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CHEMICAL EQUILIBRIA AND REACTION RATES FOR HYDROFLUORINATION
OF UO_2 FROM "AMMONIUM DIURANATE" AND FROM UO_3

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ABSTRACT

Reaction rates for the hydrofluorination of UO_2 derived from two widely different source materials (sulfated pot-denitrated UO_3 and "ammonium diuranate," (ADU) were determined in a thermobalance over a wide range of temperatures (460°F to 1150°F) and with several $\text{HF}-\text{H}_2\text{O}$ gas phase mixtures varying from 20 to 100 per cent HF . These data were then organized to yield single plots for each type of feed material. From these plots, maximum instantaneous reaction rates may be determined. These values may be applied to problems dealing with the estimation of minimum retention times required for hydrofluorination in counter-current gas-solid contactors.

In addition to the rate studies, the thermobalance was used to establish temperatures corresponding to equilibrium in the system, $\text{UO}_2(\text{s})-\text{UF}_4(\text{s})-\text{HF}(\text{g})-\text{H}_2\text{O}(\text{g})$, at several selected $\text{HF}/\text{H}_2\text{O}$ ratios in the gas phase. These data, together with thermodynamic theory, were employed to calculate equilibrium conditions at total pressures other than one atmosphere and for various dilutions of the gas phase with an inert gas.

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INTRODUCTION

In the refining of uranium ores or concentrates to either uranium metal or uranium hexafluoride (for subsequent use in the production of fissionable materials), the hydrofluorination of uranium dioxide to uranium tetrafluoride (green salt) is one of the more difficult steps. From the standpoint of economical operation, it is desirable (particularly when making metal-grade UF_4) that the reaction proceed rapidly to a conversion level of 96 per cent or better.¹ Present methods of producing UF_4 in large tonnages involve contacting the UO_2 with hydrogen fluoride at elevated temperatures in an essentially countercurrent continuous system. The reaction is performed in "screw-type" reactors at sites engaged in producing metal-grade UF_4 .² Vibrating tray-type reactors are employed at Oak Ridge, where the product is used for UF_6 manufacture.³ More recently, effort has been directed towards the development of vertical moving-bed type reactors^{4,5} and multistage fluid-bed contactors.⁶ Efforts to improve the process have centered upon (1) the exploration of new types of processing equipment, primarily to improve gas-solid contact, temperature control, and heat removal, and (2) the development of feeds from which UO_2 of greater reactivity towards hydrofluorination may be derived.

The reactivity problem is very complex and has received much attention. Some of the factors which bear upon this problem are discussed briefly below:

1. The UO_2 may be produced by a number of different processes, all of which start with an aqueous solution of uranyl nitrate. If certain impurities (notably the alkali metals) are not removed in subsequent processing steps, they can significantly diminish the hydrofluorination efficiency of the UO_2 which will be produced.^{7,8,9}

2. Two principal techniques exist for the production (from uranyl nitrate solution) of intermediates from which UO_2 may be derived. The first is thermal denitration of the uranyl nitrate solution to form uranium trioxide. The solution is

heated to evaporate water and excess nitric acid. Eventually solid phases appear ("dough stage") and heating is continued until the oxides of nitrogen have been driven off. The "reactivity" and other physical characteristics of the product are affected by the technique and by the particular type of equipment employed. Various techniques which are being used or which have been explored to some extent include: (1) batch heating in large gas-fired or electrically heated "pots,"¹⁰ (2) continuous calcination in which molten uranyl nitrate is added to a mechanically agitated bed of UO_3 in a heated trough-type reactor,¹¹ (3) spray denitration,¹² (4) fluidized-bed denitration,¹³ and (5) denitration in a drum dryer or rotary calciner.¹⁴

The second general technique is that of precipitating an intermediate from uranyl nitrate solution by the addition of reagents such as hydrogen peroxide, gaseous ammonia, or ammonium hydroxide. These precipitated materials may be subsequently dried and reduced (by hydrogen) to UO_2 which, in general, possesses a higher surface area and hence greater reactivity than many of the thermally denitrated materials. However, the lower bulk density of these precipitated materials increases the difficulty of producing UF_4 of high density, which is desired for subsequent processing to uranium metal. In this country, precipitation processes have not found acceptance for large-scale production of feed for the hydrofluorination step, but the British have employed precipitation with ammonium hydroxide to furnish "ammonium diuranate" (ADU) for their "Dry-Way" process.¹⁵

3. Associated with thermal denitration has been the use of additives which enhance the efficiency of conversion of UO_2 to UF_4 . Sulfur in some form (usually sulfuric acid), when added in small amounts to the uranyl nitrate solution prior to denitration, has a marked effect upon the reactivity of the UO_2 .¹⁶ More recently, beneficial effects have been observed when ammonium hydroxide is added to the uranyl nitrate.¹⁷ Thermally denitrated

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UO₃ has also been activated by hydrating the UO₃, and then dehydrating to produce a product of relatively low density.¹⁸

4. The reactivity of the UO₂ may also be affected by the procedures employed during the reduction of UO₃ or an intermediate to UO₂. The reduction is usually done at elevated temperatures with hydrogen or cracked ammonia.

In general, uncontrolled high temperature during reduction can bring about a serious loss of reactivity, particularly for those feeds consisting of the relatively dense, low-surface-area types of UO₃ (e.g., pot-denitrated UO₃).¹⁹ On the other hand, relatively high reduction temperatures need not be avoided in processing certain types of precipitated feeds. Moreover, prior conversion of such feeds to U₃O₈ at temperatures near 1400°F before hydrogen reduction appears to be beneficial.²⁰

It is possible to produce uranium dioxides differing very greatly in reactivity towards hydrofluorination. Thus, it is evident that attempts to improve the hydrofluorination process must take into consideration the mode of feed preparation.

Improvements which may be sought in the hydrofluorination process include the following: (1) increased throughput per reactor, consistent with high quality of the product, (2) lowering of the excess HF requirements—preferably to a point at which the off-gases may be disposed of economically by neutralization,* (3) improved temperature control and heat removal, (4) minimizing the dust carry-out from the reactors, and (5) elimination of caking and plugging in the reactors.²¹ All of these desired improvements depend largely upon the reactivity and physical characteristics of the feed.

In the laboratory, the hydrofluorination reaction has been studied extensively. Attempts have been made to elucidate the reaction mechanism.²² Other studies²³⁻²⁵ have involved use of the thermobalance to measure reaction rates of various UO₂ feeds in anhydrous HF or in mixtures of this gas with steam or inert gases.** Much of the work

has been limited to the characterization of particular feed materials by short, semi-empirical tests. One such test involves the determination of a "reactivity ratio" in which a given sample of UO₂ is reacted simultaneously with a "standard" sample of UO₂ in a small tube furnace. The resulting conversions to UF₄ after a given interval of time are compared.²⁷ Relatively few of the studies have been sufficiently complete, nor have the data been presented in a sufficiently organized manner to make them very useful in estimating the performance of plant-scale hydrofluorination equipment operating with various types of feeds.

The primary aims of the present study were to develop relatively complete reaction rate data for the hydrofluorination of two types of UO₂ which differ greatly in physical properties and to organize these data into a form useful in carrying out calculations for reaction in a countercurrent system. The two basic types of UO₂ studied were: (1) that derived from UO₃ which had been produced in the plant by pot denitration and which contained sulfate for activation, and (2) that derived from U₃O₈ which had been prepared from ADU formed by the addition of ammonium hydroxide to uranyl nitrate solution. The latter material was chosen for study since it is known to be inherently much more reactive than the pot-denitrated UO₃. In addition, hydrofluorinations were performed with ADU-source UO₂ which had been prepared by a technique which increased the density and particle size of the UO₂.

* Present practice requires the recovery of HF in the off-gases as 70 per cent acid, which is resold. The selling price of the 70 per cent acid is about 5 cents less (per pound of contained HF) than is the cost of 100 per cent HF.

** Probably the most detailed reaction rate study which has been made was that carried out at the AEC's New Brunswick Laboratory, in which pelletized UO₃ feeds were investigated in connection with the development of a moving-bed reactor system.²⁶

The investigation of reaction rates was carried out in a thermobalance constructed specifically for hydrofluorination work. The reactions were performed at several selected temperatures and with the gas phase consisting of several mixtures of HF and steam. A few rate determinations were made with nitrogen diluting the gas phase.

The hydrofluorination reaction, represented by the following equation,

is reversible, and in order to produce UF_4 it is necessary to maintain temperatures below those corresponding to equilibrium in the system. The temperature at which equilibrium exists is a function of the composition of the gas phase (which will contain HF, steam, and possibly an inert gas)

and the total pressure. Since the equilibria define the limiting conditions which cannot be exceeded if UF_4 is to be produced, a portion of the present study was devoted to the experimental and mathematical determination of equilibrium conditions.

In a final section of this report, the rate data were used to calculate the minimum retention times required for the hydrofluorination of the two types of UO_2 to 95 per cent UF_4 in an ideal counter-current system. Reaction conditions were selected to show the effect of diminishing the HF feed rate to a very low stoichiometric excess. From the results of these calculations and other considerations, it is possible to make certain predictions regarding the performance of the two types of feed materials in typical screw reactors.

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SUMMARY AND CONCLUSIONS

1. For the reversible gas-solid reaction,

equilibrium temperatures were determined over a range of HF concentrations (in the HF-H₂O gas phase) between 5 and 75 mole per cent at a pressure of essentially one atmosphere. With these data as a starting point, equilibrium conditions were calculated (1) for higher HF concentrations at one atmosphere, (2) for total pressures other than one atmosphere, and (3) for the gas phase containing an inert diluent gas in addition to HF and H₂O.

2. Using the chemical equilibrium data, a value of -50.6 kcal was calculated for the standard heat of reaction, ΔH° . This represents an average value over the temperature range of 660°F to 1260°F.

3. Hydrofluorination rates were measured for thin-bed samples of UO₂ in a thermobalance over wide ranges of temperature and HF-H₂O gas phase composition. Rates were obtained for two types of UO₂ differing greatly in physical characteristics; one type was derived from sulfated pot-denitrated UO₃ produced at this site, while the other was derived from laboratory-prepared "ammonium diuranate" (ADU). The ADU-source UO₂ (which was of lower bulk density and which possessed a relatively large specific surface area) was far more reactive than the pot-denitrated UO₃. With the ADU-source material, the maximum hydrofluorination rates occurred at lower temperatures. Although the initial reaction rates for the two types of UO₂ were not greatly different, the ADU-source material reacted far more readily during the final stages of the reaction.

4. The temperatures corresponding to the maximum instantaneous reaction rates are functions not only of the gas phase composition but also of the conversion level reached during the reaction. As a result, it is necessary to increase the temperature during the course of the reaction in order to complete the reaction in the shortest possible time.

5. The maximum instantaneous reaction rates

for each type of UO₂ may be conveniently represented upon a single chart as functions of the HF concentration in the HF-H₂O gas phase, the temperature, and the fraction of the solid phases converted to UF₄. This method of plotting the data facilitates the calculation of minimum retention times required for hydrofluorination in an ideal countercurrent gas-solid contactor.

6. Minimum retention times were calculated for four cases of countercurrent hydrofluorination in which the selected variables were the off-gas composition and the types of UO₂ feed. The results indicated that the ADU-type feed can be hydrofluorinated to 95 per cent UF₄ in a given ideal countercurrent reactor at throughputs approximately 3.5 times greater than that possible with the pot-denitrated feed and when operating with no greater than 7 per cent excess HF (based on 100 per cent reaction). Moreover, the heat of reaction would be developed more uniformly over the full length of the reactor.

7. Poor gas-solids contact in plant screw-type reactors appears to be primarily responsible for conversion rates that are one-sixth to one-eighth those found for the hydrofluorination of thin-bed samples in the thermobalance.

8. Based upon the thermobalance rate data alone, it appears possible to react the pot-denitrated UO₃ to 95 per cent UF₄ using much lower excesses of HF than are presently employed in standard practice. Thus the data indicate that the HF excess may be lowered from 185 per cent (approximate present practice) to at least 7 per cent while increasing the time required for conversion by about 15 per cent.

9. Samples of an ADU-source feed consisting of relatively large dense particles hydrofluorinated at rates almost identical with those observed for ADU-source samples of low density and fine particle size.

10. Two thermobalance runs in which nitrogen was used to dilute the HF-H₂O gas phase indicated (a) that the reaction rate with ADU-source

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UO₂ was diminished in the presence of nitrogen by an almost constant factor at all levels of conversion, and (b) that with pot-source UO₂, the reaction rate was similarly slowed during the

initial phases of reaction, but at conversion levels greater than 70 per cent, the instantaneous reaction rates were actually greater than those observed when the gas phase contained no nitrogen.

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DESCRIPTION OF EQUIPMENT

The major piece of equipment employed in this work was a thermobalance which was specifically designed and fabricated for the hydrofluorination of uranium compounds. With this equipment, it is possible to measure reaction rates in gas-solid reactions by observing continuously the change in weight of a sample while it is suspended from an analytical balance in an atmosphere containing the reactant gas.

The thermobalance and its associated equipment are shown in Figures 1 through 8. The reaction chamber consists of a vertically mounted section of standard 4-inch Monel pipe, the bottom of which is closed with $\frac{1}{2}$ -inch Monel plate. The upper end is flanged to accommodate a Monel cover plate which is $\frac{3}{4}$ inch thick. A gas-tight closure is

provided by a Flexitallic-type gasket consisting of asbestos compressed between spirally wound turns of thin Monel. Welded to the cover plate is an assembly (Fig. 3) which is provided with openings for the introduction of the suspension wire holding the sample basket. The off-gases pass to the laboratory hood through the lower horizontal pipe section and a connected piece of $\frac{3}{8}$ -inch copper tubing. The upper horizontal pipe section was originally connected to the nitrogen supply for the purpose of providing a buffer so that hydrogen fluoride would not escape from the reaction chamber into the room through the openings provided for the suspension wire. In practice, the buffer system was found to be unnecessary because the off-gases are exhausted to the labor-

FIGURE 1 Thermobalance Layout, Showing the Means of Introducing the Various Gases

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FIGURE 2 Thermobalance with Associated Electrical Equipment and Means for Introducing Various Gases

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FIGURE 3 Head Assembly for Reaction Chamber

FIGURE 5 Platinum Tray For Use With Powdered Samples

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FIGURE 4 Flash Vaporizer for Vaporizing HF-H₂O Solutions of Accurately Known Composition; Also Shown (At Left) is Equipment for Introducing Preheated Nitrogen (Used in Dilution Studies)

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FIGURE 6 Upper and Lower Baffle Assembly Used During Runs With Powdered Samples

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FIGURE 7 Platinum Mesh Basket and Baffle Assembly for Use With Pellet Samples

atryhood under a suction of about $\frac{1}{2}$ inch of water. As a result, there is a small inleakage of air when the nitrogen buffer is not used, but this air passes with the off-gases to the hood and does not enter the reaction chamber.

Fitted into the lower section of the reaction chamber is a set of three baffle plates perforated with holes $\frac{1}{8}$ inch in diameter located on $\frac{1}{4}$ -inch centers (Fig. 6 and 7). These serve to distribute and to help preheat the gases which enter through an opening in the bottom of the chamber.

Two types of sample holders were used. When equilibrium determinations were made, the samples consisted of pellets, and a basket constructed of platinum mesh was employed (Fig. 7). When reaction rates were measured, the samples (in the form of powders) were held in the shallow tray shown in the photograph of Figure 5 and in detail in Figure 8. To insure good sweeping of the gases over the sample when using this tray, a baffle

FIGURE 8 Platinum Tray Used for Powdered Samples

(Fig. 6) containing a centrally located hole $\frac{1}{2}$ inch in diameter was placed about $\frac{3}{4}$ inch above the tray.*

The reaction chamber is heated by a Hevi-duty electrical resistance furnace of 2500 watts capacity. The two halves of the furnace are mounted on vertical hinges so that they may be swung away from the reaction chamber to allow more rapid cooling. The reaction chamber can be heated to 1200°F in about 70 minutes, and to 1400°F in about 100 minutes. The highest temperature at which

* The need for the baffle above the tray and the baffles in the bottom of the reaction chamber is questionable. A series of hydrofluorination runs performed with and without the baffles when using anhydrous HF revealed no significant differences in the reaction rates. These results contradicted earlier experience, in which a similar thermo-balance had been used. The earlier experiments had indicated that baffling was necessary.

reactions can be conveniently investigated with the equipment is considered to be approximately 1400°F. Experience with similar units in this laboratory has shown that rapid oxidation and scaling of the outside surface of the Monel reaction chamber occurs at 1500°F to 1600°F.

The temperature within the reaction chamber is measured with a porcelain-insulated Chromel-Alumel thermocouple housed within a Conax $\frac{3}{16}$ -inch Monel protection tube. The thermocouple is mounted axially within the reaction chamber, with its tip extending to a point level with the sample.

The sample basket or tray is suspended on a nichrome wire from the pan of a Mettler Gram-atic analytical balance. With this balance, weight changes may be followed visually without manipulation over a range of 100 milligrams. Dial settings allow the weight reading to be changed in increments of 0.1, 1, 10, and 100 grams. The maximum capacity of the balance is 200 grams.

Figure 1 shows the method of introducing the various gases into the reaction chamber and of metering their flows. Hydrogen for reducing the samples of UO_3 or U_3O_8 to UO_2 is supplied from a commercial cylinder. The gas is passed through a catalytic (palladium) "De-Oxo" unit to remove oxygen. Moisture is removed by passage of the gas through a section of pipe filled with Drierite. Nitrogen, supplied from a commercial cylinder, also passes through the drying tube, but is not further purified. Anhydrous HF is supplied from a 25-pound cylinder. The flow is metered by a small rotameter which has a capacity of about 1500 cubic centimeters per minute and which consists of a Teflon metering tube fitted with a Monel ball float.

To provide gas mixtures of HF and steam of accurately known composition, the apparatus shown in Figures 1 and 4 was constructed. It consists essentially of a Monel flash chamber made of an 8-inch length of 2-inch pipe closed at the ends with $\frac{1}{4}$ -inch plate. Aqueous solutions of HF are dripped into this chamber through a length of

$\frac{3}{4}$ -inch Monel tubing, and the vapors are expelled through $\frac{1}{4}$ -inch Monel tubing. A Fisher gas burner is used to heat the chamber, which is also fitted with a flame shield and an insulated "hat" to deflect the hot burner gases away from the plastic tubing connections at the top of the chamber. To prevent overheating of the plastic tubing, it is also necessary to cool the Monel inlet tube. This is accomplished by passing air through a section of copper tubing that is brazed to the inlet tube.

The HF solutions are siphoned from a polyethylene bottle through $\frac{3}{16}$ -inch polyethylene tubing to the inlet of the flash chamber. The end of this tube is drawn out to form a drip tip which is inserted into a short length of polyethylene tubing of larger diameter. The flow of HF solution into the flash chamber can then be controlled by adjusting a screw clamp on the feed line until the desired drip rate is obtained.

The aqueous HF feed line is fitted with a cooling water jacket of copper tubing to prevent vapor-locking in the feed line when the more volatile concentrated solutions of HF are fed. The storage bottle containing the HF solutions is also kept cool with ice.

All sections of tubing and valves through which anhydrous HF gas or HF-steam mixtures pass are heated by electrical resistance tapes, over which asbestos paper is wrapped as insulation. The assembly on the reaction chamber cover and the off-gas line to the hood are heated electrically with windings of nichrome resistance wire.

The flash vaporizer performed satisfactorily with all aqueous solutions containing 85 per cent or less HF by weight. An attempt to operate with 100 per cent HF was unsuccessful because of vapor-locking in the feed line. The only other difficulty was corrosion of the valves handling the HF-steam mixtures of low HF concentration. Corrosion appeared to be limited to the valve seats and stems, which were made of a nickel alloy. The Monel valve bodies were apparently unaffected.

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Electrical equipment includes (1) a Brown Electronik Circular-Chart Recorder and Controller for regulating the power input to the furnace that heats the reaction chamber, (2) a time switch that can be set to turn on the furnace so that the reaction chamber will be at temperature and ready for use at the start of the working day, (3) a timer

(reading in hundredths of a minute) for timing the weight readings, (4) three variacs for controlling input to the several heating tapes, and (5) a 750-watt tube furnace for pre-heating the gases just before they enter the reaction chamber of the thermobalance.

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EXPERIMENTAL PROCEDURES

PREPARATION OF UO_2 SOURCE MATERIALS

The primary aim of this investigation was to obtain information concerning the hydrofluorination behavior of UO_2 derived from two widely different source materials. The first of these source materials was plant-produced uranium trioxide (UO_3) prepared from purified uranyl nitrate solution by thermal evaporation and denitration (commonly referred to as "pot" denitration). For the laboratory study, a representative quantity of this pot-denitrated oxide was prepared by blending 100-gram amounts of each of ten consecutive production lots. The material contained sulfate added for activation (nominally, 625 ppm on a uranium basis). Chemical analyses and physical properties of this material are given in Table I.

The second source of material was black oxide (U_3O_8) prepared in the laboratory from so-called "ammonium diuranate" (ADU) which was precipitated from uranyl nitrate solution with ammonium hydroxide.* The ADU was prepared in accordance with recommended procedures developed at this site in an investigation of the precipitation reaction.²⁸

Purified uranyl nitrate boil-down liquor was obtained from the plant and was diluted to a concentration of 160 grams uranium per liter. Ammonium hydroxide (28 per cent NH_3) was added slowly to

the agitated solution in a stainless steel beaker at a temperature of $65^\circ C$. The reagent was added in large excess until the pH rose to 8.6, as measured by a portable Beckman pH meter. The yellow precipitate was recovered by filtration on No. 41 Whatman filter paper and was then reslurried with distilled water and refiltered five times. The slurry filtered rapidly during the first four filtrations, but the last two filtrations became progressively slower due to the formation of a small quantity of colloidal material which tended to clog the filter paper and pass through with the filtrate. The washed ADU was then dried at $110^\circ C$ and was pulverized to break up soft lumps. A portion of the material was fired at $1400^\circ F$ in a muffle furnace for 40 minutes to convert it to an olive-colored U_3O_8 . This oxide was the starting material for the thermobalance study of the hydrofluorination rates of ADU-source UO_2 . Certain physical properties of the material are given in Table II.

Some of the ADU was used to prepare a quantity of U_3O_8 having a greater bulk density and from which a sample of relatively large mean particle size could be obtained. A paste was prepared by mixing with ADU a solution of uranyl nitrate in a ratio such that 15 grams of uranium as uranyl nitrate were combined with 100 grams of uranium as ADU. The paste was then heated in a crucible

* The true compound, ammonium diuranate, if it exists at all, is not prepared by the procedure outlined above. The yellow precipitate after drying at $100^\circ C$ contains less ammonia than is indicated by the formula, $(NH_4)_2U_2O_7$, and also contains water which is slowly lost upon heating. When heated to about 700° to $800^\circ F$, the water and ammonia are driven off and the color changes to orange. X-ray diffraction patterns of both the original dried precipitate and the heated material contain very few lines, indicating a poorly defined crystal structure. Conversion of the

material to UO_2 by hydrogen reduction however, yields a sharply defined X-ray diffraction pattern which is indistinguishable from that obtained with UO_2 derived from pot-denitrated UO_3 . When the heated ADU is dropped into water, it evolves copious quantities of a gas, the nature of which has not yet been investigated. Upon being heated to higher temperatures, the ADU undergoes transformation to U_3O_8 ; this transformation begins at much lower temperatures than that observed for the similar decomposition of the pot-denitrated UO_3 .

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TABLE I Chemical Analyses and Physical Properties of Plant-Produced, Pot-Denitrated UO_3

Chemical Analyses, Density, Etc.	Spectrochemical Analyses*		Dry Screen Analysis*	
	A*	B**	(ppm)	Mesh Wt %***
U (%)	—	81.44	Al <4 Mo <4	+40 0.5
UO_3 (%)	97.52	97.3	B <0.2 Na 2	+60, -40 0.8
H_2O (%)	1.25	1.49	Ba <1 N1 9	+80, -60 1.2
NO_3^- (%)	0.87	0.65	B1 <1 P <20	+100, -80 1.4
HCl-Insoluble (U_3O_8) (%)	0.44	0.56	Ca <10 Pb <1	+200, -100 6.9
Fe (ppm)	—	38	Cd <0.2 S1 <20	+325, -200 12.0
N1 (ppm)	—	5.8	Co <2 Sn <1	-325, 77.2
Th (ppm)	81	91	Cr 6 Sr <12	Surface Area by BET (nitrogen adsorption)
Na (ppm)	23	10	Cu 2 V <20	
SO_4 (ppm)	990	—	Fe 30 Zn <20	3.2 $\text{m}^2/\text{g}^\dagger$
on 40 mesh (%)	0.8	—	L1 <3 Dy 0.2	
Density (g/cc)	2.33	(Bulk)	Mg 6 Gd <0.02	1.7 $\text{m}^2/\text{g}^\ddagger$
Density (g/cc)	3.0	(Tap)	Mn <4	

* Analyses made on composite sample prepared for the thermobalance studies.

** Routine plant quality control analyses performed on a separate composite sample which was prepared from the same ten lots of UO_3 .

*** Screening done on a Rotap for 30 minutes.

† Performed on a sample of UO_3 heated to 750°F .

‡ Performed on a sample of UO_3 heated to U_3O_8 at 1400°F .

TABLE II Physical Properties of ADU and of U_3O_8 Derived from the ADU

Tap density of ADU = 1.3 g/cc

Tap density of U_3O_8 prepared from ADU = 1.5 g/cc

BET surface area (nitrogen adsorption)

ADU heated to 750°F ADU heated to U_3O_8 at 1400°F

S. A. = 15.2 m^2/g S A = 6.3 m^2/g

Dry screen analysis of U_3O_8 prepared from ADU*

Mesh	Wt %
+40	2.9
+60, - 40	2.0
+80, - 60	3.4
+100, - 80	2.1
+200, -100	5.2
+325, -200	10.0
-325	74.4

Density of U_3O_8 prepared from ADU that had been densified by the addition of uranyl nitrate

-80 mesh fraction, $\rho(\text{Tap}) = 2.1 \text{ g/cc}$

+80, -40 mesh fraction, $\rho(\text{Tap}) = 1.8 \text{ g/cc}$

+80, -40 mesh fraction, $\rho(\text{Bulk}) = 1.7 \text{ g/cc}$

* The coarser fractions actually consisted of weak agglomerates which could be crushed easily to fine powder.

to 1400°F forming U_3O_8 . After the material was completely converted to U_3O_8 , heating was continued for an additional 30 minutes at 1400°F . The lumps were then crushed and screened in such a manner as to recover as much as possible of the material as 40 to 80-mesh particles.

To achieve a greater sensitivity in the thermobalance determinations of equilibrium in the reversible hydrofluorination reaction, the UO_3 pellets used were prepared by the following procedure:

Plant-produced, nonsulfated, pot-denitrated UO_3 powder was mixed with sufficient water (13 grams H_2O per 100 grams UO_3) to form a stiff paste. The paste was then spread into a layer approximately $\frac{1}{4}$ inch thick on a piece of aluminum foil. After a few minutes, the oxide began to hydrate and harden in a manner analogous to the setting of plaster of Paris. While still sufficiently soft, the layer was sliced with a spatula knife to form cube-shaped pellets. The pellets were then detached from the foil and

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placed in a capped bottle overnight to allow sufficient time for complete hydration. Finally, they were dehydrated by heating in an oven to 750°F for several hours and were stored in a capped bottle.

PROCEDURE FOR DETERMINING EQUILIBRIA FOR THE REACTION

As will be shown in a later section of this paper, the temperature at which equilibrium is established for this reversible heterogeneous reaction is dependent upon (1) the total pressure of the system and (2) the composition of the gas phase in contact with the two solid phases (which consist of essentially pure UO_2 and pure UF_4). In this study, equilibria were established experimentally in the thermobalance at a total pressure of essentially one atmosphere and at several compositions of the binary $\text{HF}-\text{H}_2\text{O}$ gas phase. The method is outlined below.

1. A sample of UO_3 pellets (varying from 11.6 to 16.0 grams in weight) was reduced with hydrogen to UO_2 in the thermobalance at approximately 1150°F.

2. The reaction chamber was then cooled to a temperature known to be considerably less than that corresponding to equilibrium for the particular concentration of the $\text{HF}-\text{H}_2\text{O}$ gas mixture to be employed in the experiment. During cooling, a flow of nitrogen was maintained through the reaction chamber.*

* Under these conditions, any gain in weight of the sample during cooling indicated the presence of air, which causes reoxidation of the UO_2 sample. Occasionally, slow oxidation of the sample was observed. This difficulty was apparently caused by the presence of traces of oxygen in the nitrogen supply. Therefore, when oxidation was observed, the reduction step was repeated with a new sample and the UO_2 was cooled in nitrogen supplied from a newly installed cylinder.

3. While the reaction chamber was cooled, feeding of the aqueous HF solution to the heated flash vaporizer was begun. While the drip rate was being adjusted, the flashed vapors were by-passed to the laboratory hood.

4. The $\text{HF}-\text{H}_2\text{O}$ vapors were then diverted into the reaction chamber, and the nitrogen flow was discontinued. Since the temperature was well below the equilibrium value, the sample gained in weight as the UO_2 converted to UF_4 . Reaction was allowed to proceed until approximately 25 per cent of the reaction had been completed, and then the temperature of the reaction chamber was slowly increased by setting the temperature control up in increments of 10°F to 20°F at 2 to 4-minute intervals, depending upon the proximity to equilibrium.

5. As the temperature increased and as the equilibrium condition was approached, the rate of the reaction diminished rapidly (although reaction was far from complete) until finally, reversal of the reaction was indicated by a steady decrease in weight of the sample. The temperature at which the weight of the sample had reached a maximum and at which the net rate of reaction had fallen to zero was the equilibrium temperature corresponding to the particular composition of the gas phase.

6. In some instances, the equilibrium was also re-approached from the high temperature side by cooling the reaction chamber slowly until the sample weight passed through a minimum. In general, approach to equilibrium from the low-temperature and from the high-temperature side yielded consistent results.

Equilibrium temperatures were determined experimentally for several compositions of the gas phase between 5 and 75 mole per cent HF . The chief source of error was probably that due to the difficulty of determining the precise temperature at which the net reaction rate became zero, since the rate of weight change of the sample near the equilibrium condition was very low, particularly in those experiments in which low concentrations of HF were employed. One of the reasons for using

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pelletized samples rather than powder samples in the equilibrium determinations was to diminish this source of error, since the use of pellets made it more convenient to employ a large weight of sample and thus provide a greater weight change during reaction. Also, it is somewhat simpler to load the sample basket with pellets and to then introduce the sample basket into the reaction chamber.

The aqueous solutions of HF were prepared by appropriate dilution or by combination of 70 per cent or 100 per cent acids, which were available in the plant. The HF concentration of these solutions was determined to an accuracy of ± 0.1 per cent or better, by titration against a standardized solution of carbonate-free sodium hydroxide. The solutions were stored in polyethylene bottles in a dry-ice box. It was discovered that prolonged refrigeration at temperatures sufficiently low to cause separation of ice from the HF solutions resulted in saturation of these solutions with air. When the solution was then fed to the HF vaporizer, air bubbles would form in the feed line, making control of the drip rate difficult. The presence of the air also was undesirable because this would cause some oxidation of the samples during the equilibrium determinations. These difficulties were eliminated either by preparing the solutions just prior to the equilibrium determinations or by storing them at temperatures well above freezing.

During the equilibrium determinations, the HF solutions were fed to the vaporizer at a rate of roughly 0.08 gram mole per minute, which corresponds to a gas flow of about 5 liters per minute at a temperature of 850°F.

Prior to making the equilibrium determinations, calibration runs were made to establish the temperature corrections which should be applied to the indicated temperatures measured by the thermocouple in the reaction chamber. To do this, two types of thermocouples of thin-wire construction were introduced into the reaction chamber through the holes provided for the suspension wire. One of these auxiliary thermocouples was of the

"Ceramco" type, consisting of very thin Chromel and Alumel wires completely encased in a small thin-walled Monel tube filled with magnesia. The other thermocouple consisted of fine wires of Chromel and Alumel contained within a woven fiber-glass insulation, which was stripped away near the fused hot junction. The hot junctions were located at the level within the reaction chamber normally occupied by the sample to be reacted. Cold junctions were immersed in a Dewar flask containing an ice-water mixture; the e.m.f.'s were measured with a portable potentiometer. The calibration procedure consisted of measuring the temperatures indicated by the auxiliary thermocouple as the temperature indicated by the control thermocouple (Fig. 1) was lowered in 100°F increments from 1300°F to 500°F. During these runs, steam generated in the flash vaporizer was passed through the reaction chamber to simulate the effect of HF-steam flows during the subsequent equilibrium and reaction rate determinations. It was found that the temperatures measured by the thin auxiliary thermocouples were lower than those indicated by the control thermocouple; the difference, which at 1300°F was about 55°F, diminished linearly to about 40°F at a control setting of 500°F. This difference was considered to be a result of heat transfer between the hot furnace walls and the thermocouples, complicated by thermal gradients in the furnace walls.

The corrections indicated by these tests were applied to all temperatures indicated by the control thermocouple during subsequent thermobalance runs dealing with the measurement of equilibrium temperatures or reaction rates. In making these corrections, it was assumed that the temperature indicated by the thin auxiliary test thermocouples more accurately represented the true average temperature of the gas stream at the position occupied by the sample than did the temperature indicated by the bulkier control thermocouple. In the application of these corrections to the temperatures measured during runs dealing with the measurement of reaction rates, it is recognized

that inaccuracies arise from the fact that the gas stream temperature may differ considerably from that of the sample, due to the heat of reaction generated within the sample (particularly when the rate of reaction is high).

PROCEDURE FOR MEASURING REACTION RATES

In the measurement of reaction rates during the hydrofluorination of UO_2 in the thermobalance, the sample weight of pot-denitrated UO_3 or of U_3O_8 from ADU was approximately five grams. The bed depth of the UO_3 powder, when spread evenly on the sample tray, was about one millimeter; the bed depth of the less dense U_3O_8 powder was about 2 millimeters. (These bed depths, after reduction to UO_2 in the thermobalance, were considerably less as a result of shrinkage.)

The UO_3 samples were reduced in the thermobalance, using undiluted hydrogen. To insure that the UO_2 would possess maximum reactivity towards subsequent hydrofluorination, the reduction was performed with the temperature rising from about 850°F to 1150°F at the maximum heating rate. Under these conditions, the reduction proceeds rather slowly and the reaction rate is never suf-

ficiently great to cause overheating of the sample (which may adversely affect the reactivity of the UO_2).

The ADU-source U_3O_8 was reduced rapidly at a temperature setting of 1150°F . Although the hydrogen was diluted with nitrogen, the reaction was very rapid and was normally complete in about one minute. With the ADU-source material, reduction to UO_2 at low temperatures is not particularly desirable. In fact, it has been shown that it is desirable to process the ADU to UO_2 in such a manner as to purposely diminish the specific surface area of the material. Conversion of the ADU to U_3O_8 at 1400°F accomplishes this.*

After reduction of the sample to UO_2 in the thermobalance was completed, the temperature was readjusted to that chosen for the particular hydrofluorination run. During this readjustment, an atmosphere of nitrogen was maintained in the reaction chamber, and if any appreciable gain in weight of the sample occurred due to oxidation, the run was abandoned and a fresh cylinder of nitrogen was installed in accordance with the procedure discussed previously for making the equilibrium runs.**

*Previous work at this site²⁹ has shown that ADU which has been reduced directly to UO_2 by heating the material in a stream of hydrogen is extremely reactive. The UO_2 is pyrophoric and oxidizes rapidly upon exposure to air at room temperature. This material does not hydrofluorinate well when the reaction is carried out at elevated temperatures (ca 1000°F); the reaction is characterized by slow tail-end conversion rates, probably because of excessive sintering (which is commonly associated with materials possessing high specific surface areas). If the ADU is converted to U_3O_8 at elevated temperatures prior to its reduction, the UO_2 becomes less sensitive toward oxidation and its hydrofluorination to UF_4 at elevated temperatures is readily achieved. Experimental evidence gathered at this and other laboratories has shown that calcination of U_3O_8 at elevated temperatures is accompanied by rapid sintering^{30,31} (Also, see the specific surface data of Tables I and II.) It is therefore to be expected that UO_2 derived from ADU via U_3O_8 will possess a smaller specific surface area than that of UO_2 derived directly from ADU by low-temperature reduction.

**In early exploratory runs, cooling to lower temperatures had been done while a flow of hydrogen was maintained through the reactor chamber. However, it was observed that samples cooled below 600°F to 700°F slowly gained weight, and it was suspected that the samples were being reoxidized by traces of oxygen. At the time, it was not known whether the oxygen was introduced as a contaminant in the hydrogen or whether it was the result of leakage through the suspension wire holes or head gasket. Since the substitution of nitrogen for hydrogen eliminated the difficulty, it was concluded that the hydrogen contained oxygen despite the fact that it had been passed through a catalytic "De-Oxo" unit. The use of nitrogen during the period of temperature readjustment was therefore made standard practice. With nitrogen used, it would also be possible to detect leakage of air if a leak should develop in the equipment.

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During each hydrofluorination run, the temperature was maintained as constant as possible at the desired control setting. The drip rate of HF solution into the flash vaporizer was held as steady as possible to maintain a flow of about 0.08 gram mole of solution per minute, which is equivalent to a gas flow of about 5 liters per minute (computed at 850°F for a 60 per cent by weight solution of HF). The latter figure is only approximate, since the flows depended on a number of factors, such as (1) the size of the drops (which may have varied somewhat with HF concentration and viscosity of the solution) and (2) the densities of the solutions. In order to maintain the gas composition near the surface of the reacting sample at very nearly the same composition as that of the HF solution fed to the vaporizer, it was necessary to maintain a flow of HF such that the total quantity of HF fed to the reaction chamber during the course of the reaction was several times the stoichiometric amount required to react the sample. The faster the reaction rate, the less excess over stoichiometric requirements is actually supplied and the greater is the difference between the feed gas concentration and the gas concentration near the sample. It is estimated that in the fastest reactions, at least ten times the stoichiometric requirement of HF was supplied by the flashing apparatus. In those runs made with anhydrous HF supplied from a commercial cylinder, the excess for the most rapid reaction performed with the ADU-

source material may have been somewhat less than ten times the stoichiometric requirement.

With each of the two UO_2 -source materials, a large number of hydrofluorination runs were performed, covering a range of temperature settings from 455°F to 1150°F and with selected HF concentrations of 20, 30, 45, 60, 75, 85, and 100 per cent by weight. A few additional runs were performed at various HF concentrations, using the coarse 40 to 80-mesh fraction of U_3O_8 prepared from ADU-uranyl nitrate mixture. The effect (upon reaction rates) of nitrogen dilution of the HF- H_2O gas phase was also explored in two experiments.

During the hydrofluorination runs, the weight gain of the sample was recorded at time intervals of from one to ten minutes, depending upon the rate of the reaction. The per cent completion of the reaction at anytime was determined by dividing the observed gain in weight by the calculated theoretical gain in weight for 100 per cent reaction. In the calculation of theoretical weight gain, it was assumed that the sample consisted of pure UO_2 after reduction. (The weight of the sample as UO_2 is accurately determined from (1) the sum of the weights of the sample holder, suspension wire and sample before reduction, and (2) the observed weight loss during reduction.)

The hydrofluorination data for each thermo-balance run are tabulated in Appendix B.

EXPERIMENTAL RESULTS; DISCUSSION

EQUILIBRIUM DETERMINATION FOR THE REACTION,

In Figure 9 are plotted the experimentally determined equilibrium temperatures corresponding to a number of gas phase mixtures containing hydrogen fluoride and steam. For convenience in making certain calculations, HF concentrations are expressed as mole fractions. Similar data reported by Kuhlman³² and by the New Brunswick Laboratory³³ are also plotted in Figure 9 for comparison. Excellent agreement between the results of the present study and those reported by the New Brunswick Laboratory is indicated. The equilibrium temperatures reported by Kuhlman lie about 50°F below those determined in the present study.

The experimental equilibrium data define a curve along which the net rate of the reversible

FIGURE 9 Chemical Equilibria for the Reaction,
 $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightleftharpoons \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

hydrofluorination reaction is zero when the total pressure exerted by the gas phase is one atmosphere. The region lying to the left of the curve represents a region of temperature and HF concentration in which it is thermodynamically possible to convert UO_2 completely to UF_4 . In the region lying to the right of the curve, it is possible only to convert UF_4 to UO_2 .

By combining the results of the experimental equilibrium determinations with thermodynamic theory, it was possible to calculate equilibrium conditions (1) at HF concentrations greater than 75 mole per cent in the HF-H₂O gas phase, (2) at total pressures other than one atmosphere, and (3) for a gas phase containing an additional inert diluent gas. The standard heat of reaction may also be computed. The detailed thermodynamic theory and calculations are presented in Appendix A, and the results are summarized by the curves of Figures 10 and 11.

FIGURE 10 Effect of Pressure on Chemical Equilibria for the Reaction,
 $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightleftharpoons \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

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FIGURE 11 Effect of an Inert Diluent Gas on Chemical Equilibrium in the Reaction,
 $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightleftharpoons \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

The isobaric equilibrium curves of Figure 10 which were calculated for total pressures of 0.5, 1.0, 2.0, and 4.0 atmospheres illustrate the shift in equilibrium towards higher temperatures when the pressure is increased.

The curves of Figure 11 show that equilibrium is shifted toward lower temperatures when the gas phase contains an inert diluent gas.

On the basis of experimental equilibrium data, a value of -50.6 kcal was calculated for the standard heat of reaction, ΔH° . This value was obtained from the slope of the familiar straight line plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature and represents an average value over the temperature range of 660°F to 1260°F .

REACTION RATES IN THE HYDRO- FLUORINATION OF UO_2

From a practical standpoint, the equilibrium data are useful in that they define the limiting

conditions under which it is possible to convert UO_2 to UF_4 with gaseous HF . For example, one can conclude from the equilibrium data of Figure 9 that conversion of UO_2 to UF_4 cannot be accomplished at a temperature of 1100°F when the gas phase in contact with the UO_2 contains 30 mole per cent HF and 70 mole per cent steam and when the total pressure is one atmosphere. Reaction becomes possible when the temperature is lowered to 925°F , but since the system is then very nearly at equilibrium, the reaction will probably not proceed at a sufficient rate to be practical. One may therefore expect that optimum rate conditions must be sought at temperatures lower than 925°F . In other words, the net reaction rate approaches zero as equilibrium conditions are approached and becomes zero at equilibrium; the equilibrium data are inadequate for determining quantitatively the reaction rates at conditions displaced from equilibrium.

The term "reaction rate," as applied in this paper to the hydrofluorination of UO_2 , will be taken to mean the instantaneous rate of reaction as measured by taking the slope at any point on a curve relating the mole fraction of UO_2 reacted to UF_4 with time. This rate may then be expressed in the following units: moles of UF_4 produced per hour per mole of uranium. For a typical isothermal hydrofluorination, as carried out in the thermobalance (Fig. 14), the instantaneous rate may be plotted as a function of the conversion level.

In presenting the rate data, no attempt has been made to correlate these data in the form of kinetic equations. Other investigators have attempted simplification by methods such as expressing their isothermal rate data in terms of pseudo first-order kinetics, although there is no sound theoretical basis for doing so in reactions involving solids with gases. A good "fit" of the experimental results with first order kinetics would be entirely fortuitous since the method cannot take into account the many complex factors which actually determine the rates of gas-solid reactions. In the section to follow, the author will attempt to demon-

FIGURE 12 Maximum Hydrofluorination Rates of UO_2 Prepared from Sulfated Pot-Denitrated UO_3

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FIGURE 13 Maximum Hydrofluorination Rates of UO_2 Prepared from
ADU-Source U_3O_8

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strate how the reaction rate data may be put into useful form while avoiding the inaccuracies which result when such data are fitted to empirical equations.

Plotting of Reaction Rate Data

Several types of plots of the thermobalance reaction rate data may be prepared to illustrate aspects of the hydrofluorination reaction. The most detailed and useful of these are those presented in Figures 12 and 13 (one for each type of UO_2 studied). In these figures, the maximum instantaneous reaction rates may be determined as functions of (1) the mole fraction of HF in the binary HF- H_2O gas phase, (2) the mole fraction of solids converted to UF_4 , and (3) the temperature. The procedure employed in preparing these plots from the data obtained in the thermobalance runs is outlined below:

1. For each thermobalance run which was made at a particular temperature setting and a particular gas mixture of HF and steam, the reaction curve illustrated in Figure 14 was constructed. The conversion of the sample to UF_4 (expressed in mole per cent) was plotted against time in minutes.

2. Using a slope reader ("Derivimeter"), the instantaneous reaction rates (expressed in units of

moles UF_4 produced per hour per mole uranium) were obtained from the reaction curves. These values were then plotted against mole per cent conversion (Fig. 14).

3. Next, plots such as that illustrated by Figure 15 were prepared in which the instantaneous reaction rates were plotted against reaction temperature. A family of curves was produced, each curve corresponding to a given level of conversion reached during the course of the reaction. Similar plots were prepared for each of the seven gas phase compositions used in making the thermobalance runs.

4. The instantaneous rates corresponding to the maxima in the curves of the above plots and the temperatures corresponding to these maxima were transferred to the co-ordinates of Figures 12 and 13. Then it was possible to construct two sets of curves; each curve of the one set corresponding to a constant conversion level, and each curve of the second set representing a constant value of temperature.

In preparing the subplots and the final plots of Figures 12 and 13, some smoothing of the experimental data was necessary, but no serious discrepancies were observed. There is some doubt as to the accuracy and form of the constant temperature lines, particularly in the region of HF concentration above 85 mole per cent. Therefore, the temperatures are indicated as dashed lines in this region of relatively high uncertainty (Fig. 12). It will also be observed that some of the constant conversion lines or portions of them are shown as dashed lines, and that a constant value of temperature is indicated along these dashed portions. This was done to indicate that the reaction rates are those observed at the temperature indicated along the dashed curves and are not necessarily the maximum rates. As can be seen from the subplot of Figure 15, the temperatures at which the rates would reach maximum values at low levels of conversion would lie below the lowest temperature employed in the thermobalance runs.

FIGURE 14 Typical Thermobalance Conversion of UO_2 to UF_4

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FIGURE 15 Thermobalance Hydrofluorination of Pot-Source UO₂, Illustrating Method for Establishing Maximum Reaction Rates and Corresponding Temperatures

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Relation of Reaction Rate to Per Cent Conversion and Gas Composition

The principal points of interest concerning the thermobalance hydrofluorination lie in the comparisons which can be made between the hydrofluorination behavior of the two types of UO_2 . It will be seen from Figures 12 and 13 that maximum reaction rates occur at lower temperatures with the ADU-source material and that the rates are greater than those observed for pot-source UO_2 . At low conversion levels, the differences in the rates for the two materials are not great, but at higher conversion levels, the ADU reacts much more rapidly.

Another type of plot which may aid visualization of the hydrofluorination reaction is illustrated by Figures 16 and 17. Here the inverse of time (hours) to reach a conversion of 90 mole per cent is plotted against the temperature at which the reaction is carried out. The experimental data define a set of curves, each curve corresponding to a particular composition of the gas phase. (In the case of the pot-source material reacted with 20 per cent HF, a curve could not be plotted, since the thermobalance runs were terminated before the samples had reached 90 per cent conversion to UF_4). Each of the curves intersects the temperature axis at the equilibrium temperature. Again it is evident that the optimum hydrofluorination conditions for ADU-source UO_2 lie at temperatures considerably lower than those found for optimum hydrofluorination of pot-source UO_2 .

Sets of curves similar to those shown in Figures 16 and 17 may be plotted for levels of conversion other than 90 per cent. The maxima in the curves would shift towards lower temperatures for lower conversion levels.

It should be clear from the foregoing that the over-all time required to hydrofluorinate a given type of UO_2 will be minimized by programming the temperature in such a manner that the instantaneous rate is a maximum at all times during the course of the reaction. To accomplish this, the tempera-

FIGURE 16 Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3 , Showing the Effect of HF Concentration and Temperature on the Reaction Rates

FIGURE 17 Hydrofluorination of UO_3 Derived from ADU Showing the Effect of HF Concentration and Temperature on the Reaction Rates

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ture must be increased continuously in a definite manner as the reaction progresses. This is true even when a constant ratio of HF and H_2O is maintained in the gas phase.*

* By the use of a thermobalance, it has been demonstrated in this laboratory³⁴ and by others³⁵ that the hydrofluorination of UO_2 with anhydrous HF is accomplished most rapidly when the temperature is varied during the course of the reaction from an initially low value to a relatively high finishing temperature (600°F to 1100°F, for example). Runs performed isothermally at the high limit of temperature require more time for completion. The initial reaction rates at the lower temperature during the temperature-programmed runs are greater than those observed during the initial phases of the high temperature isothermal runs. These results agree with those deduced from thermobalance runs made at several constant temperature settings.

Factors Affecting the Reaction Mechanism: Driving Forces

The effect of temperature upon reaction rates in the hydrofluorination of UO_2 is further illustrated by the set of isothermal reaction curves shown in Figure 18. This particular set of reaction curves was obtained with an HF- H_2O gas mixture containing 28.2 mole per cent HF and when reacting the ADU-source UO_2 . Similar sets of curves were obtained with pot-source UO_2 and with other gas phase compositions. In accordance with the previous discussion, it will be observed that the initial rates of reaction increased as the temperature was reduced. However, it is apparent that the final rates of conversion diminished as the temperature was lowered below about 600°F.

FIGURE 18 Thermobalance Hydrofluorination of ADU-Source UO_2 at Various Temperatures

Let us consider the reversible reaction as written below:

Kinetically, it may be considered that two reactions are proceeding simultaneously; the forward reaction produces UF_4 while the reverse reaction produces UO_2 . The net reaction will produce either UF_4 or UO_2 , depending upon the ratio between HF and H_2O in the gas phase, the pressure, and the temperature. The rates of both the forward and the reverse reactions will increase with temperature in accordance with classical kinetic theory, but the rate of the forward reaction does not increase with temperature as rapidly as does that of the reverse reaction. Hence, it is possible that a temperature will exist at which the two rates are identical and the net reaction rate will then be zero. This point corresponds to that at which the free energy, ΔF , for the net reaction is zero. ΔF may be considered as a "chemical potential" or thermodynamic driving force for the net reaction.

At conditions displaced from equilibrium, ΔF for the reaction with the products and reactants in any arbitrary states is given by the equation,³⁶

$$\Delta F = RT \ln \frac{Q}{K}$$

where ΔF = free energy change for the reaction in calories. (The direction of the reaction must be specified; the direction that produces UF_4 will be chosen.)

T = absolute temperature ($^{\circ}\text{K}$)

K = the equilibrium constant

Q = the arbitrary reaction quotient

The terms, K and Q , must be clarified. The equilibrium constant is given by

$$K = \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{HF}})^4}$$

where the activities, $a_{\text{H}_2\text{O}}$ and a_{HF} , of HF and H_2O in the gas phase are those required to produce equilibrium in the system at temperature, T . The reaction quotient, Q , is given by

$$Q = \frac{(a'_{\text{H}_2\text{O}})^2}{(a'_{\text{HF}})^4}$$

where the activities, $a'_{\text{H}_2\text{O}}$ and a'_{HF} , are those at the arbitrarily selected concentration of HF and H_2O in the gas mixture employed for the reaction at the same temperature, T .

As shown in Appendix A, the activities of the HF and H_2O may be expressed as follows, since activity coefficients are essentially unity:

$$a_{\text{HF}} \cong N_{\text{HF}} \Pi, \quad a'_{\text{HF}} \cong N'_{\text{HF}} \Pi$$

$$a_{\text{H}_2\text{O}} \cong N_{\text{H}_2\text{O}} \Pi, \quad a'_{\text{H}_2\text{O}} \cong N'_{\text{H}_2\text{O}} \Pi$$

where N is the mole fraction of the component gas in the gas phase and Π is the total pressure.

Therefore, by substitution,

$$\Delta F = RT \ln \frac{(N_{\text{HF}})^4 (N'_{\text{H}_2\text{O}})^2}{(N_{\text{H}_2\text{O}})^2 (N'_{\text{HF}})^4} \quad (\text{at } \Pi = 1 \text{ atmosphere})$$

By use of the above equation, values of ΔF were calculated at various temperatures for the gas phase containing 28.2 per cent HF and 71.8 mole per cent H_2O . Values of N_{HF} and $N_{\text{H}_2\text{O}}$ may be found from Figures 9 or 10. The results are tabulated below.

TABLE III Free Energy Change, ΔF , for Hydrofluorination at Total Pressure of One Atmosphere with a Gas Phase Containing 28.2 Mole % HF and 71.8 Mole % H_2O

Temperature ($^{\circ}\text{F}$)	ΔF (cal)
1200	9,980
1100	6,110
1000	2,450
940	0 (equilibrium)
900	-1,345
800	-5,170
700	-8,890

It will be seen that ΔF rapidly becomes negative as the temperature is lowered. The more negative ΔF becomes, the greater is the chemical potential or driving force for the reaction proceeding in a direction such that UF_4 is produced.

It cannot be said that the rate at which UF_4 is formed should be directly proportional to the negative value of free energy change over a large interval of temperature. However, if the temperature

is lowered below that corresponding to equilibrium, ΔF is the basic driving force responsible for the reaction rate during the initial phases of the reaction.

In reactions between gases and solids, it may be expected that the rates will also be affected by diffusional resistances. In the hydrofluorination of UO_2 , the fluoride reactant must penetrate to the reaction sites within the solid particles or crystallites while the oxygen reaction product must escape by reverse diffusion. Further, it is to be expected that the diffusional resistance will increase as reaction proceeds, since the diffusing species must be transferred to or from reaction sites located at greater and greater depths within the solid particles.

An increase in diffusion rates should be accomplished by increasing the temperature and/or the concentration of HF in the gas phase. Temperature, together with HF concentration, may then be considered as a second driving force in the hydrofluorination reaction, and the importance of this driving force should increase as the reaction progresses towards completion.

By use of the concept of two driving forces, it is possible to explain in a qualitative manner why the temperature should be increased during the reaction in order to maintain maximum instantaneous reaction rates. During the initial phases of reaction, the temperature should be relatively low in order to take advantage of the large driving

force due to chemical potential. However, as the reaction proceeds, the diffusional resistance increases so that it becomes necessary to raise the temperature to provide an increasing driving force to overcome this diffusional resistance. Raising the temperature will be at the expense of diminishing the chemical potential. Obviously, then, there will be an optimum temperature at each level of conversion at which the two driving forces combine to give the highest rate of reaction.

In comparing the relative hydrofluorination behavior of pot-source UO_2 and ADU-source UO_2 , one may conclude that the chemical driving force is the same for both materials, since the two materials do not differ chemically or in crystal structure. Hence, the initial reaction rates of both forms of UO_2 should not differ if chemical potential provides the chief driving force for reaction. However, since the UO_2 from ADU exists in a state of much finer subdivision (as indicated by the difference in specific surface areas of the two materials), its diffusional resistance must be less than that of the pot-source UO_2 at all stages of the reaction. As a result, lower temperatures will suffice to maintain optimum rates. Furthermore, because it is not necessary to greatly increase the temperature of ADU-source UO_2 during reaction in order to overcome diffusional resistance, it is possible to take more complete advantage of the greater driving force due to chemical potential at the lower temperatures, and thus to enhance reaction rates.

MISCELLANEOUS REACTION RATE DETERMINATIONS

EFFECT OF DENSIFICATION AND PARTICLE SIZE ON THE HYDROFLUORINATION RATES OF ADU-SOURCE UO_2

As explained in the section dealing with the preparation of the UO_2 -source materials, (Table II), a portion of the ADU was mixed with uranyl nitrate solution and then converted to U_3O_8 at 1400°F to produce a product having a tap density about 40 per cent greater than that of U_3O_8 prepared from ADU without uranyl nitrate addition. Furthermore, the more dense form of U_3O_8 was crushed and screened to yield a large percentage of material in the range of particle size between 40 and 80 mesh. This fraction was reduced and hydrofluorinated in three thermobalance runs, using anhydrous HF, 60 per cent HF, and 30 per cent HF. The results may be compared with those of runs made with the less dense U_3O_8 at the same temperatures and HF concentrations (Fig. 19).

The reaction curves of Figure 19 indicate that

the material of relatively large particle size and greater particle density hydrofluorinated very similarly to the material of lower density and smaller average particle size. In the runs with 100 per cent HF and 60 per cent HF, the coarse material was apparently slightly less reactive than the fine material, but the trend was reversed in the run made with 30 per cent HF. The small differences observed between the two sets of runs may not be significant within the limits of experimental precision.

The results indicate that particle size has a relatively minor effect upon reaction rates when the feed material is derived from ADU. This is true, probably, because the particles possess sufficient porosity so that the gases meet very little resistance in penetrating to the actual crystallites which make up the particles, and it is likely that the reaction rate is primarily determined by the size of these crystallites. In the case of

FIGURE 19 Hydrofluorination of UO_2 Derived from ADU

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UO₂ derived from ADU, these crystallites are small, as is apparent from the relatively high value of 6.3 m²/g measured for the specific surface area of the parent U₃O₈.

Actually, part of the UO₂ of greater particle density (i.e., 13 per cent of the material) had been derived from uranyl nitrate by a process involving thermal denitration. The hydrofluorination results indicated that the presence of this thermally denitrated portion did not significantly alter the reactivity of the mixture.

The findings discussed above may have practical significance in considering the use of precipitated or low-density feed materials for the production of green salt (UF₄). Normally, these feeds (when directly processed) yield a green salt less dense than the green salt produced from pot-denitrated UO₃. This low density is undesirable* in the subsequent bomb reduction step (in which the UF₄ is reduced to massive uranium metal). Although densification of the UF₄ may be accomplished by sintering at high temperatures, this would involve perhaps a separate processing step and additional equipment. On the other hand, the feed may be densified (prior to its reduction to UO₂ and hydrofluorination) in a manner such as that described in this report for the densification of ADU. The degree of densification that may be achieved is indicated by the following tapped densities of samples of UF₄ (which were produced in thermobalance runs from the two ADU-source feeds). The tapped density of the densified form was 2.7 g/cc (after the relatively coarse particles were ground to a fine powder), and the tapped density of the less dense ADU-source material was 2.2 g/cc. This is not necessarily the optimum densification that may be achieved by the uranyl nitrate addition technique consistent with maintaining high reactivity of the UO₂.

* The low density of the green salt diminishes the quantity of the UF₄-magnesium charge which may be placed in each reduction bomb.

The tapped density of UF₄ prepared from pot-denitrated UO₃ is normally about 3.5 g/cc. A tapped density of 3.0 g/cc has been proposed as acceptable for metal-grade green salt.³⁷

Predensification of low-density feeds may be incorporated as an integral part of the process employed in producing the feed and may not constitute a separate additional step. For example, in producing an ADU-type feed, the wet precipitate must be dried to yield a powder which may be fed to the reduction reactors in the green salt plant. In a densification procedure based upon the addition of uranyl nitrate, the wet filter cake could be mixed with a concentrated uranyl nitrate solution in a pugging operation and then fired to U₃O₈. The latter process might prove to be more economical than the slower, lower temperature drying process which it would replace.

The fact that particle size has little effect upon the hydrofluorination rates of densified ADU-source UO₂ suggests that it would be advantageous to employ such a feed in a relatively coarse form in order to reduce the carry-out of dust from the hydrofluorination reactors. Moreover, the use of a coarse grind* may help to eliminate caking and plugging in these reactors.

EFFECT OF DILUTING THE GAS PHASE WITH NITROGEN

Two thermobalance runs were made with a gas phase containing nitrogen, HF, and steam. The apparatus used to introduce the nitrogen gas may be seen in Figures 2 and 4. The gas was metered with a calibrated Brooks rotameter (shown mounted on the side of the hood) and was passed through a coil of heated copper tubing before being fed into

* In contrast, some exploratory tests at this site have been directed towards finer grinding of pot-denitrated UO₃ in an effort to increase reactivity. Extremely fine grinding (micronizing) has been investigated at the St. Louis Production Center.³⁸

the line carrying the mixture of HF and steam which had been generated in the flash chamber. In both runs, the solution of HF fed to the flash chamber contained 60 per cent by weight HF, and the flows of nitrogen and HF solution were adjusted to maintain (as nearly as possible) an equimolar ratio between the nitrogen and the HF-H₂O mixture. Expressed as molar percentages, the flows were adjusted to yield a gas mixture containing 28.7 per cent HF, 21.3 per cent H₂O and 50 per cent N₂. In both of these experiments, the total gas flow was set at about 0.076 gram mole per minute.

In order to adjust the flow rate of HF solution to the flash chamber, it was necessary to establish a relationship between the rate at which drops of the solution were fed into the flash chamber and the weight of solution fed. This was done by weighing the quantity of solution delivered from the drip tip during an interval of three minutes and noting the number of drops delivered in this interval. During these determinations, the polyethylene feed line was disconnected from the inlet of the flash chamber, and the solution was dripped into a small preweighed polyethylene bottle containing water. (The water served to dilute the HF and to minimize evaporation losses.) It was determined that the weight of solution delivered per drop was 0.0244 gram and was constant over a rather large range of feed rate.*

One of the thermobalance runs was performed with UO₂ derived from the pot-denitrated UO₃, with the temperature held at 925°F. The other run was made at 760°F with the 40 to 80-mesh fraction

of the densified U₃O₈ which had been prepared from ADU-uranyl nitrate mixture. The reaction curves for the hydrofluorinations are shown in Figure 20. For purposes of comparison, the reaction curves are also shown for runs made with the same UO₂ - source materials and at the same temperatures but with the gas phase containing no diluent nitrogen. (In all four runs, the HF/H₂O ratio was the same.)

With the ADU-source material, dilution of the HF-H₂O gas phase with an equimolar amount of nitrogen reduced the rate of hydrofluorination by a factor of roughly 2.5 during the entire course of the reaction. With the pot-source UO₂, the initial rate of reaction was slowed by a factor of about three. However, by the time that the reaction had become about 70 per cent complete, the instantaneous rate in the diluted gas (as measured from the slope of the reaction curve) had become equal to that observed for the run performed without nitrogen dilution. At conversion levels above 70 per cent, the instantaneous rate in the diluted gas actually surpassed that observed for the undiluted run, and the reaction finally reached a slightly higher level of conversion.

The mechanism that improved the reaction rate of UO₂ derived from pot-denitrated UO₃ during the late stages of hydrofluorination in nitrogen-diluted gas cannot be deduced from the few experiments which have been described. This effect has previously been reported by at least one other investigating group, however.³⁹ It has been hypothesized that diluting the reactant HF gas may alleviate sintering during the initial stages of the reaction, when it is possible that relatively high temperatures may be developed within the rapidly reacting particles. Any sintering might increase the diffusional resistance offered by the particles to the gases and thus tend to slow the reaction during its late stages. On the basis of this hypothesis, one might expect the ADU-source UO₂ to be more readily sintered than the pot-source material, since it reacts faster and possesses a much greater specific surface area.

* During the thermobalance runs, it was possible to hold the drip rate within only about 10 per cent of the desired 30 drops per minute. Furthermore, other factors, such as slight back pressure and higher temperatures at the drop tip, may have altered the size of the drops while the HF solution was fed into the flash chamber. Therefore, it is possible that the actual ratio of nitrogen to HF-H₂O mixture may have experienced a corresponding variation from the scheduled value.

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However, the factors of particle density and porosity may modify the effect of sintering. Even though sintering may occur with both types of UO_2 , its effect in reducing the rate of hydro-

fluorination during the late stages of reaction may be more serious with that UO_2 possessing the greater particle density and lower porosity.

FIGURE 20 Effect of Nitrogen Dilution on Hydrofluorination Rates

APPLICATION OF THE REACTION RATE DATA TO CALCULATIONS OF HYDROFLUORINATION IN A COUNTERCURRENT SYSTEM

The main purpose of this section is to illustrate general methods by which the reaction rate data derived from the laboratory thermobalance investigation can be applied, together with other information, to estimate the performance to be expected when hydrofluorination is conducted under countercurrent conditions in typical plant reactors. These illustrations will pertain most closely to hydrofluorination conducted in an idealized countercurrent reactor. Four problems will be solved in which the primary variables will be the type of UO_2 feed and the HF excess employed. The solution of these problems will yield quantitative information regarding (1) the feasibility of employing low excesses of HF (which is desirable from an economic standpoint), and (2) the desirability of employing more reactive feed types to increase production rates.

Four cases are to be considered, the conditions of which are specified below:

Case A — The feed is UO_2 derived from pot-denitrated UO_3 , to which the reaction rate data of Figure 12 are applicable. The product from the reactor is to be 95 mole per cent UF_4 , with the balance assumed to be unreacted UO_2 . The feed gas is 100 per cent HF, and the off-gas composition is selected to be 20 mole per cent HF and 80 mole per cent H_2O .

tion is selected to be 20 mole per cent HF and 80 mole per cent H_2O . The temperature distribution along the length of the reactor is such that the maximum reaction rate is realized at each point.

Case B — All conditions are the same as Case A, except that the feed is UO_2 derived from ADU to which the rate data of Figure 13 apply.

Case C — The feed is UO_2 derived from pot source UO_3 . The product is to be 95 mole per cent UF_4 , 5 mole per cent UO_2 . The feed gas is 100 per cent HF, and the off-gas composition is selected to be 80 mole per cent HF and 20 mole per cent H_2O . The temperature distribution corresponds with that required for maximum reaction rates.

Case D — All conditions are the same as Case C, except that the feed is UO_2 derived from ADU.

It is desired to calculate first, the minimum retention time required in each of the above cases to react the UO_2 to 95 mole per cent UF_4 . The method of calculating these minimum residence times follows.

Consider a countercurrent hydrofluorination process taking place in an idealized reactor under the conditions specified in Case A.

CASE A Idealized Countercurrent Reactor

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Over the length, ds , the rate of formation of UF_4 is given by,

$$R = \frac{d N_{UF_4}}{dt}$$

where N_{UF_4} = mole fraction of UF_4 in the bed of solids at ds .

t = time (hours)

R = instantaneous reaction rate at ds , moles UF_4 formed/hour, per mole of solids entering ds .

With the quantities defined as above, R is independent of the UO_2 feed rate. Solving for dt and integrating,

$$t = \int_{N_{UF_4}=0}^{N_{UF_4}=0.95} \left(\frac{1}{R} \right) d N_{UF_4}$$

Since the temperature distribution is selected such that the reaction rates are maximum at all points along the reactor, the time required for reaction is a minimum, and we may write

$$t \text{ (min)} = \int_{N_{UF_4}=0}^{N_{UF_4}=0.95} \left(\frac{1}{R_{\max}} \right) d N_{UF_4}$$

Solution of the integral involves graphical integration. A plot of $\frac{1}{R_{\max}}$ against N_{UF_4} is prepared, and the area under the curve is the required minimum retention time. First, however, it is necessary to relate $\frac{1}{R_{\max}}$ and N_{UF_4} . This is accomplished by making appropriate material balances as follows:

Over-all Material Balance Around the Reactor

Basis: One mole UO_2 entering the reactor.

$$\begin{aligned} \text{Moles } H_2O \text{ produced by reaction} &= 2 \times 0.95 \\ &= 1.90 \end{aligned}$$

$$\text{Moles off-gas} = \frac{1.90}{0.80}$$

$$= 2.375$$

$$\begin{aligned} \text{Moles HF in off-gas} &= 2.375 - 1.90 \\ &= 0.475 \end{aligned}$$

$$\begin{aligned} \text{Moles HF used in the reaction} &= 4 \times 0.95 \\ &= 3.80 \end{aligned}$$

$$\begin{aligned} \text{Moles HF fed to the reactor} &= 3.80 + 0.475 \\ &= 4.275 \end{aligned}$$

$$\begin{aligned} \text{Excess HF} &= \frac{0.275}{4} \times 100 \\ \text{(based on 100\% conversion)} &= 6.9\% \end{aligned}$$

Next, any value of N_{UF_4} is selected between the limits, $N_{UF_4} = 0$ and $N_{UF_4} = 0.95$. A material balance around the section of reactor shown in solid line below, yields the composition of the gas phase in contact with the bed of solids corresponding to the selected value of N_{UF_4} .

$$\begin{aligned} \text{Let } N_{UF_4} &= 0.400. \text{ For the reactor section shown,} \\ \text{Moles } H_2O \text{ produced by reaction} &= (0.950 - 0.400) \times 2 \\ &= 1.100 \end{aligned}$$

$$\begin{aligned} \text{Moles HF used in reaction} &= (0.950 - 0.400) \times 4 \\ &= 2.200 \end{aligned}$$

$$\begin{aligned} \text{Moles HF left at } ds &= 4.275 - 2.200 \\ &= 2.075 \end{aligned}$$

$$\begin{aligned} N_{HF} \text{ at } ds &= \frac{2.075}{2.075 + 1.100} \\ &= 0.654 \\ &= \underline{65.4} \text{ mole \% HF} \end{aligned}$$

The reaction rate, $R_{\max}$, can now be obtained from Figure 12 for $N_{\text{UF}_4} = 40$ mole per cent and $N_{\text{HF}} = 65.4$ mole per cent. Thus, $R_{\max}$ is found to be 7.52 moles UF_4 per hour per mole of UO_2 fed to the reactor, and the temperature at which this rate occurs is 780°F .

The calculation is repeated for several selected values of N_{UF_4} ; the results are presented in Table IV.

In Figure 21, $\frac{1}{R_{\max}}$ is plotted against N_{UF_4} . The area under the curve between $N_{\text{UF}_4} = 0$ and $N_{\text{UF}_4} = 0.95$ is equivalent to the minimum retention time.

$$\begin{aligned} t_{\min} &= 0.467 \text{ hour} \\ &= 28.0 \text{ minutes} \end{aligned}$$

The same procedure was employed in calculating the minimum residence times for cases B, C, and D. The results are given in Table V, which includes additional information pertinent to later discussion.

Figures 22 through 29 were also prepared for each of the four cases under consideration. The first four plots show the percentage of the minimum retention time required to reach a given level of

conversion within the bed of solids. The additional plots illustrate the temperature profiles corresponding to the maximum reaction rates and the degree of conversion reached in the solids as they travel through the reactor. In preparing the latter four plots, it was assumed (1) that the full length of the reactor is utilized in producing a 95 mole per cent product, and (2) that the solids velocity (moles/hour) is constant.

FIGURE 21 Plot of $\frac{1}{R_{\max}}$ Versus Mole Fraction UF_4 in Bed of Solids. Countercurrent Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3 (Case A).

TABLE IV

Mole Fraction UF_4 in Bed, N_{UF_4}	Mole % HF in Gas Phase, N_{HF}	Maximum Reaction Rate, Moles UF_4 /hr, $R_{\max}$	Temperature Corresponding to Max Rate, $T_{\max}$ ($^\circ\text{F}$)	$\frac{1}{R_{\max}}$
0	20.0	2.65	650—	0.377
0.10	34.0	4.50	650—	0.222
0.20	46.0	5.87	650	0.170
0.30	56.3	6.95	750—	0.144
0.40	65.4	7.52	780	0.133
0.50	73.3	7.88	810	0.127
0.60	80.4	6.40	880	0.156
0.70	86.8	3.13	950	0.319
0.80	92.5	1.42	970+	0.704
0.85	95.1	0.93	980+	1.075
0.90	97.6	0.50	1000—	2.00
0.925	98.5	0.33	1000	3.03
0.95	100.0	0.16	1000+	6.25

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FIGURE 22 Countercurrent Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3

FIGURE 24 Countercurrent Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3

FIGURE 23 Countercurrent Hydrofluorination of UO_2 Derived from ADU

FIGURE 25 Countercurrent Hydrofluorination of UO_2 Derived from ADU

MINIMUM RETENTION TIME

In Table V, it will be observed that solids feed rates, HF feed rates, and off-gas rates for each of the four cases are given relative to those calculated for Case C. This comparison with Case C is made because the conditions chosen for the calculation of minimum residence time in Case C approximate those for which experience in plant-scale screw reactors is available.

The minimum retention times calculated from the thermobalance rate data are obviously much shorter than those which are required in actual plant-scale screw reactors. This is to be expected, since a number of factors tend to reduce the reaction rates in the plant equipment. Foremost among these, probably, is the "bed effect," in which the reaction rate within the bed of powder (which averages a few inches in depth) is diminished due to the limited rate at which the reactant gas penetrates to points within the bed. It is probable that only a thin surface layer of the bed undergoes reaction at rates comparable with those measured for thin beds of powder in the thermobalance. Another factor which should tend to reduce the rate of reaction is the presence, within the bed (and perhaps even above the bed surface),

of an appreciable HF concentration gradient normal to the direction of bed movement. Such gradients are minimized in the thermobalance, since the bed depth is small and a relatively high gas velocity is maintained over the surface of the sample to sweep away the water vapor formed in the reaction. It is thus apparent that the reactors now in use, while utilizing countercurrent feed, are not the true countercurrent contactors assumed in the calculations.

Another factor which may tend to diminish the over-all conversion rate is deviation from the temperature profile required to yield maximum rates at each point within the bed. This may in turn be related to difficulties in removing the heat of reaction, which is removed primarily by conduction through the reactor shell. If the rate of heat removal is insufficient in any zone, the bed temperature tends to rise and the reaction temperatures approach more closely the temperatures corresponding to thermodynamic equilibrium at which the reaction rates are zero.

There has been plant experience with the operation of screw reactors employing feeds similar in reactivity to the pot-source UO_2 employed in the present study. When operating under conditions of

TABLE V Countercurrent Hydrofluorination of Two Types of UO_2
(Minimum retention times based on thermobalance reaction rate data)

Case	UO_2 Source	Mole % HF in Off-Gas*	Calculated Per Cent Excess HF**	Minimum Retention Time [†] Required (min)	UO_2 Feed Rate Ratio ^{††}	HF Feed Rate Ratio [‡]	Off-Gas Rate Ratio ^{‡‡}
A	Pot- UO_3	20	6.9	28.0	0.84	0.32	0.21
B	ADU	20	6.9	6.65	3.55	1.33	0.89
C	Pot- UO_3	80	185	23.6	1.00	1.00	1.00
D	ADU	80	185	3.81	6.19	6.19	6.19

* Mole % H_2O in off-gas = 100 - mole % HF

** Per cent excess HF, based on 100% conversion of UO_2 to UF_4

† Minimum retention time to reach 95 mole % UF_4

†† Feed rates are maximum values, relative to Case C. Maximum feed rates are assumed to be inversely proportional to the minimum residence times. Molar holdup of the reactor is assumed to be independent of feed rate and feed type.

‡ Moles HF feed gas relative to Case C when operating at the maximum UO_2 feed rate.

‡‡ Moles off-gas relative to Case C when operating at the maximum UO_2 feed rate.

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HF excess and off-gas concentration similar to those chosen in calculating the minimum residence time for Case C, it is estimated that the actual retention times required are 4 to 6 hours. This indicates that the actual retention times are greater than those calculated from the thermobalance rate data by a factor of roughly six to eight. The magnitude of this factor suggests that there is a large potential for increasing the productive capacity of the screw-type reactor by means of enhanced gas-solid contact. Suggested possibilities include the use of lifting flights to increase the surface of the solids exposed to the gas and the use of baffling to increase the gas velocities.

Since the conditions chosen in computing the minimum retention time in Case C parallel those for which production experience is available, it is of interest to compare the results of the calculations performed for Cases A, B, and D with those of Case C. A comparison between Cases A and C indicates that the pot-source UO_2 can be hydrofluorinated to 95 mole per cent UF_4 under conditions such that the HF concentration in the off-gas is only 20 mole per cent, but that the UO_2 feed rate must be diminished by 15 per cent. The feed rate might have to be lowered more than 15 per cent because the calculation does not take into account the effect upon the reaction rates of lowering the velocity of the gas stream over the bed of solids. Thus, from the data presented in the last two columns of Table V, it is seen that the flow rate of the gases in Case A will average approximately only one-quarter of the flow rate in Case C. This may result in much less effective contact of the solids with the reactant HF gas, and may make necessary a lowering of the solids feed rate well below that calculated for Case A. It is concluded that lowering of the HF feed rate to the point at which it is economical to neutralize the off-gases rather than to recover the excess HF as 70 per cent acid may be accompanied by a loss in conversion capacity of the order of 15 per cent or greater.

The reverse situation is indicated by a comparison of the results of Case D with those of Case C. Here, a very great increase in the production capacity of a screw-type reactor should result if the pot-source UO_2 is replaced by a feed derived from ADU. The increase may be somewhat greater than that indicated by the calculations because the gas velocity would be increased in proportion to the solids feed rate. On the other hand, a six-fold increase in the gas velocity may not actually be feasible in existing screw reactors because of the accompanying increase in dust carry-out.

The most interesting and significant comparisons are those which can be made between the results of Cases B and C. Here, the use of the more reactive feed, coupled with a lowering of the off-gas concentration from 80 to 20 mole per cent HF, results in a three to four-fold increase in productive capacity. At the same time, the average gas velocities within the reactor for the two cases do not differ greatly; this fact increases the confidence with which the calculated increase of throughput can be extrapolated to plant-scale equipment. Since the gas velocities for Cases B and C do not differ greatly, it is also reasonable to predict little difference in the carry-out of dust for these two cases.*

TEMPERATURE PROFILES

Figures 26, 27, 28, and 29 illustrate for each of the four cases the temperature profiles which should be imposed upon the countercurrent gas-solids reactor to insure maximum reaction rates. The conversion level is also indicated as a function of reactor length when operating at maximum throughput consistent with the production of 95 mole per cent UF_4 .

* The assumption is that of the magnitude of dust carry-out is primarily determined by the gas phase velocity. Actually, differences in the two types of UO_2 feeds such as particle size distribution and particle density must be considered in any detailed analysis.

FIGURE 26 Countercurrent Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3

FIGURE 28 Countercurrent Hydrofluorination of UO_2 Derived from Pot-Denitrated UO_3 . Optimum Temperature Profile for Case "C"

FIGURE 27 Countercurrent Hydrofluorination of UO_2 Derived from ADU. Optimum Temperature Profile for Case "B"

FIGURE 29 Countercurrent Hydrofluorination of UO_2 Derived from ADU. Optimum Temperature Profile for Case "D"

Figures 26 and 28 for Cases A and C, respectively, show that with pot-source UO_2 , most of the conversion should occur near the feed end of the

reactor, even when low excesses of HF are employed. The optimum temperature profiles do not differ greatly, despite the large differences in the

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HF excess. However, it is far more important to maintain low bed temperatures near the feed end of the reactor when low excesses of HF are employed because the equilibrium temperatures will be relatively low near the feed end.

Figures 27 and 29 for Cases B and D illustrate that conversion should occur much more evenly

along the length of the reactor when the feed is ADU-source UO_2 . Temperatures should be kept low over most of the length of the reactor, but should increase sharply near the product-discharge point in order to maintain high tail-end conversion rates. Heat removal and the control of bed temperatures should be facilitated when this feed is used, since the reaction is more evenly "spread out" with respect to distance along the reactor.

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CONCLUDING REMARKS

In the method illustrated in this report for calculating the residence time required for hydrofluorinating in an ideal countercurrent system, the assumption was made that the maximum instantaneous reaction rate at any given instant could be represented as a function of only two independent variables. For a given type of feed material being hydrofluorinated at a fixed total pressure of one atmosphere, these variables are: (1) the HF/H₂O ratio in the gas phase which is in contact with the solids and (2) the mole fraction of UF₄ in the bed of solids (Fig. 12 and 13). This assumption implies that the reaction rate at any given instant during the reaction is independent of the conditions imposed prior to that instant (i.e., temperature, HF concentration etc.). As an illustration, the reaction rate at the instant that the reaction passes through the conversion level of 80 per cent while the material is in contact with a gas phase containing 75 per cent HF and 25 per cent steam at 1000°F is assumed to be the same, whether the material had been reacted to the 80 per cent conversion level with the temperature held constant at 1000°F or had been reacted to the same point while the temperature was increased from 500°F to 1000°F.

It is possible that this assumption leads to considerable error in calculations performed with rate data derived from hydrofluorination experiments in which the conditions imposed differed greatly from those for the particular case being calculated. The instantaneous rate determinations whose errors may be greatest are those pertaining to the final stages of hydrofluorination in thermobalance runs made under essentially isothermal conditions at relatively high temperatures. These tail-end rates may be low because of sintering or "thermal damage" suffered during the initial stages of the thermobalance runs; when these rates are applied to calculations involving hydrofluorination in a countercurrent system operating with low excesses of HF so that the initial reaction temperatures are held to relatively low values, correspondingly large errors may be introduced. That significantly large errors of this nature are possible is indicated by the previously described results of the two thermobalance runs performed with the HF-H₂O gas phase diluted with nitrogen.

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APPENDIX A

THERMODYNAMIC DERIVATIONS. CALCULATION OF EQUILIBRIA IN THE SYSTEM,
 $\text{UO}_2(\text{s}) - \text{UF}_4(\text{s}) - \text{HF}(\text{g}) - \text{H}_2\text{O}(\text{g})$

APPLICATION OF THE PHASE RULE

System: $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightleftharpoons \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

$$F = C + 2 - P$$

$$C = I - r$$

where

F = degrees of freedom for the system at equilibrium

C = number of components

P = number of phases

I = number of chemical species

r = restrictions

For the system under consideration,

$$I = 4 (\text{UO}_2, \text{UF}_4, \text{H}_2\text{O}, \text{HF})$$

$$r = 1 \text{ (one chemical reaction)}$$

$$C = I - r$$

$$= 3$$

$$P = 3 \text{ (two solid phases, one gas phase)}$$

$$F = 3 + 2 - 3$$

$$= 2$$

Since $F = 2$, only two of the intensive variables (temperature, T ; total pressure, Π ; HF or H_2O concentration in the gas phase) need be selected to define completely the state of the system at equilibrium. The selection of concentration variables is restricted to the gas phase, since the solids, UO_2 and UF_4 , may be assumed to be mutually insoluble in each other.⁴⁰

If Π and T are selected, the gas phase composition is fixed at a particular ratio of HF and H_2O .

If Π and the gas phase composition are selected, T becomes fixed at one particular value.

If T and the gas phase composition are selected, Π can assume only one particular value.

If the system also includes an inert gas, the degrees of freedom are increased to three, and it becomes necessary to select three intensive variables (which now include the concentration of the inert gas in the gas phase) before the state of the system at equilibrium becomes completely defined.

THERMODYNAMIC DERIVATIONS

For the reaction, $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightarrow \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$,

$$\Delta F^\circ = -RT \ln K$$

where ΔF° = the free energy change for the reaction in which the products and reactants are in their standard states (i.e., pure gases and pure solids at one atmosphere), calories.

K = equilibrium constant (a function only of temperature)

T = absolute temperature ($^\circ\text{K}$)

R = gas constant (calories/gram mole $^\circ\text{K}$)

ΔF° and K are functions only of temperature when the standard states are specified, as above.

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$$K = \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{HF}})^4} \quad \text{where } a = \text{activity at equilibrium } a_{\text{UO}_2} \text{ and } a_{\text{UF}_4} = 1 \text{ (no solid solutions)}$$

$$a = \frac{f}{f^\circ} \quad \text{where } f^\circ \text{ is the fugacity of the component gas in the standard state (one atmosphere) and } f \text{ is the fugacity of the component gas in the equilibrium state.}$$

Substituting,

$$\begin{aligned} \Delta F^\circ &= -RT \ln \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{HF}})^4} \\ &= -RT \ln \left[\frac{(f_{\text{H}_2\text{O}})^2}{(f_{\text{HF}})^4} \cdot \frac{(f^\circ_{\text{HF}})^4}{(f^\circ_{\text{H}_2\text{O}})^2} \right] \end{aligned}$$

The fugacities of gaseous HF and water in their standard states may be considered equal to one atmosphere. Hence,

$$\begin{aligned} K_a &= K_f \\ &= \frac{(f_{\text{H}_2\text{O}})^2}{(f_{\text{HF}})^4} \end{aligned}$$

If the gas phase is an ideal solution,

$$f_{\text{H}_2\text{O}} = f^*_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}}$$

where $f^*_{\text{H}_2\text{O}}$ = fugacity of gaseous water at the total pressure Π and temperature T of the system at equilibrium.

$N_{\text{H}_2\text{O}}$ = mole fraction of H_2O in the gas phase.

Similarly,

$$f_{\text{HF}} = f^*_{\text{HF}} N_{\text{HF}}$$

In addition,

$$\begin{aligned} f_{\text{H}_2\text{O}} &= N_{\text{H}_2\text{O}} \gamma^*_{\text{H}_2\text{O}} \Pi \\ f_{\text{HF}} &= N_{\text{HF}} \gamma^*_{\text{HF}} \Pi \end{aligned}$$

where γ^* is the fugacity coefficient for the pure component gas at Π and T of the system in the equilibrium state. At elevated temperature and moderate pressures, $\gamma^* \approx 1$.

Substituting,

$$\begin{aligned} K &\approx \frac{(N_{\text{H}_2\text{O}} \Pi)^2}{(N_{\text{HF}} \Pi)^4} \\ &\approx \frac{1}{\Pi^2} \frac{(N_{\text{H}_2\text{O}})^2}{(N_{\text{HF}})^4} \end{aligned}$$

where Π is expressed in atmospheres.

Finally,

$$\frac{(N_{\text{H}_2\text{O}})^2}{(N_{\text{HF}})^4} = \Pi^2 K = \Pi^2 e^{\frac{-\Delta F^\circ}{RT}} \quad (1)$$

According to the above equation, selecting values for the gas phase composition and Π determines a value of K . Since K is a function only of temperature, the temperature at equilibrium becomes fixed. This is in agreement with the phase rule.

EQUILIBRIUM CALCULATIONS

Data for the standard free energies of formation of the compounds UO_2 , UF_4 , HF and H_2O are tabulated below.

TABLE VI Standard Free Energies⁴¹ of Formation, F° (kcal/gram mole)

Temperature (°K)	UO_2 (Solid)	UF_4 (Solid)	HF (gas)	H_2O (gas)
298	-247	-421	-64.7	-54.62
500	-238	-407	-65.0	-52.36
1000	-218	-373	-65.8	-46.03
1500	-198	-339	-66.6	-39.26

For the reaction as written below,

the values of ΔF° are calculated from the relation,

$$\Delta F^\circ = F^\circ_{\text{UF}_4} + 2F^\circ_{\text{H}_2\text{O}} - F^\circ_{\text{UO}_2} - 4F^\circ_{\text{HF}}$$

and are tabulated below.

TABLE VII Calculated Standard Free Energy Change of Reaction (ΔF°)

T (°K)	ΔF° (kcal)
298	-24.4
500	-13.7
1000	+16.1
1500	+46.9

ΔF° is plotted versus T (Fig. 30).

Experimentally, it was found that equilibrium was established at a temperature of 1130°F with a gas phase composition of 59.7 mole per cent HF , 40.3 mole per cent H_2O , and $\Pi = 1$ atmosphere. Equation 1 is employed to calculate a corresponding "experimental" value of ΔF° at 1130°F (883°K).

$$\frac{(N_{\text{H}_2\text{O}})^2}{(N_{\text{HF}})^4} = \Pi^2 e^{\frac{-\Delta F^\circ}{RT}}$$

Solving for ΔF° , noting that $N_{\text{H}_2\text{O}} = 1 - N_{\text{HF}}$,

$$\Delta F^\circ = -2.303 RT \left[\log \frac{(N_{\text{H}_2\text{O}})^2}{(N_{\text{HF}})^4} - 2 \log \Pi \right]$$

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At $\Pi = 1$ atmosphere; $R = 1.987$ cal/g mole, $^{\circ}\text{K}$; $T = 883^{\circ}\text{K}$; and $N_{\text{HF}} = 0.597$, we have,

$$\Delta F^{\circ} = -(2.303) (1.987) (883) \left[\log \frac{(0.403)^2}{(0.597)^4} - 2 \log 1 \right]$$

$$\Delta F^{\circ} = -0.432 \text{ kcal at } 883^{\circ}\text{K}$$

The value of ΔF° at 883°K from Figure 30 is $+9.1$ kcal. Thus, to obtain a "fit" with the experimental equilibrium determination, the value of ΔF° calculated from free energy of formation data must be corrected by an amount, $-(9.1 + 0.4) = -9.5$ kcal at $T = 883^{\circ}\text{K}$.

Equation (2) is next employed to calculate the set of equilibrium curves presented in Figure 10, thus allowing extension of the experimental equilibrium data to HF concentrations greater than 75 mole per cent and also to show the effects upon equilibrium of pressure changes and of dilution with an inert gas. The ΔF° correction of -9.5 kcal found to be necessary to force agreement between equation (1) and one selected experimental equilibrium determination is applied without change to yield the corrected values of ΔF° over the entire range of temperature under consideration. The justification of the use of a constant value for this correction is based upon the assumption that the change with temperature of the free energy of formation of a compound should be known with much greater precision than the free energy itself. A "corrected" curve relating ΔF° and T is shown in Figure 30.

The steps involved in calculating the data from which the curves of Figure 10 were constructed are outlined below:

Calculation of Values of K:

$$K = e^{\frac{-\Delta F^{\circ}}{RT}}$$

$$\log K = \frac{-\Delta F^{\circ}}{2.303 RT}$$

$$= \frac{-\Delta F^{\circ}}{4.576 T}$$

Taking values of ΔF° and corresponding values of T from the "corrected" curve of Figure 30, values of K were determined at 100°F intervals from 600°F to 1400°F . K was then plotted versus temperature on semi-logarithmic coordinates (Fig. 31).

Sample calculation: At 1400°F (1033.2°K), ΔF° (corrected) = $+8700$ calories

$$\log K = \frac{-8700}{(4.576) (1033.2)}$$

$$= -1.840$$

$$\log K = 8.160 - 10$$

$$K = 0.01445$$

$$= 1.45 \times 10^{-2}$$

Data from which the curves of Figure 31 were constructed are given in Table VIII.

FIGURE 30 Standard Free Energy Change, ΔF° , Versus Temperature for Reaction:

FIGURE 31 Plot of Equilibrium Constant Versus Temperature for the Reaction:

TABLE VIII Calculated Values* of K

Temperature (°F)	K
600	4.05×10^6
700	8.96×10^4
800	3.37×10^3
900	2.06×10^2
1000	1.905×10^1
1100	2.26
1200	3.55×10^{-1}
1300	6.21×10^{-2}
1400	1.45×10^{-2}

* Data used in Figure 31.

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Calculation of Values of $\Pi^2 K$ and Data of Table IX

$$\Pi^2 K \approx \frac{(N_{H_2O})^2}{(N_{HF})^4}$$

$N_{H_2O} = 1 - N_{HF}$ for the case when the gas phase contains no inert diluent gas.

Sample Calculation: Let $N_{HF} = 0.05$. Then

$$\begin{aligned} N_{H_2O} &= 1 - 0.05 \\ &= 0.95 \end{aligned}$$

$$\Pi^2 K = \frac{(0.95)^2}{(0.05)^4}$$

$$\Pi^2 K = 144,400$$

Values of $\Pi^2 K$ and corresponding values of N_{HF} are given in the first two columns of Table IX.

TABLE IX Calculated Values of Equilibrium Temperatures at Selected Values of Total Pressure and Mole Fraction HF in the Gas Phase (Gas Phase Contains only HF and H_2O)

N_{HF}	$\Pi^2 K$	π (atm)	K	T (°F)	π (atm)	K	T (°F)	π (atm)	K	T (°F)	π (atm)	K	T (°F)
0.05	144,400	0.5	576,000	650	1.0	144,400	687	2.0	36,000	727	4.0	9,000	769
0.10	8,100	0.5	32,400	730	1.0	8,100	772	2.0	203	816	4.0	506	864
0.20	400	0.5	1,600	824	1.0	400	873	2.0	100.0	930	4.0	25.0	988
0.30	60.5	0.5	242	894	1.0	60.5	951	2.0	15.12	1010	4.0	3.78	1074
0.40	14.06	0.5	56.2	954	1.0	14.06	1013	2.0	3.52	1078	4.0	0.879	1151
0.50	4.00	0.5	16.00	1007	1.0	4.00	1072	2.0	1.000	1144	4.0	0.250	1219
0.60	1.235	0.5	4.94	1062	1.0	1.235	1133	2.0	0.309	1207	4.0	0.0772	1288
0.70	0.375	0.5	1.499	1123	1.0	0.375	1196	2.0	0.0937	1275	4.0	0.0234	1366
0.80	0.0977	0.5	0.391	1194	1.0	0.0977	1273	2.0	0.0244	1363	4.0	0.00610	—
0.90	0.01524	0.5	0.0610	1303	1.0	0.01524	1397	2.0	0.00381	—	4.0	0.000953	—
0.95	0.00307	0.5	0.01228	1412									

The remaining calculations are indicated in the remaining columns of Table IX. Since values of $\Pi^2 K$ are known, values of K are calculated corresponding to chosen values of Π . The equilibrium temperature corresponding to the values of K are found from Figure 31. The data of Table IX were employed in plotting the isobaric equilibrium curves of Figure 10.

Calculation of Effect Upon Equilibrium of an Inert Diluent Gas

Data from which the equilibrium curves of Figure 11 were plotted are tabulated in Table X. Equation 1 was employed to calculate values of K; corresponding equilibrium temperatures were then available from Figure 31. The method is illustrated below:

$$\frac{(N_{H_2O})^2}{(N_{HF})^4} = \Pi^2 K$$

TABLE X* Effect of an Inert Diluent Gas on Equilibria in the Hydrofluorination of UO_2

Total Pressure: one atmosphere.

 $N_{\text{HF}}^\dagger$ denotes mole fraction HF in gas phase, inert gas - present basis.

N_{HF} (Inert Gas - Free Basis)	N_i	$N_{\text{HF}}^\dagger$	K	T (°F)	N_i	$N_{\text{HF}}^\dagger$	K	T (°F)	N_i	$N_{\text{HF}}^\dagger$	K	T (°F)
0.05	0.75	0.0125	2.31×10^6	614	0.50	0.025	5.78×10^5	650	0.25	0.0375	2.57×10^5	672
0.10	0.75	0.025	1.296×10^5	691	0.50	0.050	3.24×10^4	730	0.25	0.075	1.440×10^4	755
0.20	0.75	0.050	6.40×10^3	780	0.50	0.100	1.600×10^3	824	0.25	0.150	7.11×10^2	853
0.30	0.75	0.075	9.68×10^2	842	0.50	0.150	2.42×10^2	894	0.25	0.225	1.075×10^2	928
0.40	0.75	0.100	2.25×10^2	897	0.50	0.200	5.63×10^1	954	0.25	0.300	2.50×10^1	988
0.50	0.75	0.125	6.40×10^1	948	0.50	0.250	1.600×10^1	1007	0.25	0.375	7.11	1045
0.60	0.75	0.150	1.975×10^1	998	0.50	0.300	4.94	1062	0.25	0.450	2.19	1103
0.70	0.75	0.175	6.00	1052	0.50	0.350	1.499	1123	0.25	0.525	6.67×10^1	1165
0.80	0.75	0.200	1.563	1121	0.50	0.400	3.91×10^{-1}	1194	0.25	0.600	1.736×10^{-1}	1240
0.90	0.75	0.225	2.44×10^{-1}	1221	0.50	0.450	6.10×10^{-2}	1303	0.25	0.675	2.71×10^{-2}	1356
0.95	0.75	0.2375	4.91×10^{-2}	1317	0.50	0.475	1.228×10^{-2}	1412	0.25	0.7125	5.45×10^{-3}	—

* Calculated data for Figure 11.

If N_i denotes the mole fraction of inert diluent gas in the gas phase, the mole fraction H_2O in the gas phase becomes

$$N_{\text{H}_2\text{O}} = 1 - N_i - N_{\text{HF}}$$

Hence,

$$\frac{(1 - N_i - N_{\text{HF}})^2}{(N_{\text{HF}})^4} = \Pi^2 K$$

Sample Calculation:

Let the total pressure $\Pi = 1$ atmosphere. Let $N_i = 0.75$. Let the mole fraction of HF in the gas phase be 0.40 on an inert gas - free basis.

$$N_{\text{HF}} = (0.40)(1 - 0.75)$$

$$= 0.100$$

$$\frac{(1 - 0.75 - 0.100)^2}{(0.100)^4} = K$$

$$K = 2.25 \times 10^2$$

From Figure 31, the equilibrium temperature is found to be 897°F .

Calculation of Standard Heat of Reaction, ΔH°

The standard heat of reaction may be determined from the following equation:

$$\Delta H^\circ = -R \left[\frac{\partial \ln K}{\partial \left(\frac{1}{T} \right)} \right]_P$$

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For the reaction under consideration, the standard states selected were those of the pure solids and gases at one atmosphere. Under this condition, K is not a function of pressure, so that the equation may be written,

$$\Delta H^\circ = -R \frac{d \ln K}{d\left(\frac{1}{T}\right)}$$

or

$$\frac{d \log K}{d\left(\frac{1}{T}\right)} = \frac{\Delta H^\circ}{2.303 R}$$

The right side of the above equation equals the slope at any point on a plot of log K versus $\frac{1}{T}$. The data for such a plot are given in Table XI. Values of K were obtained from Figure 31 for temperatures greater than 600°K; at temperatures of 300°, 400°, and 500°K, values of log K were computed by using ΔF° values from Figure 30 and the relation,

$$\log K = -\frac{\Delta F^\circ}{2.303 RT}$$

The plot of Figure 32 is almost a straight line. Taking slopes at $\frac{1}{T} = 0.00100$ and $\frac{1}{T} = 0.00333$, the following values of ΔH° were computed:

$$\Delta H^\circ_{300^\circ K} = 47.3 \text{ kcal}$$

$$\Delta H^\circ_{1000^\circ K} = 53.3 \text{ kcal}$$

The above calculation of ΔH° was not based solely upon the experimental equilibrium data, although the values of K were derived using "corrected" values of ΔF° which involved the use of one particular experimental equilibrium determination. Figure 33 was prepared, using only the experimental data. Values of K were calculated from the relation:

$$K = \frac{(1 - N_{HF})^2}{(N_{HF})^4} \quad \text{at } \Pi = 1 \text{ atmosphere}$$

The experimental equilibrium data and the values of log K and $\frac{1}{T}$ derived from these data are given in Table XII.

A straight line is drawn through the points of Figure 33. From the slope of this line, a value of -50.6 kcal was obtained for the value of ΔH° ; this represents an average value over the temperature range between 660° and 1260°F.

TABLE XI

T (°K)	T (°F)	log K	$\frac{1}{T}$ (°K)
1000	1340	-1.45	0.00100
900	1160	-0.13	0.00111
800	980	1.48	0.00125
700	800	3.53	0.00143
600	620	6.26	0.00167
500	440	10.1	0.00200
400	260	15.6	0.00250
300	80	24.6	0.00333

FIGURE 32 Plot of Logarithm of the Equilibrium Constant, K, Versus $\frac{1}{T}$ for the Reaction:

TABLE XII Experimental Equilibrium Data

Equilibrium		K	log K	$\frac{1}{T}$ (°K)
N _{HF}	T (°K)			
0.045	619.4	2.22×10^5	5.347	0.001614
0.091	677.8	1.205×10^4	4.081	0.001475
0.185	736.1	5.67×10^2	2.754	0.001359
0.250	777.8	1.440×10^2	2.158	0.001286
0.275	780.6	9.19×10^1	1.963	0.001281
0.433	841.7	9.15	0.961	0.001188
0.585	880.6	1.471	0.168	0.001136
0.596	883.3	1.293	0.112	0.001132
0.586	886.1	1.454	0.163	0.001129
0.758	958.3	1.773×10^{-1}	-0.751	0.001044

FIGURE 33 Plot of the Logarithm of the Equilibrium Constant, K, Versus $\frac{1}{T}$ for the Reaction: $\text{UO}_2(\text{s}) + 4\text{HF}(\text{g}) \rightleftharpoons \text{UF}_4(\text{s}) + 2\text{H}_2\text{O}(\text{g})$ Based Upon the Experimental Equilibrium Data of Table XII.

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APPENDIX B

TABULATION OF THERMOBALANCE DATA FOR HYDROFLUORINATION RUNS

Table XIII of this appendix contains hydrofluorination data for isothermal runs made with UO_2 derived from sulfated pot-denitrated UO_3 , the properties of which are given in Table I. Table XIV contains similar data obtained with UO_2 derived from the lower density form of U_3O_8 which had been prepared from ADU (Table II). Conversions to UF_4 are given in mole per cent. Composition of the binary $\text{HF}-\text{H}_2\text{O}$ gas phase is given in weight per cent. The data given in this section were used to prepare the reaction rate diagrams of Figures 12 and 13.

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TABLE XIII Thermobalance Runs Made With UO_2 From Pot-Denitrated UO_3

20% HF — 80% H ₂ O								30.0 HF — 70% H ₂ O								45.0% HF — 55.0% H ₂ O								
560°F		655°F		755°F		800°F		560°F		655°F		755°F		850°F		655°F		755°F		850°F		950°F		
Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	
2	5.4	2	5.4	2	4.4	4	2.7	2	10.7	2	8.1	2	4.2	2	2.6	2	18.9	2	8.5	2	4.9	2	1.9	
4	13.9	4	12.6	4	9.7	8	6.0	4	23.1	4	20.1	4	13.4	4	6.2	4	35.1	4	25.1	4	18.7	4	7.3	
6	21.5	6	19.2	6	15.6	12	9.9	6	30.2	6	30.5	6	22.0	6	10.2	6	44.5	6	39.6	6	31.3	6	13.3	
8	26.8	8	25.1	8	21.8	16	13.3	8	33.4	8	38.0	8	30.7	8	14.9	8	50.4	8	50.5	8	43.4	8	19.8	
12	31.7	12	34.2	10	26.2	20	17.2	10	35.9	10	42.7	10	37.8	10	19.3	10	54.0	10	57.0	10	53.1	10	25.3	
16	34.6	16	40.3	12	30.7	24	21.2	12	38.1	14	48.9	12	44.2	12	23.8	12	56.9	12	61.6	12	60.1	12	30.9	
20	36.9	20	44.3	14	35.6	28	24.7	16	41.2	18	53.7	14	49.1	14	27.5	14	59.3	14	65.5	14	65.0	14	36.0	
30	41.2	30	51.5	16	39.3	32	27.7	20	44.4	22	57.7	16	53.1	16	31.3	16	61.3	16	68.1	16	69.0	16	41.1	
40	45.1	40	56.8	18	42.8	36	31.3	24	46.9	26	60.5	20	59.2	18	34.8	18	63.4	18	70.5	18	72.0	18	45.9	
60	50.4	60	63.7	20	45.6	40	34.6	28	49.2	30	62.8	24	63.9	20	38.6	20	65.0	20	72.4	20	74.7	20	50.1	
80	54.9	80	68.3	24	49.7	50	41.6	32	51.5	40	66.9	28	67.7	24	45.8	22	66.5	22	74.0	24	78.2	22	54.4	
100	58.2	100	71.5	28	53.2	60	47.6	36	53.2	50	70.2	32	70.5	28	51.7	26	68.9	26	76.6	28	81.7	24	58.6	
120	60.9	120	74.3	32	56.2	70	51.9	40	54.6	60	72.7	36	72.5	32	56.1	30	70.9	30	78.8	32	83.8	26	62.0	
140	63.1	140	76.4	36	58.8	80	56.2	50	58.0	70	74.7	40	74.4	36	59.5	35	72.9	35	80.6	36	85.7	28	64.9	
160	65.1	160	78.1	40	61.0	90	58.6	60	60.6	80	76.3	50	78.2	40	62.6	40	74.7	40	82.2	40	86.9	32	69.5	
180	66.8	180	79.8	50	65.3	100	60.9	70	62.9	90	77.9	60	81.1	50	67.9	45	76.5	45	83.7	50	89.5	36	72.6	
200	68.3	200	81.0	60	68.7	120	64.5	80	64.9	100	79.1	70	83.5	60	72.0	50	77.5	50	84.7	60	91.0	40	75.4	
220	69.5	220	82.2	70	71.6	140	67.6	90	66.6	120	81.4	80	85.1	70	75.1	55	78.3	60	86.7	70	92.2	50	80.1	
240	70.7	240	83.3	80	73.7	160	69.9	100	68.0	140	83.0	90	86.5	80	77.5	65	80.5	70	87.9	80	93.0	60	83.0	
260	72.0	260	84.1	90	75.9	180	72.0	120	70.6	160	84.3	100	87.6	90	79.5	70	81.3	80	89.1	90	93.4	70	85.2	
280	73.2	280	84.9	100	77.4	200	73.9	140	72.0	180	85.5	120	89.4	100	81.2	80	82.6	90	90.2	100	94.0	80	86.6	
300	74.1	300	84.9	110	78.5	225	75.9	160	73.6	200	86.6	140	90.6	120	83.7	97	85.4	100	91.0	110	94.7	90	87.4	
		320	86.3	120	79.9			180	75.5	220	87.6	160	91.5	140	85.7	110	86.7					110	89.8	
										240	88.0	180	92.6	160	87.2								130	91.1
										260	88.7			180	88.2								150	92.2
										280	89.4			200	89.3									
										300	90.0			220	90.1									
														240	90.5									
														260	91.0									

(Continued)

TABLE XIII Thermobalance Runs Made With UO_2 From Pot-Denitrated UO_3 (Continued)

60.0% HF — 40.0% H ₂ O								75.0% HF — 25.0% H ₂ O									
755°F		850°F		925°F		1000°F		750°F		850°F		950°F		1050°F		1150°F	
Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄
1	14.5	1	12.2	1	8.9	1	6.5	1	17.3	1	16.5	1	13.7	1	11.2	2	6.9
2	28.0	2	25.1	2	19.4	2	13.0	2	35.6	2	33.9	2	28.1	2	22.7	4	13.5
3	39.4	3	36.7	3	28.7	3	19.5	3	50.3	3	48.5	3	41.1	3	32.8	6	20.2
4	49.4	4	46.4	4	38.0	4	26.1	4	59.3	4	60.4	4	51.5	4	42.4	8	27.0
5	56.8	5	54.9	5	46.8	5	32.4	5	64.4	5	66.8	5	60.9	5	50.1	10	34.3
6	61.0	6	61.2	6	54.0	6	38.6	6	67.8	6	71.0	6	67.2	6	56.6	12	39.8
7	64.3	7	65.4	7	60.1	7	44.1	7	70.3	7	73.8	7	71.4	7	61.8	14	45.9
8	66.8	8	68.2	8	64.8	8	49.5	8	72.3	8	76.1	8	74.6	8	65.8	16	51.1
9	68.7	9	70.9	9	68.4	9	54.3	9	74.2	9	77.9	9	77.1	9	69.1	18	55.9
10	70.5	10	73.0	10	71.3	10	58.4	10	75.6	10	79.5	10	79.0	10	71.3	20	60.2
12	73.2	12	76.5	12	75.8	12	64.8	12	78.3	12	82.0	12	82.6	12	75.0	22	63.1
14	75.3	14	79.1	14	79.1	14	69.4	14	80.3	14	84.2	14	85.1	14	77.8	26	67.2
16	77.3	16	81.3	16	81.4	16	72.9	16	82.3	16	85.9	16	86.8	16	79.8	30	71.2
18	78.9	18	82.8	18	83.4	18	75.5	18	83.8	18	87.4	18	88.4	18	81.4	36	74.8
20	80.3	20	84.4	20	85.2	20	78.1	20	85.0	20	88.4	20	89.6	20	83.0	40	76.5
22	81.7	22	85.4	22	86.4	22	79.8	22	86.2	22	89.5	22	90.5	22	84.3	50	80.1
26	83.7	26	87.2	24	87.5	26	82.3	24	87.1	26	91.0	24	91.5	26	86.2	60	83.0
30	85.4	30	88.8	26	88.6	30	84.8	26	88.0	30	92.2	26	92.0	30	87.8	70	84.7
40	87.0	40	91.5	28	89.2	40	88.3	28	88.7	35	93.4	30	93.2	40	90.4	80	86.5
50	90.6	50	93.2	30	90.0	52	91.1	30	89.3	40	94.3	40	95.1	50	92.2	92	88.0
60	91.9	60	94.3	40	92.7	60	92.3	40	92.0	50	95.5	50	96.0	60	93.2	100	88.6
70	93.1	70	95.2	50	94.3	70	93.4	50	93.6	60	96.4	60	96.7	70	94.3	110	89.4
80	94.2	80	95.7	60	95.3	80	94.1	60	95.1	65	96.7			80	94.9	120	90.3
90	94.8			70	95.9	90	94.7	70	95.9					90	95.4		
105	95.5					110	95.5	80	96.4								

(Continued)

TABLE XIII Thermobalance Runs Made With UO_2 From Pot-Denitrated UO_3 (Continued)

85.0% HF — 15.0% H_2O										100.0% HF									
755°F		850°F		950°F		1050°F		1150°F		755°F		850°F		950°F		1050°F		1150°F	
Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4
1	13.8	1	12.0	1	12.3	1	11.2	1	11.2	1	28.5	1	25.4	1	21.7	1	16.7	1	7.5
2	35.6	2	26.8	2	28.9	2	23.5	2	21.9	2	55.1	2	53.5	2	46.9	2	38.9	2	21.5
3	54.2	3	41.7	3	43.5	3	34.4	3	30.7	3	66.2	3	68.4	3	64.0	3	56.3	3	35.1
4	63.6	4	55.9	4	56.3	4	45.2	4	39.1	4	70.4	4	74.2	4	72.0	4	67.2	4	46.9
5	68.6	5	65.2	5	65.6	5	55.1	5	46.4	5	73.2	5	72.6	5	76.1	5	72.3	5	55.6
6	71.8	6	70.7	6	71.2	6	63.0	6	52.9	6	75.4	6	80.0	6	79.3	6	76.8	6	61.1
8	76.3	7	74.2	7	75.1	7	69.4	7	58.6	7	77.0	7	82.0	7	81.7	7	79.9	7	65.3
10	79.2	8	76.8	8	77.9	8	73.3	8	62.6	8	78.4	8	83.5	8	83.3	8	82.3	8	68.7
12	81.6	9	78.8	9	80.3	9	76.2	9	66.2	9	79.8	9	84.8	9	85.2	9	84.3	9	71.5
14	83.4	10	80.4	10	82.3	10	78.6	10	68.8	10	81.1	10	86.0	10	86.7	10	86.0	10	73.9
16	85.0	12	83.2	12	85.4	12	82.4	12	72.6	12	83.0	12	88.1	12	88.7	12	88.7	12	77.9
18	86.3	14	85.4	14	87.6	14	85.0	14	75.7	14	84.6	14	89.5	14	90.4	14	90.5	14	81.2
20	87.4	16	86.8	16	89.2	16	87.2	16	78.2	16	85.8	16	90.7	18	92.8	16	92.1	16	83.7
22	88.3	18	88.3	18	90.7	18	88.7	18	80.1	18	86.8	18	91.7	22	94.2	18	93.3	18	85.9
26	90.1	20	89.6	20	91.9	20	90.0	20	81.8	22	88.4	20	92.4	26	95.3	22	94.7	20	87.5
30	91.3	22	90.5	22	92.7	22	91.1	22	83.4	26	90.0	22	93.1	30	96.1	26	95.7	22	88.7
35	92.5	26	92.0	26	94.0	26	92.7	26	85.6	30	90.9	26	94.1	35	96.8	30	96.5	24	89.9
40	93.5	30	93.1	30	94.9	30	93.8	30	87.5	35	91.9	30	94.9	40	97.2	35	97.1	26	90.8
45	94.3	35	94.1	35	96.1	35	94.8	36	89.8	40	92.7	35	95.9	45	97.6	40	97.5	30	92.4
50	94.9	40	94.9	40	96.5	40	95.5	40	90.7	50	94.0	40	96.4			45	98.0	40	94.4
60	96.0	50	96.1	50	97.3	50	96.3	50	92.6	60	94.9	45	96.7					50	95.6
70	96.7	60	96.8	60	97.7	60	96.9	60	93.9									60	96.1
								70	94.7										
								80	95.2										
								90	95.6										

TABLE XIV Thermobalance Runs Made With UO_2 Derived From ADU

20.0% HF — 80.0% H ₂ O								30.0% HF — 70.0% H ₂ O									
460°F		560°F		655°F		755°F		460°F		560°F		655°F		755°F		850°F	
Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄
2	6.9	2	5.8	2	6.7	2	2.2	2	7.6	2	8.1	2	6.7	2	5.6	2	3.2
4	13.3	4	16.1	4	14.9	4	5.5	4	18.0	4	23.5	4	18.9	4	15.6	4	7.8
6	19.6	6	26.0	6	22.5	6	9.6	6	30.6	6	36.5	6	30.8	6	25.6	6	12.9
8	25.9	8	34.8	8	29.6	8	13.5	8	43.3	8	47.8	8	42.0	8	36.1	8	17.7
10	32.3	10	42.4	10	36.6	10	17.7	10	51.3	10	57.0	10	52.8	10	44.7	10	22.5
12	39.5	12	49.1	12	42.7	12	21.3	12	55.6	12	63.8	12	61.5	12	53.5	14	32.6
14	46.1	14	54.5	14	48.6	14	24.8	14	58.4	14	69.1	14	70.2	14	61.0	18	41.2
16	50.8	16	58.6	16	53.9	18	31.4	16	60.9	16	73.5	16	75.9	16	68.4	22	49.4
18	53.6	18	61.7	18	59.0	22	37.9	20	65.0	18	77.2	18	80.8	18	75.8	26	57.4
20	55.3	20	64.5	20	63.5	26	44.4	24	68.4	20	80.0	20	85.0	20	80.6	30	64.7
24	58.1	24	69.8	22	67.5	30	50.5	28	71.3	24	84.5	22	87.9	22	85.5	34	71.4
28	60.4	28	74.3	24	71.1	34	56.2	32	74.3	28	87.5	24	90.1	24	88.5	38	77.6
32	62.8	32	77.9	26	74.1	38	61.6	36	76.3	32	89.6	26	91.8	26	90.5	42	82.7
36	64.8	36	80.6	28	76.9	42	66.7	40	78.5	36	91.2	28	92.8	28	92.1	46	87.2
40	66.8	40	82.9	30	79.3	46	71.3	50	83.4	40	92.6	30	93.6	30	93.1	50	90.5
44	68.3	44	85.0	34	83.4	50	75.8	60	86.3	50	94.6	32	94.2	34	94.4	55	92.8
50	70.7	48	86.8	38	86.2	54	79.4	70	88.5	60	95.4	36	95.1	40	95.2	60	94.2
60	74.5	52	88.2	42	88.4	58	82.3	90	90.4	70	96.0	40	95.7	50	96.0	70	95.1
70	77.8	56	89.3	46	89.8	60	83.6	90	91.5	80	96.5	50	96.6	60	96.4	80	95.6
80	80.1	60	90.2	50	91.1	65	86.0	100	92.3	90	96.9	60	96.9	70	96.7	90	96.1
90	82.2	70	91.8	60	98.0	70	88.0	120	94.0					80	96.9	100	96.3
100	84.2	80	93.1	70	94.1	80	90.5							90	96.9	120	96.7
110	85.6	90	94.0	90	95.3	90	92.3										
120	86.9	100	94.6	110	95.9	100	93.4										
130	88.1	110	95.2			110	94.0										
140	89.0					120	94.6										
160	90.7					130	95.0										

(Continued)

TABLE XIV Thermobalance Runs Made With UO_2 Derived From ADU (Continued)

45.0% HF - 55.0% H ₂ O										60.0% HF - 40.0% H ₂ O											
560°F		655°F		755°F		850°F		950°F		560°F		655°F		755°F		850°F		950°F		1050°F	
Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄
2	12.5	2	14.3	2	13.1	2	10.9	2	2.8	2	33.4	1	13.8	1	1.7	1	8.9	1	5.6	2	4.6
4	35.6	4	35.7	4	30.3	4	22.3	4	7.5	3	49.9	2	31.5	2	24.8	2	20.2	2	13.5	4	9.4
6	54.0	6	54.4	6	46.6	6	33.1	6	11.7	4	63.8	3	46.5	3	39.0	3	31.2	3	21.0	6	14.6
8	68.6	8	70.3	8	62.4	8	42.7	8	17.4	5	74.8	4	60.1	4	52.7	4	41.9	5	34.7	8	19.9
10	77.8	10	82.1	10	75.8	10	52.5	10	23.1	6	82.2	5	72.0	5	65.3	5	51.8	6	41.2	10	25.6
12	83.3	12	88.7	12	85.7	12	61.1	12	29.1	7	86.1	6	81.7	6	76.9	6	61.0	7	47.9	12	30.2
14	86.9	14	91.5	14	91.0	14	70.3	14	34.7	8	88.3	7	88.4	7	86.2	7	69.4	8	54.1	14	35.0
16	89.2	16	93.5	16	94.0	16	78.3	16	40.3	9	89.8	8	91.9	8	91.8	8	77.0	9	59.9	16	39.5
18	91.0	18	94.7	18	95.2	18	85.0	18	45.6	10	91.0	9	93.7	9	94.6	9	83.7	10	65.5	18	43.6
20	92.1	20	95.5	20	95.9	20	90.2	20	50.7	12	92.6	10	94.8	10	95.8	10	90.0	11	70.9	20	47.5
22	92.9	22	95.9	22	96.4	22	93.6	22	55.5	14	93.7	12	96.0	11	96.4	11	93.8	12	75.6	22	51.8
24	93.8	26	96.6	26	96.9	24	95.0	24	60.0	16	94.5	14	96.6	12	96.8	12	95.8	13	80.2	24	55.8
26	94.3	30	97.1	30	97.3	26	95.8	26	64.4	18	95.1	16	97.0	13	97.3	13	96.7	14	84.4	26	59.8
28	94.7	35	97.3	35	97.7	28	96.3	28	68.6	20	95.5	18	97.4	14	97.4	14	97.2	15	88.2	28	63.7
30	95.2	40	97.6	40	98.0	30	96.7	30	72.7	22	95.8	20	97.6	15	97.7	15	97.4	16	91.3	30	67.5
35	96.0	45	97.8	45	98.0	40	97.3	32	76.5	26	96.4	30	98.4	18	98.2	16	97.8	17	93.9	32	70.9
45	96.8					45	97.5	34	80.1	30	96.8			22	98.5	20	98.3	18	95.5	34	74.4
								36	82.8					26	98.7	25	98.5	19	96.2	36	77.8
								38	85.8					30	99.0			20	96.9	38	80.8
								40	88.4					40	99.0			22	97.3	40	83.7
								42	90.7									26	97.9	45	89.2
								46	93.3									30	98.2	50	93.3
								50	94.5											55	95.4
								60	95.6											60	96.0
								70	96.1											65	96.2

(Continued)

TABLE XIV Thermobalance Runs Made With UO₂ Derived From ADU (Continued)

75.0% HF — 25.0% H ₂ O												85.0% HF — 15.0% H ₂ O													
560°F		705°F		850°F		950°F		1050°F		1150°F		560°F		655°F		755°F		850°F		950°F		1050°F		1150°F	
Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄	Time (min.)	% UF ₄
1	19.2	1	18.4	1	17.5	1	13.6	1	7.9	1	4.3	1	25.6	1	15.0	1	21.2	1	18.5	1	12.2	1	11.5	1	6.9
2	42.3	2	37.1	2	36.3	2	27.2	2	17.9	2	7.9	2	56.1	2	41.3	2	43.3	2	37.6	2	28.0	2	23.8	2	16.5
3	62.5	3	55.1	3	52.9	3	39.9	3	27.2	3	11.4	3	77.0	3	65.8	3	64.1	3	54.9	3	43.6	3	35.7	3	25.7
4	78.5	4	71.5	4	68.1	4	53.3	4	37.0	4	14.9	4	89.5	4	84.8	4	81.7	4	72.1	4	58.4	4	47.9	4	34.5
5	87.4	5	85.5	5	81.0	5	65.4	5	45.9	5	18.4	5	93.5	5	94.8	5	94.3	5	86.3	5	72.8	5	59.3	5	43.0
6	90.5	6	93.2	6	90.8	6	76.5	6	54.5	6	22.6	6	94.5	6	97.0	6	97.3	6	95.3	6	85.3	6	69.7	6	51.1
7	92.0	7	95.4	7	95.8	7	85.7	7	62.5	7	26.4	7	95.5	7	97.4	7	98.1	7	98.0	7	94.9	7	80.1	7	58.8
8	93.0	8	96.3	8	97.0	8	92.2	8	69.8	8	30.6	8	96.1	8	97.7	8	98.4	8	98.4	8	97.7	8	88.3	8	65.9
9	93.7	9	96.7	9	97.6	9	95.9	9	76.7	9	34.7	9	96.4	9	98.0	9	98.6	9	98.8	9	98.4	9	94.4	9	72.7
10	94.2	10	97.1	10	98.1	10	97.0	10	83.0	10	38.0	10	96.7	10	98.3	10	98.8	10	98.9	10	98.9	10	97.3	10	78.6
12	95.1	12	97.6	12	98.5	12	98.1	11	88.6	12	45.2	12	97.1	12	98.4	12	99.0	12	99.1	12	99.0	11	98.1	11	84.1
14	95.7	14	97.9	14	98.8	14	98.4	12	93.3	14	51.7	14	97.3	14	98.6	14	99.0			14	99.2	12	98.4	12	89.1
16	96.2	16	98.2	16	98.9	16	98.6	14	97.8	16	58.0	16	97.6	16	98.7					16	99.2	14	98.8	13	92.5
18	96.7			18	99.0	18	98.9	16	98.4	18	63.7											16	98.8	14	95.4
20	97.0					25	99.0	18	98.6	20	69.3													15	96.9
25	97.5							20	98.9	22	74.1													16	97.4
30	97.9							25	99.1	24	78.8													18	97.9
										26	83.0													20	98.0
										28	87.0													25	98.2
										30	90.2														
										32	92.9														
										34	94.7														
										36	95.4														
										38	95.9														
										40	96.3														
										50	97.0														
										60	97.6														
										65	97.8														

(Continued)

TABLE XIV Thermobalance Runs Made With UO_2 Derived From ADU (Continued)

100.0% HF									
755°F		850°F		950°F		1050°F		1150°F	
Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4	Time (min.)	% UF_4
1	33.3	1	31.7	1	22.4	1	20.3	1	12.9
2	66.2	2	62.2	2	49.4	2	44.6	2	32.0
3	90.5	3	86.1	3	72.8	3	65.8	3	49.9
4	97.7	4	97.8	4	90.8	4	83.5	4	66.3
5	98.1	5	98.4	5	98.1	5	95.4	5	80.2
6	98.4	6	98.6	6	98.4	6	98.4	6	91.1
7	98.5	10	98.6	7	98.6	7	98.8	7	96.1
8	98.7			10	98.6	10	98.8	8	97.2
9	98.7							9	97.7
10	98.7							10	97.8
								12	98.1
								14	98.4
								16	98.4