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LABORATORY DEVELOPMENT OF THE FLUOROX PROCESS: THE REACTION OF UF_4 WITH DRY O_2

I. SIDE REACTIONS AND THERMODYNAMICS

L. M. Ferris

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

LABORATORY DEVELOPMENT OF THE FLUOROX PROCESS: THE REACTION OF UF_4 WITH DRY O_2. I. SIDE REACTIONS AND THERMODYNAMICS

L. M. Ferris

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1.0 ABSTRACT

UO_2F_2, UF_4, and U_3O_8 are deposited on the quartz reactor walls in the reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$ at temperatures above 700°C. Experiments indicated that the first two compounds arise chiefly from decomposition of UF_5 and U_2OF_8, which are possible intermediates in the oxidation reaction. The U_3O_8 appeared to result from reaction of the UF_6 with the quartz. Estimated thermodynamic data were consistent with these results. Preliminary kinetic data were accumulated during the course of this work.

2.0 INTRODUCTION

The use of dry oxygen, instead of fluorine, to convert UF_4 to UF_6 is being studied as one step of the Fluorox process.[1] This conversion is perhaps the most expensive step in the process for preparing UF_6 when elemental fluorine is used. Reported here are the results of batch experiments made to provide a clearer understanding of the nature of the reaction with dry O_2, with emphasis on side reactions. This type of study is a necessary precursor to a detailed study of the kinetics of the reaction. It was therefore expedient to determine the source of the UO_2F_2, UF_4, and U_3O_8 found deposited inside a reaction vessel. Thermodynamic estimates were made to aid in the explanation of the experimental observations. Preliminary data were obtained on the rate of the reaction.

In 1945 it was shown[2] that UF_6 is a product of the reaction of UF_4 with dry oxygen at 800°C. The reaction is, essentially, $2\ UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$ and has been considered intermittently[3,4] during the past 10 years as the basis for new schemes for producing UF_6. Moving-bed reactors are presently utilized in the Fluorox process. Fluid-bed and

flame reactors have also been suggested for reacting UF_4 with O_2.

The author expresses appreciation for the x-ray analyses made by the late Dr. G. E. Klein of the Solid State Division, and to Dr. R. G. Wymer for his valuable comments and criticisms.

3.0 EXPERIMENTAL PROCEDURE

The experiments were carried out batchwise in 1-in.-dia quartz tubes heated by a 750-watt tube furnace. The 10-g UF_4 samples were contained in platinum boats. The temperature inside the furnace was maintained to within 10°C of the specified temperature by use of a Pyrovane controller. Connected to the reaction tubes were 0.5-in.-dia quartz U tubes which, when immersed in trichloroethylene--dry ice slush, served as cold traps for collecting the UF_6. The oxygen and helium gases were dried by passage through a train consisting of a trichloroethylene--dry ice cold trap, a fuming sulfuric acid trap, and two Drierite bulbs.

In a typical oxidation experiment a UF_4 sample was heated to temperature in a stream of dry helium. At the desired temperature, the helium was replaced by dry oxygen flowing at a rate of 100-300 ml/min. After a predetermined length of time, the system was cooled in helium and the results of the oxidation were studied.

Some experiments were performed to evaluate the extent of UF_4 vaporization under the conditions used. In these experiments no O_2 was used, but, rather, the weight loss produced by contact with a flowing stream of helium was obtained. A platinum liner was used in some experiments to determine whether the UF_6 reacted with quartz to produce the observed U_3O_8 deposits.

4.0 SOURCE OF URANIUM DEPOSITS ON REACTOR WALL

Throughout studies of the overall oxidation reaction

$$2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$$

at temperatures above 700°C, uranium compounds have been found on the walls of the reaction vessel. Their presence has generally been attributed[2,4] to sublimation of UF_4 and UO_2F_2 from the reaction mixture and to reaction of UF_6 with the vessel wall. The same deposits---UO_2F_2, UF_4, and U_3O_8 (Fig. 1)---were noted in the experiments reported here. The U_3O_8 is considered to have resulted from reaction of UF_6 with the quartz vessel, since the reactors used were severely attacked, particularly in the high-temperature regions. However, the volatilities of both UF_4 and UO_2F_2 were too low under process conditions to entirely account for the large amounts of the compounds found on the reactor walls. They are thought to have been formed primarily by decomposition of UF_5 and U_2OF_8, which may be[4] intermediates involved in a mechanism similar to the following:

$$4UF_4 + O_2 \longrightarrow 2U_2OF_8 \longrightarrow 2UF_5 + UF_4 + UO_2F_2$$

$$2UF_5 \longrightarrow UF_6 + UF_4$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$$

4.1 Isolation of Intermediate Reaction Products

In separate studies,* two pentavalent uranium compounds, UF_5 and U_2OF_8, have been isolated from the oxidation system, under different conditions.

UF_5. A brown material, later shown to contain UF_5, was evolved simultaneously with the UF_6 as the oxygen was passed through the reactor, and some of it condensed before it reached the cold trap. It was always found when the reaction was carried out above 750°C,

*The present and reference 4.

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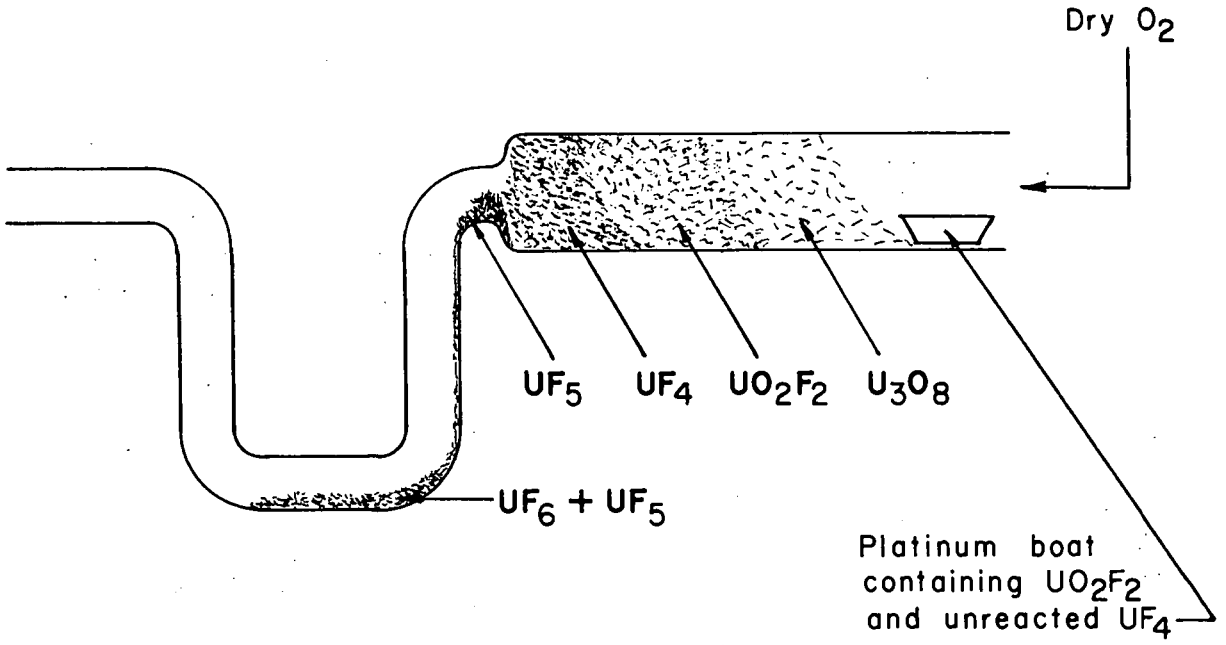

Fig. 1. Distribution of Compounds Inside a Quartz Reactor after Reaction of UF_4 with Dry Oxygen. Regions were actually somewhat less distinct with some UO_2F_2 in nearly all parts of the tube.

regardless of the source of the UF_4. It could be separated from the UF_6 by passing a dry gas over the two compounds while they were held at about 60°C, under which conditions the UF_6 sublimed while the brown material remained in the vessel. In a moisture-free vessel, the brown substance apparently volatilized when heated gently with a bunsen burner, but when heated strongly in the presence of dry oxygen it was converted to UF_4 plus some UO_2F_2. When it was heated in a closed quartz capillary tube, the molten tip of the tube burst, showing a relatively high gas pressure which is indicative of the presence of UF_6. In the presence of moisture, the brown material rapidly hydrolyzed to UO_2F_2 and UF_4. The composition (determined by both x-ray and chemical analysis) of the hydrolysis product indicated it to be a 1-to-1 mixture of UO_2F_2 and UF_4:

	Amount (wt %)		
	Total U	U(IV)	F^-
Hydrolysis product	63.4*	38.9	17.8
UO_2F_2-UF_4, 1 to 1	76.6	37.9	18.3
UF_5	71.5	35.7	28.6
UO_2F_2	77.3	0	12.3
UF_4	75.8	75.8	24.2

*Analysis undoubtedly low.

The brown substance was not soluble in acetone or anhydrous ether, and it imparted a slight green color to cold ammonium oxalate.

The chemical and physical properties of the brown substance coincided with those of UF_5, and the presence of UF_5 as a reaction by-product can be predicted from thermodynamic considerations (Sec. 5.0). The presence of β-UF_5 in the brown material was confirmed by x-ray-diffraction analysis.

Although the presence of UF_5 was definitely established and its formation as an intermediate in the oxidation reaction is postulated, formation by other reactions is possible. As mentioned above, UF_4 is vaporized to a measurable extent above 700°C under the experimental

conditions employed. It is therefore conceivable that UF_5 is formed by a UF_4-UF_6 reaction, either in the vapor phase or by direct contact of UF_6 gas with solid UF_4. Thermodynamically UF_5 could be formed by a simple oxidation of UF_4 (Eq. 10, Sec. 5.0) without U_2OF_8 as an intermediate.

U_2OF_8. This compound was isolated and identified by other workers,[4] in 1950, only when pressure cycling was very rapid, i.e., when the pressure of the system was changed from oxygen at 1 atm to a high vacuum in a few seconds. Its chemical properties were found to be similar to those of UF_5, but its x-ray-diffraction pattern is different.

4.2 Volatilization of UF_4 and UO_2F_2

Gram quantities of UF_4 and UO_2F_2 were found on the walls of the reactor after each run, and in some cases single crystals of UO_2F_2 were found adhering to the sides of the platinum boat. However, only a few hundred milligrams of either compound volatilized from samples held for 1 hr at 800°C in a stream of dry helium. It is interesting to note, however, that the UF_4 sample weight losses showed an order-of-magnitude agreement with those predicted from the reported[7] vapor pressures of UF_4 (Fig. 2), assuming that the gas stream is saturated at the specified flow rate. At 800°C, the experimental points all fell within the range predicted by gas flow rates of 100-300 ml/min, while at 600 and 700°C the values were appreciably higher. If the vapor pressure values used for these lower temperatures are low by a factor of 2 or 3, all results would fall in the predicted range.

4.3 Decomposition of UF_6 and UO_2F_2

Deposition of a measurable amount of UF_4 as a result of

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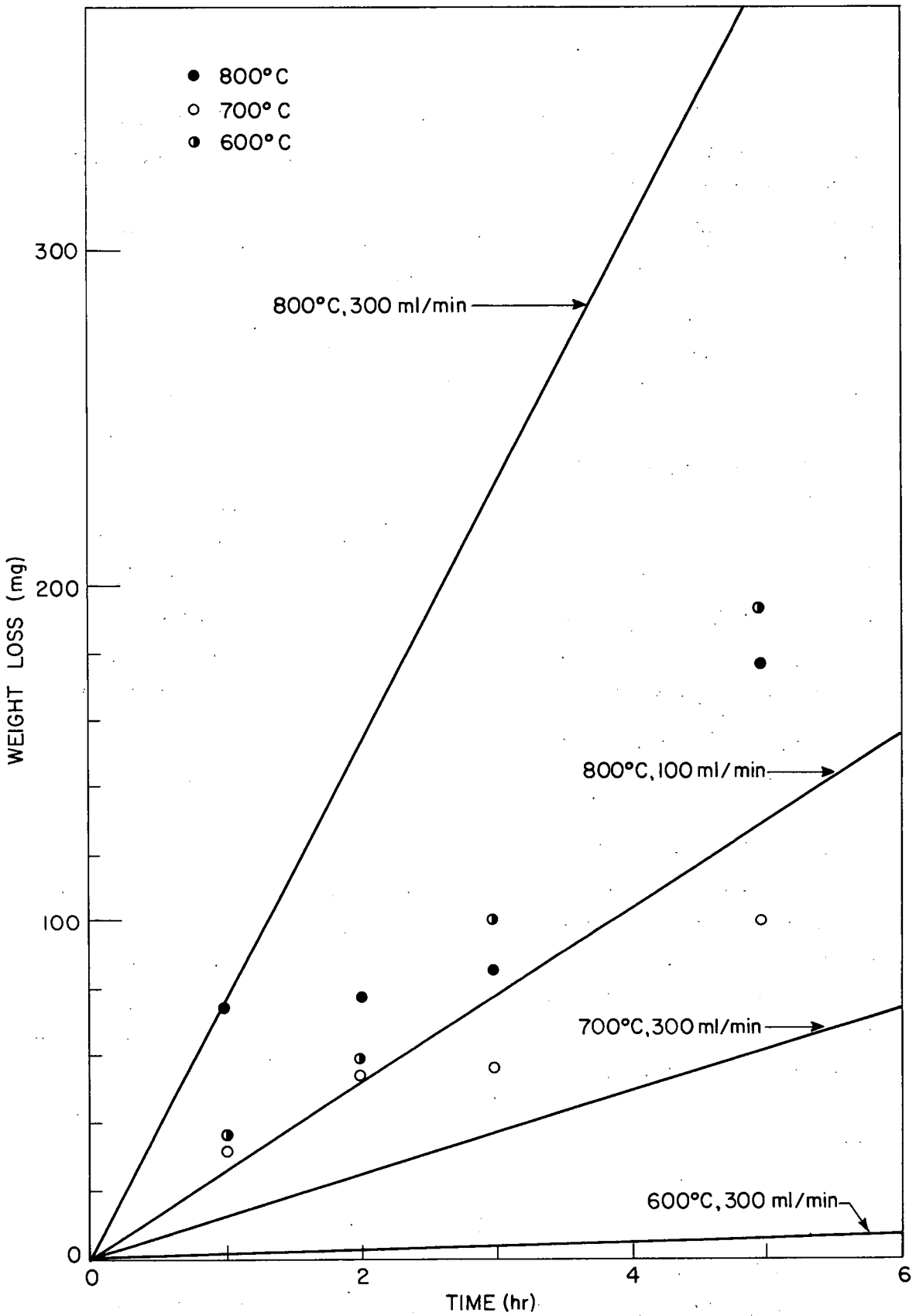

Fig. 2. UF_4 Weight Loss in Flowing Oxygen as a Function of Time. The lines show values predicted from vapor pressure data, and points show values obtained with +60 mesh UF_4 and oxygen flow rates of 100-300 ml/min.

dissociation of UF_6 is thermodynamically improbable (Sec. 5.0), and only a small amount of U_3O_8 and no UF_4 were noted when UO_2F_2 was heated at 800°C.

It has been reported[5,6] that UO_2F_2 thermally decomposes in both oxygen and a vacuum. Two possible reactions are

$$3UO_2F_2 \longrightarrow UF_6 + 2/3\ U_3O_8 + 1/3\ O_2$$

$$2UO_2F_2 \longrightarrow UF_4 + UO_2 + O_2$$

Some decomposition was observed when UO_2F_2 was heated in a stream of dry oxygen, nitrogen, or helium. The decomposition apparently began at about 600°C but the rate was very slow even at 800°C. In 5 hr at 800°C only a thin surface layer of U_3O_8 was observed, and the only decomposition product isolated was U_3O_8. The rate of decomposition apparently increased markedly as the temperature was raised above 800°C, for only U_3O_8 was found as a solid product after a 1-hr oxidation of UF_4 at 1100-1200°C. In contrast, UO_2F_2 was completely pyrohydrolyzed to U_3O_8 in less than 1.5 hr at 800°C.

4.4 Reaction of UF_6 with Quartz

When the oxidation was carried out in quartz reactors, relatively large amounts of U_3O_8 were formed. When the reaction was carried out inside a platinum liner inserted in the quartz tube, only two compounds, UO_2F_2 and UF_4, were found on the liner. Apparently, no U_3O_8 was formed. When an Inconel tube was used as the reactor, some NiF_2 was formed as a slag.

5.0 THERMODYNAMICS

Some of the various reactions which may be written to account for the observed results in the oxidation of UF_4 to UF_6 are:

Eq. No.	Reaction	ΔF^{o} (kcal/mole ± 10 kcal)				
		25°C	500°C	700°C	800°C	900°C
1	$2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$	-11	-9.5	-7.5	-6	-4
2	$3SiO_2 + 2UF_6 \longrightarrow 3SiF_4 + 2UO_3$	-102	-116	-127	-126	-121
3	$UO_3 \longrightarrow \frac{1}{3}U_3O_8 + \frac{1}{6}O_2$	+4	+1	-1	-2	-3
4	$UO_2F_2 \longrightarrow UO_2 + F_2$	+114	+96	+90	+86	+83
5	$2UO_2F_2 \longrightarrow UO_2 + UF_4 + O_2$	+63	+41	+33	+27	+23
6	$3UO_2F_2 \longrightarrow UF_6 + \frac{2}{3}U_3O_8 + \frac{1}{3}O_2$	+55	+26	+27	+20	+16
7	$4UO_2F_2 \longrightarrow UF_4 + U_3O_8 + 2F_2$	+215	+178	+166	+156	+150
8	$3UO_2F_2 + \frac{5}{2}O_2 \longrightarrow U_3O_8 + 3F_2O$	+296	+284	+281	+278	+278
9	$UF_6 \longrightarrow UF_4 + F_2$	+62	+65	+64	+63	+64
10	$3UF_4 + O_2 \longrightarrow UO_2F_2 + 2UF_5$	-27	-11	-9	-11	-14
11	$2UF_5 \longrightarrow UF_4 + UF_6$	+16	+1	+2	+5	+10

Only those reactions with negative free-energy changes would be expected to occur spontaneously at constant temperature and pressure.*

Reaction 1 is thermodynamically more favorable at low temperatures. The fact that UF_4 is not appreciably oxidized below 700°C possibly indicates a complex mechanism and a high energy of activation. From the variation of the heat of reaction with temperature (Fig. 3), it is

*The free energies of formation of all uranium compounds except UO_2F_2 and UF_5 were taken from reference 8. Values for UF_5 and silicon compounds were obtained from reference 9. Values for UO_2F_2 at various temperatures were calculated from data given in references 8 and 9 and the ΔF^{o} for reaction 1 from reference 10. The values for UO_2F_2 thus obtained agreed within 5 kcal with those estimated by Kirslis et al.[34] Most of the values tabulated above were estimated by extrapolation of low-temperature heat-capacity data and therefore cannot be considered accurate to more than ± 10 kcal. The fact that reaction 1 does occur at 800°C and lower, as predicted by the negative, though small, free-energy change, lends some support to the validity of the extrapolations. Data for F_2O are found in reference 12.

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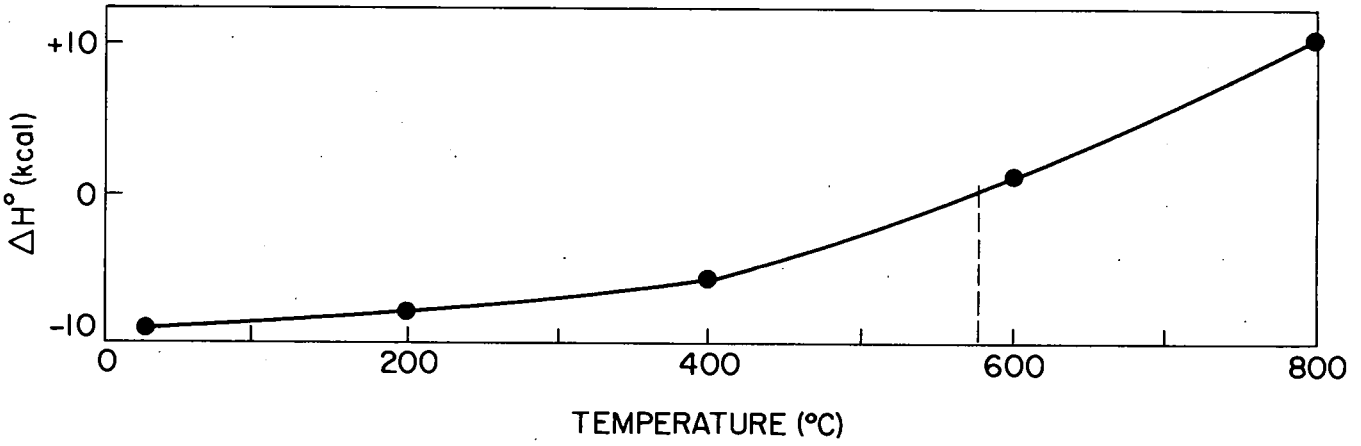

Fig. 3. Temperature Variation of the Standard Enthalpy Change for the Reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$.

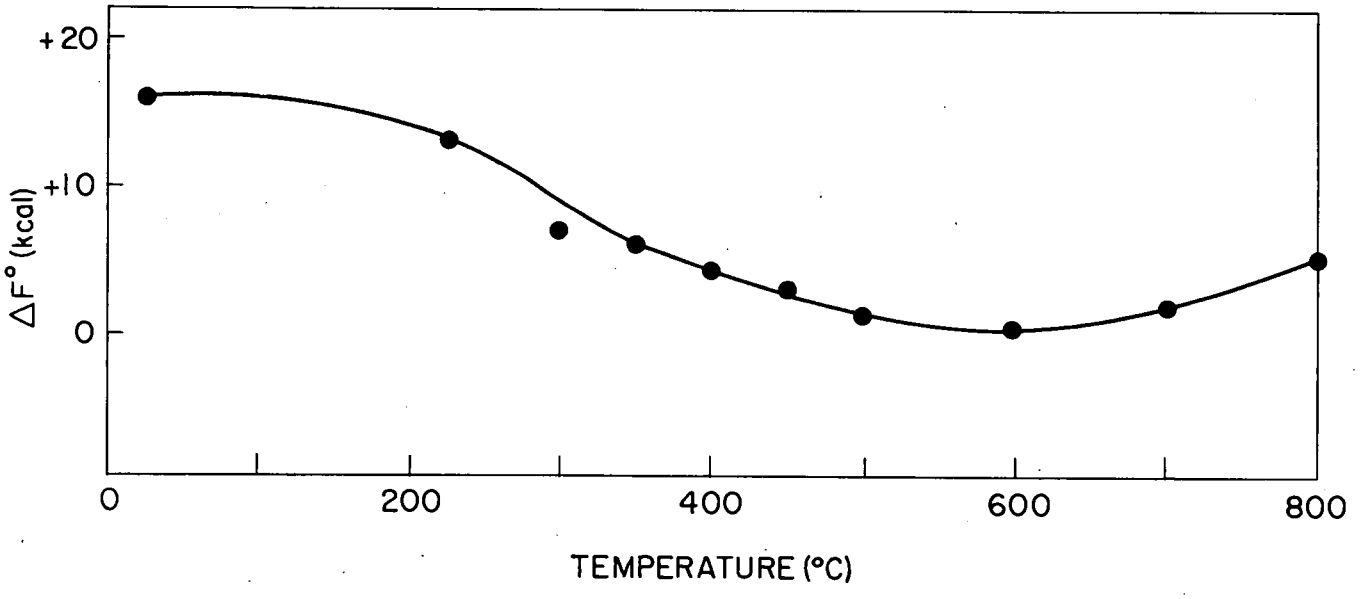

Fig. 4. Temperature Variation of the Standard Free Energy Change for the Reaction $2UF_5 \longrightarrow UF_4 + UF_6$.

evident that the reaction is nearly adiabatic over a wide temperature range within the limits of accuracy of the thermochemical quantities.

Reaction 2 strongly suggests that the quartz reaction tubes are attacked by UF_6. Uranium hexafluoride is known to attack glass, and this would account for the U_3O_8 deposits, which were not found when a platinum liner was used in the reaction tube. The absence of UO_3 in the system is accounted for by the rapid rate[11] of reaction 3.

Possible routes of decomposition of UO_2F_2 are shown in reactions 4-7. Reactions 5 and 6 are the most likely choices for explaining the slight decomposition observed at 800°C, but all four reactions are thermodynamically unfavorable. The calculated equilibrium constants for reactions 4 and 7 show that immeasurable amounts of the products would be formed, even in a flowing-gas system. Formation of U_3O_8 by direct reaction of UO_2F_2 with oxygen appears unlikely, as shown by Eq. 8.

The formation of UF_4 as a product of the disproportionation of UF_6 is shown by reaction 9 to be nearly a thermodynamic impossibility. Brewer[7] has calculated that UF_6 should be stable to at least 1200°C.

Isolation of UF_5 from the system is not surprising in light of the negative free-energy values for reactions 10 and the reverse of reaction 11. That it can be formed during the oxidation of UF_4 is predicted by reaction 10, and its stability at 800°C is predicted by reaction 11. However, a closer look at the free-energy change for reaction 11 (Fig. 4) shows that, in the neighborhood of 600°C, UF_5 goes through a region where it is relatively unstable. This phenomenon could account for the separate deposits of UF_4 and UO_2F_2 in the reaction tube. By use of a thermocouple probe, it was ascertained that the UF_4 appeared only in regions where the temperature was below 600°C. Any UF_4 deposited in a region where the temperature was above 600°C could be slowly oxidized to UO_2F_2. It should be noted also that the free-energy change for reaction 10 does not exclude the possibility of the existence of the

compound U_2OF_8 as reported by Kirslis,[16] since the free-energy change is based only on initial and final conditions, and any intermediate situations are ignored.

6.0 CATALYSIS

The rate of the reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$ is very low at temperatures below 800°C despite the fact that the reaction is thermodynamically more favorable at low temperatures (Sec. 5.0). Catalysis of the reaction would be desirable in a production scheme because high-temperature problems such as corrosion and preheating requirements could be reduced. In laboratory-scale experiments at 600°C, 1 wt % platinum black approximately doubled the reaction rate. However, owing to the relatively large amount of platinum needed to produce a small rate increase, the cost would be prohibitive for a production scheme. The same amount of Fe_2O_3 or V_2O_5 had no detectable catalytic effect.

7.0 PRELIMINARY KINETIC DATA

Approximate specific reaction rate constants for the reaction $2UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6$ may be calculated from batch oxidation data. If the reaction rate is assumed to be proportional to the surface area of the UF_4 and to the oxygen partial pressure, the following equation may be derived:

$$\frac{-dN}{N} = kSMp_{O_2}\, dt \qquad (1)$$

where N is the number of moles of UF_4

p_{O_2} is the partial pressure of the oxygen, mm Hg

S is the specific surface area of the UF_4, m^2/g
M is the molecular weight of UF_4
k is the specific reaction rate constant, moles/min·atm·m^2
t is the oxidation time, min

Integration of this equation, assuming that the UF_4 specific surface area is independent of time, gives

$$k = \frac{-2.3 \log \left(1.00 - \frac{\%\ UF_4\ \text{oxidized}}{100}\right)}{SMp_{O_2} t} \qquad (2)$$

for the reaction rate constant at a given temperature. The percentage UF_4 of known specific surface area oxidized in a given time is easily obtained from chemical analyses of reactants and products and the total sample weight loss by assuming that all tetravalent uranium remaining in the UO_2F_2 product exists as UF_4. The specific surface area may be obtained by N_2 adsorption. It must be understood that the rate constants calculated from Eq. 2 are valid only for oxygen at ~1 atm since no experimental work was done to evaluate the effect of various pressures.

Reaction rate constants were calculated from data (Table 1) obtained by reacting 10-g samples of UF_4, in a platinum boat, for a predetermined length of time with dry oxygen at several temperatures. The oxygen pressure was usually about 745 mm Hg, slightly above that in the laboratory, and the linear velocity of the oxygen in all cases was between 0.33 and 1.0 cm/sec, as measured at 25°C. The specific surface areas used in the calculations (Fig. 5) were those obtained by N_2 adsorption for UF_4 which was ~99% pure.

An Arrhenius plot of the rate constants is found in Fig. 6. The scatter in the experimental points is due mainly to differences in sintering of the packed powdered samples. The lines shown are drawn through points representing the upper and lower extremities of the temperature dependence of the rate of reaction. The calculated range of activation energy extends from 30-40 kcal/mole. No mechanistic

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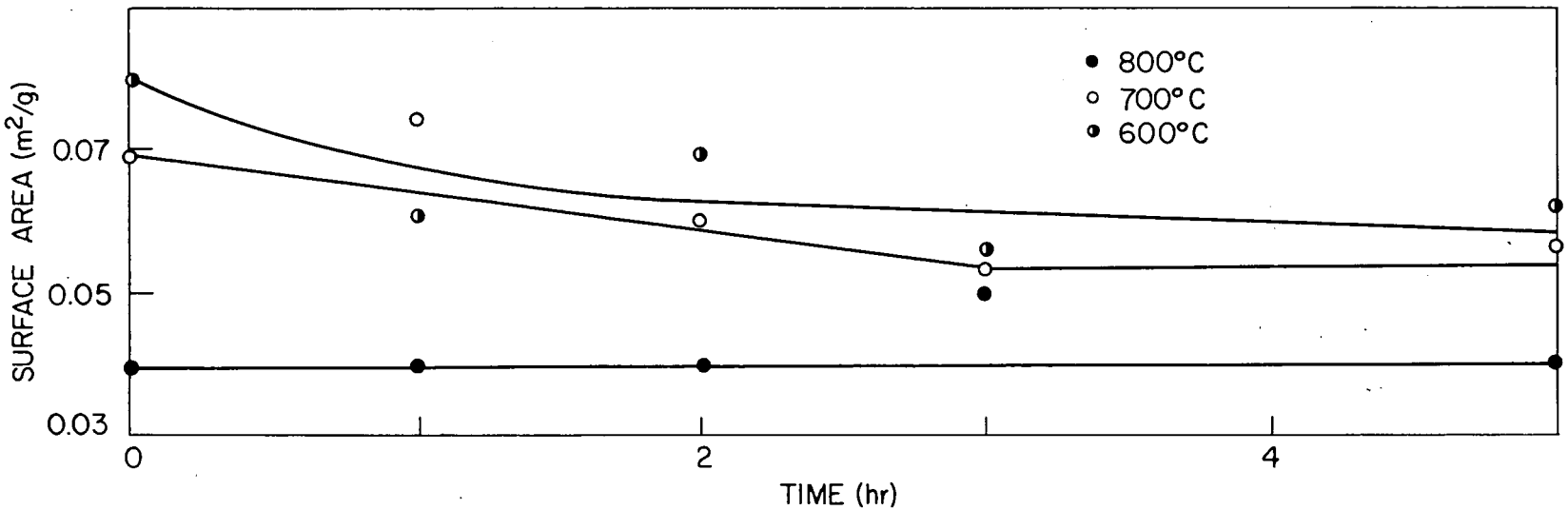

Table 1. Specific Reaction Rate Constants for Oxidation of UF_4 with Dry Oxygen

Various UF_4 powders (98%), ~10-g samples
Oxygen partial pressure: ~745 mm Hg

T (°K)	1/T	Oxidation Time (hr)	UF_4 Oxidized (%)	Particle Size (mesh)	S (m^2/g)	k (moles/min·atm·m^2)	log k
873	0.00114	1.0	2.67	-325	0.08	1.8×10^{-5}	-4.74
		2.0	13.4	-325	0.07	5.5×10^{-5}	-4.26
973	0.00103	1.0	11.7	-325	0.07	9.4×10^{-5}	-4.03
		1.0	16.9	-325	0.07	1.4×10^{-4}	-3.85
		1.5	68.8	-325	0.07	5.9×10^{-4}	-3.23
		3.0	30.0	-325	0.07	9.0×10^{-5}	-4.04
		4.0	69.7	-325	0.07	2.3×10^{-4}	-3.65
1073	0.00093	0.25	68.2	-325	0.04	6.1×10^{-3}	-2.22
		0.5	32.8	---	0.04	1.1×10^{-3}	-2.98
		0.5	85.1	-325	0.04	5.1×10^{-3}	-2.30
		1.0	70.2	-325	0.04	1.6×10^{-3}	-2.80
		1.0	29.1	+60	0.04	4.6×10^{-4}	-3.34
		1.3	82.4	+60	0.04	1.7×10^{-3}	-2.75
1173	0.00085	1.0	89.5	+60	0.04	3.0×10^{-3}	-2.53

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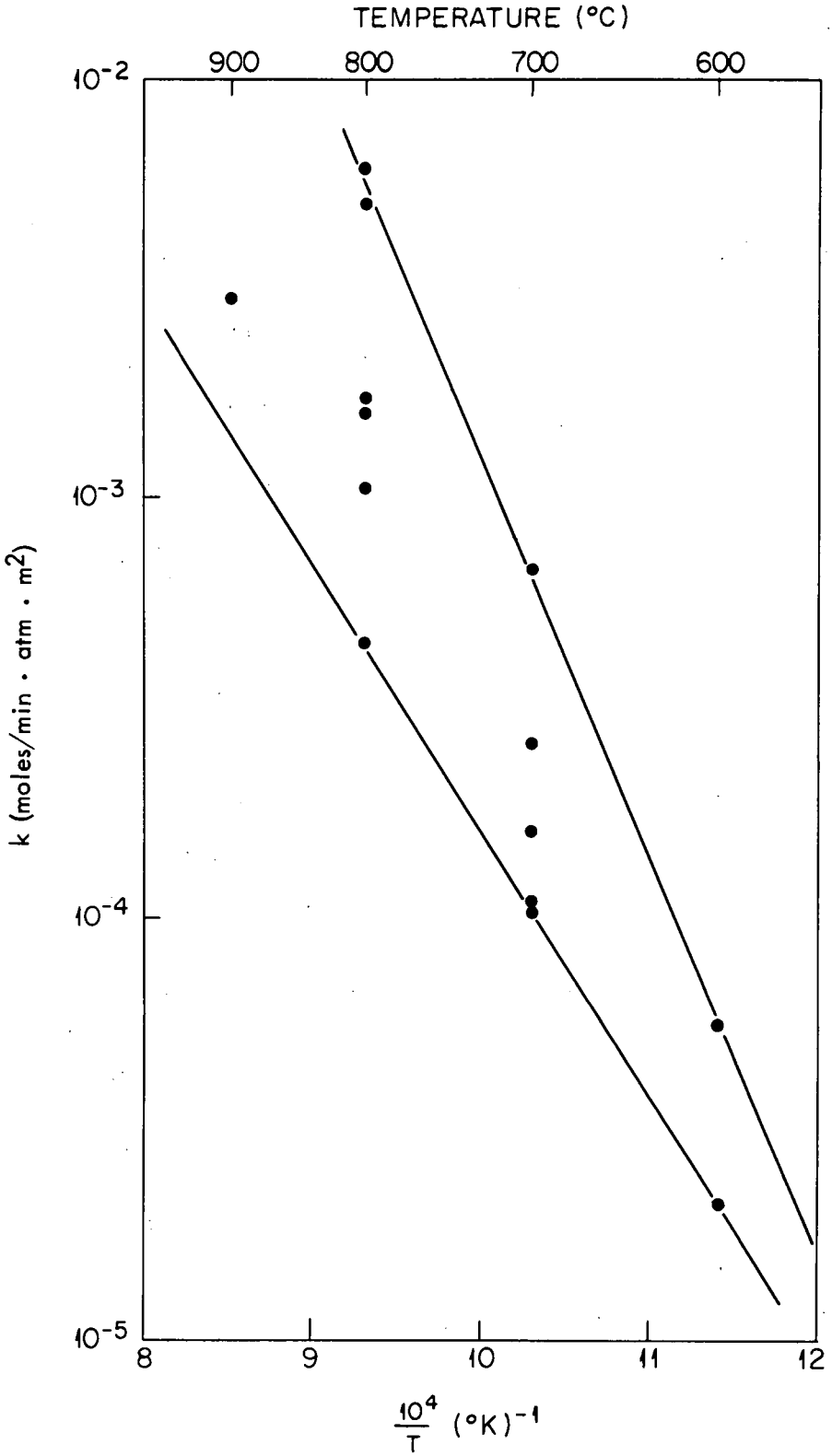

Fig. 6. Approximate Rate Constants For The Reaction $2\,UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$.

explanation can be offered at this time. However, it is felt that the rate constants obtained under the specified conditions are not in error by more than a factor of 10 despite the fact that surface areas of the UF_4 samples used were not actually measured because of their UO_2F_2 content and that platinum boats, which have a slight catalytic effect, were used. UF_4 samples containing about 2% UO_2F_2 had specific surface areas higher by a factor of 4 than the >99% UF_4. The surface areas used for the powdered UF_4 should be accurate since the material of 99% purity was prepared by leaching most of the UO_2F_2 from the original 98% UF_4. It is evident that the arbitrary choice of a surface area only changes the position of the curve but not the slope. It may be preferred to view the preliminary data from the standpoint of the amount of UF_4 oxidized in a given time since the surface area effects have not been elucidated. Certainly an order-of-magnitude rate of oxidation can be obtained from the batch data.

A catalyst that would reduce the temperature needed for rapid oxidation from 800 to 600°C would be extremely advantageous because: (1) The corrosive effect of UF_6 and O_2 should be lessened; (2) the vapor pressure of UF_4 is extremely low at the lower temperature, so that the formation of UF_5 by a UF_6-UF_4 reaction might be avoided, and the thermal stability of UF_5 appears to be at a minimum at 600°C; (3) uranium tetrafluoride does not seem to sinter appreciably at the lower temperature.

The formation of UF_5 by a UF_4-UF_6 vapor-phase reaction might also be controlled by feeding the oxygen at a stoichiometric rate so that little UF_4 could be vaporized and carried in a stream of excess gas.

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