

Fluorination of Uranium Compounds by Gaseous  
Bromine Trifluoride and a Bromine-Fluorine  
Mixture

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March, 1976

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日本原子力研究所

Japan Atomic Energy Research Institute

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# Fluorination of Uranium Compounds by Gaseous Bromine Trifluoride and a Bromine-Fluorine Mixture

Tsutomu SAKURAI

Tokai Research Establishment  
Japan Atomic Energy Research Institute

Received September 29, 1975

## Summary

This report summarizes the studies of fluorination of uranium compounds by gaseous  $\text{BrF}_3$  and a  $\text{Br}_2\text{-F}_2$  mixture, which were carried out in Fluorine Chemistry Laboratory of JAERI in connection with the reprocessing method of nuclear fuels.

Although thermodynamically more stable than  $\text{F}_2$ ,  $\text{BrF}_3$  has higher reactivity at relatively low temperatures: fluorination of uranium compounds can be carried out at  $100^\circ \sim 200^\circ\text{C}$  by using gaseous  $\text{BrF}_3$ . This fluorination temperature is lower than those of  $\text{F}_2$ ,  $\text{BrF}_5$ ,  $\text{ClF}$  and  $\text{SF}_4$ , and close to that of  $\text{ClF}_3$ .

The usage of  $\text{BrF}_3$  has however the drawbacks that it requires additional devices to heat the corrosive liquid and to remove  $\text{Br}_2$  produced as a byproduct. In order to eliminate the difficulties indicated, a new method of fluorination was developed—the use of a  $\text{Br}_2\text{-F}_2$  mixture. Addition of small amounts of  $\text{Br}_2$  to the fluorine flow (about 6% in relation to the fluorine concentration) gives marked effects on the rate of fluorination.

## 三フッ化臭素および臭素-フッ素混合ガスによる ウラン化合物のフッ素化反応

日本原子力研究所 東海研究所

桜 井 勉

1975年9月29日受理

核燃料再処理に関連してフッ素化学研究室で進めてきた、三フッ化臭素ガスによるウラン化合物のフッ素化およびその関連研究をまとめた。三フッ化臭素ガスによりウラン化合物を  $100^{\circ}\sim 200^{\circ}\text{C}$  で六フッ化ウランにフッ素化することができる。このフッ素化温度は、単体フッ素、五フッ化臭素、一フッ化塩素および四フッ化イオウによる場合より低く、三フッ化塩素のそれに近い。このことは熱力学的にフッ素より安定な三フッ化臭素が、比較的低温領域で、それより高い反応性をもつことを示す。しかし、三フッ化臭素を使用すると、その液体の加熱および副生成物臭素の処理という操作が加わる。これら欠点を補う方法として、臭素-フッ素混合ガスによるフッ素化方法を開発した。フッ素気流中に少量の臭素（フッ素濃度の約6%）を添加することにより、大きなフッ素化速度を得ることができる。

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## 1. Introduction

The fluoride-volatility process is one of the reprocessing methods for nuclear fuels, which utilizes the volatilities of  $UF_6$  and  $PuF_6$ . Since most fission products (except Sb, Nb, Mo, Tc, Ru, Te, I and Np) form non-volatile fluorides, U and Pu in spent fuels can be separated from them by fluorination. Fluorine Chemistry Laboratory of JAERI started research on the process in 1958. In this, the present author has studied fluorination of nuclear fuels with the two purposes.

(i) **Development of an appropriate method of the fluorination.** The fluorination process must meet the following requirements. Since the fluorinating agents and the fluorination products are very corrosive and toxic, it is desirable to carry out the fluorination under as mild conditions as possible. On the other hand, rapid fluorination would be necessary from the standpoint of economy; long period of the fluorination results in loss of  $PuF_6$  due to its radiolysis. And, the fluorinating agent must facilitate recovery and purification of U and Pu.

(ii) **Contribution to fluorine chemistry.** Because of corrosive and toxic properties of the fluorinating agents, very few laboratories can treat these materials. Consequently, the fluorination is a relatively unknown branch of chemical reactions. Through the study, the author intended to provide other workers with the information.

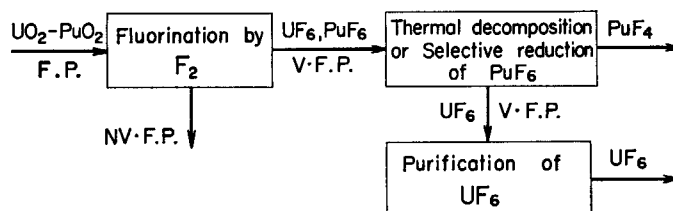
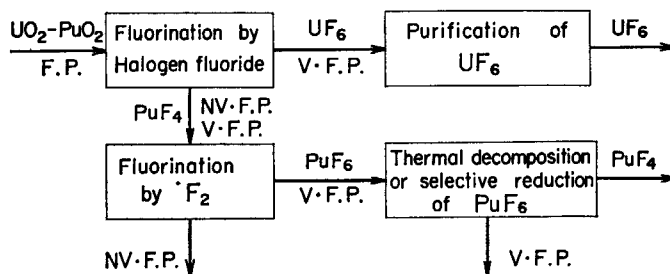
Fluorine Chemistry Laboratory took up two fluorinating agents of different types—a gaseous fluorinating agent  $F_2$  and a liquid one  $BrF_3$ . In the early stage, the present author attempted to use liquid  $BrF_3$  for fluorination of uranium compounds by diluting it with liquid bromine. However, it was difficult to treat quantitatively this corrosive and toxic liquid, and little data were obtained from these experiments. In the course of studies, the author found that the fluorination could be carried out more easily with gaseous  $BrF_3$  than with the liquid form. Since then, the fluorination by gaseous  $BrF_3$  has been studied in order to see whether or not there are any possibilities of its application to the fluoride-volatility process. Interesting results have been obtained. Recently, this method has been modified into a new method of the fluorination using a  $Br_2-F_2$  mixture.

In the present report, the author intends to clarify characteristics of the two fluorinating agents ( $BrF_3$  and a  $Br_2-F_2$  mixture), and also to discuss their application to the fluoride-volatility process. References are also made to reactivities of other fluorinating agents. The fluoride-volatility process is outlined later in this chapter. Chapter 2 deals with the fluorination of uranium compounds by gaseous  $BrF_3$ . The experimental procedure and the kinetics of reactions are described. In chapter 3, on the basis of the experimental results, the reactivity of  $BrF_3$  is compared with those of some other fluorinating agents. The difference in reactivity between  $BrF_3$  and  $F_2$  is interesting from a chemical point of view; it is therefore discussed in detail. The usage of  $BrF_3$  is however accompanied by some technical difficulties. In order to eliminate these drawbacks, the fluorination by a  $Br_2-F_2$  mixture has been developed; chapter 4 describes this new method of fluorination. Finally, chapter 5 summarizes the studies made to this day.

The fluorination of uranium compounds is important in the field of nuclear engineering. Although the present study was carried out for fuel reprocessing, the results obtained may apply to other aspects in fluorination of uranium compounds and other inorganic substances.

## Introductory remarks for the fluoride-volatility process

This process may be classified into the two alternative methods, depending upon the fluorinating agent used (see Fig. 1).

(A) Elemental Fluorine ( $F_2$ )(B) Halogen fluoride ( $ClF_3, ClF, BrF_3$  or  $BrF_5$ )

F.P. ----- Fission products.

V·F.P.----- Volatile fluorides of fission products.

NV·F.P.--- Non-volatile fluorides of fission products.

Fig. 1 Flowsheet of the fluoride-volatility process. The fluorinating agent used is  $F_2$  in (A) and a halogen fluoride in (B)

(i) In the case of  $F_2$  being the fluorinating agent, both U and Pu are fluorinated into  $UF_6$  and  $PuF_6$ , respectively. The separation of  $UF_6$  from  $PuF_6$  is done by either thermal decomposition or selective reduction of  $PuF_6$  into non-volatile  $PuF_4$  (see Fig. 1(A)).

(ii) When such a halogen fluoride as  $ClF_3$ ,  $BrF_3$  or  $BrF_5$  is used, the separation of U from Pu is achieved in the step of fluorination, because only U volatilizes as  $UF_6$  and Pu remains in the reactor as non-volatile  $PuF_4$  (see Fig. 1(B)).

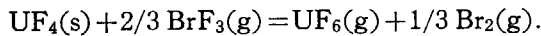
One of the earliest methods of the fluoride-volatility process used liquid  $BrF_3$ , because the liquid was considered to be suitable for removal of the heat of reaction. Brookhaven National Laboratory (U. S. A.) carried out engineering-scale experiments with this liquid in the 1950's<sup>1)</sup>. However, this process was soon discarded, possibly because the fluorination by liquid  $BrF_3$  was too vigorous to control. Following this effort, the method of fluorination has been developed along a different line—the use of gaseous fluorinating agents in combination with fluidization techniques. Argonne National Laboratory (U. S. A.) carried out extensive experiments with  $F_2$  and gaseous  $BrF_5$  in 1958~1969<sup>2)</sup>. Centre d'Etude de l'Energie Nucléaire, Mol (Belgium) studied the fluorination by  $ClF_3$  in 1960~1969<sup>3)</sup>. Then, JAERI and Centre d'Etude Nucléaire de Fontenay-aux-Roses (France) are still continuing the engineering-scale experiments using  $F_2$ <sup>4), 5)</sup>.



The most important problems encountered in these methods are (i) to increase Pu recovery and (ii) to prevent contamination of Pu by Ru. Details of the fluoride-volatility process have been reviewed frequently in the literature<sup>6</sup>.

## 2. Results of the Kinetic Study of Fluorination Using Gaseous $\text{BrF}_3$

Fluorination of uranium compounds by gaseous bromine trifluoride is one of the gas-solid reactions in which the products are entirely gaseous, e. g.



Therefore, a reaction rate can be obtained by tracing the weight change of the solid during the reaction. An experimental apparatus was devised, and the kinetics of these reactions was studied.

### 2. 1 Experimental Apparatus and Procedure

Fig. 2 shows the apparatus used for the study of fluorination by gaseous  $\text{BrF}_3$ . It consists

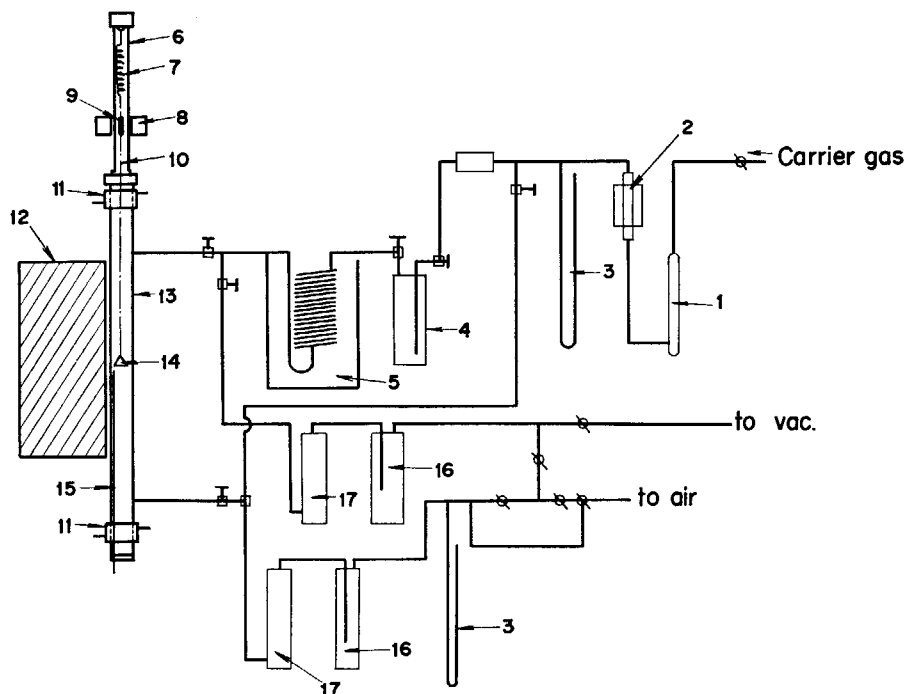


Fig. 2 An experimental apparatus for the fluorination by gaseous  $\text{BrF}_3$ .

1. Molecular sieve
2. Rotameter
3. Hg manometer
4. Vessel for liquid  $\text{BrF}_3$
5. Thermostat
6. Spring column (Kel-F or Teflon)
7. Nickel spring
8. Differential transformer
9. Ferrite core sealed with Teflon-100X tube
10. Nickel chain
11. Jacket for cooling water
12. Electric furnace
13. Reaction tube (Monel)
14. Nickel pan for the sample
15. Thermocouple well
16. Chemical trap charged with active carbon
17. Chemical trap charged with soda lime

of a vessel for liq- $\text{BrF}_3$ , a spiral tube immersed in a thermostat, a thermobalance, and chemical traps. The liq- $\text{BrF}_3$ , 70~80 mm deep in the vessel, should be purified in advance by distillation<sup>7)</sup>. Gaseous  $\text{BrF}_3$  with a constant partial pressure was supplied to the reaction tube in the following manner. The liq- $\text{BrF}_3$  in the vessel was bubbled with the stream of an inert gas ( $\text{N}_2$ , Ar or He) with a fixed flow rate less than 15 l/hr. The gas containing  $\text{BrF}_3$  vapor was then passed through the thermostat; during the passage through it the stream was saturated with  $\text{BrF}_3$  vapor because the thermostat was maintained at a temperature 15~20°C lower than the temperature of the liq- $\text{BrF}_3$  vessel. Thus, the gas containing a constant amount of  $\text{BrF}_3$  was supplied to the reaction tube at a fixed flow rate. The connecting line must be heated moderately to prevent condensation of  $\text{BrF}_3$ .

The thermobalance corrosion-resistant to  $\text{BrF}_3$  was devised in our laboratory by Tsujimura, Fujisawa and Takahashi<sup>8)</sup>. Its spring column was made of a Kel-F or Teflon tube and the sensing element was a nickel spring whose extension was measured with a differential transformer and recorded automatically. In an experimental run, 70~100 mg of the solid sample was mounted in the nickel pan. The spring column must be maintained at a temperature higher than that of the thermostat by means of a thermostated air-bath in order to avoid the influence of change in ambient temperature on the spring sensitivity and also to prevent condensation of gaseous  $\text{BrF}_3$ .

Besides the thermobalance, all valves and connecting lines in contact with  $\text{BrF}_3$  were made of corrosion-resistant materials such as Monel, nickel, Kel-F or Teflon. The chemical traps were charged with soda-lime and active carbon; the latter was necessary for removing free bromine.

## 2. 2 Rate of the Reaction

In the case of the gas-solid reaction in which the products are entirely gaseous, the dimin-

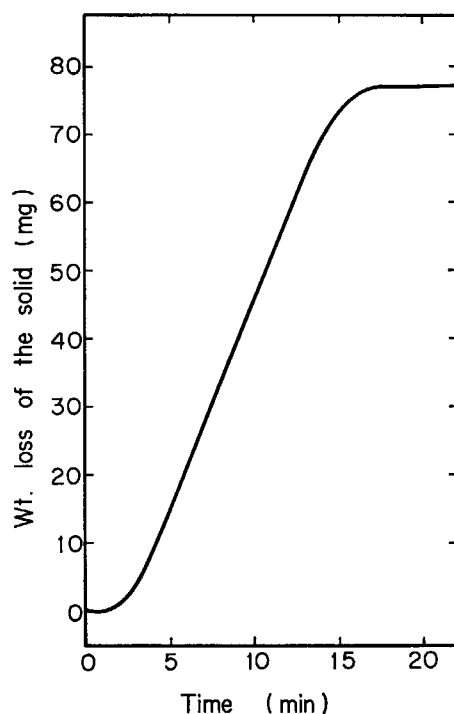


Fig. 3 An example of the "weight change vs. time" curve in the  $\text{UF}_4$ - $\text{BrF}_3$  reaction. Initial weight of  $\text{UF}_4$ =77mg, temperature=110°C,  $\text{BrF}_3$  partial pressure=15 mmHg, carrier gas=Ar, and linear gas velocity=1 cm/sec

ishing sphere model can be used for analysis of the results<sup>9)~12)</sup>. The final equation derived from this kinetic model is

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

where  $F$  is the fraction of reaction that takes place in time  $t$  and  $k'$  a rate constant. The "weight change vs. time" curve as shown in Fig. 3 gives the fraction of reaction expressed as

$$F=(W_0-W)/W_0, \quad (2)$$

where  $W_0$  and  $W$  are the weights of the solid at time 0 and  $t$ , respectively. When this model applies,  $k'$  is obtained from the slope of a straight line in the plot of  $(1-F)^{1/3}$  vs. time.

However, in the present case, the plot of  $(1-F)$  but not  $(1-F)^{1/3}$  vs. time fits in a linear relationship as Fig. 4 shows<sup>13)</sup>. This fact means that weight of sample decreases at a nearly constant rate with time, i. e.

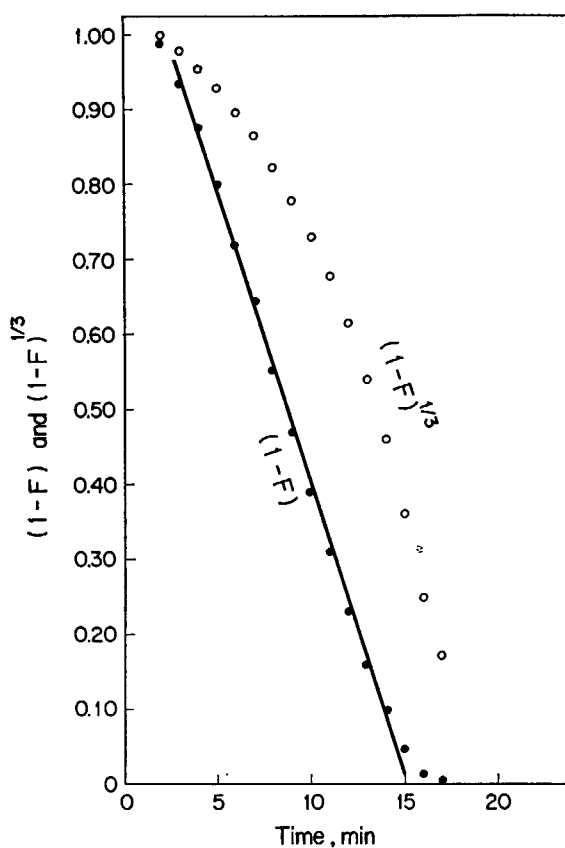


Fig. 4 Plots of  $(1-F)$  and  $(1-F)^{1/3}$  vs. time for the "weight change vs. time" curve in Fig. 3<sup>13)</sup>.

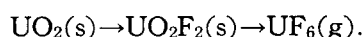
$$-dW/dt=K(=\text{const.}), \quad (3)$$

for integration of eq. (3) leads to the following relation:<sup>13)</sup>

$$(1-F)=1-(K/W_0)t. \quad (4)$$

Deviation of the plot of  $(1-F)^{1/3}$  vs. time from a straight line is ascribable to the situation that the powdered sample bed in the pan is considerably deep in comparison with particle sizes of the powder. It seems likely that  $\text{UF}_6$  is produced in a relatively thin layer at the surface of the bed. As this reaction zone proceeds downward through the bed the rate of reaction appears linear with time. This situation holds also for other uranium compounds. Therefore,  $K$  in eqs. (3) and (4) was used as a reaction rate in the present study.

In Fig. 4, the initial and final portions of the plot of  $(1-F)$  vs. time deviate from the straight line. Of these, the initial deviation is attributed to the facts that it takes 1~2 min for the gaseous reactant to reach its fixed concentration in the reaction tube and that the fluorination of uranium compounds is a consecutive reaction. UF<sub>4</sub> and UO<sub>2</sub> are fluorinated into UF<sub>6</sub> through the following steps, respectively:<sup>13),14)</sup>



In the former reaction, the weight of the sample is kept almost constant for 1~2 min before it begins to decrease, while in the latter case the weight increases slightly before it decreases<sup>14)</sup>. On the other hand, the deviation at the end of reaction may be caused by a number of variables, one of which is a small amount of the sample remaining. Chemisorption of BrF<sub>3</sub> on the surface of the remaining solid may contribute significantly to the final weight of the sample thereby biasing the results.

## 2. 3 Factors Influencing the Reaction Rate

### 2. 3. 1 Diffusion rate

In most of the literature treating the kinetics of fluorination of uranium compounds, it has been postulated that the diffusion of the reactant gas onto the solid surface does not limit the reaction any way, for diffusion in the gaseous state would be fast involving little or no activation energy<sup>9),10)</sup>.

However, the present author found that the change of the carrier gas of BrF<sub>3</sub> from Ar or N<sub>2</sub> to He brought about the reaction rate twice as high (see TABLE 1)<sup>14),15)</sup>. This finding indicates that the transport of BrF<sub>3</sub> to the solid surface influences the reaction rate. Transport of UF<sub>6</sub> away from the surface is not attributed to this phenomenon, because vapor pressure of UF<sub>6</sub> is very high ( $3 \times 10^3$  mmHg at 100°C)<sup>16)</sup> and the reaction rate depends upon BrF<sub>3</sub> partial pressure as described later<sup>17)</sup>. Calculation with Gilliland's formula leads to the following relationships between diffusion coefficients for the binary systems of BrF<sub>3</sub> and its carrier gases:<sup>15)</sup>

TABLE 1 Dependence of the reaction rate  $K$  upon the carrier gas of BrF<sub>3</sub>

Sample	Carrier gas of BrF <sub>3</sub>	Reaction temperature (°C)	Reaction rate, $K$ (mg/min)
UO <sub>2</sub>	He	209	5.5
"	Ar	"	2.7
U <sub>3</sub> O <sub>8</sub>	He	110	3.4
"	"	"	3.1
"	N <sub>2</sub>	"	1.7
"	Ar	"	1.6
UF <sub>4</sub>	He	"	12.5
"	"	"	12.2
"	"	"	12.7
"	N <sub>2</sub>	"	6.0
"	"	"	"
"	Ar	"	6.1
"	"	"	5.7

Initial weight of the sample  $81 \pm 1$  mg. BrF<sub>3</sub> partial pressure 15 mmHg.  
Linear gas velocity 66 cm/min.

$$D_{\text{He}}/D_{\text{Ar}}=2.7, D_{\text{He}}/D_{\text{N}_2}=2.5 \text{ and } D_{\text{N}_2}/D_{\text{Ar}}=1.1,$$

where  $D_{\text{He}}$ ,  $D_{\text{N}_2}$  and  $D_{\text{Ar}}$  denote the diffusion coefficients for He-BrF<sub>3</sub>, N<sub>2</sub>-BrF<sub>3</sub> and Ar-BrF<sub>3</sub> systems, respectively. These values are close to those of the corresponding ratio of the reaction rate as shown in TABLE 1.

### 2. 3. 2 Gas flow rate

Fig. 5 shows a typical example of gas flow rate dependence of the reaction rate. The reaction rate increases with an increase in linear gas velocity up to about 1 cm/sec, and then becomes nearly independent of it thereafter for the three carrier gases. Doubling the gas velocity only increases the reaction rate by 4% at most. This phenomenon arises from the fact that the sample is mounted in a pan and the gas is stagnant in it. When the linear gas velocity is increased to the extent of obliterating the BrF<sub>3</sub> concentration gradient outside the pan, the reaction rate would not be further changed by additional increase of the gas velocity, and it would be controlled by the diffusion rate of BrF<sub>3</sub> through the stagnant gas layer in the pan.

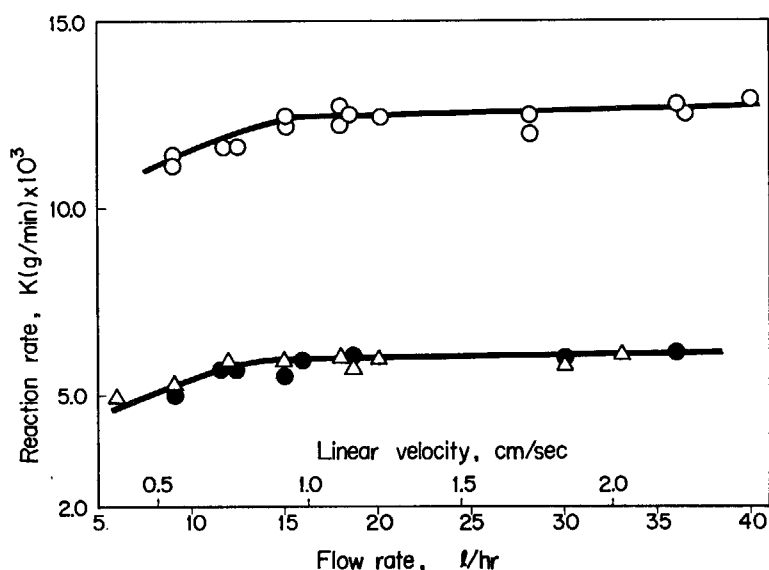


Fig. 5 Effect of gas velocity on the reaction rate<sup>15)</sup>.  
Initial weight of UF<sub>6</sub> = 80 ± 1 mg, reaction temperature = 110°C, BrF<sub>3</sub> partial pressure = 15 mmHg. Carrier gas used: ○, He; ●, N<sub>2</sub>; △, Ar.

If a sample spherical in shape is placed in a stream of reactant gas with a velocity  $V$  and the rate determining step is gas diffusion in the boundary layer, the reaction rate is proportional to  $V^{0.5}$ .<sup>18)</sup>

### 2. 3. 3 Partial pressure of the reactant gas

The reaction rate was proportional to 0.8th power of BrF<sub>3</sub> partial pressure in its range of 7 to 45 mmHg<sup>13), 15)</sup>. This partial pressure dependence may be explained as follows. As the partial pressure of BrF<sub>3</sub> increases, that of UF<sub>6</sub> also increases in the stagnant gas layer in the pan. This increase of UF<sub>6</sub> concentration causes the decrease of diffusion rate of BrF<sub>3</sub>, because of the large difference in molecular weight of the carrier gas and UF<sub>6</sub><sup>17)</sup>. As a result, the rate of increase of the reaction rate decreases as the partial pressure of BrF<sub>3</sub> increases.

### 2. 3. 4 Temperature

Fluorination by gaseous  $\text{BrF}_3$  proceeds even at room temperature, and the temperature dependence of its rate is very small: the apparent activation energy, calculated from the Arrhenius plot, is of the order of 1 kcal/mol, irrespective of the carrier gas used<sup>(13)~(15), (19)</sup>.

Since the fluorination temperature by  $\text{BrF}_3$  is considerably low in comparison with that by  $\text{F}_2$ , an anomalous temperature-dependence of the reaction rate appears in the case of  $\text{UF}_4$ - $\text{BrF}_3$  reaction. Fig. 6 (a) shows the relation between the reaction rate  $K$  and temperature:  $K$  increases slightly with increasing temperature up to 185°C, falls to a minimum at 220°C, and then remains almost constant thereafter. On the other hand, when the average rate of weight loss—(initial weight of  $\text{UF}_4$ )/(the time required for the reaction to complete)—is plotted against temperature, no anomaly is observed as Fig. 6 (b) shows. These facts indicate the presence of concurrent reactions, viz. the reaction of  $\text{UF}_6$  with the remaining  $\text{UF}_4$  to produce such intermediate fluorides as  $\text{UF}_5$ ,  $\text{UF}_{4.5}$  and  $\text{UF}_{4.25}$ .<sup>(16)</sup>

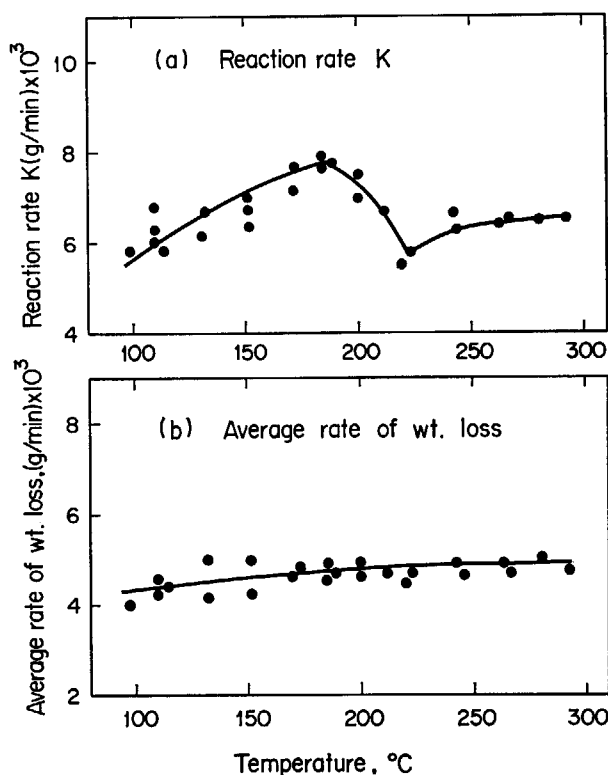
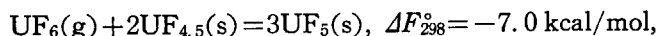
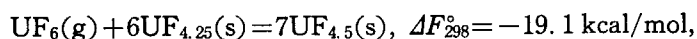
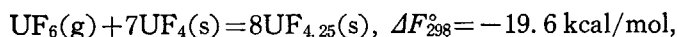


Fig. 6 Temperature-dependence of (a) the reaction rate  $K$  and (b) the average rate of weight loss\*.

Initial weight of  $\text{UF}_4$  = 77 mg,  $\text{BrF}_3$  partial pressure = 15 mmHg, carrier gas = Ar, and linear gas velocity = 1 cm/sec.

\* (Initial weight of  $\text{UF}_4$ )/(the time required for the reaction to complete)



where  $\Delta F_{298}^\circ$  is the free energy increase by each reaction at 25°C. Since these reactions proceed favorably at low temperatures<sup>(16)</sup>, an induction period appears on the "weight change vs. time" curve obtained in the runs at temperatures below 200°C<sup>(13)</sup>. This induction period causes the anomalous temperature-dependence of the reaction rate  $K$ .

The small temperature-dependence of the reaction rate and its dependence on the diffusion coefficient of gas phase indicate that the rate controlling step of  $\text{BrF}_3$  reactions is the transport of  $\text{BrF}_3$  onto the solid surface<sup>15)</sup>. Similar relationship between temperature and the reaction rate is observed in the fluorination of fission-product oxides by gaseous  $\text{BrF}_3$ <sup>20)</sup>.

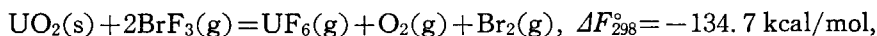
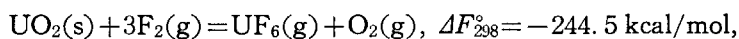


### 3. Comparison of BrF<sub>3</sub> with Some Other Fluorinating Agents

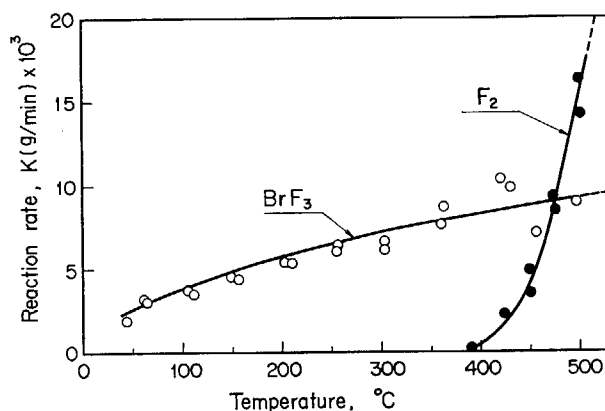
Besides BrF<sub>3</sub>, such a reagent as F<sub>2</sub>, ClF<sub>3</sub>, ClF, BrF<sub>5</sub>, or SF<sub>4</sub> can be used for fluorination of nuclear fuels. Their reactivities are compared here with that of gaseous BrF<sub>3</sub>.

#### 3.1 Elemental Fluorine

Fluorine is the only fluorinating agent that can fluorinate plutonium and its compounds into PuF<sub>6</sub>. Unlike BrF<sub>3</sub>, F<sub>2</sub> itself does not form by-products in the fluorination. Further, such reaction products as UF<sub>6</sub> and PuF<sub>6</sub> can easily be separated from the excess F<sub>2</sub>. Consequently, the use of F<sub>2</sub> may reduce the number of the unit processes in the fluoride-volatility process. Both BrF<sub>3</sub> and F<sub>2</sub> fluorinate uranium compounds into UF<sub>6</sub>, e. g.



where  $\Delta F_{298}^\circ$  is a free energy increase by each reaction at 298°K<sup>(21), (22)</sup>. The change of the carrier gas from He to Ar or N<sub>2</sub> reduces the rates of both reactions<sup>(14)</sup>.



**Fig. 7** Temperature-dependence of the rates of UO<sub>2</sub>-F<sub>2</sub> and UO<sub>2</sub>-BrF<sub>3</sub> reaction. Initial weight of UO<sub>2</sub>=100 mg, BrF<sub>3</sub> partial pressure=15 mmHg, F<sub>2</sub> partial pressure=152 mmHg, carrier gas=He, and linear gas velocity =1 cm/sec.

However, there are marked differences in reaction rate between the two fluorinating agents. **Fig. 7** shows the temperature-dependence of the rates of UO<sub>2</sub>-F<sub>2</sub> and UO<sub>2</sub>-BrF<sub>3</sub> reaction. Although the BrF<sub>3</sub> partial pressure is 1/10 as high as that of F<sub>2</sub>, the reaction by BrF<sub>3</sub> proceeds even at 40°C; however, its rate increases only slightly with increasing temperature. In contrast with this, the reaction by F<sub>2</sub> is not observable up to 390°C; its rate however increases markedly with temperature above this temperature and exceeds that of the UO<sub>2</sub>-BrF<sub>3</sub> reaction beyond 480°C. Similar relations have been obtained for fluorinations of other uranium compounds and also MoO<sub>3</sub><sup>(20)</sup>. These facts indicate that the reactivity of BrF<sub>3</sub> is greater than that of F<sub>2</sub> in a relatively low temperature region and, further that the two fluorinating agents act in different way on these materials. Since BrF<sub>3</sub> molecules have a dipole moment ( $\mu=1.0 \text{ D}$ )<sup>(23)</sup>, this polarity is considered to play an important role in their reactions. The present author has reported

elsewhere that gaseous  $\text{BrF}_3$  is sorbed by such ionic crystals as  $\text{NaF}$  under the same partial pressure as used in the present study<sup>24</sup>, i.e.  $P/P_s \leq 0.02$ , where  $P_s$  is the saturation vapor pressure of  $\text{BrF}_3$ . This process is a non-activated one and heating is necessary for the desorption of  $\text{BrF}_3$ ; therefore, the adsorption of  $\text{BrF}_3$  has a feature of "weak" chemisorption<sup>25</sup>. The use of potential energy curves may permit the following interpretation of the reactivities of  $\text{BrF}_3$  and  $\text{F}_2$ .

Fig. 8 (a) and (b) show the potential energy curves for the adsorption of  $\text{F}_2$  and  $\text{BrF}_3$ , respectively, which were inferred from the experimental results. In both (a) and (b), curve I gives the potential energy for physical adsorption and curve II that for chemisorption as a function of the distance from the surface to the adsorbed unit. Since physical adsorption is related to the process of liquefaction, it only occurs to an appreciable extent at pressures and temperatures close to those required for liquefaction. Physical adsorption of  $\text{F}_2$  may take place at temperatures in the vicinity of  $-188^\circ\text{C}$  (its boiling point); this temperature is very low in comparison with the reaction temperature shown in Fig. 7. Therefore, the reaction of  $\text{F}_2$  does not involve its physical adsorption; it proceeds through activated and dissociative adsorption of  $\text{F}_2$ . In this case, the two potential curves cross each other after the van der Waals force already changed repulsive, as Fig. 8 (a) shows. An activation energy,  $E$ , is necessary for physically adsorbed molecules to switch from curve I to II. Actually, physically adsorbed molecules are unlikely to pass over to the chemisorbed state in this case, because the molecules rather desorb when they gain enough translational energy to escape from the potential well of curve I<sup>26</sup>.

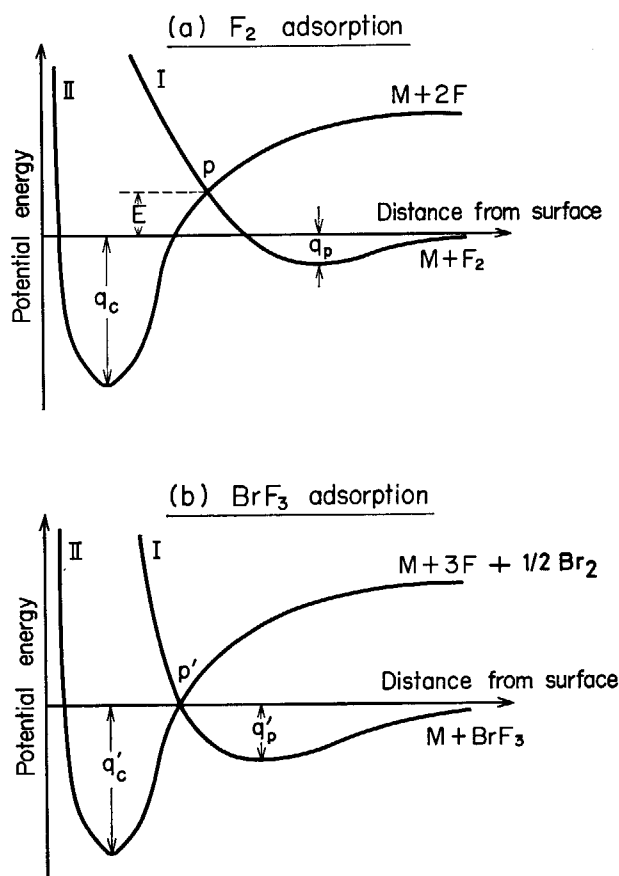


Fig. 8 Potential energy curves for the adsorption of (a)  $\text{F}_2$  and (b)  $\text{BrF}_3$ , as a function of the distance from surface to adsorbed unit. In both (a) and (b), curve I represents the potential energy curve for physical adsorption and curve II that for chemisorption.

The F<sub>2</sub> molecules in gas phase are directly chemisorbed, and for this they must gain in advance translational energies greater than  $E$ . The heating, necessary for the initiation of F<sub>2</sub> reactions, may be attributed to this energy of stretching the interatomic distance of F<sub>2</sub> molecules so as to match the distances between metal ion sites on the solid surface. Since the number of the energetic F<sub>2</sub> molecules increases exponentially with increasing temperature<sup>27)</sup>, a rise in reaction temperature results in an exponential increase in the reaction rate (see Fig. 7).

On the other hand, the temperature range of BrF<sub>3</sub> reactions involves temperatures at which the physical adsorption of BrF<sub>3</sub> can take place, i.e. temperatures in the vicinity of its boiling point (126°C). BrF<sub>3</sub> molecules are attracted to the solid surface by an electrostatic force exerted between their dipoles and the surface ions of solids. They can approach closer to the surface than F<sub>2</sub> molecules, because their physical adsorption combines "weak" chemisorption. Hence, in the case of BrF<sub>3</sub>, the two curves are considered to cross before the van der Waals force changes repulsive, as Fig. 8 (b) shows. The point p' in the figure corresponds to a transition state, in which a Br-Br bond is formed between the two neighboring BrF<sub>3</sub> molecules adsorbed and, simultaneously, acceptor bonds are formed between the surface and the fluorine atoms of each molecule. Little activation energy will be anticipated for the BrF<sub>3</sub> molecules adsorbed to switch from curve I to II, and therefore BrF<sub>3</sub> reactions can proceed even at room temperature.

On the consideration that the physical adsorption of BrF<sub>3</sub> functions as the precursor to its chemisorption, the small temperature-dependence of the rate of BrF<sub>3</sub> reactions may be explained as follows. Of the BrF<sub>3</sub> molecules in the gas phase, only a fraction with total translational energies less than the heat of adsorption,  $q_p'$  erg, is attracted to the solid surface by the electrostatic force. On the assumption that the BrF<sub>3</sub> molecules in the inert gas behave as an ideal gas, such a fraction,  $f(q_p', T)$ , as described above is given as<sup>27)</sup>

$$f(q_p', T) = \text{Erf}[(q_p'/kT)^{1/2}] - 2/\pi^{1/2}(q_p'/kT)^{1/2} \exp(-q_p'/kT), \quad (5)$$

where  $k$  is the Boltzmann's constant,  $T$  temperature in °K and  $\text{Erf}(x)$  the error function. The rate of a gas-solid reaction is proportional to  $D_{12}(C_b - C_s)$ , where  $D_{12}$  is the diffusion coefficient of binary gas system, and  $C_b$  and  $C_s$  are the concentration of the reactant gas in the main gas stream and that in the gas phase at the solid surface, respectively<sup>28)</sup>. In the present case,  $C_s$  can be taken as  $C_b[1 - f(q_p', T)]$ . In theoretical equations,  $D_{12}$  is related to temperature as

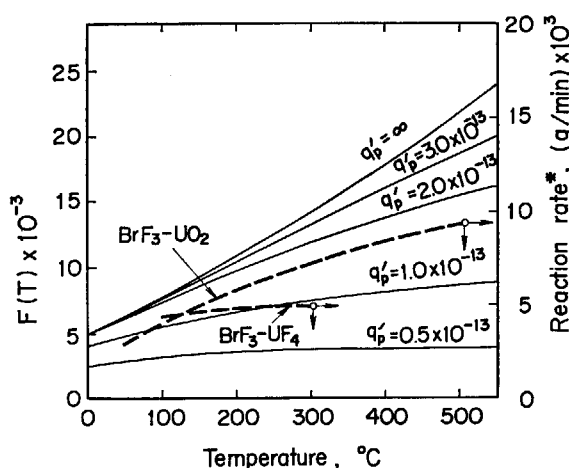


Fig. 9 Comparison of the temperature-dependence of the  $F(T)$  function for  $q_p' \geq 0.5 \times 10^{-13}$  erg with those of the rates of BrF<sub>3</sub>-UO<sub>2</sub> and BrF<sub>3</sub>-UF<sub>4</sub> reaction.

\* The average rate of weight loss in Fig. 6 (b) is used here as the rate of BrF<sub>3</sub>-UF<sub>4</sub> reaction, and  $K$  in Fig. 7 is used as that of BrF<sub>3</sub>-UO<sub>2</sub> reaction.

$T^{3/2}$ .<sup>29)</sup> Therefore, the temperature-function of the reaction rate,  $F(T)$ , is expressed as

$$F(T) = T^{3/2} f(q_p', T). \quad (6)$$

Since  $f(q_p', T)$  decreases with increasing temperature,  $F(T)$  increases slightly or decreases, depending upon the value of  $q_p'$ , when temperature increases.

Some  $F(T)$  curves for  $q_p' \geq 0.5 \times 10^{-13}$  erg are shown in Fig. 9, together with temperature-dependence curves of the rates of  $\text{BrF}_3\text{-UO}_2$  and  $\text{BrF}_3\text{-UF}_4$  reaction. The rate of  $\text{BrF}_3\text{-UO}_2$  reaction in this figure is the  $K$  (see Fig. 7), and that of  $\text{BrF}_3\text{-UF}_4$  reaction is represented by the average rate of weight loss shown in Fig. 6 (b), because the  $K$  for the  $\text{BrF}_3\text{-UF}_4$  reaction involves the rate of the concurrent reaction (see Fig. 6 (a)). The shape of the  $F(T)$  curve for  $q_p' = 2.0 \times 10^{-13}$  erg is similar to the temperature-dependence curve for the  $\text{BrF}_3\text{-UO}_2$  reaction. The values of  $f(q_p', T)$  for  $q_p' = 2.0 \times 10^{-13}$  erg are 0.94 at 400°K, 0.82 at 600°K and 0.70 at 800°K. More detailed expression for the temperature-dependence of  $\text{BrF}_3$  reaction rate remains undetermined.

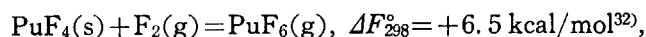
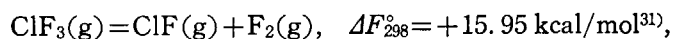
### 3. 2 Chlorine Trifluoride

Reactivity of  $\text{ClF}_3$  with uranium compounds is similar to that of  $\text{BrF}_3$ . Labaton studied the reaction of  $\text{ClF}_3$  with  $\text{UF}_4$  in the temperature range of 17° to 193°C<sup>30)</sup>. This reaction proceeds even at 17°C and its rate shows an anomalous temperature-dependence—the rate passes through a maximum at 105°C, falls to minimum at 148°C and then rises again. The apparent activation energy was 5.6 kcal/mol in the range 15°~58°C and 3.4 kcal/mol in the range 156°~194°C. These values and the shape of the temperature-dependence curve are similar to those of  $\text{BrF}_3\text{-UF}_4$  reaction (see Fig. 6 (a)). In addition, Schmetz *et al.* reported that  $\text{ClF}_3$  fluorinated  $\text{U}_3\text{O}_8$  and  $\text{UO}_2$  into  $\text{UF}_6$  at temperatures as low as 50°C<sup>3)</sup>.

However, the fluorination method using  $\text{ClF}_3$  has the drawback that, from temperatures of 250°C, a part of plutonium contained in the fuels is volatilized as  $\text{PuF}_6$ , so that it is practically impossible to obtain quantitative separation of the uranium and plutonium. According to Schmetz *et al.*, the rate of  $\text{PuF}_6$  volatilization in  $\text{ClF}_3\text{-PuF}_4$  reaction,  $V$  (mg cm<sup>-2</sup>·h<sup>-1</sup>), is expressed as

$$\log V = -(3846/T) + 6.8845, \quad (7)$$

in the temperature range of 200° to 375°C<sup>3)</sup>. This volatilization of  $\text{PuF}_6$  occurs because  $\text{ClF}_3$  partly dissociates into  $\text{ClF}$  and  $\text{F}_2$  with increasing temperature and the latter fluorinates  $\text{PuF}_4$  into  $\text{PuF}_6$ :



where  $\Delta F_{298}^\circ$  denotes the free energy increase by each step at 298°K. The addition of  $\text{Cl}_2$  or  $\text{ClF}$  to  $\text{ClF}_3$  is effective to inhibit formation of free fluorine: the former reacts with fluorine to produce  $\text{ClF}$  and the latter shifts the equilibrium of  $\text{ClF}_3$  dissociation towards the formation of  $\text{ClF}_3$ . On the other hand, no experimental data have been presented as to the dissociation of  $\text{BrF}_3$  below 500°C.

Particular attention should be given to disposal operation of  $\text{ClF}_3$ , because this material may produce explosive chlorine oxides through its reaction with water, moist surfaces or reactive oxides<sup>33)</sup>. (The presence of fluorine makes it possible to destroy the dangerous  $\text{Cl}_2\text{O}$  and  $\text{ClO}_2$  compounds<sup>34)</sup>.) On the contrary, the instability of bromine oxides at temperatures above

0°C makes their presence highly improbable<sup>35</sup>).

### 3.3 Chlorine Monofluoride

ClF can be regarded as a fluorinating agent selective for uranium : it does not fluorinate PuF<sub>4</sub> into PuF<sub>6</sub> even at 550°C<sup>3</sup>). However, owing to the low reactivity, its use would require an operation temperature far higher than that required for the fluorination by ClF<sub>3</sub> or BrF<sub>3</sub>. The use of ClF is thus very limited from the viewpoint of the corrosion of the apparatus at the higher operation temperature.

On the other hand, the use of ClF has the merit that the surplus ClF can be easily recycled to continue its reaction with nuclear fuels, because it does not condense with UF<sub>6</sub> in the process<sup>36</sup>).

### 3.4 Bromine Pentafluoride

BrF<sub>5</sub> does not fluorinate plutonium into PuF<sub>6</sub> at least up to 400°C<sup>37</sup>) and is therefore used for the selective fluorination of uranium in nuclear fuels (see Fig. 1). Fluorination of uranium compounds by BrF<sub>5</sub> proceeds at lower temperatures than that by F<sub>2</sub>, however, at higher temperatures than those by ClF<sub>3</sub> and by BrF<sub>3</sub>. Jarry and Steindler studied the fluorination of uranium compounds by BrF<sub>5</sub> in the temperature range 175°~300°C<sup>12</sup>). They represented the temperature and BrF<sub>5</sub> partial pressure dependence of these reactions in the form of

$$\log k' = A \log P_{\text{BrF}_5} (\text{torr}) - B/T(^{\circ}\text{K}) + C, \quad (8)$$

where  $k'$  is the rate constant in eq. (1). The values of A, B and C for each reaction are given in TABLE 2.

TABLE 2 Values of A, B and C in eq. (8)<sup>12</sup>)

Sample	A	B	C
UF <sub>4</sub>	0.38	3690	4.286
UO <sub>2</sub> F <sub>2</sub>	0.71	1810	0
U <sub>3</sub> O <sub>8</sub>	0.90	2000	-0.220
UO <sub>2</sub>	0.84	1630	-0.270
UO <sub>3</sub>	1.05	1680	-0.767

TABLE 3 Comparison of the fluorination by BrF<sub>5</sub> with that by BrF<sub>3</sub><sup>12</sup>)

Sample	Reaction temperature (°C)	BrF <sub>5</sub> reaction		BrF <sub>3</sub> reaction	
		BrF <sub>5</sub> partial pressure (torr)	Rate const. $k'$ (min <sup>-1</sup> )	BrF <sub>3</sub> partial pressure (torr)	Rate const. $k'$ (min <sup>-1</sup> )
UF <sub>4</sub>	200	198	0.00235	105	0.0145
U <sub>3</sub> O <sub>8</sub>	200	18	0.0006	18	0.025

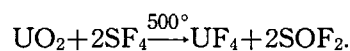
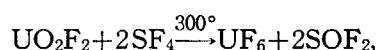
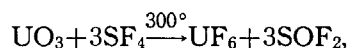
TABLE 3 compares the reactivity of BrF<sub>5</sub> with that of BrF<sub>3</sub>. Although the BrF<sub>3</sub> partial pressure in the fluorination of UF<sub>4</sub> is nearly half as high as that of BrF<sub>5</sub>, the rate constant of the former reaction is about 50 times as great as that of the latter. Also in the case of U<sub>3</sub>O<sub>8</sub>, the fluorination by BrF<sub>3</sub> proceeds much more rapidly than the other. These experimental data

show that  $\text{BrF}_3$  is more reactive than  $\text{BrF}_5$ .

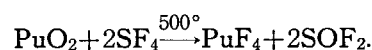
However, the handling of  $\text{BrF}_5$  is easier than that of  $\text{BrF}_3$  because of the higher volatility of  $\text{BrF}_5$ .

### 3. 5 Sulfur Tetrafluoride

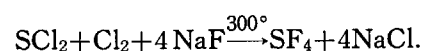
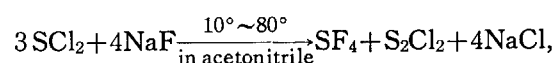
Johnson *et al.* studied the reaction of  $\text{SF}_4$  with various fluorides, oxyfluorides and oxides of uranium and plutonium<sup>10),38)</sup>. Its reactions with some uranium compounds are expressed as follows :



In all of these reactions, the only gaseous sulfur product is thionyl fluoride. Since  $\text{SF}_4$  does not act as an oxidizing agent,  $\text{UF}_6$  is formed only when hexavalent uranium compounds are used as the starting material. This is the most important difference between the reactivities of  $\text{SF}_4$  and  $\text{BrF}_3$ . The reaction-temperature of  $\text{SF}_4$  is considerably higher than that of  $\text{BrF}_3$  and close to that of  $\text{F}_2$ . Reactions of  $\text{SF}_4$  with plutonium are similar to those of  $\text{BrF}_3$ , for  $\text{PuF}_6$  is not formed.<sup>38)</sup>



Important characteristic of  $\text{SF}_4$  lies in that it is a fluorinating agent that does not need fluorine for its preparation.<sup>39)</sup>



Some works on the fluorination of uranium compounds are listed in Appendix.

#### 4. Improvement of the Fluorination Method Using Gaseous $\text{BrF}_3$

The foregoing results show that the fluorination by gaseous  $\text{BrF}_3$  proceeds under milder experimental conditions than that by  $\text{F}_2$  (see 3. 1). However, the use of  $\text{BrF}_3$  brings about the following drawbacks: it requires an additional device to remove considerable amounts of bromine produced as a reaction byproduct, and heating of the connecting line is necessary to prevent condensation of  $\text{BrF}_3$  therein. In order to reduce these drawbacks, the present author has developed a new fluorination method using a  $\text{Br}_2\text{-F}_2$  mixture. This improved method is described here as applied to fluorination of  $\text{UO}_2^{40)}$ .

##### 4. 1 Effect of Bromine

Fig. 10 shows the experimental apparatus used.  $\text{F}_2$  and  $\text{Br}_2$ , diluted with  $\text{N}_2$ , are introduced directly into the reaction tube through the separate inlets. The proceeding of fluorination was traced continuously with a thermobalance, or by direct weighing of the reaction residue at regular time intervals when a horizontal reaction tube was used. The horizontal reaction tube, 100 cm long, consists of four flanged Monel pipes (2.4 cm i. d.) so that an infrared absorption cell can be inserted between the flanges, as Fig. 10 (b) shows. The fluorine-to-bromine ratio in the reaction tube is varied by controlling the flow rates of  $\text{F}_2$  and the two nitrogen flows.

Fig. 11 shows the change in weight of the sample with time at  $200^\circ\text{C}$ . In the case of  $\text{F}_2$  alone, unaccompanied by  $\text{Br}_2$ , no weight decrease is observed, no  $\text{UF}_6$  being formed in this case (the dotted line A in the figure). Upon addition of  $\text{Br}_2$  to the fluorine flow, the weight starts to decrease immediately (the full line in the figure). Turning off the bromine flow in the midst of reaction, e. g. at the point p, stops the fluorination. Thus, it is evident that the addition of bromine induces the fluorination. Infrared analysis confirmed that the main component of the

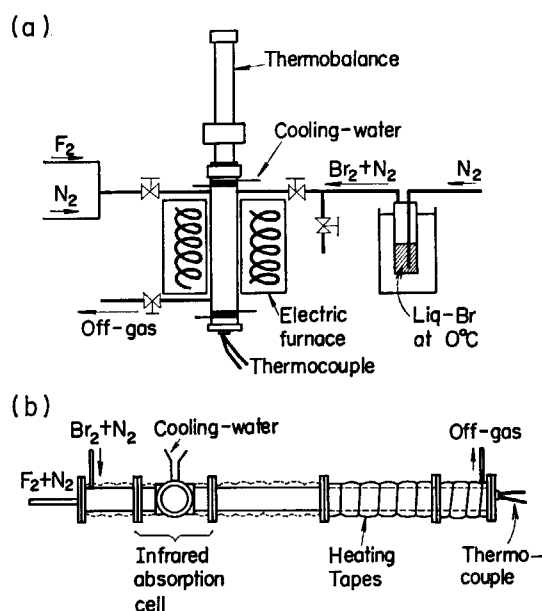


Fig. 10 Apparatus for the fluorination by a fluorine-bromine mixture. (a) Outline of the apparatus including a thermobalance. (b) A horizontal tubular reactor, 100 cm long, including an infrared absorption cell.

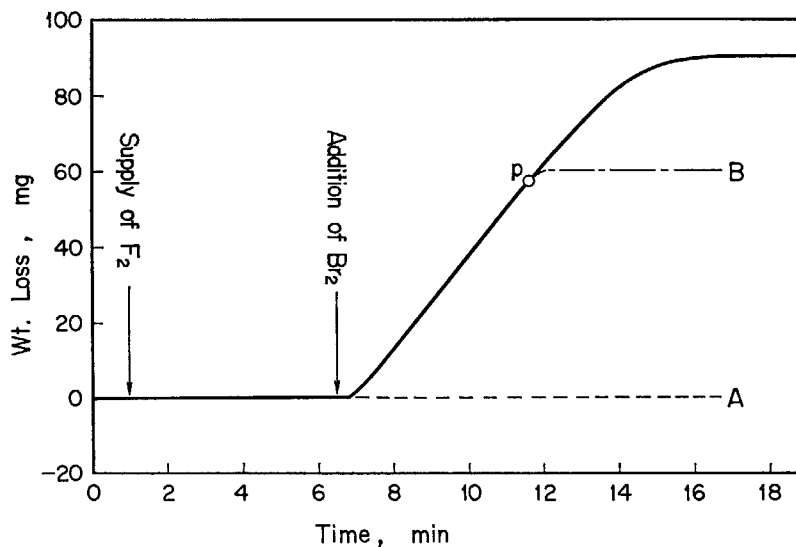


Fig. 11 Effect of  $\text{Br}_2$  on the fluorination of  $\text{UO}_2$  at  $200^\circ\text{C}$ .

Fluorination by  $\text{F}_2$  alone does not occur at this temperature (A). Upon addition of  $\text{Br}_2$  to the  $\text{F}_2$  flow, the weight begins to decrease immediately due to volatilization of  $\text{UF}_6$  (the full line). Turning off the  $\text{Br}_2$  at the point P stops the fluorination (B).

Initial weight of  $\text{UO}_2 = 91$  mg,  $\text{F}_2$  partial pressure\* = 118 mmHg,  $\text{Br}_2$  partial pressure\* = 14 mmHg, and linear gas velocity = 1 cm/sec.

\* The presumed partial pressure which would be exerted in the reaction tube if no interaction took place between  $\text{F}_2$  and  $\text{Br}_2$ .

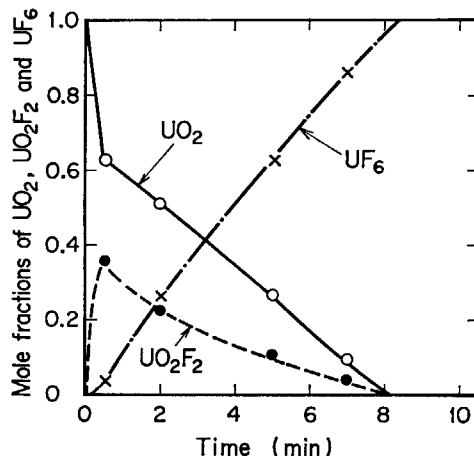
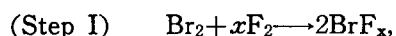


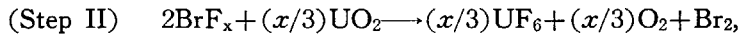
Fig. 12 Change of the mole fractions of  $\text{UO}_2$ ,  $\text{UO}_2\text{F}_2$  and  $\text{UF}_6$  during the reaction at  $210^\circ\text{C}$ .

Initial weight of  $\text{UO}_2 = 100$  mg,  $P_{\text{F}_2}^* = 118$  mmHg,  $P_{\text{Br}_2}^* = 14$  mmHg, and linear gas velocity = 1.7 cm/sec. The mixed gas takes 3 sec to reach the sample. ( $P_{\text{F}_2}^*$  and  $P_{\text{Br}_2}^*$  are the presumed partial pressures of  $\text{F}_2$  and  $\text{Br}_2$ , respectively, which would be exerted in the reaction tube if no interaction took place between them.)

reactant gas was  $\text{BrF}_3$ . Hence, the fluorination by a  $\text{Br}_2$ - $\text{F}_2$  mixture can be divided into two steps—rapid reaction of  $\text{Br}_2$  with  $\text{F}_2$  to produce bromine fluorides, and their reaction with the solid:<sup>40)</sup>







where  $x=3$  or  $5$ .

Chemical analysis of the solid phase shows that its bromine content is negligible, i. e. less than  $10 \mu\text{g}$ , and  $\text{UO}_2\text{F}_2$  is formed as an intermediate. Fig. 12 shows the change in mole fraction of  $\text{UO}_2$ ,  $\text{UO}_2\text{F}_2$  and  $\text{UF}_6$  during the reaction carried out at  $210^\circ\text{C}$ .

#### 4. 2 Factors Influencing the Reaction Rate

Fig. 13 shows the influence of the fluorine-to-bromine ratio on the reaction rate. The symbols  $P_{\text{F}_2}^*$  and  $P_{\text{Br}_2}^*$  in the figure represent the presumed partial pressure of  $\text{F}_2$  and  $\text{Br}_2$ , respectively, which would prevail in the reaction tube if there were no interaction between them. Under a constant  $P_{\text{Br}_2}^*$  ( $=14 \text{ mmHg}$ ), the reaction rate  $K$  increases markedly with  $P_{\text{F}_2}^*$ . On the other hand, when  $P_{\text{Br}_2}^*$  is varied under a constant  $P_{\text{F}_2}^*$  ( $=118 \text{ mmHg}$ ), the reaction rate acquires its greatest value at a fluorine-to-bromine ratio around 17. The rate declines with either the increase or decrease of bromine concentration from this maximum point. This is because the excess fluorine contributes to the reaction rate much more significantly than the concentration of bromine fluorides themselves. (The increase of  $P_{\text{Br}_2}^*$  brings about that of the concentration of bromine fluorides and, conversely, the decrease of excess fluorine.) These findings would indicate that the addition of bromine corresponding to about 6% of the fluorine concentration should suffice to enhance the fluorination.

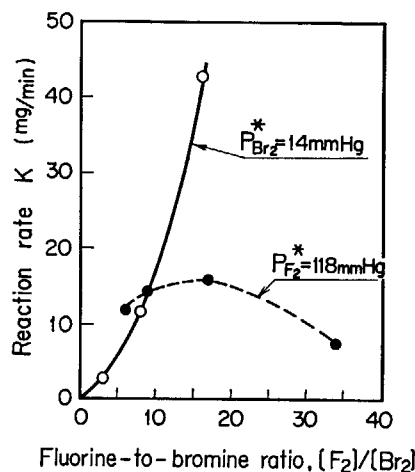


Fig. 13 Influence of fluorine-to-bromine ratio on the reaction rate.

Initial weight of  $\text{UO}_2$  90mg,  $P_{\text{F}_2}^* = 118 \text{ mmHg}$ ,  $P_{\text{Br}_2}^* = 14 \text{ mmHg}$ , and linear gas velocity = 1 cm/sec.

\* Presumed partial pressure which would be exerted if no interaction took place between  $\text{F}_2$  and  $\text{Br}_2$  in the reaction tube.

Fig. 14 shows the temperature-dependence of the reaction rate in the range of  $100^\circ$  to  $500^\circ\text{C}$ . The reaction proceeds even at  $100^\circ\text{C}$ , and its rate increases gradually with temperature up to  $400^\circ\text{C}$ ; beyond which point, the further increase of temperature no longer accelerates the reaction.

The horizontal reaction tube was used to examine the dependence of the reaction rate on the time taken by the mixed gas to reach the solid sample. As a result, it was found that

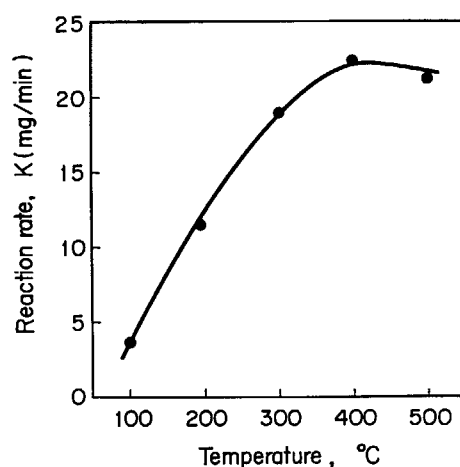


Fig. 14 Temperature-dependence of the reaction rate  $K$ . Initial weight of  $\text{UO}_2$ : 89 mg.  $\text{F}_2$  partial pressure\*: 118 mmHg.  $\text{Br}_2$  partial pressure\*: 14 mmHg. Carrier gas:  $\text{N}_2$ . Linear gas velocity: 1 cm/sec.

\* The presumed partial pressure which would be exerted if no interaction took place between  $\text{F}_2$  and  $\text{Br}_2$  in the reactor.

greater reaction rates were obtained when the mixed gas was held for 3~20 sec before arriving at the sample. Further increase of the time causes a decrease of the reaction rate, because the  $\text{BrF}_3$  produced is subsequently fluorinated into less reactive  $\text{BrF}_5$  as the time elapses<sup>40</sup>.

#### 4.3 Comparison of the Present Fluorination with That by Gaseous $\text{BrF}_3$

TABLE 4 compares the rate of the present reaction with that by gaseous  $\text{BrF}_3$ . The symbol  $P_{\text{BrF}_x}^*$  means the partial pressure of bromine fluorides formed in the reaction tube by direct combination of the  $\text{F}_2$  and the  $\text{Br}_2$  added. While the  $P_{\text{BrF}_x}^*$  is indicated to be almost equal to the  $P_{\text{BrF}_3}$  ( $\text{BrF}_3$  partial pressure in the  $\text{UO}_2$ - $\text{BrF}_3$  reaction), the reaction by a  $\text{Br}_2$ - $\text{F}_2$  mixture proceeds much more rapidly than the  $\text{UO}_2$ - $\text{BrF}_3$  reaction; the reaction rate  $K$  is 17.1 mg/min for the former and only 2.7 mg/min for the latter reaction. The resulting actual effect of bromine hence becomes much greater than would result from  $P_{\text{BrF}_x}^*$ . This indicates that a part of the bromine produced in the "Step II" takes part again in the fluorination of the solid through its rapid reaction with excess fluorine: bromine acts as if it were a catalyst of fluorination.

TABLE 4 Comparison of the fluorination by a  $\text{Br}_2$ - $\text{F}_2$  mixture with that by  $\text{BrF}_3$

Fluorinating agent	Partial pressure of bromine fluoride (mmHg)	Wt. of sample $\text{UO}_2$ (mg)	Temperature (°C)	Reaction rate, $K$ (mg/min)
$\text{BrF}_3$	$P_{\text{BrF}_3} = 15$	81.5	200	2.7
$\text{Br}_2$ - $\text{F}_2$ mixture	$P_{\text{BrF}_x}^* = 14$ $\left\{ \begin{array}{l} P_{\text{F}_2}^* = 118 \\ P_{\text{Br}_2}^* = 7 \end{array} \right.$	91.5	200	17.1

Linear gas velocity 1 cm/sec. Carrier gas  $\text{N}_2$ .  $P_{\text{BrF}_x}^*$  is the partial pressure of bromine fluorides produced by direct combination of  $\text{F}_2$  and  $\text{Br}_2$  in the reaction tube.  $P_{\text{F}_2}^*$  and  $P_{\text{Br}_2}^*$  are the presumed partial pressures of  $\text{F}_2$  and  $\text{Br}_2$ , respectively, which would be exerted if no interaction took place between them in the reaction tube.

#### 4. 4 Comparison of the Present Method with Those Using F<sub>2</sub>-halogen Fluoride Mixtures

Holmes *et al.* have reported<sup>41)</sup> that UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> can be fluorinated to UF<sub>6</sub> by the action of F<sub>2</sub> with catalytic amounts of halogen fluoride at temperatures of about 200°C. The halogen fluoride used is BrF<sub>5</sub>, BrF<sub>3</sub>, ClF<sub>3</sub> or IF<sub>7</sub>, and its concentration is less than 15 volume percent in relation to fluorine concentration. Similarly, Pierni *et al.* have proposed a fluorination method using the mixture of F<sub>2</sub> and ClF<sub>3</sub>.<sup>34)</sup>

These methods are essentially the same as that using a Br<sub>2</sub>-F<sub>2</sub> mixture, because chlorine or iodine of the halogen fluoride added acts as if it were a catalyst of the fluorination. However, no use of toxic and corrosive halogen fluorides makes the present method more favorable from a technical point of view.

## 5. Significance of the Present Study

The present study is the first attempt to use gaseous  $\text{BrF}_3$  as a fluorinating agent for nuclear fuels. It revealed kinetics and mechanism of the reactions in some degree and also the differences in reactivity between  $\text{BrF}_3$  and some other fluorinating agents. Though thermodynamically more stable than  $\text{F}_2$ ,  $\text{BrF}_3$  was found to have higher reactivity with uranium compounds at relatively low temperatures. The fluorination could be carried out at temperatures as low as  $100^\circ\sim 200^\circ\text{C}$  by using gaseous  $\text{BrF}_3$ . A low concentration of this reactant gas was sufficient to give moderate rate of the fluorination. These findings indicate that the polarity of the reactant gas plays an important role in the fluorination; this may be interesting in chemistry. On the other hand, low fluorination temperature is technically favorable because it makes the operation easier and also it might increase the Pu recovery in the process. The usage of gaseous  $\text{BrF}_3$  has however the following drawbacks in the fluoride-volatility process: (i) a facility for disposing of the bromine (byproduct) is necessary; (ii) the connecting lines of the apparatus must be warmed to prevent condensation of the  $\text{BrF}_3$ ; and (iii) heating of the very corrosive liquid is necessary to obtain high concentration of the reactant gas.

Use of the bromine-fluorine mixture, instead of gaseous  $\text{BrF}_3$ , eliminates significantly the difficulties indicated, because the amount of bromine added to the fluorine flow is very small. It is concluded that the fluorination by a  $\text{Br}_2\text{-F}_2$  mixture is technically advantageous over that by gaseous  $\text{BrF}_3$ . It is desired to develop a fluorinating reactor in which a small amount of  $\text{Br}_2$  is recycled and made to act as the catalyst in fluorination. When the  $\text{Br}_2\text{-F}_2$  mixture is applied practically in reprocessing of nuclear fuels, the fluorination will be carried out in two steps: (i) the first fluorination by a  $\text{Br}_2\text{-F}_2$  mixture at  $200^\circ\sim 300^\circ\text{C}$  for volatilizing U and some fission products (Ru, Nb, I, etc.) as  $\text{UF}_6$  and their volatile fluorides, respectively, and (ii) the second fluorination by  $\text{F}_2$  alone at temperatures over  $350^\circ\text{C}$  for volatilizing Pu as  $\text{PuF}_6$ . In the future, it must be clarified how the use of a  $\text{Br}_2\text{-F}_2$  mixture influences the recovery of Pu and its contamination by Ru. This is because both are the most important aspects to be solved in the development of the fluoride-volatility process.

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## Appendix: Some Kinetic Studies on the Fluorination of Uranium Compounds

Uranium compound	Fluorinating agent and its partial pressure (mmHg)	Temperature range (°C)	Apparent activation energy (kcal/mol)	Workers	No. of the reference
UO <sub>2</sub> (powder)	F <sub>2</sub> , 85~340	300~430	29.4, 33.1	Yahata, Iwasaki	11
" "	" 152	350~500	26.0	Sakurai	14
" "	BrF <sub>3</sub> , 15	40~500	1.0	"	"
" "	BrF <sub>5</sub> , 74~369	225~375	7.5	Jarry, Steindler	12
" "	ClF <sub>3</sub> , 76~380	71~165	11.1	Schmetz <i>et al.</i>	3
U <sub>3</sub> O <sub>8</sub> (powder)	F <sub>2</sub> , 80~360	350~440	21.3	Iwasaki	11
" "	BrF <sub>3</sub> , 7~23	50~300	0.9(50~200°C)	Iwasaki, Sakurai	19
" "	BrF <sub>5</sub> , 89~369	225~350	9.2	Jarry, Steindler	12
" "	ClF <sub>3</sub> , 76	50~300	1.6	Schmetz <i>et al.</i>	3
UO <sub>3</sub> (powder)	F <sub>2</sub> , 80~360	350~440	22.0	Iwasaki	11
" "	BrF <sub>5</sub> , 90~227	225~300	7.7	Jarry, Steindler	12
" "	SF <sub>4</sub> , 152~760	255~370	6.0	Johnson, Fischer	10
UO <sub>2</sub> F <sub>2</sub> (powder)	BrF <sub>5</sub> , 130~370	175~300	8.3	Jarry, Steindler	12
" "	SF <sub>4</sub> , 152~760	255~370	32.0	Johnson, Fischer	10
UF <sub>4</sub> (powder)	F <sub>2</sub> , 70~760	265~348	15.5, 19.1, 19.9	Labaton, Johnson	9
" "	BrF <sub>3</sub> , 6~45	30~300	1.0(90~190°C)	Sakurai, Iwasaki	13
" "	BrF <sub>5</sub> , 130~370	175~300	16.9	Jarry, Steindler	12
" "	ClF <sub>3</sub> , 39~74	17~193	5.6( 17~ 58°C) 3.4(156~194°C)	Labaton	30
UC (powder)	F <sub>2</sub> , 34~135	240~300	22.4	Iwasaki, Sakurai. Ishikawa	*
UC <sub>2</sub> (powder)	F <sub>2</sub> , 38~114	220~300	19.5	Iwasaki, Sakurai. Ishikawa	**
UO <sub>2</sub> (pellet)	F <sub>2</sub> , 76~304	300~540	14 (360~400°C) 23 (460~540°C)	Iwasaki	***
" "	BrF <sub>3</sub> , 10~33	100~250	3.9	Iwasaki, Sakurai	****
U <sub>3</sub> O <sub>8</sub> (pellet)	" "	" "	0.95	Iwasaki, Sakurai	****

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