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THE REACTION BETWEEN DISSOCIATED FLUORINE AND OXIDES OF URANIUM

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ABSTRACT

Fluorine at 1-5 torr pressure was dissociated with a microwave discharge and passed over samples of UO_2 or U_3O_8. The only reaction products were UF_6 and O_2. The reaction rates were independent of particle size and sample depth, but depended upon the geometric surface of the sample. Kinetic studies were interpreted to show that F-atoms react immediately upon contact with the surface, and that both F_2-molecules and F-atoms react with the sample. When the ratio, F/F_2, is relatively low, the partial pressure of F-atoms is rate determining. When the ratio, F/F_2, is relatively high the rate of diffusion of total fluorine ($F+F_2$) to the surface is rate determining.

INTRODUCTION

The great reactivity of fluorine combined with the high volatility of many fluorine compounds make elemental fluorine an attractive reagent for use in separating and purifying certain elements. Although molecular fluorine has frequently been used for this purpose, the technique has seldom been extended to the use of F-atoms. F-atoms have the advantage of being one of the most potent oxidizing agents known; in some cases its reactivity exceeds that of molecular fluorine by an order of magnitude [1].

There have been a substantial number of studies in which molecular fluorine was used to fluorinate uranium oxides or uranium oxide fuel elements for the Fluoride Volatility Process [2,3,4]. The purpose of this work was to investigate the merits of converting UO_2 and U_3O_8 to UF_6 by the use of atomic-F at ambient room temperature.

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F-atoms have been generated from F_2 by various techniques, including thermal dissociation [5], electrical discharge [6], UHF [7,8] and microwave [1,9] discharges, electron beam [10], and photochemical dissociation [11]. In this work the microwave technique was selected for its simplicity and freedom from contamination.

EXPERIMENTAL

Fluorination studies were carried out in a cell machined from a 10 cm aluminum cube as shown in Fig. 1. Connections were made with stainless steel tubing equipped with Cajon fittings or Viton O-ring seals. Samples were held in a shallow 3.3 cm i.d. Teflon dish or a 7 cm deep conical Teflon cup with a 1.8 cm i.d. flat bottom shown in Fig. 2a. The deep cup was used at high flow velocities to prevent loss of sample. The fluorine was dissociated by passing the gases through a 1.27 cm o.d. alumina or sapphire tube equipped with an Evanson microwave discharge cavity operated at 2450 MHz and energized by a Kiva (Model MPF-4M, 100 W) power supply. The exit end of the alumina or sapphire tube was directly above the solid sample. The gas flow passed from the cell into a -78°C trap and on to the vacuum pump. Cell pressures were measured with a manometer (MKS Baratron) and regulated in the 1 to 5 torr range by throttling the vacuum pump. Gas temperatures in the vicinity of the sample were measured with a thermocouple during preliminary experiments to be approximately 30 to 60°C. Flow rates were measured with a mass flowmeter (Hastings 0-50 Std. cm^3/min).

Fluorine (Matheson, 98% pure) was passed through a sodium bifluoride trap and a -78°C trap to remove HF impurity. The UO_2 (99.99% pure) was synthesized at this laboratory, and particle sizes were characterized.

U_3O_8 of small particle size was prepared by flowing O_2 for ~10 minutes over UO_2 heated to 400-500°C. During this exothermic reaction the temperature would increase significantly. The resulting fine powder of U_3O_8 had a density that was only 23% of crystal density. The increase in mass closely corresponded to the stoichiometric oxygen uptake. The particle size range was 5 to 50 µm.

A sample of UO_2 with a total of approximately 2% of a selected group of metal oxide impurities was prepared by sintering the oxide mixture in a closed molybdenum tube at 1650°C. The 98% pure UO_2 was pulverized and used for estimating the effects of nonvolatile impurities upon fluorination rates of UO_2. The UF_6 product was collected in a -78°C trap and quantitatively

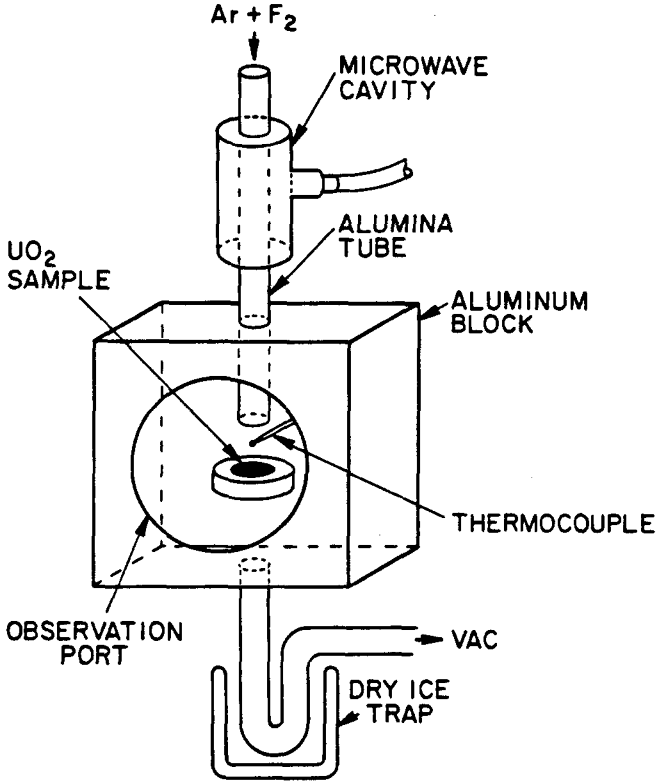

Fig. 1. Schematic of fluorination cell. The 5.7 cm diameter observation port was covered by a sapphire window. The thermocouple was removed during kinetics experiments.

determined from pressure after expanding it into a calibrated and well passivated volume at ambient room temperature. This technique was validated by collecting identical samples in the trap in the presence of excess frozen H_2O, allowing the UF_6 to completely hydrolyze upon warming and weighing the dried UO_2F_2 product [12].

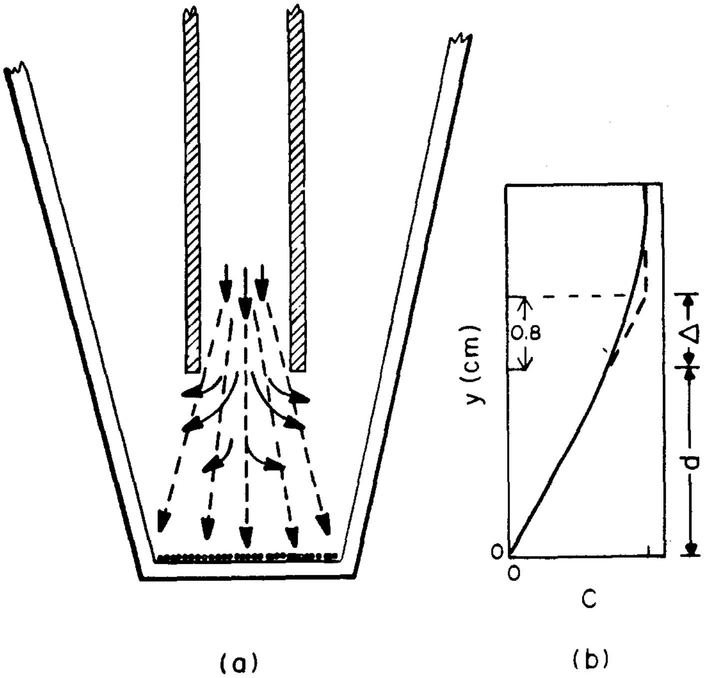

Fig. 2.(a) Deep Teflon sample cup showing lines of flow (solid arrows) and concentration gradient (dashed arrows).(b) The variation of concentration of fluorine atoms, C, with distance, d. Extrapolation to limiting value of C falls 0.8 cm into the tube.

The duration of an experiment was typically 15 minutes, during which time only part of the uranium oxide was allowed to react so that the geometric surface area of the sample was maintained constant. Mass spectrometric analysis of the gaseous products passing through the -78°C trap indicated the presence of N_2, O_2, CO_2 and traces of BF_3 and SiF_4. No OF_2 was found. The N_2 and CO_2 levels correspond to impurity levels in the F_2, and the O_2 level is consistent with products derived from the UO_2 and from impurities in the F_2. The yield of UF_6 calculated from PVT analysis usually agreed with mass loss of the uranium oxide sample within ±3%. Average reaction rates were calculated from UF_6 yields.

When UO_2 was fluorinated the color of the surface changed from dark brown to yellow-red, which could be UOF_4. The coating was too thin to give an identifiable X-ray diffraction pattern.

RESULTS AND DISCUSSION

The reaction product was identified by the fact that UF_6 is the only volatile product of uranium that could be formed. Material balance gave approximately 100% recovery of uranium. Since O_2 was the only oxygen containing product detected, the stoichiometries of the fluorination reactions are given by:

$$3F_2 + UO_2 \longrightarrow O_2 + UF_6 \tag{1}$$

$$3F_2 + \frac{1}{3} U_3O_8 \longrightarrow \frac{4}{3} O_2 + UF_6 \tag{2}$$

During preliminary experiments it was found that at certain flow rates and pressures the conversion of F_2 to UF_6 increased with increasing microwave power at relatively low microwave powers, but approached a limiting threshold at relatively high microwave powers. The threshold appears to result from microwave power saturation associated with a maximum degree of dissociation of F_2. Previous work [13] showed that when the microwave power was sufficiently high the dissociation of F_2 varied from approximately 100% at relatively low pressures and/or low flow rates to 60-70% at relatively high pressures and/or high flow rates.

All experiments were done with approximately 100 W of microwave power. This power level was typically 30-fold greater than the power required to dissociate 100% of the F_2, at the flow rates used. Therefore all experiments were made under conditions of high excess microwave power and the degree of dissociation of F_2 in the region of the microwave cavity was 60-100%.

Changing the fraction of carrier gas while keeping the pressure constant had very little effect upon rates of fluorination, i.e., when the Ar fraction was decreased two fold the rate of fluorination of U_3O_8 increased by only ~3%.

Vibration of pure U_3O_8 samples via a piston and bellows beneath the sample dish, causing the particles to move and expose new surface, had no detectable effect upon fluorination rates.

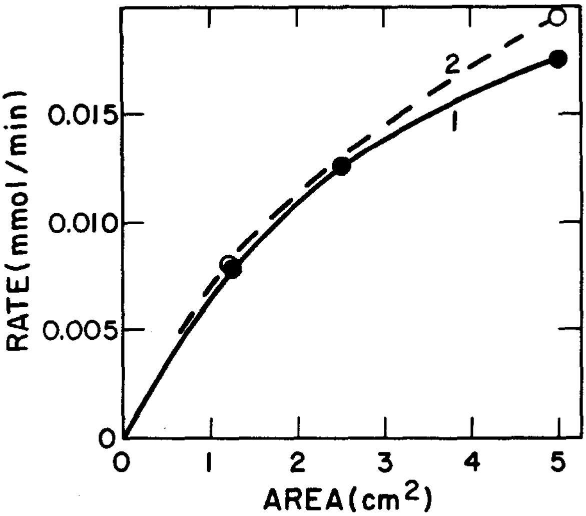

Fig. 3. Average reaction rates of UF_6 formation as a function of geometric sample area of U_3O_8. Line 1 is at 4.5 torr pressure, 2.9 mol% F_2, and 165 std cm^3/min; line 2 at 10.3 torr, 2.4 mol% F_2, and 308 std cm^3/min.

The variation of the rate of fluorination of U_3O_8 with the geometric area of the sample was measured using pie-shaped samples covering fractions of the surface of the sample dish. Results given in Fig. 3 indicate that the reaction rate increases slightly less than linearly with increasing geometric area of the sample. Additional experiments using samples of different depths or partially reacted samples showed that the average rates of fluorination are independent of both sample depth and fractional sample depletion.

In several experiments the samples of UO_2 having ~2% impurities were fluorinated in the same manner as the pure UO_2 or U_3O_8. During the reaction the samples became coated with a fluffy white residue of nonvolatile oxides or fluorides of the impurity metals. The particle size range was either 0.1 - 0.5 cm or 0.5 - 2.0 cm. The average rates of fluorination were approximately half as great as the rates with pure UO_2, and the rates were independent of particle size. Vibration of the samples caused the average rates of fluorination to increase to near that of pure UO_2. Apparently the nonvolatile residue inhibited the reaction by occluding part of the surface, unless it was removed by vibration.

The above experiments indicate that the rate of fluorination depends not upon the particulate surface area of the U_3O_8 but rather upon non-occluded geometric surface area facing the stream of dissociated fluorine. Evidently the dissociated fluorine reacts rapidly at or near the point of first contact with the U_3O_8 surface.

In a series of experiments, the distance between the tube exit and U_3O_8 sample surface was varied between 0.80 and 4.70 cm, and the reaction rate was found to depend strongly upon this distance. At the minimum distance of 0.80 cm and with relatively high volumetric flow rates the conversion of F_2 to UF_6 was as high as 61%. If the tube to sample distance could be made sufficiently close without entraining particles there is no reason not to expect a conversion approaching 100%.

At relatively low flow rates the rate of fluorination decreased with increased residence time, τ, of the dissociated fluorine in the alumina or sapphire tube. Results given in Fig. 4 show the variation of fluorination rate of U_3O_8 with the length of the tube, at a nearly constant pressure of

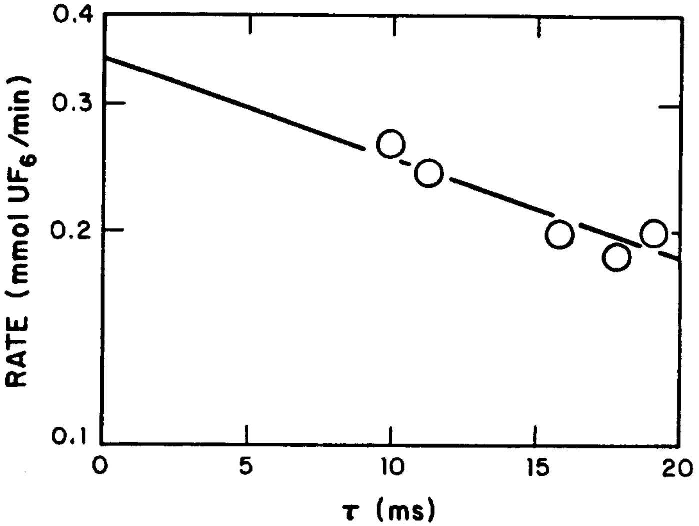

Fig. 4. Log_{10} of rate of fluorination of U_3O_8 vs gas residence time in the 0.95 cm i.d. alumina tube, τ. The location of the microwave cavity was varied between 10.6 and 20 cm from the tube exit, and the tube-to-sample distance was 0.8 cm. The gas, composed of 56.5 mol% F_2 in Ar, was flowed at 2.20 mmol/min and a pressure of 0.82 to 1.00 torr. Slope x 2.303 = 32.2 ± 4.6 s^{-1}.

0.82-1.00 torr. The residence time is given by τ = PV/mRT, where P is total pressure, V is the volume of the alumina or sapphire tube between the microwave cavity and tube exit, m is flow rate in mol/s, R is the gas constant and T = 295 K. The straight line of log RATE vs τ is consistent with a first order reaction rate. The reaction rate constant derived from the slope, 32 s^{-1}, approximately agrees with a previously measured value of 42 s^{-1} for the heterogeneous F-atom recombination rate constant on alumina [13]. The difference between the values is not significant because the heterogeneous recombination rate is highly dependent upon the previous history and degree of passivation of the surface. The rate of fluorination of U_3O_8 decreases with τ in the same way that the partial pressure of F-atoms decreases with τ. Thus the rate of fluorination is directly proportional to the partial pressure of F-atoms emerging from the exit of the alumina tube.

The variation of the reaction rate with residence time was also studied by varying the pressure and keeping the tube length and mass flow rates constant. Results given in Fig. 5 show the variation of log RATE with τ at three different tube-to-sample distances. Here the reaction rates have a first order dependence upon τ at relatively long τ and a zero order dependence at relatively short τ. At long τ the data can be fit to straight lines, the slopes of which are in approximate agreement with the F-atom recombination rate on the alumina tube walls. However, at short τ the fluorination rates reach a threshold value that is independent of τ.

It is unlikely that the abrupt change in order shown here, and also observed in other data, could be explained by any process occurring in the microwave discharge. The fractional dissociation of fluorine in this type of microwave discharge varies only slowly with flow rate and pressure. By comparing the experimental conditions of the data given in Fig. 5 with former measurements of F-atom concentrations made under very similar conditions [14], we estimate that the degree of dissociation of the fluorine is 72 % ± 6%.

If the first-order portions of the curves for tube to sample distances of 0.80 and 4.70 cm in Fig. 5 are extrapolated to τ=0 the intercepts fall above the zero-order intercepts by factors of 2.1 and 2.0 respectively. Therefore in time, τ, the fractional dissociation of the fluorine must decrease from its initial value by approximately a factor of 2, so that the fractional dissociation at residence times corresponding to the breaks in the curves must be approximately 1/2 of 72%.

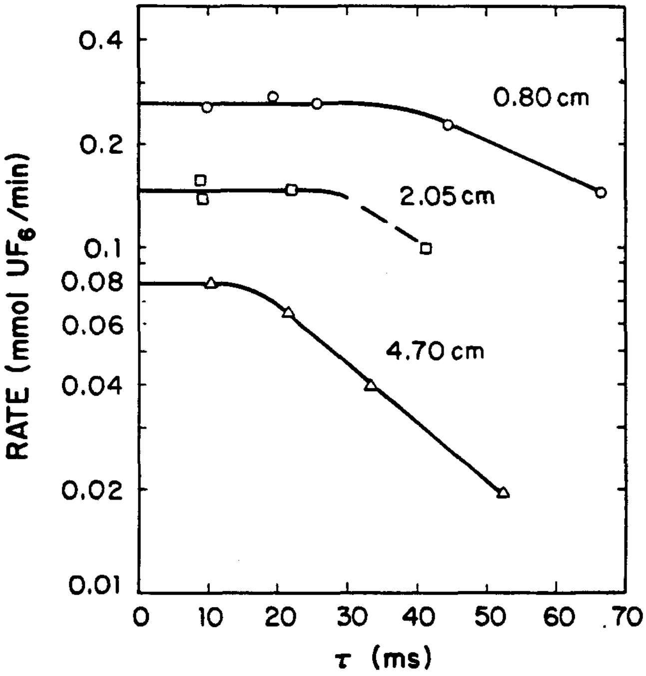

Fig. 5. Log_{10} of rate of fluorination of U_3O_8 vs τ. τ was regulated by adjusting pressure between 0.85 and 6.0 torr. The gas, composed of 56.5% F_2 in Ar flowed at 2.20 m mol/min through a 0.95 cm i.d. alumina tube. The distance from microwave cavity to tube exit was 10.6 cm, and the distance from tube exit to sample is given in the figure. For the 4.70 cm line, slope x 2.303 = 39 s^{-1}.

Suppose that the overall reactions that produce UF_6 were initiated by F-atoms and could be completed with either F-atoms or F_2-molecules, and that the activation energy was supplied by the reaction with the F-atoms. Then the overall reaction rate would depend upon the concentration of F-atoms at relatively low fractional dissociation where F_2-molecules would be in excess, and would depend upon the concentration of F + F_2 at relatively high fractional dissociation where F-atoms would be in excess. The former rate would correspond to the region of first order kinetics and the latter rate to the region of zero order kinetics. The transition between the two regions would occur where the ratio of the two reacting species, F/F_2, was just great enough supply the minimum activation energy.

Assuming this mechanism we may write reactions (1) and (2) in a more general way as follows:

$$x\ F + \left(\frac{6 - x}{2}\right) F_2 + UO_2 \longrightarrow O_2 + UF_6 \qquad (1A)$$

$$x\ F + \left(\frac{6 - x}{2}\right) F_2 + \frac{1}{3} U_3O_8 \longrightarrow \frac{4}{3} O_2 + UF_6 \qquad (2A)$$

where $x_o \leq x \leq 6$ and x_o is the minimum number of F-atoms capable of supplying sufficient activation energy for the overall reaction. In the first order region only x_o F-atoms react per UF_6 and the fluorination rate is limited by the availability of F-atoms at the gas-solid interface. In the zero order region, F-atoms are in excess and the reaction rate is limited only by the total fluorine ($F + F_2$) at the gas-solid interface.

It is instructive to compare the zero order rates with a calculated rate of diffusion of fluorine from the tube exit to the sample surface. One dimensional diffusion is given by Fick's first law as

$$J = -DA \frac{dc}{dy} \cong - DA \frac{c - c_s}{y} \qquad (3)$$

where J is the flux (mol/s) diffusing normal to the surface of area A, c, and c_s are F-atom concentrations (mol/cm^3) at the tube end and at the sample surface respectively, y is the length of diffusion path (cm) and D is the diffusion coefficient (cm^2/s). We assume that the rate of reaction at the surface is fast, relative to the diffusion rate, so that $c_s \cong 0$, and the rate of the fluorination reaction is approximately equal to the flux. It follows from Eq. (3) that the fluorination rate is proportional to 1/y. Figure 6 shows that a plot of the zero order rate versus the reciprocal of the tube to sample distances, 1/d, is a nearly linear relationship. We may conclude that the zero order rates are consistent with a diffusion controlled mechanism. A more linear relationship was obtained by plotting the ordinate vs $1/(d + \Delta)$, where Δ is an empirical constant equal to 0.8 cm. It turns out that Δ approximately equals the inside diameter of the tube, which suggests that the diffusion equation fits if the beginning of the diffusion path is located on the inside walls of the tube approximately one diameter into the tube, as shown in Fig. 2b.

Equation (3) was approximately evaluated from the diffusion coefficient, calculated in the appendix, the surface area, 3.3 cm^2, and $c = 5.34 \times 10^{-8}\ P_F$, where P_F is the partial pressure of F-atoms (torr). The resulting equation is

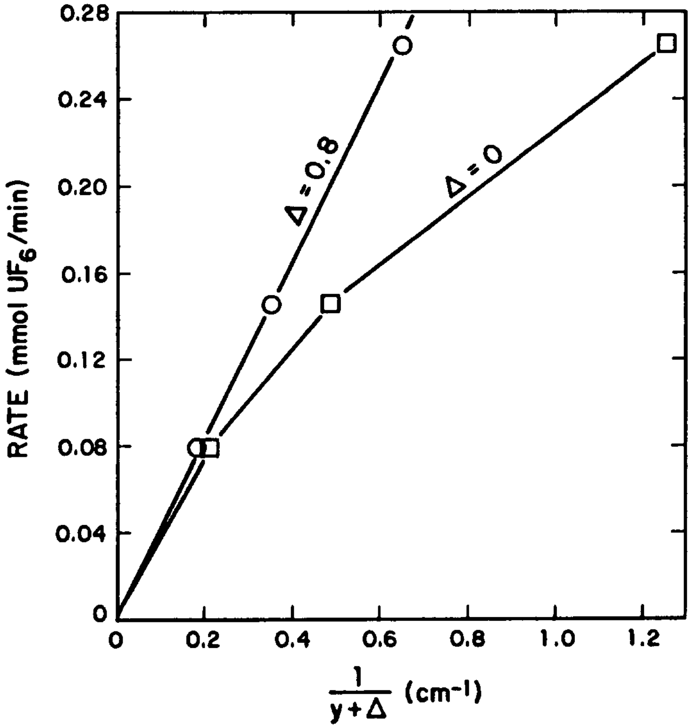

Fig. 6. Variation of rate of fluorination with reciprocal of the tube to sample distance, y, for the data given in Fig. 5. Δ is an empirical constant.

$$J = \frac{3.10}{y}\,\frac{P_F}{P} \quad . \tag{4}$$

The fractional dissociation of fluorine, f, is given by $f = 2P_F/(2P_F + P_{F_2})$, where P_F and P_{F_2} are partial pressures of F and F_2 respectively. It follows that

$$P_F = \frac{P_{F_2}}{2}\,\frac{f}{1 - f} \tag{5}$$

Since we estimated that $f \cong 0.36$ at the breaks in the curves in Fig 5, $P_F \cong 0.28\, P_{F_2}$; and from the pressure of the undissociated gas we know that $P_{F_2}/P \overset{\sim}{<} 0.565$. Substituting these values into Eq. (4) gives $J \overset{\sim}{<} 0.49/y$.

TABLE I

Comparison of diffusion rate and zero-order rate

d (cm)	y (cm)	$\left(\frac{J}{\frac{\text{m mol F}}{\text{min}}}\right)$	$\left(\frac{R^{(1)}}{\frac{\text{m mol } UF_6}{\text{min}}}\right)$	J/R
0.8	1.60	0.307	0.265	1.16
2.05	2.85	0.172	0.145	1.19
4.7	5.5	0.089	0.079	1.13

(1) R = zero order rate from Fig. 5

The calculated values of J and the zero order rates are given in Table I for each value of y. The ratio J/R would in principle give the minimum number of F-atoms that must react per UF_6 molecule formed. However, undetermined errors in the diffusion coefficient and in the model of linear diffusion make it impossible to evaluate the error in this ratio from our data. On the other hand, it is significant that the ratios are in good agreement and their average value is much less than six. In this sense the diffusion calculation supports the hypothesis that both F-atoms and F_2 molecules react at the sample surface.

CONCLUSION

The use of dissociated fluorine is an effective method for quantitatively converting both pure and impure oxides of uranium into the gaseous product, UF_6. This relatively simple technique is potentially useful for separating and purifying uranium and other metals capable of forming volatile fluorides or oxyfluorides. The reaction with both UO_2 and U_3O_8 is fast at ambient room temperature. Rate studies indicate that F-atoms react immediately upon contact with the UO_2 or U_3O_8 surface. When the degree of dissociation of the fluorine reaching the sample surface is relatively high, the rate of fluorination is limited by the concentration of total fluorine ($F + F_2$) at the surface and depends upon the rate diffusion of total fluorine. When the degree of dissociation is relatively low, the rate of fluorination is limited only by the concentration of F-atoms at the surface and depends upon the rate of diffusion of F-atoms to the surface.

SUPPLEMENTARY FINDINGS

The diffusion coefficient, D_{12} for F-atoms in mixture of F,F_2 and Ar may be approximated by using an equation for a binary mixture of F (component 1) in a gas with average properties of Ar and F_2 (component 2) because F_2 and Ar have nearly the same molecular weights. The Stephen-Maxwell theory [15] leads to the expression,

$$D_{12} = \frac{\bar{C}_2\sqrt{\frac{M_1}{M_1 + M_2}} + \bar{C}_1\sqrt{\frac{M_2}{M_1 + M_2}}}{3\,\Pi\,(N_1 + N_2)\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2} \tag{A1}$$

where C_1 and C_2 are mean speeds, N_1 and N_2 are numbers of molecules/cm^3, σ, and σ_2 molecular diameters, and M_1 and M_2 molecular weights. Mean speeds were calculated at 300 K from kinetic theory; molecular diameters were calculated from gas viscosities [16] for Ar and F_2 and from VanderWaals radius for F. The calculated numbers are given in Table II. By this evaluation, Eq. (A1) may be reduced to

$$D_{12} = 392/P \tag{A2}$$

where P is total pressure in torr.

The Reynolds number for flow in the 0.95 cm o.d. alumina tube falls in the range 480 - 2800 at the gas velocities and pressure used, which is low enough that flow may be considered to be essentially laminar. Consequently diffusion equations should apply to conditions both in the tube and in the flowing gas between the tube exit and sample.

TABLE II

Molecular parameters used in calculations, with T = 300 K

	Atom or Molecule			
	F	F_2	A_r	F_2-Ar Avg
M	19	38	40	39
$C(10^4$cm/s)	5.782	4.088	3.985	4.037
$\eta(10^{-4}$poise)	--	2.285	2.259	--
$\sigma(10^{-8}$cm)	2.70	2.910	2.964	2.937

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