless steel cladding by reacting it with an HF -oxygen mixture to convert the cladding to a mixture of the solid oxides of its constituent elements; (2) fluorination of the uranium and plutonium species to the hexafluorides, UF_6 and PuF_6 ; (3) separation of the PuF_6 from UF_6 by thermal

decomposition of the PuF_6 to solid PuF_4 ; and (4) decontamination of the UF_6 by fractional distillation, aided by adsorption techniques. Considerable advantage may be gained, however, if uranium and plutonium can be separated by volatilizing separate UF_6 and PuF_6 stream from the fluorination reactor.

One method which may be applied to achieve such a separation is the selective fluorination of uranium (including most of the fission products that form volatile fluorides) without removing the plutonium from the fluorination reactor. For example, the reactions of BrF_3 (Ref. 2) and SF_4 (Ref. 3) with uranium and plutonium compounds generally result in the conversion of the uranium compounds to UF_6 and the conversion of the plutonium compounds only to nonvolatile PuF_4 . Of the various reagents that could be useful for selective fluorination, bromine pentafluoride (BrF_5) appears to hold considerable promise. Selective fluorination is expected to have the following potential advantages:

1. Shorter overall plutonium fluorination time would be possible, if plutonium (as PuF_4) from several batches of feed could be allowed to accumulate in the fluid bed before recovery by reaction with fluorine.
2. Conversion of PuF_6 to PuF_4 (by thermal decomposition or chemical reduction) would be simplified if UF_6 and fission products were absent.
3. Purification and decontamination of UF_6 would be simplified if PuF_6 were absent.
4. Collection of UF_6 in a liquid mixture with BrF_5 may be more efficient than when UF_6 , formed by reaction of uranium with fluorine, must be condensed from a gas phase containing fluorine and nitrogen.

An experimental program has been conducted to evaluate the selectivity of BrF_5 as a fluorinating agent for uranium in mixtures with plutonium compounds. The experimental program involved study of the reaction of BrF_5 with simulated fluid-bed solid reaction mixtures containing uranium compounds (UO_2F_2 , UF_4 , and U_3O_8), plutonium compounds, alumina, and non-radioactive fission-product element compounds. These experiments were performed to determine the optimum reaction conditions for the removal of >99% of the uranium as volatile UF_6 . In some experiments, stainless steel decladding product or Zircaloy decladding product was added to the solid mixtures to determine the effect of this addition on uranium removal.

Plutonium was added, as PuO_2 , to solid mixtures containing U_3O_8 to determine if any of the plutonium would be volatilized during the reaction with BrF_5 . The residue remaining after BrF_5 fluorination was subsequently treated with elemental fluorine to determine the extent of conversion of the plutonium to PuF_6 .

Finally, the kinetics of the reaction of BrF_5 with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3 were determined. Equations representing the temperature and BrF_5 concentration dependences of the several reactions and the values of the activation energies of the reaction were derived from these kinetic data.

II. EXPERIMENTAL PROCEDURE

A. Materials

1. Uranium Compounds

The specifications for the uranium compounds used in this study are listed in Table I.

TABLE I. Specifications of Uranium Compounds

Compound	Analytical Results, %						Average Particle Diameter, μ	Surface Area, m^2/g
	Found			Theoretical				
	U	O	F	U	O	F		
U_3O_8	84.7	15.2	-	84.8	15.2	-	10	0.23
ANL UO_2	88.3	12.0	-	88.2	11.9	-	81	0.46
NUMEC UO_2	88.1	12.0	-	88.2	11.9	-	81	0.04
UO_3	82.7	16.7	-	83.2	16.8	-	81	0.67
UF_4	75.6	-	23.8	75.8	-	24.2	84	0.30
UO_2F_2	77.3	12.1	a	77.3	10.4	12.3	55	12.2

^aNot determined.

2. Plutonium Dioxide

The plutonium dioxide contained 88.0% plutonium (88.2% theoretical) and had a specific activity of 8.47×10^7 counts/min-mg of plutonium.

3. Bromine Pentafluoride

The BrF_5 was obtained from the Matheson Co. and was stated to be of a purity of at least 98%. A check of the vapor pressure at 0°C and at room temperature did not show evidence of contamination by volatile substances. An infrared scan of the BrF_5 was made. The very strong peak at 644 cm^{-1} and the weak peak at 580 cm^{-1} reported by Stein⁴ were found; peaks at 1192 and 1226 cm^{-1} were noted, but not in the strength reported. Inspection of the scan did not show the very strong peak at 613 cm^{-1} for BrF_3 reported by Claassen et al.⁵

4. Fission-product Compounds

The fission-product mixture, designated Fission Product Mixture VI, contained the following compounds: Y_2O_3 , ZrO_2 , BaO , La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , MoO_3 , SrF_2 , CsF , Nb_2O_5 , and RuO_2 . The concentrations of the compounds, which are the amounts calculated to be present in partially spent Dresden-type fuel elements of specified burnup and cooling period, are listed in Table II. All compounds used to make up the fission-product mixture had purities of 99% or greater.

TABLE II. Composition of Fission-product Mixture VI

Fission Product Compound	Weight, g, of Compound ^a per 100 g of Uranium	Fission Product Compound	Weight, g, of Compound ^a per 100 g of Uranium
Y_2O_3	26.4	Eu_2O_3	1.99
ZrO_2	209.1	Gd_2O_3	0.46
BaO	66.5	MoO_3	214.8
La_2O_3	57.0	SrF_2	47.2
CeO_2	108.3	CsF	149.7
Pr_6O_{11}	50.2	Nb_2O_5	0.23
Nd_2O_3	198.2	RuO_2	106.2
Sm_2O_3	45.6		

^aBased on fission-product distribution calculated for Dresden-type low-enrichment UO_2 fuel, 10,000-MWd/ton burnup, 4-yr exposure, 30-day cooled.

5. Alumina

Alcoa T-61 tabular alumina was used. This material had a median particle size of 150 μ and a particle-size range of 80-250 μ .

6. Diluent Gas

Nitrogen was used as the diluting medium. The source of the nitrogen was the house supply, and the gas was passed through a bed of Linde Type 4A Molecular Sieve to remove water prior to use.

7. Zircaloy Decladding Product

The Zircaloy decladding product was produced by $HF-O_2$ reaction with Zircaloy-clad UO_2 pellets. X-ray analysis indicated that the principal component was ZrF_4 . The decladding product was ground, and the -200 mesh fraction was used. The uranium content of the decladding product was determined to be 0.3 w/o.

8. Stainless Steel Decladding Product

The stainless steel decladding product was produced by HF-O₂ reaction with Type 304 stainless steel. The decladding product contained 47.6% iron and 12.8% chromium as determined by chemical analysis. The material was ground, and the -200 mesh fraction was used in the experiments.

9. Activated Alumina

Grade F-1, 8-14 mesh, activated alumina produced by Alcoa Chemicals was used. This material had the following specifications: Al₂O₃, 92.00%; loss on ignition, 7.00%; Na₂O, <0.08%; SiO₂, <0.10%; Fe₂O₃, <0.10%; and TiO₂, <0.02%.

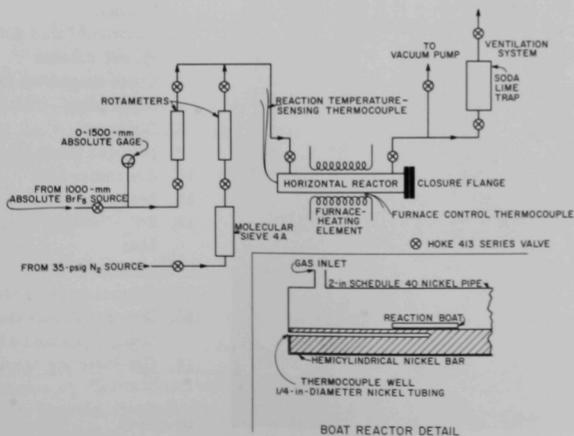
10. Soda Lime

Soda lime is a proprietary chemical and is generally described as an intimate mixture of NaOH and slaked lime. The soda lime used in this work was Mallinckrodt AR, 4-8 mesh, specified to contain no more than 1% fines with a loss on drying of 7%.

B. Apparatus

Two experimental systems were used in this work; one was a conventional boat reactor, and the other was a thermobalance. Associated with each system were a gas-metering manifold and a general-purpose manifold to which a system of cold traps and vacuum services was attached. The manifolds were constructed of nickel tubing and fittings. The valves used were Hoke 413 Series Monel with nickel diaphragms.

The boat-reactor system is shown in Fig. 1. The horizontal tubular reactor was constructed from a 1-ft length of 2-in. nominal-size nickel



pipe flanged at one end. A hemicylindrical nickel bar, with a cross section half that of the reactor, was placed in the reactor to act as a support for the nickel reaction boat and to distribute heat evenly to the bottom of the boat. A nickel boat (4 in. long, $1\frac{3}{8}$ in. wide, and $\frac{3}{16}$ in. deep) contained the solid reactants. The temperature of the boat was sensed by a Chromel-Alumel thermocouple placed in a well in the bar at the midpoint of the boat and approximately $\frac{1}{16}$ in. from the top surface of the bar.

The Sartorius thermobalance used in this work was previously described by Johnson and Fischer.⁶ The experimental setup is shown in Fig. 2, and a schematic diagram of the reactor tube is shown in Fig. 3. Briefly, the thermobalance consists of a vertical tubular reactor $1\frac{1}{2}$ in. in diameter and 20 in. long, and a Sartorius Rapid 200 analytical balance equipped with an optical-electronic weight-sensing system and a remote-recording output. The sample of the solid reactant was placed on a nickel sample pan, about $\frac{3}{4}$ in. in diameter, which was suspended below the balance pan by a Monel chain that hung through an aperture in the top of the reactor. The sample pan was positioned at about the midpoint of the heated portion of the tubular reactor. A Chromel-Alumel thermocouple in a nickel sheath, placed about $\frac{1}{8}$ in. below the sample pan, sensed the reaction temperature.

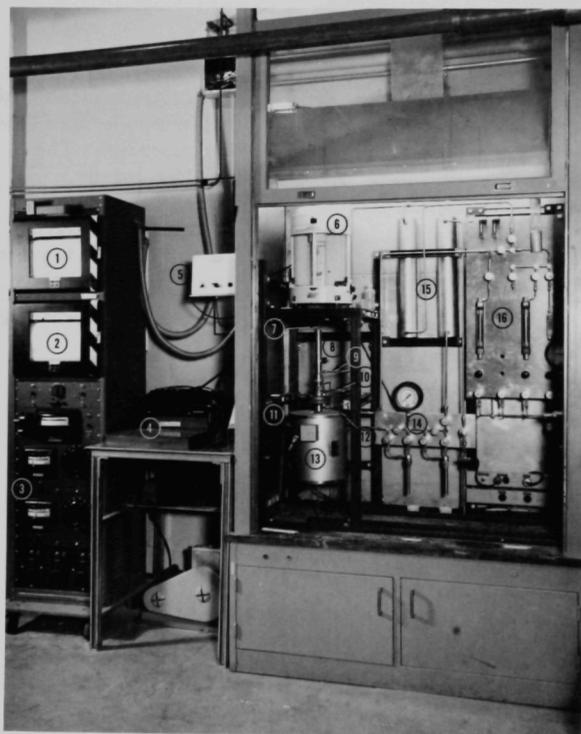
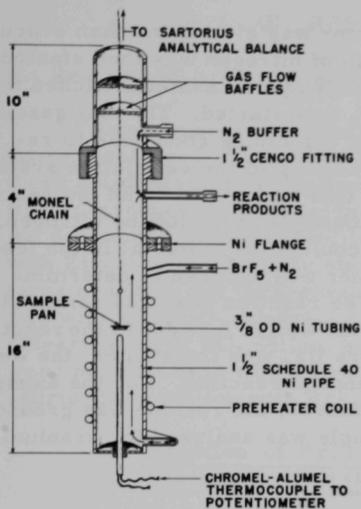


Fig. 2

Sartorius Thermobalance System

LEGEND

1. Weight-change Recorder
2. Temperature Recorder
3. Temperature-control Console
4. Potentiometer
5. Electronics for Sartorius Balance
6. Sartorius Rapid 200 Analytical Balance
7. Chain Suspension for Sample Pan
8. Chimney
9. Nitrogen Bleed Line
10. Gas Outlet Line
11. Reactor
12. BrF_5 -Nitrogen Inlet Line
13. Furnace
14. General-purpose Manifold
15. Disposal Towers (Soda Lime, Activated Alumina)
16. Gas-metering Manifold



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Fig. 3. Thermobalance Reactor Tube,
Schematic Diagram

The top of the reactor was maintained at a pressure slightly less than the inlet pressure of the reactor by pumping on the gas outlet line. The fluorinating gas, a mixture of BrF_5 and nitrogen, passed through a preheater, consisting of a section of $3/8$ -in.-diam nickel tubing coiled around the outside of the reactor tube, before entering the bottom of the reactor. A nitrogen bleed flow was brought into the reactor just above the gas outlet line to prevent any reactive gas from escaping through the open top of the reactor. The reagent gases and products were drawn off through the outlet line and passed through a trap containing soda lime. Soda lime at 100°C was a satisfactory reactant for converting BrF_5 and UF_6 to nonvolatile solids.

The gas-metering manifold contained three rotameters for metering fluorine, nitrogen, and BrF_5 . The nitrogen flowmeter was a conventional glass rotameter; the flowmeters for fluorine and BrF_5 were constructed of Kel-F.* Bromine pentafluoride was supplied to the flowmeter at an absolute pressure of 900 mm Hg from a liquid storage vessel heated to about 50°C . The tubing between the storage vessel and the flowmeter, as well as the flowmeter itself, were heated to about 70°C to prevent condensation of BrF_5 (the boiling point of BrF_5 is 40.7°C).⁷ The BrF_5 -nitrogen inlet line from the flowmeter to the reactor and the reaction-product line from the reactor to a general-purpose manifold were heated to 60 - 70°C to prevent condensation of BrF_5 , Br_2 (reaction product), and UF_6 .

The concentration of BrF_3 in the BrF_5 reagent was not known, but was thought to be of the order of <2 m/o. According to the liquid-vapor equilibria data of Long⁸ for the BrF_3 - BrF_5 system at 50°C and a pressure of ~ 1000 Torr, the vapor phase in equilibrium with the liquid would contain 99 m/o BrF_5 , even if the liquid phase contained as much as 15 m/o BrF_3 as an impurity.

C. Procedure

1. Boat Reactor

A weighed sample of solid reactant was carefully placed in the reaction boat to form a uniform layer of material in the boat. The boat

*A polymer of chlorotrifluorethylene. The flowmeter is manufactured by Brooks Instrument Division of Emerson Electric, Hatfield, Pa.

was then placed in the reactor, and the reactor was closed and then evacuated for leak-testing. A flow of about 200 ml/min of nitrogen was then started through the reactor, and the heating started. When the system reached the specified reaction temperature, flow of BrF_5 was started. The exit gases from the reactor were passed through a trap containing soda lime to remove bromine fluorides and UF_6 before exhausting to the ventilation system. After the reaction was completed, the BrF_5 flow was stopped and the reactor was cooled to room temperature under an atmosphere of flowing nitrogen. During this period, the BrF_5 container was cooled, the material in the feed lines was recondensed, and the BrF_5 container was weighed to determine the quantity of BrF_5 used in the reaction. The reaction boat was removed from the reactor and weighed to determine the weight loss due to the reaction. For experiments in which pure UO_2F_2 or pure UF_4 was fluorinated, the weight loss was sufficient for calculation of the extent of reaction. For the experiments using alumina-uranium compound mixtures, the residue was ground to ensure homogeneous sampling, and a sample was analyzed for uranium to determine the extent of reaction.

2. Thermobalance

In the thermobalance experiments, the powdered sample (about 300 mg) was weighed in the sample pan and placed in the reactor; then nitrogen flow was started. After the reaction temperature was reached, the BrF_5 flow was started. The reaction continued for 60 min or, at the higher temperatures used, for a shorter time. The recorded weight change of the loaded sample pan and the reaction time were used to determine the fraction of uranium converted to UF_6 during any increment of reaction time.

III. RESULTS AND DISCUSSION

A. Reaction of BrF₅ with Simulated Fluid-bed Solid Reaction Mixtures

Experiments were performed using solid reaction mixtures simulating those used in fluid-bed experiments. Beside uranium compounds, these solid mixtures contained alumina, a mixture of nonradioactive fission-product element oxides and fluorides and, in some experiments, the degrading product resulting from the reaction of HF-oxygen mixtures with Zircaloy or stainless steel. The uranium compounds used were mixtures of UO₂F₂ and UF₄, simulating the product of the reaction of UO₂ pellets with an HF-O₂ mixture; or U₃O₈, simulating the product of the pulverization of UO₂ pellets by reaction with oxygen. Finally, experiments were performed in which PuO₂ was added to the solid reaction mixture to affirm that reaction with BrF₅ would not produce the volatile PuF₆.

1. Reaction of BrF₅ with Mixtures of Alumina, UO₂F₂, UF₄, and Fission-product Oxides

A series of experiments was performed using a solid reaction mixture simulating those used in fluid-bed experiments. The reaction mixtures contained 10 g of T-61 alumina (48-100 mesh, nominal) and 0.07 g of fission-product mixture VI (the composition of which is listed in Table II). The alumina-to-uranium weight ratio in these solid mixtures was 2:1, and the UO₂F₂-to-UF₄ weight ratio was also 2:1. The experiments were performed using a flow rate of BrF₅ of about 0.5 g/min in a gas phase containing 26 v/o BrF₅ and 74 v/o nitrogen. The total flow rate was 250 ml/min, which was equivalent to a linear velocity in the reactor of 1.22 cm/sec. The experiments were performed at four temperatures in the range 175-250°C with reaction times of 30 min.

The results obtained from these experiments, together with the experimental conditions, used are listed in Table III. The values of the

TABLE III. Experimental Conditions and Results for Fluorination of Al₂O₃-UO₂F₂-UF₄-Fission-product Mixtures Using BrF₅

Total flow rate:	250 ml/min (26 v/o BrF ₅ , 74 v/o N ₂)						
Linear velocity:	1.22 cm/sec						
Total pressure:	1 atm						
BrF ₅ flow rate:	0.5 g/min						
Solid reaction mixture:	10.0 g of T-61 alumina; 0.07 g of fission-product oxides, ^a UF ₄ and UO ₂ F ₂ quantities shown in table ^a						
Reaction time:	30 min						
Reaction Temp, °C	U in Original Mixture, g			U in Residue, g	U Reacted, g	Fraction of U Reacted	Rate Constant, k', min ⁻¹
	As UF ₄	As UO ₂ F ₂	Total				
175	1.650	3.217	4.867	3.995	1.472	0.302	0.0038
200	1.832	3.223	5.055	2.276	2.779	0.550	0.0078
225	1.833	3.217	5.050	1.360	3.690	0.731	0.0118
	1.652	3.215	4.867	1.169	3.698	0.760	0.0126
250	1.831	3.216	5.047	0.628	4.419	0.876	0.0167
	1.649	3.219	4.868	0.575	4.293	0.882	0.0170

^aFor composition of fission-product mixture, see Table II.

fraction of uranium reacted varied from 0.3 at 175°C to 0.9 at 250°C. Values of the reaction rate constant, k' , calculated from these data varied from 0.0038 min^{-1} at 175°C to 0.017 min^{-1} at 250°C. The logarithms of the rate constants are plotted in Fig. 4 against $1/T$, together with calculated data for a mixture composed of UO_2F_2 and UF_4 in the ratio of 2:1. The theoretical plot was obtained from preliminary kinetic data for the reaction of BrF_5 with UF_4 and UO_2F_2 . The preliminary data are represented by the following equations:

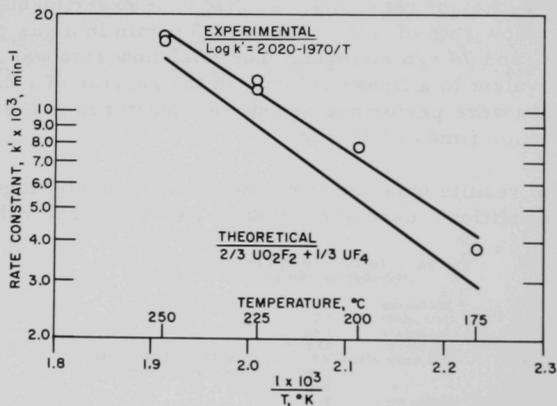
$$\text{UF}_4: \log k' = 5.719 - 3948/T, \quad E = 18 \text{ kcal/mole}; \quad (1)$$

$$\text{UO}_2\text{F}_2: \log k' = 1.493 - 1747/T, \quad E = 8.0 \text{ kcal/mole}. \quad (2)$$

The line through the experimental points was derived from the experimental data by a least-squares solution, which resulted in the following equation:

$$\log k' = 2.020 - \frac{1970}{T}. \quad (3)$$

Comparison of the experimental and calculated rate constants shows reasonably good agreement; the experimental values are about 20% higher than the calculated values. The apparent activation energy calculated by means of Eq. 3 is 9.0 kcal/mole; the apparent activation energy calculated for a mixture of $(2/3)\text{UO}_2\text{F}_2 - (1/3)\text{UF}_4$ is 11.2 kcal/mole.



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Fig. 4. Variation of Rate Constants for Reaction of Mixtures of UF_4 and UO_2F_2 with BrF_5 over Range 175-250°C

A series of experiments was performed with a solid reaction mixture similar to that described above to evaluate the effect of adding decladding product materials on the extent of uranium removal by fluorination. The reaction mixture, with and without added decladding product

materials, was reacted with BrF_5 at 250 or 300°C for reaction times of 60 min. In the first two experiments, the solid reaction mixture contained only Al_2O_3 , UO_2F_2 , UF_4 , and fission-product oxides. In the third experiment, 0.89 g of stainless steel decladding product, prepared by the HF-promoted oxidation of Type 304 stainless steel, was added to the mixture. In the fourth experiment, 2.6 g of Zircaloy decladding product, formed by the HF-promoted oxidation of Zircaloy, was added to the mixture. After reaction with BrF_5 , the uranium content of these samples was determined by means of X-ray fluorescence analysis. The data obtained are listed in Part A of Table IV. The fractional removal of uranium from the mixtures containing no decladding products was 98.2 and 99.8%

TABLE IV. Effect of Temperature and Presence of Stainless Steel or Zircaloy Decladding Product on Reaction between BrF_5 and Uranium, Alumina, and Fission-product Mixtures

		Reaction time: 60 min			
		BrF_5 flow rate: 0.5 g/min			
		Total gas flow rate: 250 ml/min at 25°C			
		(74 v/o N_2 , 26 v/o BrF_5)			
		Linear velocity of gas at 25°C: 1.22 cm/sec			
Temp, °C	Additive	Uranium Volatilized, % ^a	Temp, °C	Additive	Uranium Volatilized, % ^a
A. UO_2F_2 - UF_4 -Alumina-F.P. Mixtures ^b			B. U_3O_8 -Alumina-F.P. Mixtures ^e		
250	None	98.2	350	None	97.6
300	None	99.8	400	None	99.8
300	SS ^c	99.6	400	SS ^c	99.8
300	Zirc ^d	99.2	400	Zirc ^d	99.6

^aBased on uranium analysis of residue and uranium content of original uranium compounds.

^bMixtures contained 4.2 g of UO_2F_2 , 2.2 g of UF_4 , 10 g of alumina, and 0.07 g of fission product (see Table II for composition of fission-product mixture).

^cThe stainless steel decladding product was prepared by the HF-promoted oxidation of Type 304 stainless steel and contained 47.6% Fe and 12.8% Cr; 0.89 g of the decladding product was added to the solid mixtures described in b and e.

^dThe Zircaloy decladding product was prepared by the HF-promoted oxidation reaction and was primarily ZrF_4 ; 2.6 g of the decladding product was added to the solid mixtures described in b and e.

^eMixtures contained 5.9 g of U_3O_8 , 10 g of alumina, 0.07 g of fission product (see footnote b).

for the experiments at 250 and 300°C, respectively. For the experiments in which decladding products were present, the fractional removal of uranium was 99.2 and 99.6% for Zircaloy decladding product and stainless steel decladding product, respectively. The concentrations of the principal elemental constituents of the decladding products (titanium and zirconium for Zircaloy and iron and chromium for stainless steel) were monitored by means of X-ray fluorescence analysis and indicated that no volatilization of the component elements occurred during the BrF_5 fluorination.

These results indicate that a reaction temperature of 300°C and a reaction time of 60 min are needed to remove more than 99% of the uranium from such solid reaction mixtures. Further, the results show that the presence of Zircaloy or stainless steel decladding product in the solid mixtures will not hinder uranium removal, and that the components of the decladding products were not volatilized during fluorination.

2. Fluorination of U_3O_8 -Alumina-Fission-product Mixture

Experiments were performed to determine the extent of uranium conversion to UF_6 by the reaction of BrF_5 with mixtures containing U_3O_8 , alumina, and fission products, and with such mixtures to which was added either stainless steel or Zircaloy decladding product prepared by the HF-promoted oxidation reaction. Preliminary fluorinations, using only U_3O_8 ,

had indicated that a temperature of 350°C or greater and a reaction time of about 60 min would be needed to convert 99% or more of the uranium to UF_6 . The solid reaction mixtures contained 5.9 g of U_3O_8 , 10 g of alumina, 0.07 g of fission-product mixture, and, in some experiments, either 0.89 g of stainless steel decladding product or 2.6 g of Zircaloy decladding product. The experiments were performed at reaction temperatures of 350 or 400°C; the reaction time was 60 min. The BrF_5 flow rate was about 0.5 g/min in a gas phase containing 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate (at 25°C) of 250 ml/min.

The results obtained for these experiments are listed in Part B of Table IV. The results show that 400°C is necessary for conversion of 99% or more of the uranium to UF_6 . The data also show that the presence of stainless steel or Zircaloy decladding product in the solid reaction mixture did not affect the conversion of uranium to UF_6 . The principal difference between the mixtures containing U_3O_8 and those containing UO_2F_2 and UF_4 was that a higher temperature was required for high conversion to UF_6 for the mixtures containing U_3O_8 . The concentrations of the principal elemental constituents of the decladding products were monitored by X-ray fluorescence analysis of the reaction residues to determine whether any of these elements were volatilized during the BrF_5 fluorination. The analyses indicated that no volatilization of the component elements had occurred during the BrF_5 fluorination.

3. Fluorination of U_3O_8 -PuO₂-Alumina-Fission-product Mixtures

In a series of experiments, solid reaction mixtures containing U_3O_8 , PuO_2 , alumina, and fission products or mixtures containing only PuO_2 and alumina were reacted with BrF_5 to determine if any of the plutonium would be converted to PuF_6 . The reaction conditions chosen (400°C, 60-min reaction time, gas phase containing 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate of 250 ml/min) were those that resulted in the conversion of more than 99% of the uranium to UF_6 in previously reported experiments. In two experiments in which the solid reactant contained U_3O_8 (5.8 g), PuO_2 (0.2 g),* fission products (0.07 g), and alumina (10 g), the reaction residue remaining after the BrF_5 reaction was fluorinated with elemental fluorine at 550°C using gas-phase recycle conditions.

To determine if plutonium was volatilized during the BrF_5 step, all the gaseous reaction products (UF_6 , excess BrF_5 , bromine, and PuF_6 if any was produced) leaving the reactor were passed through a trap, containing soda lime at 100°C, to convert the reaction products to nonvolatile material. After termination of the BrF_5 step, the contents of the trap were removed, ground to a fine powder, and homogenized, and samples were taken

*The ratio of plutonium to uranium (1:25) in these mixtures was greater by a factor of 10 than the 1:250 ratio in the nominal fuel (0.4 w/o plutonium in uranium).

and analyzed for uranium and plutonium content. To determine the background concentration of plutonium in the sample-preparation equipment, portions of unreacted, plutonium-free soda lime were also ground and sampled prior to grinding of the soda lime from the trap.

For two experiments in which the starting material contained both uranium and plutonium, the soda lime after the BrF_5 step contained 0.94×10^{-3} and 0.44×10^{-3} mg of plutonium per gram of solid. These concentrations represent 0.24 and 0.11 mg of plutonium on the soda lime, corresponding to 0.13 and 0.06% of the original plutonium in the starting material, respectively. However, blanks of soda lime ground just prior to grinding of the experimental samples had 2.8×10^{-3} and 0.56×10^{-3} mg of plutonium per gram of solid for the first and second experiments, respectively. The apparatus used to grind the soda lime samples had been previously used to grind solid samples from a fluid-bed reactor using plutonium. The level of plutonium found in the blank samples strongly suggests that the plutonium contents of the experimental samples were the result of cross-contamination during the grinding operation. In an experiment in which the solid reaction mixture contained only PuO_2 and alumina, the initial quantity of PuO_2 was greater by a factor of ten than in the other two experiments. After the BrF_5 step, the soda lime contained 0.33×10^{-3} mg of plutonium per gram of solid, which again could be attributed to cross-contamination during the grinding operation. In this experiment, the weight gain of the solid reaction mixture indicated that 88% of the PuO_2 had been converted to PuF_4 . In two separate experiments, which were terminated after the BrF_5 step, the uranium content of the solid reaction mixture after the BrF_5 fluorination period was determined. These solid residues showed an average concentration of 0.067 w/o uranium, equivalent to >99.9% removal of uranium.

The solid reaction residues remaining after the BrF_5 step for the first two experiments were fluorinated using 100% fluorine at 550°C for 5 or 8 hr under recycle conditions. The alumina residues after reaction with fluorine contained 0.011 and 0.038 w/o plutonium and 0.010 and 0.018 w/o uranium for the 8- and 5-hr fluorinations, respectively. The plutonium concentrations on the alumina correspond to removal of 99.5 and 97.7% of the plutonium originally contained in the solid mixtures for the 8- and 5-hr tests, respectively. The uranium concentrations on the alumina correspond to removal of more than 99% of the original uranium present.

These results indicate that essentially none of the plutonium is converted to a volatile form by reaction with BrF_5 at 400°C for 1 hr, and that 99% or more of the plutonium remaining in the solid mixture can be converted to PuF_6 by a subsequent fluorination using fluorine at 550°C and a reaction period of less than 10 hr.

4. Comparison of Reactivity of BrF₅ and Fluorine

A series of experiments was performed in which UF₄ or UO₂F₂ or mixtures containing UF₄, UO₂F₂, alumina, and fission-product oxides were reacted with fluorine to obtain reaction data suitable for comparison with similar rate data obtained with BrF₅. The data obtained are listed in Table V. The reactions with fluorine were carried out using the reaction conditions listed in Table III.

TABLE V. Reaction Rate Constants, k' , for Reactions Using BrF₅ or Fluorine as Fluorinating Agent

Temp, °C	Reaction Rate Constant, k' , min ⁻¹					
	UO ₂ F ₂		UF ₄		UF ₄ -UO ₂ F ₂ -Al ₂ O ₃ F.P. Oxides	
	BrF ₅	F ₂	BrF ₅	F ₂	BrF ₅	F ₂
200	0.0064	0.0005	-	-	-	-
250	-	-	0.0145	0.0010	0.0169	0.0013
275	-	-	0.0344	0.0040	-	-
300	0.0276	0.0008	-	-	-	-

The data show that the rate constants for reactions with fluorine are an order of magnitude lower than those for the reactions using BrF₅ as the fluorinating agent. For example, considering a 30-min reaction period: for UO₂F₂ at 300°C, the fractions reacted would be 0.995 for BrF₅ and 0.070 for fluorine; for UF₄ at 250°C, the fractions reacted would be 0.820 for BrF₅ and 0.087 for fluorine; and for the UF₄-UO₂F₂-alumina-F.P. mixtures at 250°C, the fractions reacted would be 0.873 for BrF₅ and 0.112 for fluorine. The increased reaction rates when BrF₅ is employed as the fluorinating agent for uranium should shorten the time required to process a batch of oxide fuel.

B. Kinetic Studies

The kinetics of the reaction of gaseous BrF₅ with the compounds, UF₄, UO₂F₂, U₃O₈, UO₂, and UO₃ has been studied. No previous study of these reactions has been reported. Both the temperature and pressure dependence of the reaction rates have been determined. These basic data on materials of interest to the FBFVP will allow estimation of the rates of reaction in process equipment.

Previously reported studies of the reactions of uranium compounds with interhalogen compound have included reactions of ClF₃ with UF₄,⁹⁻¹² UO₂F₂,^{13,14} and various uranium oxides,¹⁵ and the reaction between BrF₃ and U₃O₈.¹⁶

It has been found convenient to treat the data obtained from such gas-solid heterogeneous reactions by means of the "diminishing-sphere" model developed by Anderson.¹⁷ Two examples of the use of this reaction model are the work of Labaton⁹ on the UF_4-CIF_3 reactions and that of Johnson and Fischer⁶ on the reaction of SF_4 with UO_3 and UO_2F_2 . The following development of the kinetic equation for the diminishing sphere model is from the paper of Johnson and Fischer.⁶

Assuming a solid reactant consisting of uniform spherical particles upon which the gaseous reactant acts, and assuming that the reaction starts at $t = 0$ on all particles, we can deduce the following relationship:

If the initial mass of a solid particle $M_0 = (4/3)\pi r_0^3 \rho$, where $r_0 =$ initial radius and $\rho =$ bulk density, then the rate of reduction in mass at a given temperature is assumed to be proportional to the surface area of the particle. That is,

$$-\frac{dM}{dt} = 4\pi r^2 k, \quad (4)$$

where r is the radius of the particle at time t , and k is the constant for a given temperature and a given partial pressure of reactant gas.

The fraction of reaction F that has taken place in time t is given by

$$F = \frac{M_0 - M}{M_0} = 1 - \left(\frac{r}{r_0}\right)^3,$$

which when substituted in Eq. 4 becomes

$$\left. \begin{aligned} \frac{dM}{dt} &= -4\pi r_0^2 k (1 - F)^{2/3}; \\ \frac{dF}{dt} &= \frac{1}{M_0} \frac{dM}{dt} = \frac{3k}{r_0 \rho} (1 - F)^{2/3}. \end{aligned} \right\} \quad (5)$$

Integrating Eq. 5, we obtain

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

where $k' = k/r_0 \rho$.

When $(1 - F)^{1/3}$ is plotted against the reaction time t for a typical experiment, the points lie on a straight line in agreement with the equation, with the exception of small deviations at the beginning and end of the experiment, which are considered to be due to experimental conditions. The deviation at the beginning, for example, is due to the presence of an inert gas in

the reactor, and its displacement by the reacting gas requires a small but finite time interval. The deviation at the end of the experiment is usually ascribed to the small amount of solid reactant remaining, or to the presence of a proportionally large fraction of solid intermediate product of lower reactivity.

The kinetics of the reactions with UF_4 , U_3O_8 , UO_2 , and UO_3 were determined using the thermobalance system; the kinetics for the reaction with UO_2F_2 were determined using the boat-reactor system. It was not possible to use the thermobalance for the UO_2F_2 experiments because of the large temperature rise and concurrent very rapid reaction rate in the initial stages of the reaction. This effect was considered to result from the high surface area of the UO_2F_2 . In the boat reactor, the initial temperature rise was damped out by the greater mass of the reactor (see Section II.B above), and the effect of an initially high rate would be minimized by the greater size of the UO_2F_2 sample (5 g for the boat reactor versus 0.3 g for the thermobalance).

The quantity of solid reactant used, 300 mg for the thermobalance and about 5 g for the boat reactor, was chosen so that the reaction time at the higher temperatures would not be too short to measure accurately and to provide approximately a one-particle-deep layer of solid on the reaction pan. The thin layer of solid reactant tended to minimize any effect of the formation of intermediates on the rate of reaction. This quantity of solid reactant was also found to be suitable in work by Johnson and Fischer⁶ in a thermobalance study of the kinetics of the reaction of SF_4 with UO_3 and UO_2F_2 .

1. UF_4 - BrF_5 Reaction

Kinetic data for the UF_4 - BrF_5 reaction were determined over the nominal range 200-275°C and a BrF_5 partial-pressure range of 138-370 Torr (corresponding to BrF_5 concentrations of 18-49 v/o). The reaction conditions and the values of the rate constant are listed in Table VI.

TABLE VI. Reaction Rate Constants, k' , for UF_4 - BrF_5 Reaction
Linear velocity of gas phase, 0.64 cm/sec;
 UF_4 sample size, 300 mg.

Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3,$ min^{-1}	Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3,$ min^{-1}	Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3,$ min^{-1}
	Exp	Calc ^a			Exp	Calc ^a			Exp	Calc ^a	
A. $P_{BrF_5} = 138 \text{ Torr (18 v/o } BrF_5, 82 \text{ v/o } N_2)$ $\log k' = 5.157 - 3720/T$				B. $P_{BrF_5} = 239 \text{ Torr (31 v/o } BrF_5, 69 \text{ v/o } N_2)$ $\log k' = 5.181 - 3690/T$				C. $P_{BrF_5} = 370 \text{ Torr (49 v/o } BrF_5, 51 \text{ v/o } N_2)$ $\log k' = 5.185 - 3650/T$			
200	1.97	1.98	+0.01	200	2.42	2.45	+0.03	199	2.82	2.84	+0.02
225	4.92	4.92	0.00	210	3.62	3.55	-0.07	219	5.90	5.85	-0.05
250	11.3	11.2	-0.1	230	6.87	7.14	+0.27	234	10.0	9.69	-0.31
274	22.7	22.9	+0.2	240	10.4	9.9	-0.5	249	15.2	15.6	+0.4
				262	19.0	19.6	+0.6	260	22.2	21.8	-0.4
				274	28.2	27.7	+0.5				

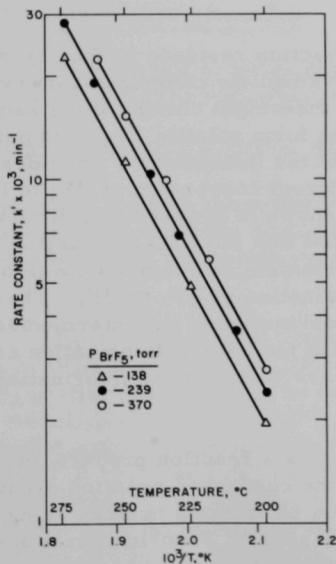
^aValues in this column were calculated by use of the equations in headings A, B, and C.

The effect of temperature on the rate constant is shown in Fig. 5. The integrated form of the Arrhenius equation was fitted to the data by the method of least squares, resulting in the equations listed in Table VI, which represent the temperature dependence of the reaction rates. Values of the apparent activation energy were 17.0, 16.9, and 16.7 kcal/mole for BrF_5 partial pressures of 138, 239, and 370 Torr, respectively.

Values of the rate constant were calculated at selected temperatures; the values are shown in Fig. 6 as plots of $\log k'$ versus the log of the BrF_5 partial pressure. Values of the coefficient n , of the pressure term of the equation $k' = Ae^{-E/RT}P^n$ were calculated using the slopes of the plots in Fig. 6. The values of n obtained ranged from 0.36 to 0.40. Averaging the constants for the Arrhenius equations and using the average value of the coefficient, n , we derived the following equation to represent the simultaneous temperature and pressure dependence of the rate constant for the $\text{UF}_4\text{-BrF}_5$ reaction:

$$\log k' = 4.286 - 3690/T(^{\circ}\text{K}) + 0.38 \log P_{\text{BrF}_5} (\text{Torr}).$$

The activation energy calculated using the above equation is 16.9 kcal/mole.



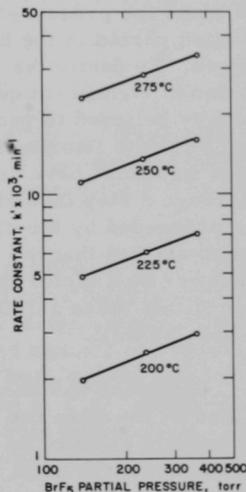
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Fig. 5. Temperature Dependence of Rate Constant for $\text{UF}_4\text{-BrF}_5$ Reaction

UF_4 sample size: 300 mg

Linear velocity

of gas phase: 0.64 cm/sec

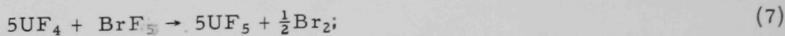


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Fig. 6. Effect of BrF_5 Partial Pressure on Rate Constant for $\text{UF}_4\text{-BrF}_5$ Reaction

Experiments were performed to determine the effect of the linear velocity of the gas phase on the reaction rate constant. The reactions were performed at 235°C using a gas phase containing 32 v/o BrF₅ (partial pressure of 243 Torr) and 68 v/o nitrogen. The values of the rate constant obtained at linear velocities of 0.46, 0.64, and 1.28 cm/sec were 6.62, 6.33, and 5.80 × 10⁻³ min⁻¹, respectively. These results show only a 13% change in the rate constant for a nearly threefold increase in the linear velocity.

The reaction between UF₄ and BrF₅ is complicated by the formation of intermediate fluorides, U₂F₉, U₄F₁₇, and UF₅, either as a result of the direct reaction or by the interaction of UF₆ with UF₄. The possible reactions, using UF₅ as the example of the intermediate fluoride, are as follows:



Although the color of the reaction residues (either brown or black) indicated the presence of the intermediate compounds, no evidence of an induction period in the history of the weight change of the samples was observed. Evidently the reaction to form volatile UF₆ does not require the formation of significant quantities of the intermediate fluorides. Hence, the reaction is believed to proceed by direct conversion of UF₄ to UF₆. The reaction of UF₄ with fluorine has been shown to proceed in a similar manner. Labaton and Johnson¹⁸ have demonstrated that the UF₄-F₂ reaction did not proceed through a step involving the formation of intermediate fluorides, but rather proceeded by the direct fluorination of UF₄ to UF₆. These workers also showed that the rate of fluorination of the intermediate fluorides was lower by a factor of 2 to 4 than the rate of fluorination of UF₄. It is assumed that these relative rates are valid for the fluorination reaction with BrF₅ as well.

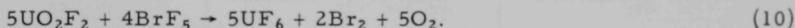
Equations 6-9 show bromine as a reaction product. Bromine was indicated by the deep red color of the condensed reaction products and was quantitatively assayed by conversion of bromine to BrF₃ using the fluorine titration method of Sheft and co-workers.¹⁹ Fluorine titrations of the condensed products from several experiments showed quantities of Br₂ corresponding to the stoichiometry of Reaction 6 above. Bromine could result from the direct reduction of BrF₅ to Br₂ or from the stepwise reduction to BrF₃, which, in turn, would react further to form Br₂. In either case, the observed kinetics would be those for the UF₄-BrF₅ reaction if the rate of the UF₄-BrF₃ reaction is higher than that of the UF₄-BrF₅ reaction. Since

no data are available in the literature for the reaction between UF_4 and BrF_3 , boat-reactor experiments were performed to obtain rate data at 200°C for the two reactions. For the UF_4 - BrF_5 reaction at a BrF_5 partial pressure of 198 Torr, the rate constant was 0.00235 min^{-1} ; for the UF_4 - BrF_3 reaction at a BrF_3 partial pressure of 105 Torr, the rate constant was 0.0145 min^{-1} . These data show clearly that the reaction rate with BrF_3 is significantly higher. Therefore, the kinetics measured represent the reaction with BrF_5 .

The value of the activation energy, 16.9 kcal/mole , found for the UF_4 - BrF_5 reaction is in the range of values reported^{18,20} for the UF_4 - F_2 reaction, 14 - 20 kcal/mole rather than the 2 - 6 kcal/mole reported for the UF_4 - ClF_3 reaction.^{9,10} The order of the UF_4 - BrF_5 reaction was fractional with respect to BrF_5 pressure, while the order of both the UF_4 - F_2 (Ref. 18) and UF_4 - ClF_3 (Ref. 9) reactions was unity with respect to the partial pressure of the fluorinating agent. Finally, the temperature dependence of the rate of the UF_4 - BrF_5 reaction did not show a minimum as was observed for the UF_4 - ClF_3 reaction;⁹ the latter was ascribed to the formation of intermediate fluorides and a consequent reduction in the rate of volatilization of UF_6 .

2. UO_2F_2 - BrF_5 Reaction

The overall reaction between UO_2F_2 and BrF_5 is considered to proceed as shown in the following equation:



In this reaction, as was shown for the UF_4 - BrF_5 reaction, Br_2 is postulated as a reaction product of the BrF_5 component of the reaction. The instability of bromine oxides at temperatures above 0°C makes their presence highly improbable.²¹

Boat-reactor experiments were performed to determine the fraction of UO_2F_2 converted to UF_6 at several time intervals, temperatures, and BrF_5 partial pressures. The data were treated using the diminishing-sphere model. Values of $(1 - F)^{1/3}$ are plotted against reaction time t in Fig. 7 for reactions performed at 250°C and BrF_5 partial pressures of 130, 197, and 357 Torr. The lines through the data in Fig. 7 represent the least-squares equations, from which values of the rate constant, k' , of 0.0116, 0.0131, and 0.0219 min^{-1} were calculated for partial pressures of BrF_5 of 130, 197, and 357 Torr, respectively.

Values of the rate constant, calculated as described above, for data obtained in the nominal temperature range 175 - 300°C and at partial pressures of BrF_5 of 130, 197, and 357 Torr are listed in Table VII and shown in Fig. 8. The integrated form of the Arrhenius equation was fitted to the data by the least-squares method; the equations obtained are listed

in Table VII along with values of k' calculated using these equations. Calculated values of the apparent activation energy are 8.4, 8.3, and 8.0 kcal/mole, for BrF_5 partial pressures of 130, 197, and 357 Torr, respectively.

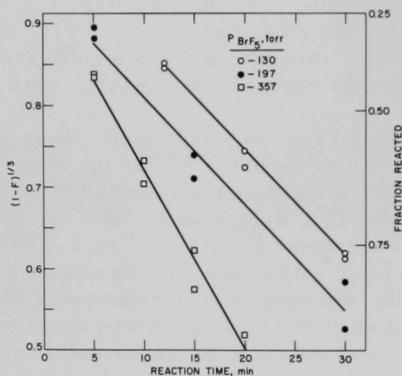


Fig. 7

Effect of BrF_5 Partial Pressure on Conversion of Uranium to UF_6 for UO_2F_2 - BrF_5 Reaction at 250°C

Sample size: 5 g
Linear velocity of gas phase: 0.85 cm/sec

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TABLE VII. Reaction Rate Constants, k' , for UO_2F_2 - BrF_5 Reaction
Linear velocity of gas phase, 0.86 cm/sec;
 UO_2F_2 sample size, 5 g.

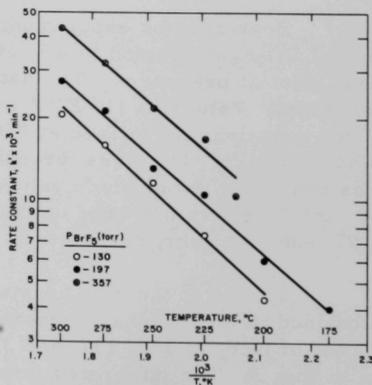
Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3, \text{min}^{-1}$	Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3, \text{min}^{-1}$	Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3, \text{min}^{-1}$
	Exp	Calc ^a			Exp	Calc ^a			Exp	Calc ^a	
A. $P_{\text{BrF}_5} = 130$ Torr (17 v/o BrF_5 , 83 v/o N_2) $\log k' = 1.561 - 1850/T$				B. $P_{\text{BrF}_5} = 197$ Torr (30 v/o BrF_5 , 70 v/o N_2) $\log k' = 1.484 - 1740/T$				C. $P_{\text{BrF}_5} = 357$ Torr (47 v/o BrF_5 , 53 v/o N_2) $\log k' = 1.848 - 1830/T$			
200	4.30	4.57	+0.27	175	4.04	3.99	-0.05	212	10.4	11.7	+1.3
225	7.42	7.17	-0.25	200	5.97	6.41	+0.44	225	16.9	14.7	-2.2
250	11.6	10.8	-0.8	225	10.5	9.8	-0.7	250	21.9	22.0	+0.1
275	15.9	15.6	-0.3	250	13.1	14.4	+1.3	275	32.0	31.8	-0.2
300	20.5	21.9	+1.4	275	21.2	20.4	-0.8	300	43.2	44.5	+1.3
				300	27.6	28.1	+0.5				

^aValues in this column were calculated by use of the equations in headings A, B, and C.

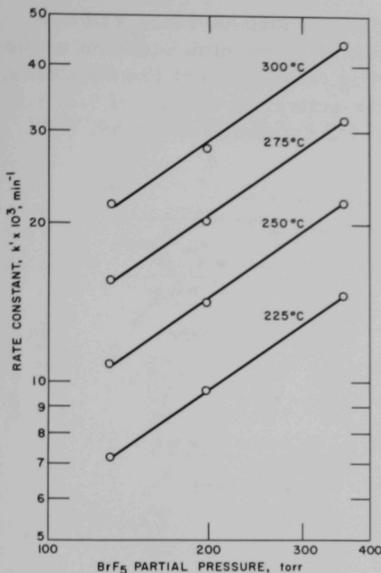
Fig. 8

Temperature Dependence of Rate Constant for UO_2F_2 - BrF_5 Reaction

Sample size: 5 g
Linear velocity of gas phase: 0.86 cm/sec



308-96



308-82

Fig. 9. Effect of BrF₅ Partial Pressure on Rate Constant for UO₂F₂-BrF₅ Reaction

and 0.0122 min⁻¹ at gas-phase linear velocities of 0.86, 1.28, and 2.92 cm/sec, respectively. These results show less than a 10% change in the rate constant for a greater than threefold increase in the linear velocity, indicating a small effect of the linear velocity on the rate constant.

Previous studies of fluorinations of UO₂F₂ include the reaction with ClF₃ (Refs. 13 and 22), with fluorine,^{21,24} and with SF₄ (Ref. 6). Activation energies for these reactions are ClF₃, 10.2 kcal/mole;²² fluorine, 19.5 kcal/mole;²⁴ and SF₄, 32 kcal/mole.⁶ The dependence of the rate constant on the partial pressure of the fluorinating gas was first order for the UO₂F₂-ClF₃ reaction²² and proportional to the 1.5 power for the UO₂F₂-SF₄ reaction.⁶ The present investigation of the UO₂F₂-BrF₅ reaction showed an activation energy of 8.3 kcal/mole and an order of pressure dependence of 0.71, which is similar to the results for the UO₂F₂-ClF₃ reaction rather than those for the UO₂F₂-SF₄ reactions.

3. U₃O₈-BrF₅ Reaction

The kinetics of the U₃O₈-BrF₅ reaction were determined at BrF₅ partial pressures of 89, 108, 189, 241, and 369 Torr, and in the nominal temperature range 225-360°C. The values of the rate constant are

Values of the rate constant were calculated at selected temperatures, and Fig. 9 shows the values as plots of log k' versus the log of the partial pressure of BrF₅. Values of the coefficient, n, of the pressure term of the equation $k' = Ae^{-E/RT}P^n$ were calculated using the slope of the plots of Fig. 9. The values obtained range from 0.70 to 0.71. The following equation was derived to represent the simultaneous temperature and pressure dependence of the rate constant for the UO₂F₂-BrF₅ reaction:

$$\log k' = -\frac{1810}{T(^{\circ}\text{K})} + 0.71 \log P_{\text{BrF}_5} (\text{Torr}). \quad (11)$$

The activation energy calculated using the above equation is 8.3 kcal/mole.

The effect of the linear velocity of the gas phase upon the rate constant was investigated in a series of experiments performed at 250°C with a BrF₅ partial pressure of 197 Torr. Values of the rate constant were 0.0135, 0.0131,

listed in Table VIII and plotted in Fig. 10. Also listed in Table VIII are equations derived by least-squares fitting of the Arrhenius equation to the data. The lines through the data points in Fig. 10 represent the equations. From the slopes of these lines, values of the activation energy of 9.1, 9.8, 9.5, 8.9, and 8.5 kcal/mole were calculated for data obtained at 89, 108, 189, 241, and 369 Torr, respectively.

TABLE VIII. Reaction Rate Constants, k' , for U_3O_8 - BrF_5 Reaction

Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3, \text{min}^{-1}$	Temp, °C	Rate Constant, $k' \times 10^3, \text{min}^{-1}$		$(k'_{\text{calc}} - k'_{\text{exp}}) \times 10^3, \text{min}^{-1}$
	Exp	Calc ^a			Exp	Calc ^a	
A. $P_{BrF_5} = 89$ Torr (12 v/o BrF_5 , 88 v/o N_2)				C. $P_{BrF_5} = 189$ Torr (25 v/o BrF_5 , 75 v/o N_2)			
$\log k' = 1.516 - 2000/T$				$\log k' = 1.926 - 2080/T$			
Linear velocity: 0.76 cm/sec				Linear velocity: 0.67 cm/sec (Contd.)			
252	4.80	5.14	+0.34	262	10.7	10.9	+0.20
267	7.04	6.56	-0.48	278	15.1	14.1	-1.00
278	8.60	7.78	-0.82	286	14.5	16.0	+1.50
313	10.3	12.8	+2.50	301	20.4	20.0	-0.40
327	16.3	15.4	-0.90	302	20.7	20.3	-0.40
358	23.5	22.4	-1.10				
B. $P_{BrF_5} = 108$ Torr (14 v/o BrF_5 , 86 v/o N_2)				D. $P_{BrF_5} = 241$ Torr (32 v/o BrF_5 , 68 v/o N_2)			
$\log k' = 1.892 - 2130/T$				$\log k' = 1.809 - 1940/T$			
Linear velocity: 0.61 cm/sec				Linear velocity: 0.64 cm/sec			
253	7.10	6.88	-0.22	226	8.44	8.48	+0.04
261	8.40	7.92	-0.48	252	13.2	13.2	0.00
275 ^b	9.55	10.0	+0.45	257	14.9	14.3	-0.60
276 ^c	9.66	10.0	+0.34	278	18.7	19.7	+1.00
277	9.67	10.3	+0.63	302	28.2	27.6	-0.60
298	14.0	14.4	+0.40				
316	18.4	18.7	+0.30				
329	22.7	22.4	-0.30				
E. $P_{BrF_5} = 369$ Torr (49 v/o BrF_5 , 51 v/o N_2)							
$\log k' = 1.813 - 1860/T$				$\log k' = 1.813 - 1860/T$			
Linear velocity: 0.67 cm/sec				Linear velocity: 0.67 cm/sec			
243	8.03	7.82	-0.21	223	11.5	11.5	0.00
243 ^d	7.90	7.82	-0.08	239	14.9	15.0	+0.10
244	7.70	7.96	+0.26	254 ^e	19.3	19.2	-0.10
				255	19.6	19.5	-0.10
				256 ^f	20.0	19.8	-0.20
				272	24.7	25.0	+0.30
				299	36.4	36.4	0.00

^aValues in this column were calculated by use of equations in headings A, B, C, D, and E.

^bLinear velocity of gas phase: 1.92 cm/sec.

^cLinear velocity of gas phase: 1.28 cm/sec.

^dLinear velocity of gas phase: 1.31 cm/sec.

^eLinear velocity of gas phase: 0.88 cm/sec.

^fLinear velocity of gas phase: 0.43 cm/sec.

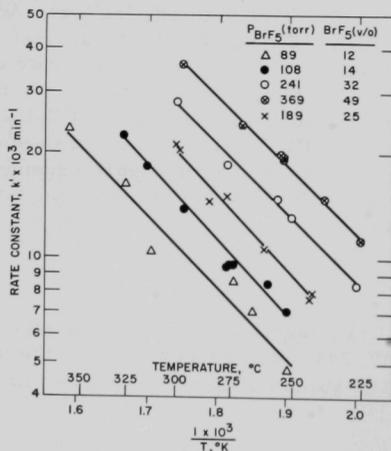
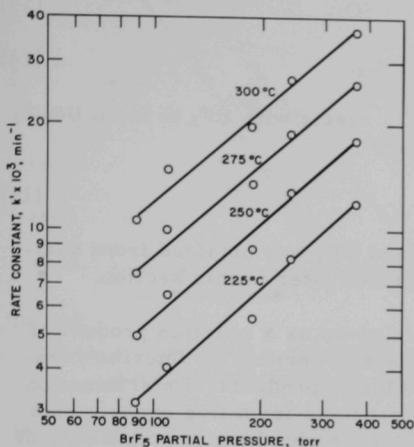


Fig. 10

Temperature Dependence of Rate Constant for U_3O_8 - BrF_5 Reaction

Values of the rate constant at selected temperatures, calculated using the equations listed in Table VIII, are plotted in Fig. 11 as $\log k'$ versus the log of the BrF_5 partial pressure. Values of the pressure dependence



308-99

Fig. 11. Effect of BrF_5 Partial Pressure on Rate Constant for U_3O_8 - BrF_5 Reaction

of the reaction were calculated from the slopes of the plots of Fig. 11 and ranged in value from 0.87 to 0.93 with an average value of 0.90. From these data, the following equation was derived for the combined temperature and pressure dependence of the U_3O_8 - BrF_5 reaction:

$$\log k' = 0.90 \log P_{\text{BrF}_5} (\text{Torr}) - 2000/T (^\circ\text{K}) - 0.220. \quad (12)$$

A value of 9.2 kcal/mole was calculated for the activation energy for the combined data.

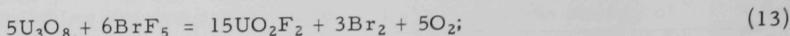
The activation energy for the U_3O_8 - BrF_5 reaction falls between the value of 21.3 kcal/mole for the reaction of U_3O_8 with fluorine²⁴ and the value of approximately 1 kcal/mole for the reaction of U_3O_8 with BrF_3 .¹⁶ The pressure dependence of all these reactions is approximately first order. In contrast to the U_3O_8 - BrF_3 reaction, the U_3O_8 - BrF_5 reaction did not exhibit a minimum in the temperature dependence of the rate constant.

Experiments were performed to determine the effect of different linear velocities of the gas phase on the reaction rate constant for the U_3O_8 - BrF_5 reaction. Three sets of experiments were performed at BrF_5 partial pressures of 108, 189, and 369 Torr, and the results are listed in Table IX. These results indicate that the effect of linear velocity of the gas phase on the rate constant is negligible.

TABLE IX. Effect of Linear Velocity of Gas Phase on Reaction Rate Constant for U_3O_8 - BrF_5 Reaction

Total system pressure: 760 Torr Quantity of U_3O_8 used: 300 mg								
Reaction Temp, $^\circ\text{C}$	Linear Velocity, cm/sec	Rate Constant, $k' \times 10^3, \text{min}^{-1}$	Reaction Temp, $^\circ\text{C}$	Linear Velocity, cm/sec	Rate Constant, $k' \times 10^3, \text{min}^{-1}$	Reaction Temp, $^\circ\text{C}$	Linear Velocity, cm/sec	Rate Constant, $k' \times 10^3, \text{min}^{-1}$
A. $P_{\text{BrF}_5} = 108$ Torr (14 v/o BrF_5 , 86 v/o N_2)			B. $P_{\text{BrF}_5} = 189$ Torr (25 v/o BrF_5 , 75 v/o N_2)			C. $P_{\text{BrF}_5} = 369$ Torr (49 v/o BrF_5 , 51 v/o N_2)		
277	0.61	9.67	243	0.67	8.03	256	0.43	20.0
276	1.28	9.66	243	1.31	7.90	255	0.67	19.6
275	1.92	9.55				254	0.88	19.3

By analogy to the U_3O_8 -fluorine reaction, the reaction between U_3O_8 and BrF_5 is considered to proceed according to the following equations:



In addition, as reported by Rampy,²⁶ U_3O_8 reacts with UF_6 to form UO_2F_2 and UF_4 as shown in the following equation:

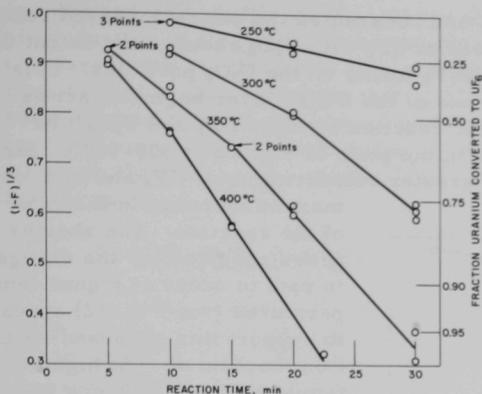


Evidence for the reaction between U_3O_8 and UF_6 was obtained from boat-reactor experiments, which will be described later in this section.

In Eqs. 13 and 14, bromine is given as a reaction product of the BrF_5 component of the reaction. This was verified by fluorine titration¹⁹ of the bromine in the condensed reaction products. Determination of the bromine content of the condensed products from five experiments resulted in an average value of $102 \pm 4\%$ of the stoichiometric quantity of bromine; individual values ranged from 94 to 108%. The stoichiometric quantity of bromine was calculated from the fraction of U_3O_8 converted to UF_6 in each experiment, based on the stoichiometry of Reactions 10 and 11.

The analytical method was tested by titrating synthetic reaction product mixtures containing only bromine and BrF_5 . The quantity of bromine added to the BrF_5 was determined from PVT relationships. Three synthetic mixtures were titrated and resulted in an average value of $100 \pm 6\%$ of the theoretical amount of bromine, with individual values of 94, 97, and 108%. These results show that the U_3O_8 - BrF_5 reaction data fall within the precision of the analytical method, and indicate that bromine is the only bromine-bearing product of the reaction.

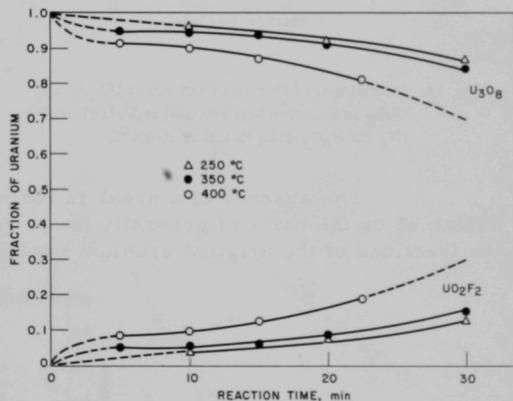
Evidence that U_3O_8 and the product UF_6 react to form a water-soluble uranium species was obtained from preliminary boat-reactor experiments over the range 250-400°C. About 5 g of U_3O_8 were used in each experiment. The gas phase contained 26 v/o BrF_5 and 74 v/o nitrogen at a total flow rate of 250 ml/min, corresponding to a linear gas velocity in the reactor of 1.22 cm/sec. The extent of reaction, i.e., conversion of U_3O_8 to UF_6 in an experiment, was calculated from the weight change of the solid. In some cases, this method for calculating the fraction reacted was checked by uranium analysis of the residues; agreement in all cases was excellent. Figure 12 shows the relationship between $(1 - F)^{1/3}$ and the reaction time at several reaction temperatures. At reaction temperatures of 300°C or greater, the plots show a change in slope, indicating an increase in the rate of uranium conversion to UF_6 with increasing reaction time.



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Fig. 12. Plots of $(1-F)^{1/3}$ vs. Reaction Time, t , for Range 250-400°C for U_3O_8 - BrF_5 Reaction

(as shown in Fig. 13). However, even after conversion of 97% of the uranium to UF_6 , most of the residue was still U_3O_8 , the water-soluble fraction of the residue constituting only about 20%. Since the unidentified phase could not be characterized, subsequent discussion of the mechanism assumes that all of the water-soluble uranium is " UO_2F_2 ." Rampy²⁶ indicated that the reaction of U_3O_8 and UF_6 is not simple but may involve undefined intermediates. It is not surprising to find no UF_4 in the residues, considering the high reaction rate that could be expected for the UF_4 - BrF_5 reaction at these temperatures. (See the plot of temperature dependence of rate for UF_4 - BrF_5 reaction in Fig. 7.)



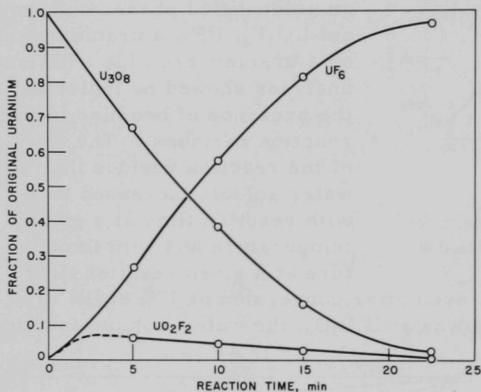
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Fig. 13. Fraction of Solid Residue Present as U_3O_8 and UO_2F_2 for U_3O_8 - BrF_5 Reaction

The rate behavior observed for the U_3O_8 - BrF_5 reaction suggests the occurrence of a concomitant reaction. This reaction initially hinders the production or volatilization of UF_6 , but its effect is diminished after a period of time and then leads to higher rates of production or volatilization of UF_6 . During the initial, lower-rate portion of the reaction,

Chemical analyses of the reaction residues for total uranium and water-soluble uranium suggested that the residues were composed of U_3O_8 and UO_2F_2 . However, X-ray diffraction analyses of the residues indicated the presence of U_3O_8 and an unidentified phase, which was not UO_2F_2 , UF_4 , a uranium oxide, or a uranium bromide. (Chemical analyses showed no indication of the presence of bromine in the reaction residues.) The fraction of the reaction residue that was water soluble increased both with reaction time at a given temperature and with temperature at a given reaction time

which was observed at 300-400°C and constituted the entire observed reaction period at 250°C, the interaction of UF_6 with U_3O_8 reduces the extent of volatilization of UF_6 ; a layer of UO_2F_2 forms on the U_3O_8 particles. This process continues until the thickness of the UO_2F_2 layer begins to act as an effective diffusion barrier to the reaction between UF_6 and U_3O_8 . At this time, indicated by the breaks in the plots of Fig. 12 at 300-400°C, further production of UF_6 results in greater volatilization of UF_6 and in a



108-9288

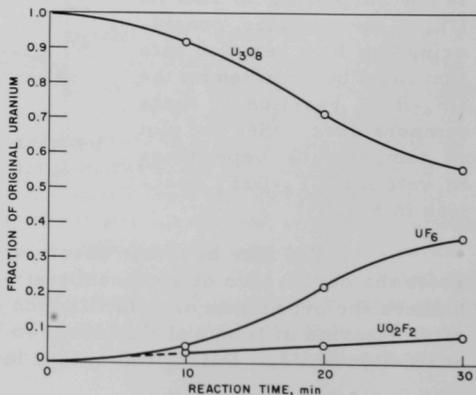
Fig. 14. Distribution of Original Uranium as UO_2F_2 and U_3O_8 in Reaction Residues and as Volatilized UF_6 for U_3O_8 - BrF_5 Reaction at 400°C

marked increase in the rate of the reaction. The shorter times required for the change in rate to occur at higher temperatures (see Fig. 12) appear to support this proposed reaction mechanism. At higher temperatures and hence increased reaction rates, the buildup of UO_2F_2 on the solid reactant should occur more quickly. Although the fraction of the original uranium present as UO_2F_2 in the solid residues decreases with reaction time (as shown in Fig. 14 for the reaction at 400°C), the fraction of UO_2F_2 in the residue increases with both reaction time and temperature (as shown in Fig. 13).

The absence of a break in the reaction rate at 250°C can be explained on the basis of generally lower reaction rates. Figure 15 shows the fractions of the original uranium present as U_3O_8 and UO_2F_2 in the solid

Fig. 15

Distribution of Original Uranium as UO_2F_2 and U_3O_8 in Reaction Residues and as Volatilized UF_6 for U_3O_8 - BrF_5 Reaction at 250°C



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residue and as volatilized UF₆. These plots show a greatly reduced rate of production of UF₆ and a steady buildup of UO₂F₂ in the residues, when compared with similar plots (Fig. 14) for the reaction at 400°C. These results lead to the conclusion that at 250°C a reaction time of 30 min was not sufficient to allow the change in rate to occur. The similar behavior in the accumulation of UO₂F₂ in the reaction residues (plotted in Fig. 13) suggests that there is no change in the reaction mechanism with changing temperature.

4. UO₂-BrF₅ Reaction

The reaction of UO₂ with BrF₅ proceeds by the formation of UO₂F₂, which, in turn, is fluorinated to UF₆. Experiments were performed at 224-302°C for ANL UO₂ and at 307-367°C for NUMEC UO₂. The partial pressure of BrF₅ in the gas phase (26 v/o BrF₅, 74 v/o nitrogen) was 181 Torr, and the linear velocity of the gas phase was about 0.7 cm/sec. The rate constants obtained are listed in Table X and are shown as a function of reciprocal temperature in Fig. 16. The products of the reaction are assumed to be UF₆ and O₂, together with elemental bromine. This assumption is in agreement with the stoichiometry previously discussed for the reactions with UF₄ and U₃O₈. From least-squares fits of the Arrhenius equation to the two sets of data, the following equations were obtained:

$$\text{ANL UO}_2: \log k' = 1.493 - \frac{1630}{T}; \quad (16)$$

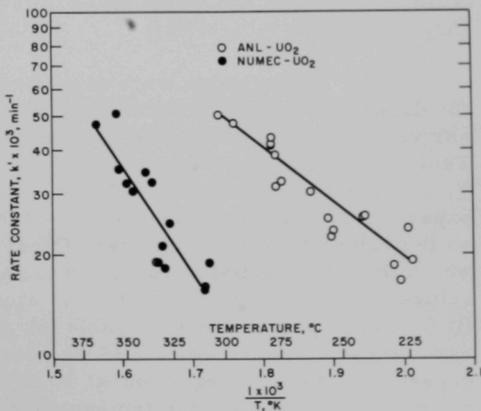
$$\text{NUMEC UO}_2: \log k' = 3.441 - \frac{3060}{T}. \quad (17)$$

TABLE X. Reaction Rate Constants, k', for UO₂-BrF₅ Reaction

Rate Constants, k' x 10 ³ , min ⁻¹		Rate Constants, k' x 10 ³ , min ⁻¹	
Temp, °C	Exp	Temp, °C	Exp
BrF ₅ partial pressure: 181 Torr Total pressure: 1 atm Linear velocity of gas phase: 0.7 cm/sec			
A. ANL UO ₂		B. NUMEC UO ₂	
224	19.3	307	19.0
225	23.8	309	16.1
228	16.8	310	15.7
230	18.7	326	24.8
241	25.9	329	18.3
242	25.4	330	21.3
253	23.3	333	19.0
254	22.3	333	19.0
255	25.3	336	32.5
262	30.2	339	34.3
274	33.5	346	30.3
277 ^a	31.2	349	32.0
277 ^b	38.4	354	35.1
279	43.4	355	51.3
279	41.6	365	46.7
279	40.6	367	47.6
295	47.9		
302	50.1		

^aLinear velocity - 0.85 cm/sec.

^bLinear velocity - 1.25 cm/sec.



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Fig. 16. Temperature Dependence of Rate Constants for UO₂-BrF₅ Reaction (P_{BrF₅} = 181 Torr)

From these equations, activation energies of 7.5 and 14 kcal/mole were calculated for the ANL and NUMEC materials, respectively.

The activation energy of 7.5 kcal/mole for the ANL UO_2 suggests that the reaction is controlled by the formation of UO_2F_2 and depletion of UO_2F_2 by fluorination. The activation energy for the UO_2F_2 reaction is 8.3 kcal/mole. For the NUMEC UO_2 , the value of 14 kcal/mole suggests the presence of UF_4 as well as UO_2F_2 on the surface of the reacting particles, since the activation energy for the UF_4 reaction is 16.9 kcal/mole. Rampy²⁶ has shown that both UO_2F_2 and UF_4 are produced by the reaction of UF_6 with UO_2 . Therefore, if in the reaction of NUMEC UO_2 , the product UF_6 reacts with the UO_2 , the solid surface would be an equimolar mixture of UO_2F_2 and UF_4 . For such an equimolar mixture, an estimate of the activation energy ($0.5 \times 8.3 + 0.5 \times 16.9$) results in a value of 12.6 kcal/mole, in reasonable agreement with the value of 14 kcal/mole obtained experimentally. Reasonable agreement of theoretical with experimental activation energies had been previously obtained for $(2/3)\text{UO}_2\text{F}_2 - (1/3)\text{UF}_4$ mixtures (see Fig. 4).

The difference in behavior of the two types of oxide probably arises from different degrees of reactivity of the two oxides. A high reactivity of ANL UO_2 may result in rapid conversion of the surface of the solid to UO_2F_2 , so that interaction at the oxide surface with UF_6 to form a mixture of UF_4 and UO_2F_2 would be essentially absent. Sintered oxide (NUMEC UO_2) is more slowly fluorinated to UO_2F_2 , and therefore some oxide surface is available for contact with UF_6 to form UF_4 and UO_2F_2 . To obtain rates comparable to those obtained for ANL UO_2 , higher temperatures are needed for NUMEC UO_2 ; this can be ascribed to the lower reactivity of the sintered UO_2 particles.

Experiments were also performed, using ANL UO_2 , to determine the dependence of the reaction rate on the BrF_5 partial pressure and the linear velocity of the gas phase. The two experiments (at 277°C in Part A of Table X) were performed at linear velocities of 0.85 and 1.25 cm/sec. Values of the rate constant of 0.0312 and 0.0384 min^{-1} obtained for these experiments indicate a small effect of the linear velocity of the gas phase on the value of the rate constant. Other experiments were performed in which the BrF_5 partial pressure in the gas phase was 74 or 369 Torr. The values of the rate constant obtained, along with those for reactions at 181 Torr BrF_5 partial pressure (from Table X), are listed in Part A of Table XI. From these data a value of 0.84 was derived for the coefficient, n , of the pressure term in the equation $k' = Ae^{-E/RT}P^n$. Combining this value of n with the equation for the temperature dependence of the ANL UO_2 - BrF_5 reaction resulted in the following equation representing the temperature and pressure dependence of the UO_2 - BrF_5 reaction:

$$\log k' = 0.84 \log P - \frac{1630}{T} - 0.270, \quad (18)$$

where P is expressed in Torr.

TABLE XI. Effect of BrF₅ Partial Pressure for Reactions with UO₂ and UO₃

Temp, °C	P ^a BrF ₅ , Torr	Rate Constant, k' x 10 ³ , min ⁻¹	Exponent, n, for BrF ₅ Pressure Term ^b	Temp, °C	P ^a BrF ₅ , Torr	Rate Constant, k' x 10 ³ , min ⁻¹	Exponent, n, for BrF ₅ Pressure Term ^b
A. UO ₂ -BrF ₅ Reaction				B. UO ₃ -BrF ₅ Reaction			
242	74	13.8		252	90	12.9	
250	74	15.5		253	90	12.9	
242	181	23.6		251	189	26.6	
250	181	27.2		252	189	31.6	
242	369	43.0		251	277	41.8	
250	369	60.1	0.84	251	277	41.8	1.05

^aTotal pressure, 1 atm.^bFor equation k' = Ae^{-E/RT}Pⁿ.TABLE XII. Reaction Rate Constants, k', for UO₃-BrF₅ Reaction

BrF₅ partial pressure: 189 Torr
 Total pressure: 1 atm
 Linear velocity of gas phase: 0.7 cm/sec

Temp, °C	Rate Constant, k' x 10 ³ , min ⁻¹		Temp, °C	Rate Constant, k' x 10 ³ , min ⁻¹	
	Exp	Calc		Exp	Calc
222	13.7	17.6	264	28.1	32.4
226	17.7	18.7	265	28.6	32.8
235	22.8	21.5	276	39.1	37.9
236	22.8	21.8	278	40.4	38.9
251	26.6	27.1	299	50.2	50.3
252	31.6	27.5	300	51.6	50.9
263	36.6	32.0			

5. UO₃-BrF₅ Reaction

The kinetics of the UO₃-BrF₅ reaction were studied over the range 222-300°C. The BrF₅ partial pressure was 189 Torr in a gas phase containing 27 v/o BrF₅ and 73 v/o nitrogen at a linear velocity of about 0.7 cm/sec. The results are listed in Table XII and are shown in the plot of Fig. 17. The products of the reaction are assumed to be UF₆ and O₂,

together with elemental bromine. The following equation representing the temperature dependence of the rate constant was obtained by a least-squares fit of the Arrhenius equation to the data:

$$\log k' = 1.636 - \frac{1680}{T} \quad (19)$$

A value of 7.7 kcal/mole was calculated for the activation energy of the UO₃-BrF₅ reaction.

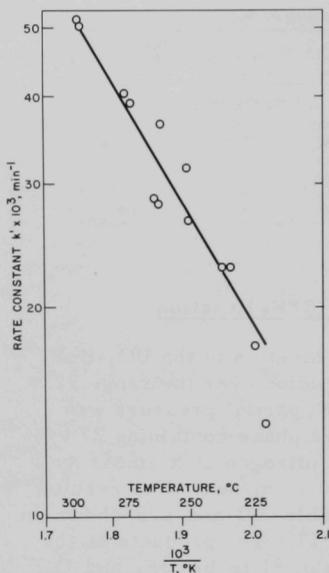
Several experiments were performed to determine the dependence of the reaction rate on the BrF₅ partial pressure. The data obtained at partial pressures of 90, 189, and 277 Torr are listed in Part B of Table XI. From these data a value of 1.05 for the coefficient n of the equation k' = Ae^{-E/RT}Pⁿ was calculated. Combining this value of n with the previous equation resulted in the following equation representing the combined temperature and pressure dependence of the reaction:

$$\log k' = 1.05 \log P - \frac{1680}{T} - 0.767, \quad (20)$$

where P is expressed in Torr.

6. Mechanisms of the UO₂-BrF₅ and UO₃-BrF₅ Reactions

Rampy²⁷ has shown that interactions between UF₆ and both UO₃ and UO₂ occur. It was therefore reasonable to postulate that the fluorination



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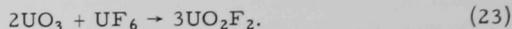
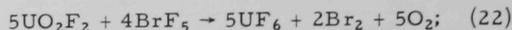
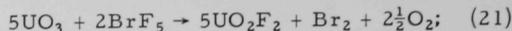
Fig. 17. Temperature Dependence of Rate Constants for $\text{UO}_3\text{-BrF}_5$ Reaction

when further interaction was hindered by the accumulation of a layer of UO_2F_2 on the surface of the oxide particles.

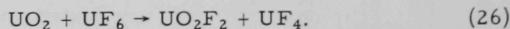
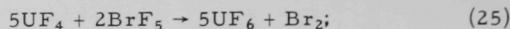
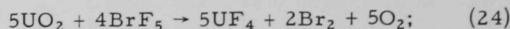
Preliminary boat-reactor data for the reactions of BrF_5 with UO_3 , UO_2 , and U_3O_8 at 300°C are compared in Fig. 18. These data show that both the $\text{UO}_3\text{-BrF}_5$ and the $\text{UO}_2\text{-BrF}_5$ reactions undergo a change in reaction rate similar to that observed for the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction.

X-ray diffraction analyses of the residue for the $\text{UO}_3\text{-BrF}_5$ reaction showed only the presence of UO_3 and UO_2F_2 . For the $\text{UO}_2\text{-BrF}_5$ reaction, X-ray diffraction analysis showed the presence of UO_2 , UO_2F_2 , UF_4 , and U_3O_8 in the residues. The U_3O_8 could be present as a result of oxidation of the UO_2 by elemental oxygen, a reaction product.

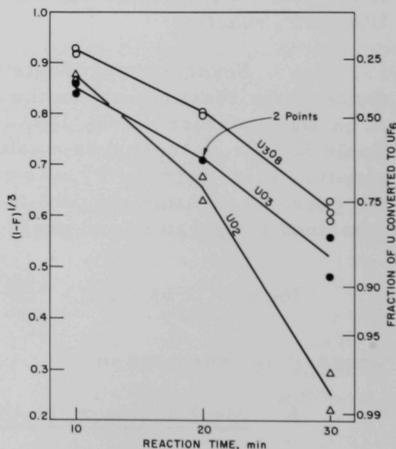
of these oxides using BrF_5 would result in the same type of rate behavior as was obtained for the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction. For the $\text{UO}_3\text{-BrF}_5$ reaction, the following reactions could be expected to occur:



For the $\text{UO}_2\text{-BrF}_5$ reaction, the following equations should apply:



In both these cases, the reaction between UF_6 and the uranium oxide would result in a low initial rate of UF_6 volatilization if the same mechanism as postulated for the $\text{U}_3\text{O}_8\text{-BrF}_5$ reaction is applied. The rate of volatilization of UF_6 would increase



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Fig. 18. Comparison of Reactions of U_3O_8 , UO_3 , and UO_2 with BrF_5 at 300°C

C. Disposal of BrF_5

Several tests were performed to evaluate suitable methods for disposal of excess BrF_5 from the laboratory experiments. Two solid materials were evaluated: commercial-grade activated alumina (8-14 mesh) and reagent-grade soda lime (4-8 mesh) which contained 7% water. The disposal experiments were performed by passing a BrF_5 - N_2 mixture through a 2-in.-diam, 6-in.-long trap containing a weighed amount of the solid disposal agent. Thermocouples to monitor the temperature of the disposal reaction were placed on the outside surface of the trap near the bottom, top, and center, and in a re-entrant well. The thermocouple in the well could be positioned from near the bottom of the solid bed to a point midway up the reaction vessel. A sodium hydroxide solution bubbler was placed downstream from the trap to indicate the breakthrough of bromine or BrF_5 .

In one experiment using activated alumina as the disposal agent, a feed stream consisting of 33 v/o BrF_5 and 67 v/o nitrogen was passed through a 4-in.-deep bed at a flow of about 0.4 g of BrF_5 /min. The reaction front was at 120°C, and after 14 g of BrF_5 had been passed through the reaction vessel bromine was noted in the effluent-gas stream. At this point in the reaction, the upper part of the reaction vessel was at 100°C. The alumina removed from the reactor showed a narrow white band (AlF_3) at the bottom of the bed, indicating that reaction with the fluorine component of the BrF_5 had occurred. There was no evidence of reaction in the upper portion of the alumina bed; instead it was found that bromine was adsorbed on the alumina. This experiment showed that 14 g of activated alumina would be needed as a disposal agent for 1 g of BrF_5 . However, the fact that the bromine is adsorbed on alumina rather than reacting with alumina suggests that activated alumina is unsuitable for use as a disposal agent.

Two experiments were performed to evaluate soda lime as a disposal agent. In one experiment the bed was 4 in. deep; in the other experiment the bed was approximately 6 in. deep. The BrF_5 flow was 1.2 g/min in a gas phase containing 50 v/o BrF_5 and 50 v/o nitrogen. Bromine was noted in the effluent-gas stream after 28 and 52 g of BrF_5 had been passed through the 4-in. (120-g) and 6-in. (220-g) beds, respectively. At this point in the reaction, the temperature of the upper portion of the soda lime bed was 100°C.* Just before bromine was noted in the effluent gas, water was observed in the effluent-gas stream. These experiments showed that about 4.3 g of soda lime is required per gram of BrF_5 reacted. Examination of the soda lime bed after the reactions indicated that BrF_5 reacted completely with the soda lime. On the basis of these tests, soda lime appears to be a suitable disposal agent.

*In subsequent use of a large soda lime trap, a temperature of at least 100°C was necessary for the bromine to react with the soda lime. If the bed temperature is not raised to this value by the heat of the fluorine reaction, the disposal trap must be heated externally.

IV. SUMMARY

A. Reactions with Simulated Fluid-bed Charges

The removal of uranium from simulated fluid-bed charges containing either UF_4 and UO_2F_2 or U_3O_8 and alumina and cold fission products was essentially complete after reaction times of 1-2 hr at 350-400°C using about 20 v/o BrF_5 in nitrogen as the fluorinating gas. The addition of Zircaloy decladding product or stainless steel decladding product did not hinder the removal of uranium. Plutonium, added to these mixtures as PuO_2 , was not volatilized during the BrF_5 fluorination, but appeared to be quantitatively converted to PuF_4 . In a fluorination with fluorine at 500-550°C following the BrF_5 step, the plutonium was satisfactorily converted to PuF_6 in a reaction time of about 8 hr.

B. Kinetics of the Reaction of BrF_5 with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3

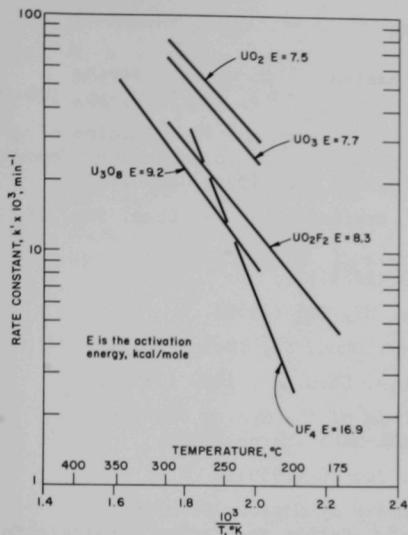
The kinetics were measured in the range 200-360°C and in the BrF_5 partial-pressure range of 74-369 Torr. Constants for the equations representing the combined temperature and pressure dependence of these reactions are listed in Table XIII. The activation energies derived from these equations are 16.9, 8.3, 9.2, 7.5, and 7.7 kcal/mole for the reactions with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3 , respectively. Values of the coefficient n for the pressure term in the equation $k' = A e^{-E/RT} P^n$ of 0.38, 0.71, 0.90, 0.84, and 1.05 were derived for the reactions with UF_4 , UO_2F_2 , U_3O_8 , UO_2 , and UO_3 , respectively. The plots of Fig. 19 show the temperature dependence of the various reactions at a BrF_5 partial pressure of 250 Torr.

TABLE XIII. Constants for Rate Equations for Reactions of BrF_5 with Uranium Compounds

	UF_4	UO_2F_2	U_3O_8	UO_2^b	UO_3
Rate equation: ^a $\log k' = n \log P - \frac{A}{T} + B$					
n	0.38	0.71	0.90	0.84	1.05
A	3690	1810	2000	1630	1680
B	4.286	0	-0.220	-0.270	-0.767
Activation Energy (kcal/mole)	16.9	8.3	9.2	7.5	7.7

^aP in Torr, k' in min^{-1} , T in °K.

^bHigh reactivity ANL UO_2 .



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Fig. 19. Temperature Dependence of Rate Constants for Reactions of BrF_5 with Uranium Compounds at a BrF_5 Partial Pressure of 250 Torr

The reactions with UF_4 and UO_2F_2 did not involve the formation of an intermediate, but the reactions with U_3O_8 , UO_2 , and UO_3 involved the formation of UO_2F_2 either directly or by the reaction of product UF_6 with the oxide.

C. Disposal of BrF_5

Soda lime (a mixture of sodium hydroxide and calcium oxide containing about 10% water) was found to be a good agent for the disposal of BrF_5 . The reaction between soda lime and BrF_5 results in the production of solid, nonvolatile reaction products, presumably mainly NaF and NaBr . The tests showed that 4.3 g of soda lime is required to completely react 1 g of BrF_5 , and that a temperature of at least 100°C is necessary for efficient reaction of the bromine component in the upper portion of the soda lime trap.

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