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RECYCLE OF UO_2F_2 IN THE FLUOROX PROCESS: REACTION OF UO_2F_2 WITH HYDROGEN

L. M. Ferris
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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

Recycle of UO_2F_2 in the Fluorox Process: Reaction of UO_2F_2 with Hydrogen

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ABSTRACT

The reaction of UO_2F_2 with hydrogen at 700-850°C was briefly investigated since it could constitute a major step in the recycle of UO_2F_2 in the Fluorox process. The reaction in this temperature range proceeds according to the equation $UO_2F_2 + H_2 \longrightarrow UO_2 + 2\ HF$. Rates of the chemical reaction were not obtained, since, with the thermogravimetric technique used, the rate-controlling process was bed diffusion. However, there is no doubt that the rate of chemical rection is sufficiently high for the desired application. No significant amount of UF_4 was formed by the back-reaction, $UO_2 + 4\ HF \longrightarrow UF_4 + 2\ H_2O$.

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1.0 INTRODUCTION

The purpose of this study was to provide the chemical information necessary to determine whether the reaction of UO_2F_2 with hydrogen is feasible as a step in the recycle of UO_2F_2 in the Fluorox process. In the Fluorox process,[1] UF_6 is produced according to the reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$, which necessitates recycle of the UO_2F_2. Two potential recycle methods are available. One of these is a "wet" method involving dissolution of the UO_2F_2, reduction of uranium(VI) to uranium(IV) in aqueous solution, and the subsequent precipitation of UF_4. The Excer process[2] is an example of the "wet" method. In a "dry" method, UO_2 would be produced by reaction of UO_2F_2 with hydrogen, and UF_4 produced by hydrofluorination of the UO_2. Considerable information is available regarding the Excer process and the hydrofluorination of UO_2. However, the reaction of UO_2F_2 with hydrogen has received only brief attention in the past.[3] Kuhlman found the reaction rapid, even at 500°C, but noted the presence of UF_4 in the reaction product. Other workers[4] found the UO_2 produced to be highly reactive.

In the present study, the stoichiometry of the reaction of UO_2F_2 with hydrogen was determined, and an attempt was made to evaluate the kinetics of the reaction.

The authors wish to acknowledge C. D. Scott of the ORNL Chemical Technology Division for his helpful discussions. W. Davis, Jr., also of the Chemical Technology Division, is due special thanks for his guidance in interpreting the rate curves. Chemical and x-ray analyses were provided by the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman of the ORNL Analytical Chemistry Division.

2.0 EXPERIMENTAL

2.1 Reagents

The UO_2F_2 was prepared by reaction of UO_3 with HF at about 300°C. The average water-insoluble content was 7.58%, this being mainly UO_3. Chemical analyses showed: uranium, 76.9%; fluoride, 11.34%; and uranium(IV), 0.001%. The UO_2F_2 content computed from the fluoride analysis was 92.2% which compares favorably with the 92.4% computed from the water insolubles. The UO_2F_2 was somewhat hygroscopic, normally containing 0.7-1.0 wt % H_2O. The water of hydration was readily lost on heating to 250°C.

Electrolytic hydrogen was further purified before use by passage through two De-Oxo units and a charcoal bed held at -196°C.

2.2 Apparatus

All weight-loss data were obtained with the semiautomatic recording thermobalance which has been described in detail elsewhere.[5] The only modification of the equipment was installation of a gas seal to prevent release of hydrogen in the vicinity of the furnace.

2.3 Experimental Technique

In each case the initial weight of the UO_2F_2 sample and the reaction basket was obtained on an analytical balance. The basket containing the sample was transferred to the thermobalance reaction chamber, which was then slowly heated to 250°C in an atmosphere of dry helium. During this heating period, the sample was essentially completely dehydrated. The heating in helium was continued until the desired reaction temperature was reached. At this temperature the helium was replaced by hydrogen and the weight change at constant ambient temperature was continuously recorded. In nearly all cases the reaction was followed until the weight was constant, i.e., until the reaction was complete. Usually the reaction product was cooled in helium before being removed for analysis.

The gas flow rate in each experiment was 1350 ml (STP)/min. The ambient temperature was maintained to ± 5°C.

3.0 RESULTS

3.1 Determination of the Stoichiometry

Interpretation of Weight-Time Curves. A weight-time plot is shown in Fig. 1, where regions A-D are interpreted as follows:

Region A: Initial loss of weight below 250°C due to dehydration of the sample

Region B: Weight loss incurred while heating the dehydrated sample in helium to the reaction temperature

Region C: Weight loss due to complete reaction of UO_2F_2 and UO_3 with hydrogen

Region D: Area of constant weight after complete reaction

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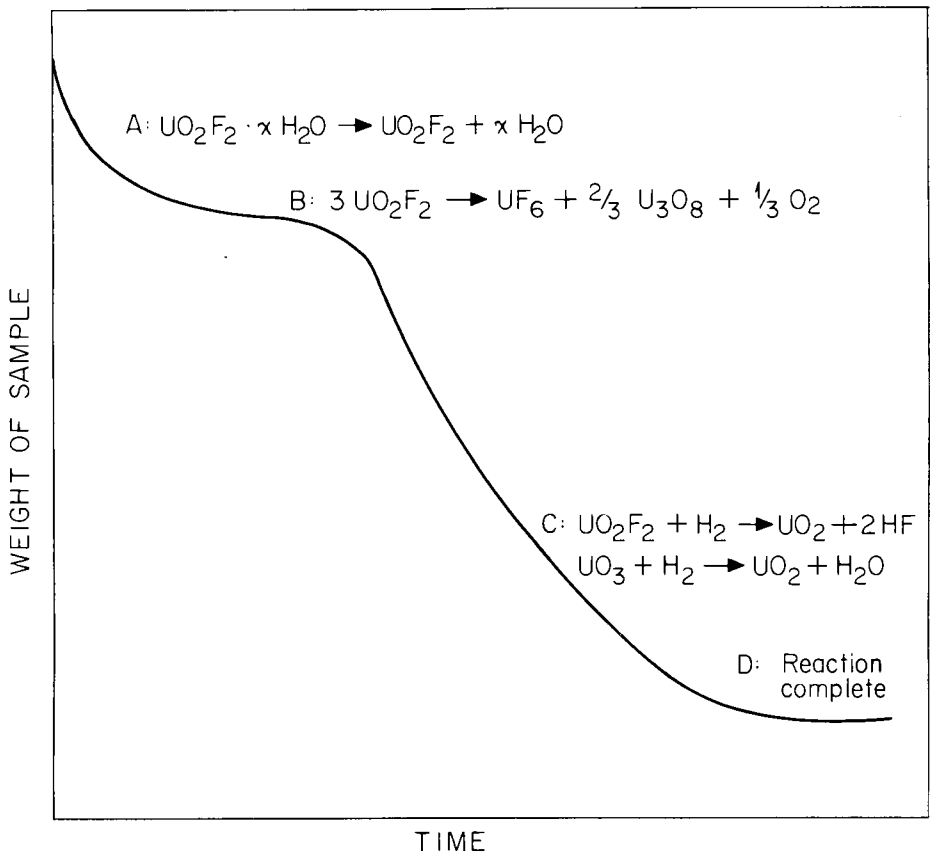

Fig. 1. Typical weight-time plot, showing the effects of reactions 1-4.

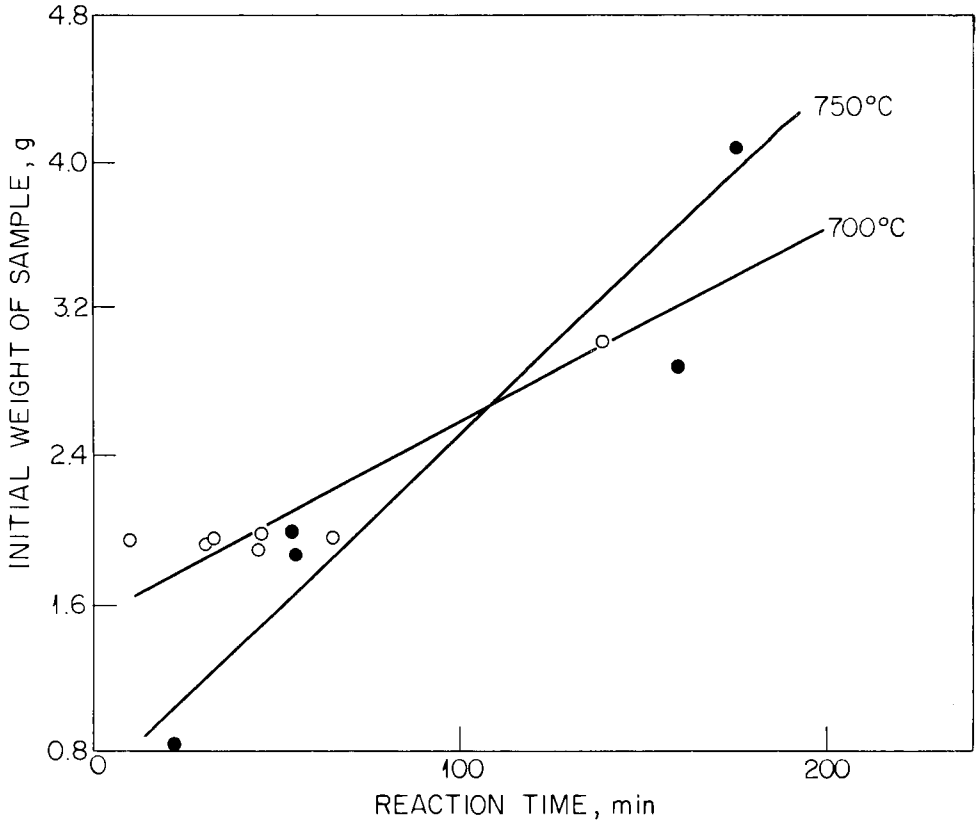

Fig. 2. Effect of sample size on time for complete reaction at 700 and 750°C. All samples -35 + 50 mesh; H_2 flow rate = 1350 ml (STP)/min.

The sequence of reactions during an experiment is thus assumed to be

Region A: $UO_2F_2 \cdot xH_2O \longrightarrow UO_2F_2 + xH_2O$ (1)

Region B: $3UO_2F_2 \longrightarrow UF_6 + 2/3\ U_3O_8 + 1/3\ O_2$ (2)

Region C: $UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$ (3)

$UO_3 + H_2 \longrightarrow UO_2 + H_2O$ (4)

In Region B the weight loss could also be attributed to the reaction

$$UO_2F_2 + H_2O \longrightarrow 1/3\ U_3O_8 + 2HF + 1/6\ O_2$$

involving the water present as a trace impurity in the helium. However, since the weight change in this region was essentially negligible (less than 0.5% of the total), it need not be considered further. Decomposition of UO_2F_2 in Region C should not seriously affect the weight change since the rate of decomposition is very low at temperatures below 800°C.[6] Therefore, the total weight loss in an experiment was attributed to dehydration (Reaction 1) and to reduction of UO_2F_2 and UO_3 (Reactions 3 and 4).

The weight change associated with the complete reduction of UO_2F_2 (Reaction 3) may be expressed as $L_1 = 0.1140\ w_o$, where w_o is the weight of solids present after dehydration. Similarly, the weight change for reduction of UO_3 (Reaction 4) is $L_2 = 0.00425\ w_o$. The total weight loss expected, if the assumptions made above are valid, is then

$$W_c = L_1 + L_2 = 0.11825\ w_o$$

Stoichiometry. The weight loss data outlined above were interpreted as indicating that the reaction of UO_2F_2 with hydrogen proceeded as follows between 700 and 850°C: $UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$. In most cases the experimental weight loss, W_e, agreed with the calculated value, W_c, within 3% (Table 1). The standard deviation was 6.5 mg. Deviations are attributed to buoyancy factors, which arise when helium is replaced with hydrogen, and to the omission of the effect of Reaction 2. The back-reaction,

$$UO_2 + 4HF \longrightarrow UF_4 + 2\ H_2O,$$

was negligible, since the highest fluoride content in the reduction product, 700 ppm, corresponds to only about 0.1% UF_4.

Table 1. Comparison of Experimental and Calculated Weight Losses

Reactions

$$UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$$

$$UO_3 + H_2 \longrightarrow UO_2 + H_2O$$

Run No.	Temp., °C	W_e, g	W_c, g	$W_e - W_c$, g	Difference,[a] %	F^- in Residue, ppm
G-8	700	0.3522	0.3521	0.0001	-0.03	-
-9	700	0.3485	0.3423	0.0062	-2.6	-
-10	700	0.2221	0.2349	-0.0128	+5.5	-
-11	750	0.2187	0.2229	-0.0042	+1.9	-
-12	800	0.2655	0.2679	-0.0024	+0.90	320
-13	850	0.2124	0.2286	-0.0162	+7.1	50
-14	700	0.2230	0.2263	-0.0033	+1.45	339
-15	750	0.2203	0.2281	-0.0078	+3.4	485
-16	750	0.4737	0.4822	-0.0085	+1.76	700
-17	750	0.0916	0.0955	-0.0039	+4.1	44
-19	700	0.2285	0.2236	0.0049	-2.2	412
-20	700	0.2396	0.2322	0.0074	-3.2	53
-21	700	0.2285	0.2266	0.0019	-0.84	10
-22	700	0.2363	0.2280	0.0083	-3.6	158
-25	700	0.2355	0.2345	0.0010	-0.42	-
-26	700	0.2360	0.2348	0.0012	-0.51	-
-27	725	0.2315	0.2347	-0.0032	+1.36	-
-28	700	0.2268	0.2335	-0.0067	+2.9	-
-29	700	0.228	0.2344	-0.0064	+2.7	-
-30	700	0.233	0.2348	-0.0018	+0.77	-
R-3	700	0.235	0.2346	0.0004	-0.17	427
-4	700	0.231	0.2341	-0.0031	+1.32	-
-5	700	0.232	0.2344	-0.0024	+1.02	-
-6	700	0.233	0.2342	-0.0012	+0.51	20
-7	700	0.2434	0.2344	0.0090	-3.8	20

[a]Defined as $100\ (W_c - W_e/W_c)$.

In two of the runs, R-6 and R-7, oxygen was admitted to the system after reduction was complete and the weight increase recorded. This increase corresponded to that expected for the reaction $3UO_2 + O_2 \longrightarrow U_3O_8$ (Table 2). The final product gained weight when cooled to room temperature in oxygen, the increase corresponding to partial conversion of the U_3O_8 to UO_3 (Table 2). Oxidation of reactive U_3O_8 on cooling in oxygen has been reported previously.[7]

X-ray analyses of residues cooled in helium showed the product of the reaction of UO_2F_2 with hydrogen to be UO_2.

Table 2. Oxidation of the UO_2 Product in Runs R-6 and R-7

Run No.	Wt. increase, mg, for $UO_2 \rightarrow U_3O_8$		Analysis of Cooled Product, %			
			Total U		U(IV)	
	Calculated	Observed	Calculated	Observed	Calculated	Observed
R-6	68.9	72.0	84.3	83.9	18.6	19.0
R-7	68.2	68.5	84.3	83.9	21.7	19.7

3.2 Interpretation of the Rate Curves

The time required for complete reaction increased markedly with increasing sample size (Fig. 2). In general, the reaction time appeared to decrease with decreasing particle size (Fig. 3, but see the two curves for -35 + 50 mesh material). In each case, however, the data best fit the parabolic equation (derived in the Appendix) for slab, or bed, diffusion,

$$F^2 = ct/w_o^2,$$

where F = fraction of solids consumed, c = a constant, t = time, and w_o = initial weight of solids. In general, the plots of F^2 vs. time were linear over the first 50% of the reaction (Fig. 4). Kuhlman's[3] data also are best fit by the parabolic equation. The fact that the bed depths in his study were 5 mm compared to about 1 mm in this study may account for his finding approximately 5% UF_4 in the product. However, the equilibrium constants for the reaction $UO_2 + 4HF \longrightarrow UF_4 + 2\,H_2O$ show that the existence of UF_4 at temperatures below about 700°C is highly favored.[8]

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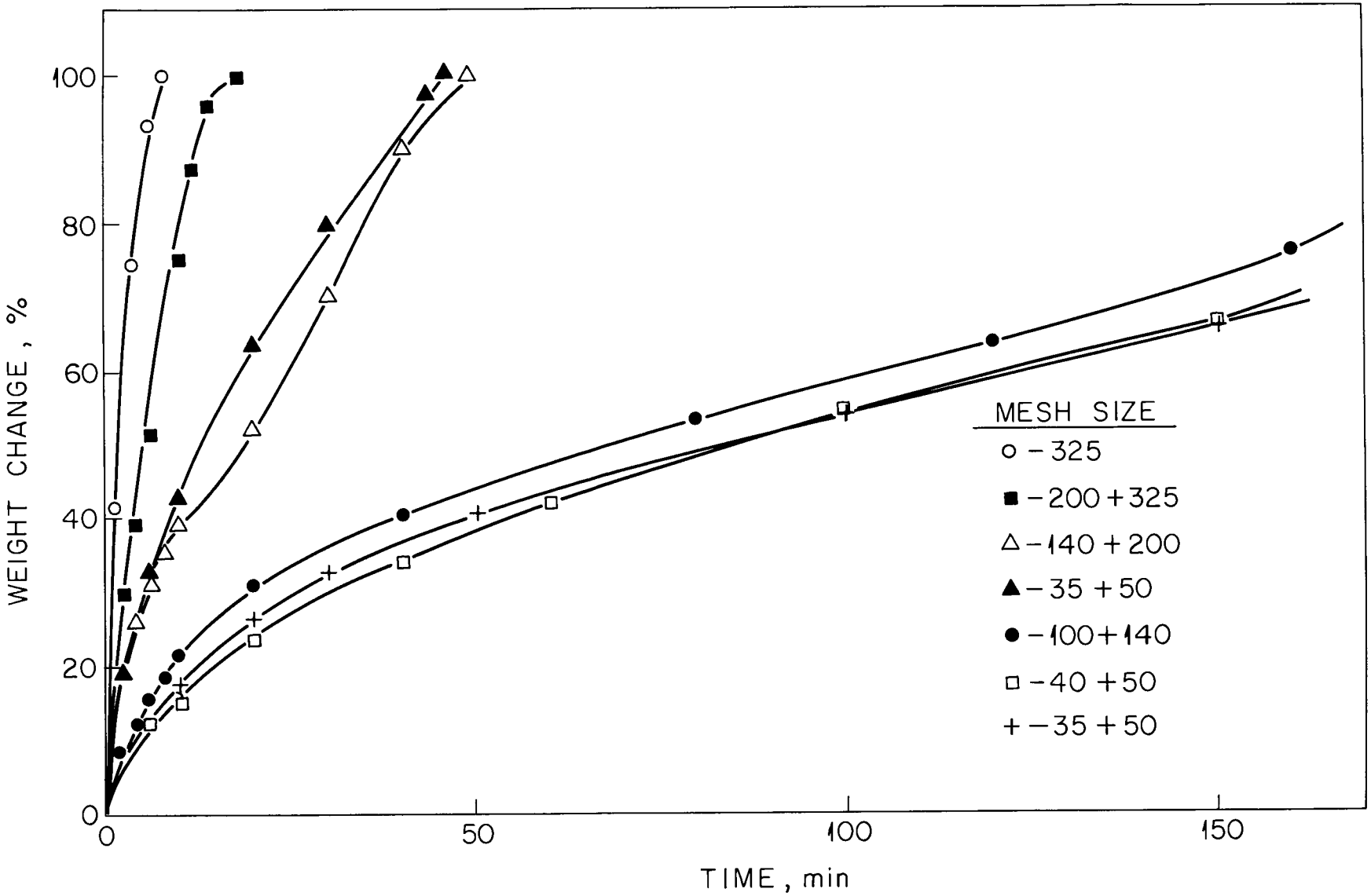

Fig. 3. Plots showing increase of time for complete reaction of 2-g samples at 700°C with increase in particle size.

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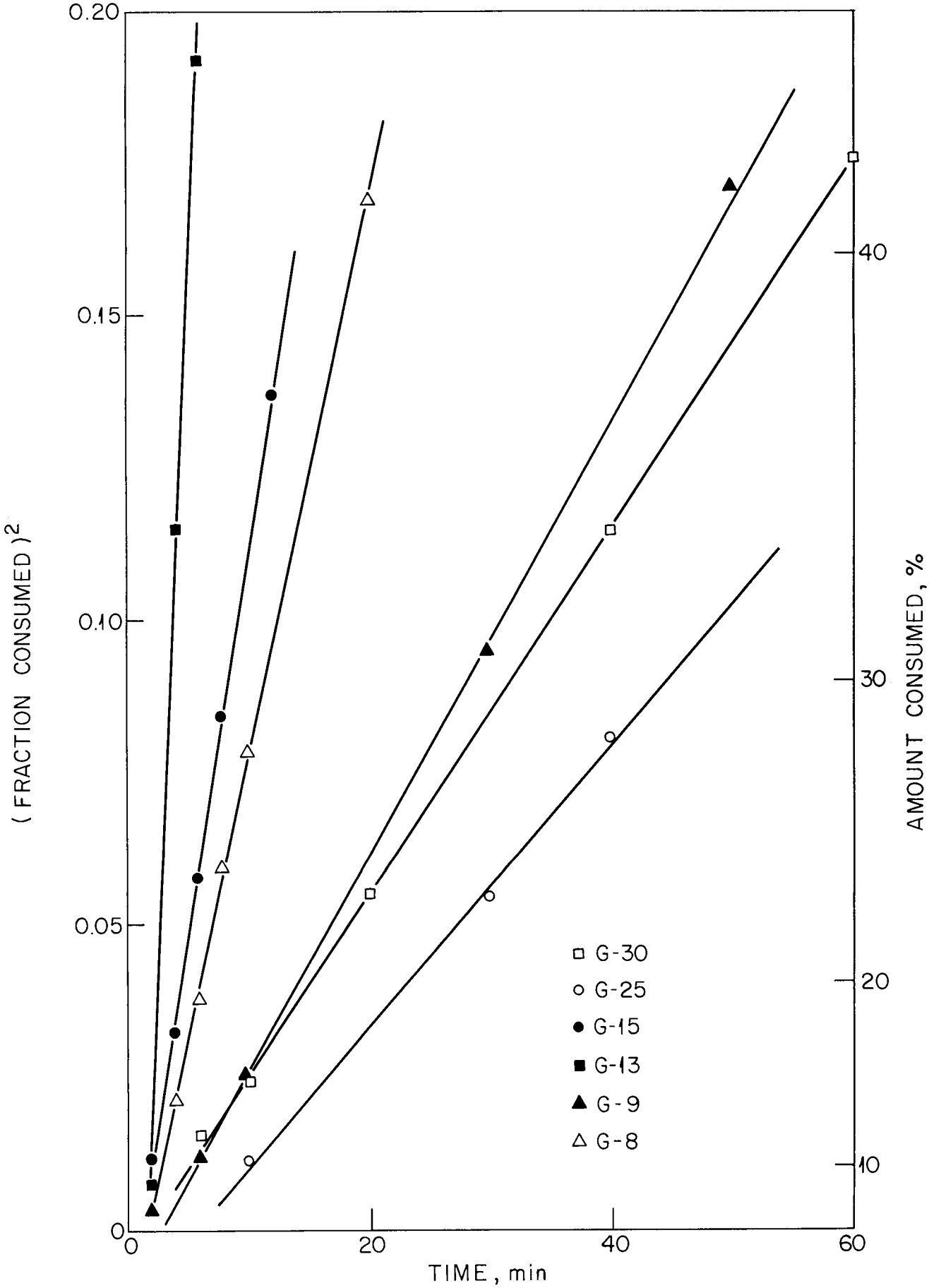

Fig. 4. Weight loss data plotted according to the parabolic law.

Values for the diffusion coefficient, computed from the slopes of the plots of F^2 vs. time by the method of Ginstling and Brounshstein,[9] are plotted vs. reciprocal absolute temperature in Fig. 5. The slope of this plot ($\sim$12 kcal/mole) is proportional to the activation energy of the rate-controlling diffusion process.

Since bed-diffusion was the rate-controlling factor in the experiments, no explicit statement regarding the rate of the reaction of UO_2F_2 with hydrogen can be made. However, since the reaction times were short it can safely be stated that the reaction of UO_2F_2 with hydrogen is rapid in the temperature range investigated.

As suggested by the lower curves in Fig. 3, the rate of reaction increased slightly during the last 40% of the reaction. This effect was observed in nearly all cases and may be due to poor heat transfer through the layer of oxide product, which eventually results in a gradual increase in reaction temperature. However, some other explanation may be more valid, since the estimated standard heat of reaction,

$$\Delta H^o_T = -2455 - 0.09\ T - 7.36 \times 10^{-3}\ T^2 - 0.61 \times 10^5\ T^{-2},$$

is relatively low (-2.5 kcal/mole at 1000°K).

4.0 CONCLUSIONS

The results of this investigation, while not yielding explicit information regarding the kinetics of the reaction of UO_2F_2 with hydrogen, point out the feasibility of using this reaction in a Fluorox recycle scheme. The reaction is obviously rapid at relatively low temperatures so that, if the reaction was carried out in a fluidized-bed reactor, the rate of reaction could probably be controlled by the rate of addition of hydrogen. Since the objective of the recycle process is to produce UF_4, it may be desirable to make use of a slow-moving bed or low reaction temperature and try to effect both reduction and hydrofluorination in the same unit.

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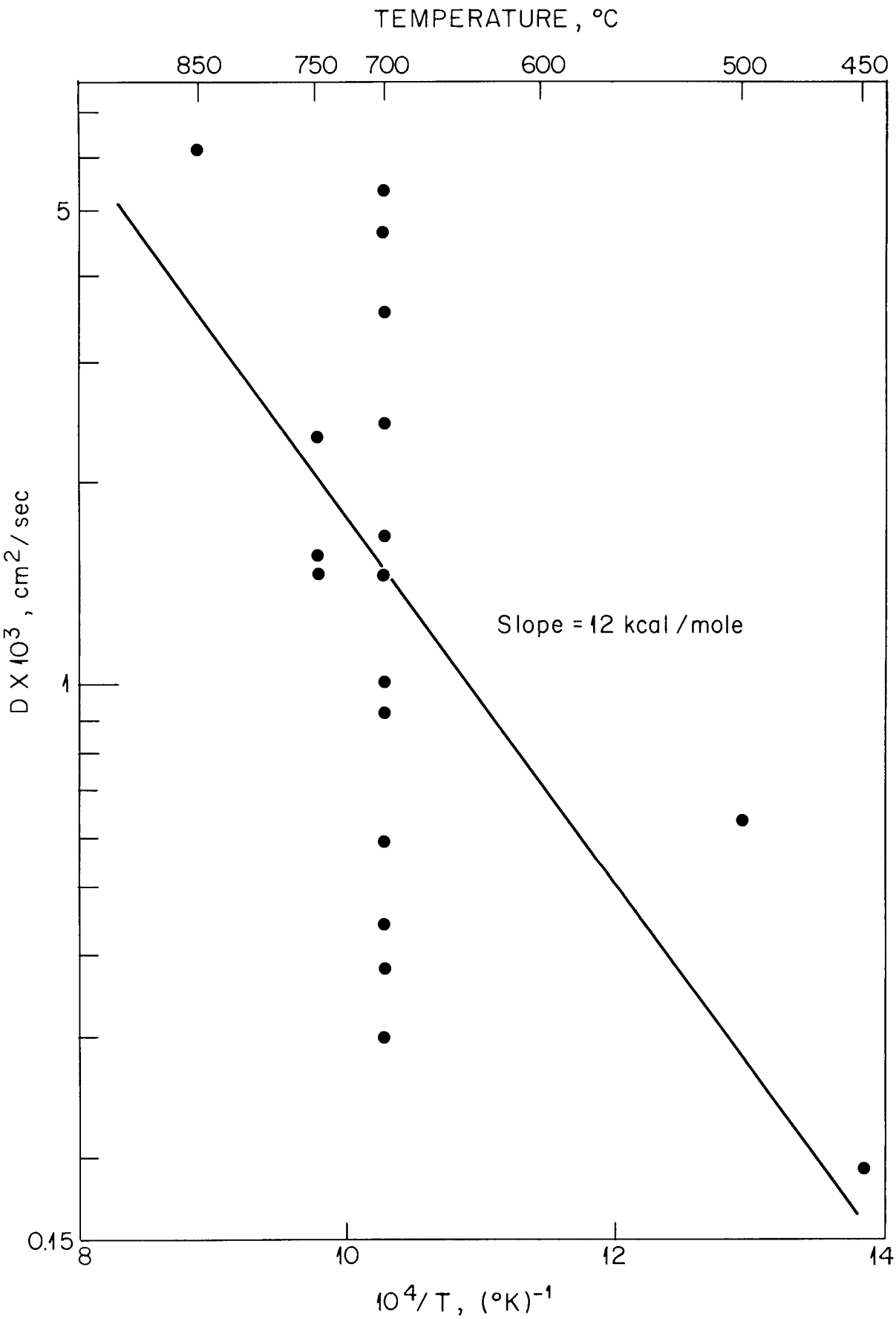

Fig. 5. Temperature dependence of the calculated diffusion coefficients.

If separate reduction and hydrofluorination steps are desired, it may be necessary to transfer UO_2 in an inert atmosphere to prevent oxidation. If the UO_2 produced is always as reactive as that obtained in this study, even trace amounts of oxygen in an inert gas can have a deleterious effect. For example, the highest purity nitrogen available at ORNL could not be used as an inert gas because the amount of oxygen contained in it caused complete oxidation to U_3O_8 of the 2-to 3-g samples of UO_2 in a matter of minutes.

It is conceded that the thermogravimetric technique attempted here is not well suited to a study of the kinetics of the reaction of UO_2F_2 with hydrogen. Any future effort to evaluate the kinetics of this reaction must be devised to avoid bed diffusion.

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6.0 APPENDIX

Derivation of the Parabolic Equation for Bed Diffusion

The following derivation is essentially that given by Jost.[10] Ginstling and Brounshstein[9] have also shown that the parabolic equation is a necessary solution of Fick's diffusion equations if the correct boundary conditions are used.

We consider a bed of solid reactant, A, to have an initial depth, x_o. It is assumed that the conversion of A, by reaction with gas G, to the solid product B takes place in such a way that there is a distinct boundary separating A and B; i.e., no A is present in B, and no B in A. The depth of unreacted A is designated as x. Since the rate of the chemical reaction occurring at the A-B interface is assumed to be extremely rapid compared to the rate of diffusion of G through B, the concentration of G at this interface is zero. The rate of change of depth of the product layer is then

$$\frac{d(x_o-x)}{dt} = \frac{k}{x_o - x} \quad \text{or} \quad \frac{-dx}{dt} = \frac{k}{x_o - x}$$

which by integration gives

$$(x_o-x)^2 = 2\,kt + c.$$

It is readily seen that $c = 0$ at $t = 0$, so

$$(x_o - x)^2 = 2\ kt.$$

If both sides of this equation are divided by x_o^2, the following equation is obtained:

$$F^2 = 2\ kt/x_o^2$$

since $(x_o - x)/x_o = F$, the fraction consumed.

Initially, the volume of solids is $V_o = S\ x_o$ where S = the cross-sectional area of the bed. Furthermore, $x_o = w_o/\rho S = \phi\ w_o$, where ρ is the bulk density of the reactant A and w_o is the initial weight of A. The final expression relating the fraction consumed to the initial sample weight is thus

$$F^2 = \frac{2kt}{\phi^2\ w_o^2} = \frac{ct}{w_o^2}.$$

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