

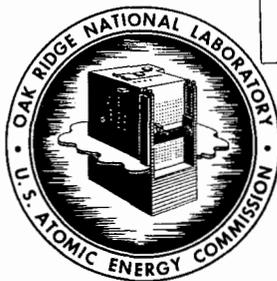
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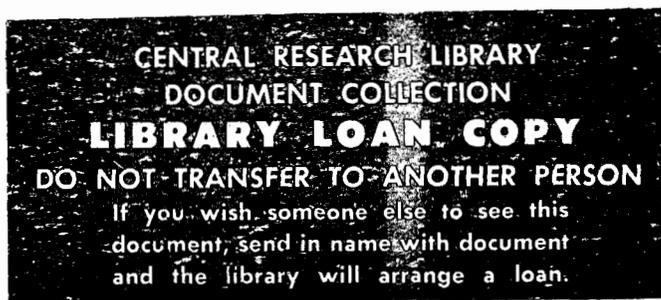
U.S. ATOMIC ENERGY COMMISSION



ORNL - TM - 1701

CONVERSION OF URANIUM CHLORIDES TO URANIA BY  
GAS-PHASE REDUCTION HYDROLYSIS

F. H. Patterson  
W. C. Robinson, Jr.  
C. F. Leitten, Jr.



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METALS AND CERAMICS DIVISION

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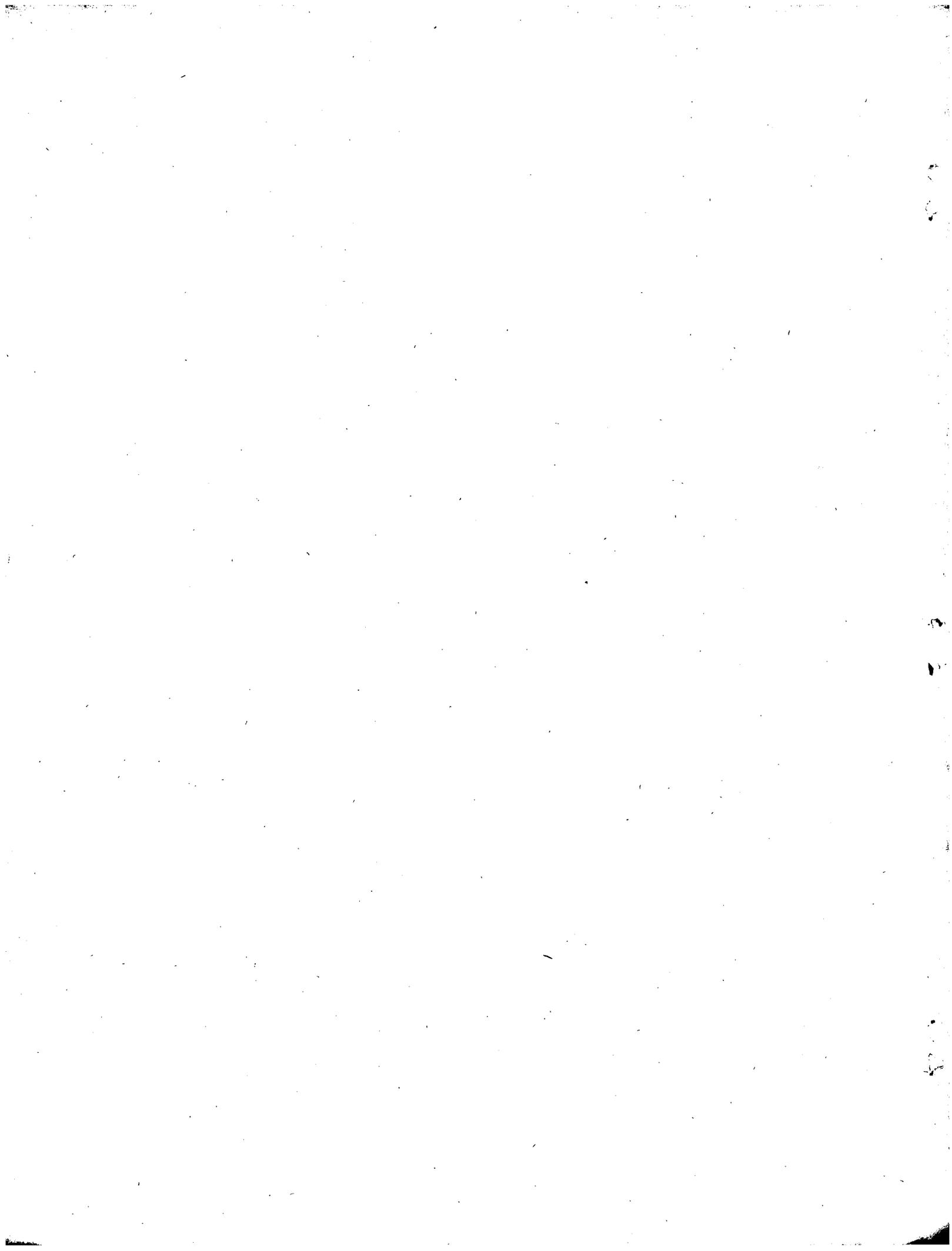
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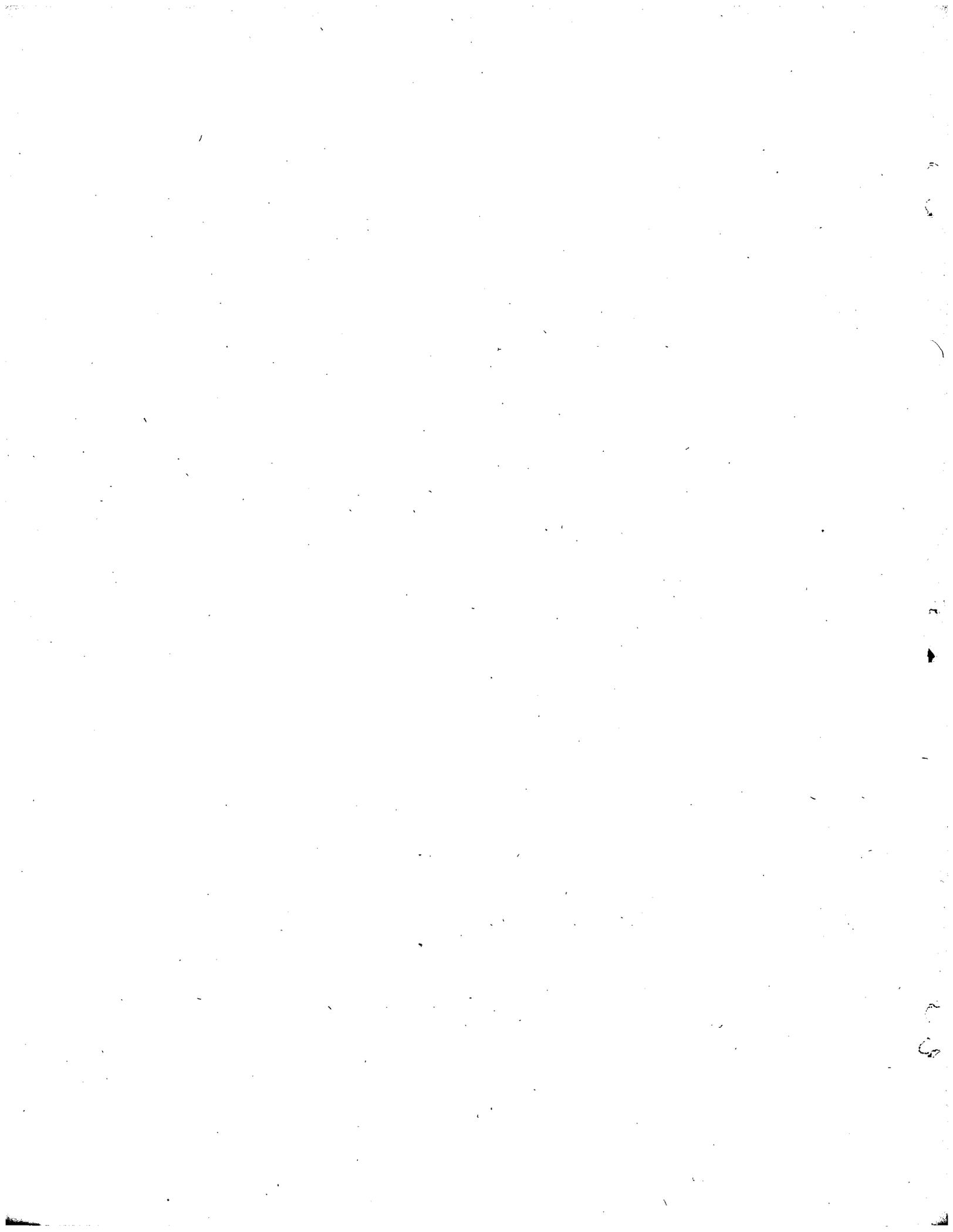


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F. H. Patterson<sup>1</sup>    W. C. Robinson, Jr.    C. F. Leitten, Jr.<sup>2</sup>

ABSTRACT

Uranium chlorides are obtained from the chlorine volatilization process presently being considered for Zircaloy-clad fuels. A program was undertaken to investigate the feasibility of converting these gaseous chlorides to uranium oxide powder by reaction with hydrogen and water vapor. The parameters investigated in these feasibility studies included a temperature range of 660 to 960°C and pressures of 1 to 6 torrs. The uranium chloride was successfully converted to microfine urania powder in this experimental range. This definitely establishes the feasibility of conversion of the product of the chloride volatilization process back to usable fuel material.

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INTRODUCTION

One of the methods being developed for recovering uranium from spent nuclear fuels involves leaching with gaseous hydrogen chloride. The volatile uranium chloride is then distilled from the less volatile chlorides of other elements. Calculations and experimentation necessary to effect this chlorination and separation have been discussed extensively by Gens.<sup>3,4</sup> The product of this separation procedure is expected to be a purified uranium chloride, which must subsequently be reconverted

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<sup>1</sup>Now with Battelle Memorial Institute, Columbus, Ohio.

<sup>2</sup>Now with Linde Division, Union Carbide Corporation.

<sup>3</sup>T. A. Gens and G. J. Atta, Thermodynamic Calculations Relating to Chloride Volatility Processing of Nuclear Fuels. I. The Gas-Phase Reduction of Uranium Tetrachloride to the Trichloride with Carbon Monoxide, ORNL-TM-829 (April 1964).

<sup>4</sup>T. A. Gens, Chloride Volatility Experimental Studies: The Reaction of U<sub>3</sub>O<sub>8</sub> with Carbon Tetrachloride and Mixtures of Carbon Tetrachloride and Chlorine, ORNL-TM-1258 (August 1965).

to fuel material. A process for converting the uranium chloride directly to uranium oxide is suggested in this report. We report thermodynamic calculations of suitable reactant compositions and deposition conditions and subsequent experimentation based on these calculations.

#### PREDICTED CHLORIDE PHASE COMPOSITION

Uranium chloride gas was obtained by direct chlorination of uranium metal at temperatures from 350 to 550°C and pressures from 2 to 5 torrs. We have used thermodynamic calculations in order to predict the phases present in the gas. Reportedly,<sup>5</sup>  $\text{UCl}_4$  has a vapor pressure of 4 torrs at 550°C; therefore, only at the highest temperature and lowest pressure would  $\text{UCl}_4$  have been a substantial component of the gas stream. Furthermore, since the transfer tube from the chlorination chamber to the hydro-reduction chamber is cooler than the chlorination chamber, the  $\text{UCl}_4$  would condense in the transfer tube. (Indeed, some condensate was observed when the experiment was performed at the extreme conditions of 2 torrs and 550°C.) The composition of the gas phase containing  $\text{Cl}_2$ ,  $\text{UCl}_5$ , and  $\text{UCl}_6$  in equilibrium with solid  $\text{UCl}_4$  can be calculated thermodynamically as a function of temperature and pressure. The free energies of formation used in the calculation and their sources are shown in Table 1. These calculations indicate that the gas-phase composition would be about 73%  $\text{Cl}_2$ , 25%  $\text{UCl}_5$ , and less than 2%  $\text{UCl}_6$  at 350°C and 79.9%  $\text{UCl}_5$  with the remainder almost totally  $\text{Cl}_2$  at 550°C, if the total system pressure is high compared to the vapor pressure of  $\text{UCl}_4$ . The thermodynamic quantities used for  $\text{UCl}_5$  were obtained using Rand and Kubaschewski's<sup>5</sup> values for the solid and Glassner's<sup>6</sup> estimation of the vapor pressure as indicated by his free energy of vaporization. The calculated compositions obtained from these quantities are somewhat uncertain, but they qualitatively demonstrate that the gas phase that we obtained by

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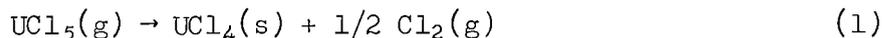
<sup>5</sup>M. H. Rand and O. Kubaschewski, The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963.

<sup>6</sup>A. Glassner, The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750 (1957).

Table 1. Thermodynamic Data Pertinent to Chlorination of Uranium Metal

Compound	Free Energy Formation (cal/mole)	Temperature Range, °K	Source
UCl <sub>4</sub> (s)	-253,100 + 112.8T - 14.3T log T	298-860	Ref. 5
UCl <sub>5</sub> (s)	-263,200 + 128.1T - 14.3T log T	298-600	Ref. 5
UCl <sub>4</sub> (g)	-201,100 + 19.85T - 0.49T log T	298-860	Calculated
UCl <sub>5</sub> (g)	-238,600 + 90.1T - 14.3T log T		Estimated from refs. 5 and 6
UCl <sub>6</sub> (g)	-250,500 + 111.3T - 14.3T log T	450-860	Ref. 5

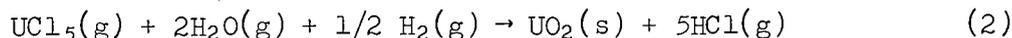
this chlorination technique consisted of UCl<sub>5</sub>, Cl<sub>2</sub>, and very little UCl<sub>6</sub> or UCl<sub>4</sub>. The gas phase was transported through a transfer tube at a lower temperature, about 450°C, into the reaction chamber. As mentioned, this should have been sufficiently low to condense a large fraction of any UCl<sub>4</sub> that might have vaporized. At temperatures below 300°C, the reaction



becomes favorable. This would cause precipitation of UCl<sub>4</sub>(s) in the transfer line, even though no UCl<sub>4</sub> was obtained in the original chlorination step. If UCl<sub>4</sub>(g) is obtained in the original chlorination step, calculations show a significant fraction will precipitate as a solid at any temperature below 525°C at our operating pressure. Hence, the gas phase entering the reaction chamber is believed to be UCl<sub>5</sub> and excess Cl<sub>2</sub>.

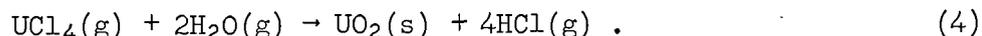
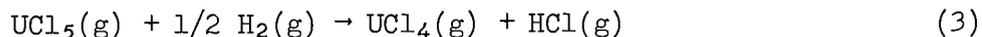
#### THERMODYNAMIC CONVERSION FEASIBILITY

The thermochemical deposition process is a stepwise process<sup>7</sup> and, therefore, the fact that the overall reaction

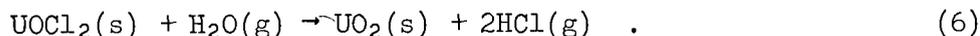
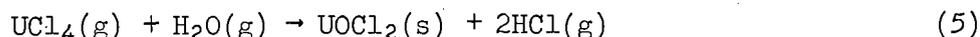


<sup>7</sup>J. D. Fleming, W. C. Robinson, Jr., and C. F. Leitten, Jr., Thermochemical Analysis of Vapor Plating Processes, ORNL-TM-1454 (July 1966).

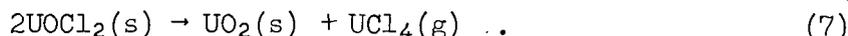
has a negative free energy is not conclusive evidence that the reaction will proceed. If stable intermediate compounds can form, these compounds can act as a sink for the reactants and little of the desired product will be obtained. Since Reaction (2) consists of both reduction and hydrolysis, we can break it down into the steps



Sufficient thermodynamic data are available to completely calculate the free energy for the Reactions (3) and (4). However, Reaction (4) indicates a trimolecular collision. Since a trimolecular collision is extremely unlikely, significant amounts of product according to Reaction (4) can only be produced as a combination of some bimolecular or monomolecular reaction such as



The free energies of Reactions (5) and (6) can also be evaluated but Reaction (5) (an intermediate reaction) involves the solid product  $\text{UOCl}_2$ . The formation of any solid product in intermediate reactions of a thermochemical deposition process usually precludes the completion of the reaction sequence. The postulation of success would seem more likely if Reaction (5) occurred to form gaseous  $\text{UOCl}_2$  which subsequently reacted. However, the species  $\text{UOCl}_2(\text{g})$  has not been reported, since solid  $\text{UOCl}_2$  vaporizes according to the reaction



The formation of  $\text{UO}_2$  via Reactions (5) and (7) offers an alternative route, which is not precluded by these arguments. The product  $\text{UCl}_4$  of Reaction (7) is subsequently recycled via Reaction (5).

One can utilize the data of Shchukarev *et al.*<sup>8</sup> to calculate the free energy of  $\text{UOCl}_2(\text{s})$  and estimate the free energy of  $\text{UOCl}_2(\text{g})$  in order to arrive at the possibility of  $\text{UOCl}_2(\text{g})$  being a stable enough intermediate to keep Reaction (4) from occurring. This somewhat detailed argument does not contribute to the purpose of this report but is given in the appendix for the sake of completeness.

The thermodynamic quantities used to calculate the free energies of Reactions (3) and (4) are shown in Table 2, and the resulting free energies of reaction are shown in Table 3. Reactions (3) and (4) appear favorable at all temperatures, and the examination of  $\text{UOCl}_2$  indicated a small likelihood of its being a sufficiently stable intermediate in either the gaseous or solid state to prevent Reaction (4).

Several other considerations were investigated before the initial experimental parameters were chosen. It was considered desirable to operate under conditions where all intermediate compounds remained gaseous. To prevent precipitation of  $\text{UOCl}_2(\text{s})$  at our operating pressures, a temperature of at least  $1000^\circ\text{K}$  was required. We desired to produce a powdered  $\text{UO}_2$  product. Previous experience<sup>9</sup> with the conversion of uranium fluoride has indicated that powder formation is enhanced by inducing a reaction route involving initial hydrolysis and subsequent reduction, instead of the reduction-hydrolysis sequence of Reactions (3) and (4). Further, since a stable intermediate is more likely if lower halides such as  $\text{UCl}_4$  and  $\text{UF}_4$  form, routes involving initial hydrolysis of a higher halide have been shown to be thermodynamically more advantageous in systems where sufficient data are available to make this calculation.<sup>7</sup> In this particular case, the lack of data on the oxychlorides formed by initial hydrolysis of  $\text{UCl}_5$  makes quantitative consideration of the reaction thermodynamics impractical. We can only suspect from previous experience that reaction sequence involving

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<sup>8</sup>S. A. Shchukarev *et al.*, Zh. Neorgan. Khim. 1, 2272-77 (1956).

<sup>9</sup>R. L. Heestand and C. F. Leitten, Jr., "Thermochemical Reduction of Uranium Hexafluoride for the Direct Fabrication of Uranium Dioxide Ceramic Fuels," Nucl. Appl. 1, 584-88 (1965).

Table 2. Thermodynamic Data Pertinent to Conversion of Uranium Chloride to Uranium Dioxide

Compound	Free Energy at Formation (cal/mole)	Temperature Range (°K)	Source
H <sub>2</sub> O	Tabulated	0-6000	Refs. 8,9
CO <sub>2</sub> (g)	Tabulated	0-6000	Ref. 9
HCl(g)	Tabulated	0-6000	Ref. 9
UO <sub>2</sub> (s)	-258,000 + 40.0T	298-1405	Ref. 5

Table 3. Calculated Free Energies of Chloride Conversion at 2 torrs

Temperature (°K)	Free Energy of Reaction, cal		
	Reaction (2)	Reaction (3)	Reaction (4)
850	-64,600	-16,700	-47,120
900	-67,600	-18,600	-49,300
950	-70,000	-19,650	-50,300
1000	-72,200	-20,800	-51,300
1050	-75,000	-22,400	-52,600
1100	-77,400	-23,750	-53,600
1150	-80,900	-25,100	-55,200

initial hydrolysis is more advantageous than (3) and (4). On the basis of these considerations, we decided to deliberately induce a reaction sequence involving the initial hydrolysis of UCl<sub>5</sub> followed by the reduction of whatever uranium oxychloride was formed.

## EXPERIMENTAL EQUIPMENT AND PROCEDURES

An experimental system was constructed to establish the feasibility of converting  $UCl_5$  directly to  $UO_2$  powder. Presumably, one would start with the mixed uranium chlorides obtained from the volatile-chloride separation process previously established for separating the residual uranium from spent fuel elements. However, to simplify material handling in this work, uranium sheet was placed in alumina boats and chlorinated in situ to obtain the equivalent uranium chlorides.

A schematic of the experimental system for the direct thermochemical conversion of  $UCl_5$  to  $UO_2$  is shown in Fig. 1. Chlorine diluted with argon was passed over hot uranium sheet. The chlorinator chamber was held at a temperature above  $450^\circ C$  and system pressure was less than about 4 torrs. The resulting uranium chlorides were passed through a heated selective-mixing injector. As shown in the detailed sketch of Fig. 2, the injector premixed the chlorides with oxygen. An interposed conical stream of argon isolated the resulting mixture until it moved away from the injector and into the hot reactor zone. The reactor chamber was held at a temperature above  $815^\circ C$  and under a partial hydrogen pressure of about 2 torrs for most operations. The reaction product was collected on the hot walls of a tubular quartz insert.

A 13.5-liter/min mechanical vacuum pump provided the necessary vacuum. Any residual chlorides and some microfine  $UO_2$  powder were arrested in a cold trap, which also condensed back-diffusing pump oil. The resulting by-products of hydrogen, hydrogen chloride, and water vapor were passed through a tower scrubber filled with berl saddles. The gaseous  $HCl$  was absorbed in the water and discharged to a drain. Excess hydrogen was burned off under a vent hood.

All the feed gases were metered through standard Pyrex-stainless steel rotameters. Transfer lines between the source bottles and the heated chambers were of 1/4-in.-diam copper tubing. All heated sections of the systems, including the injector, were constructed of quartz. The optical end caps, cold trap, vacuum line, scrubber, and mating ball-joint feed-gas couplings were constructed of Pyrex. Two thermocouple-controlled

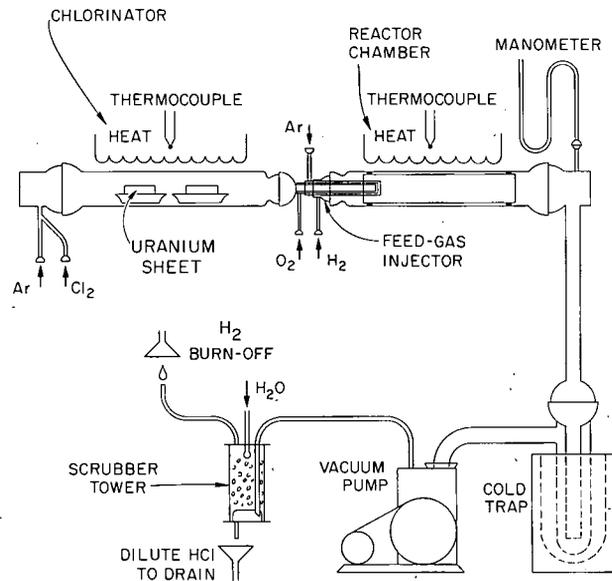


Fig. 1. Schematic of Thermochemical Deposition System for Direct Conversion of Uranium Pentachloride to Uria.

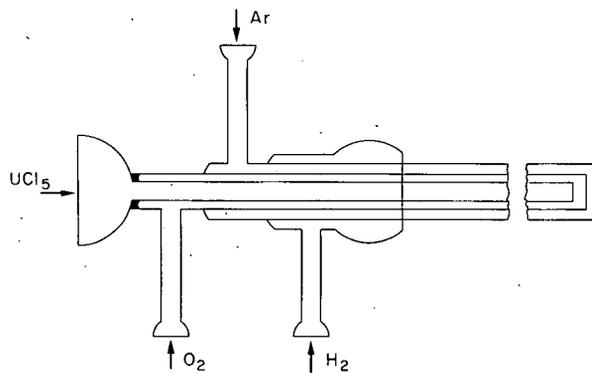


Fig. 2. Feed-Gas Injector.

Nichrome-wound shell furnaces provided heat to the chlorinator and reactor chambers. An infrared lamp and tape-type strip heater (not shown in the sketch) provided additional heat to the transfer section of the injector and to the feed-gas lines. A standard Pyrex-mercury manometer monitored the pressure on the cold exit portion of the reaction system. The completed system, mounted in a bench-type hood, is shown in Fig. 3.

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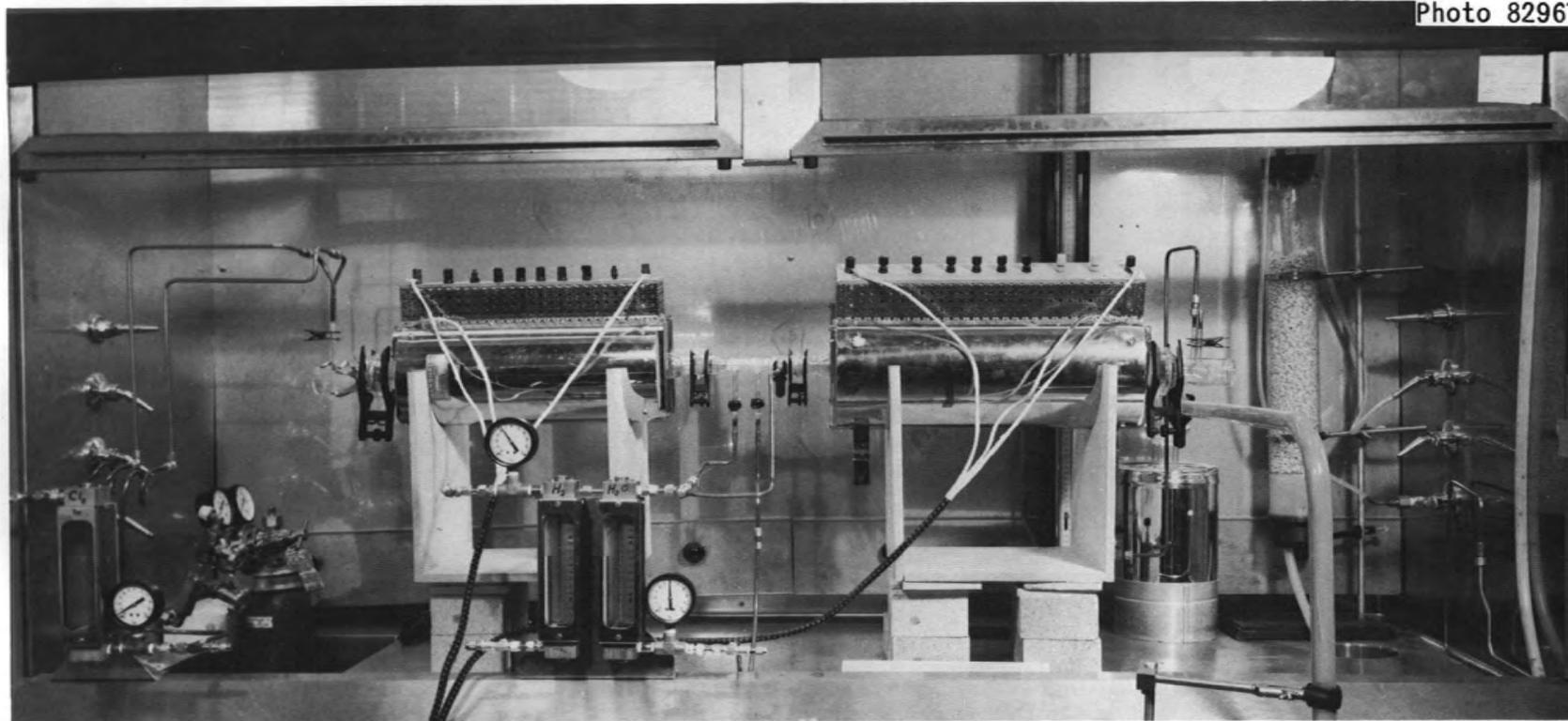


Fig. 3. Experimental System for Direct Conversion of Uranium Pentachloride to Urania by Thermochemical Deposition.

## EXPERIMENTAL CONDITIONS AND RESULTS

As the above calculations predicted, experimental system pressure and temperature could be chosen so that a suitable amount of  $UCl_5$  would be available for the subsequent hydrolysis-reduction reaction, and the  $UCl_5$  would be converted to  $UO_2$  in the presence of hydrogen and oxygen. Mole ratios of the various feed gases, however, had to be determined by trial and error.

A complete list of the experimental conditions is presented in Table 4. The temperature of the chlorinator had to be maintained at about  $520^\circ C$  to obtain adequate quantities of  $UCl_5$ . Also, the temperature of the transfer line had to be raised to about  $450^\circ C$  to prevent the  $UCl_5$  gas from converting to solid  $UCl_4$  at this point. About  $50\text{ cm}^3/\text{min}$  of argon prevented the formation of solid  $UO_2$  on the end of the injector. A reactor temperature as low as  $775^\circ C$  proved adequate for the reactions.

Table 5 presents feed-gas flow rates, expressed as mole ratios, and the chemical analysis and compound identification of the resulting deposits. Some  $UO_2$  was obtained under all experimental conditions. In all the runs at  $850^\circ C$  or above, a solid-mass annular deposit was found on the wall of the insert tube near the injector. The  $950$  and  $960^\circ C$  runs produced a crystalline annular  $UO_2$  deposit just downstream of the mass deposit along with some fine crystalline  $UO_2$  powder. However, the predominant species of all runs was a microfine  $U_3O_8$  powder. Finely divided  $UO_2$  burns to  $U_3O_8$  at the temperature of these experiments which probably accounts for these observations. The powder products of runs 1 and 9 were readily reduced to near-stoichiometric  $UO_2$  by an additional treatment, in which the powders were held at  $1000^\circ C$  for 1 hr under wet hydrogen at atmosphere pressure. In run 11, the as-deposited material was heat treated in situ by simply cutting off the chlorine flow and chlorinator heater and holding the reactor at temperature for an additional hour. This treatment produced a solid with an oxygen-to-uranium ratio of 2.582 and  $< 70$  ppm Cl.

Table 4. Experimental Conditions for Direct Conversion of Uranium Chlorides to Urania

Run	Feed-Gas Flow Rates (cm <sup>3</sup> /min)					Chamber Pressure (torrs)	Operating Temperature (°C)			Remarks
	Cl <sub>2</sub>	Ar <sub>Cl</sub> <sup>a</sup>	O <sub>2</sub>	Ar <sub>EJ</sub> <sup>b</sup>	H <sub>2</sub>		Chlorinator	Transfer Line	Reactor Chamber	
1	140	300	300	300	300	4	475	> 210	775	UCl <sub>4</sub> buildup in line
2	140	150	300	150	400	4	415	> 210	815	UCl <sub>4</sub> buildup in line
3	280	300	800	300	1800	2	530	> 210	815	UCl <sub>4</sub> buildup in line
4	140	150	450	150	300	2	532	> 210	815	UCl <sub>4</sub> buildup in line
5	140	150	450	150	300	2	360	> 210	660	Lost Cl <sub>2</sub> flow
6	140	75	450	75	300	2	450	> 210	850	UCl <sub>4</sub> buildup in line
7	175	75	450	75	300	2	500	> 210	780	UCl <sub>4</sub> buildup in line
8	280	50	540	50	540	2	545	> 210	950	UCl <sub>4</sub> buildup in line
9	280	50	280	50	1120	6	550	~ 450	960	Very little UCl <sub>4</sub> in line
10	240	50	240	50	360	2	530	~ 450	840	Very little UCl <sub>4</sub> in line
11	240	50	192	50	720	1	523	~ 450	854	Very little UCl <sub>4</sub> in line

<sup>a</sup>Amount of argon passed through the chlorinator to transport the UCl<sub>5</sub>.

<sup>b</sup>Amount of argon passed through the ejector to delay the hydrogen reaction.

Table 5. Mole Ratios of Feed Gases and Resulting Products

Run	Feed-Gas Flow (moles/mole Cl <sub>2</sub> )		Chemical Analysis				Resulting Product (By X-Ray Fink-Card Index)		Remarks <sup>a</sup>
			As-Deposited		Heat-Treated		As-Deposited	Heat-Treated	
	O <sub>2</sub>	H <sub>2</sub>	O/U	Cl (ppm)	O/U	Cl (ppm)			
1	5.4	2.1					UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub> , UO <sub>3</sub>	UO <sub>2</sub>	Separate HT (P)
2	5.4	2.9							Mostly (S)
3	7.1	6.4							Mostly (S)
4	8.0	2.1							Mostly (S)
5	8.0	2.1							Lost Cl <sub>2</sub> flow
6	8.0	2.1	2.442	50			UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub>		Mostly (S)
7	6.4	1.7							Hard particles
8	4.8	1.9	2.626	200			UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub>		(P)
9	2.5	4.0	2.662	495	2.020	593	UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub>	UO <sub>2</sub>	Crystalline UO <sub>2</sub> Separate HT (P)
10	2.5	1.5	2.673	100			UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub>		Crystalline UO <sub>2</sub>
11	2.0	3.0			2.090	<50		UO <sub>2</sub>	HT in place (S)
					2.582	<70		UO <sub>2</sub> , U <sub>3</sub> O <sub>8</sub>	HT in place (P)

<sup>a</sup>(S) = solid crystalline deposit; (P) = microfine powder; HT = heat treated in hydrogen for 1 hr.

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## DISCUSSION AND CONCLUSIONS

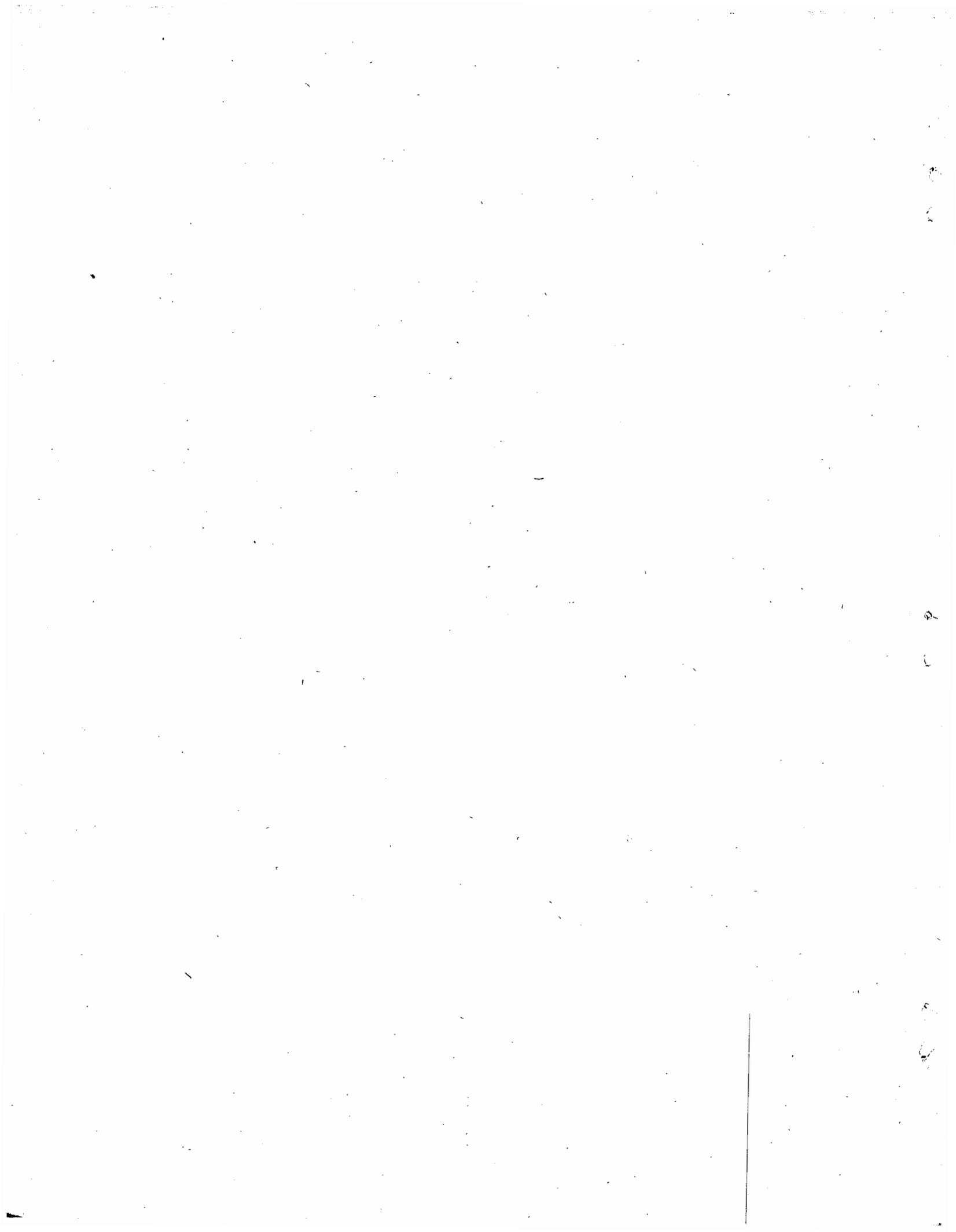
As previously stated, the objective of this work was to establish the feasibility of inexpensively converting the uranium chlorides that are obtained from the chlorine volatility process to uranium dioxide powder by a hydrolysis-reduction reaction. Should the chloride route be chosen for processing spent Zircaloy-clad uranium fuel elements, the reconversion of the resulting uranium chlorides to microfine uranium oxide powder has definitely been established. This work also suggests the possibility of obtaining "free-standing" solid deposits, deposits as coatings on other materials, and small crystallites of ultrapure uranium oxide.

Optimization of the process parameters to obtain stoichiometric  $UO_2$  powders will be left to future workers. However, we recommend for a continuous process a vertical system that would preheat all feed gases, promote gas-phase precipitation, and include an additional in-process wet-hydrogen chamber. This report concludes our work on the chloride process.

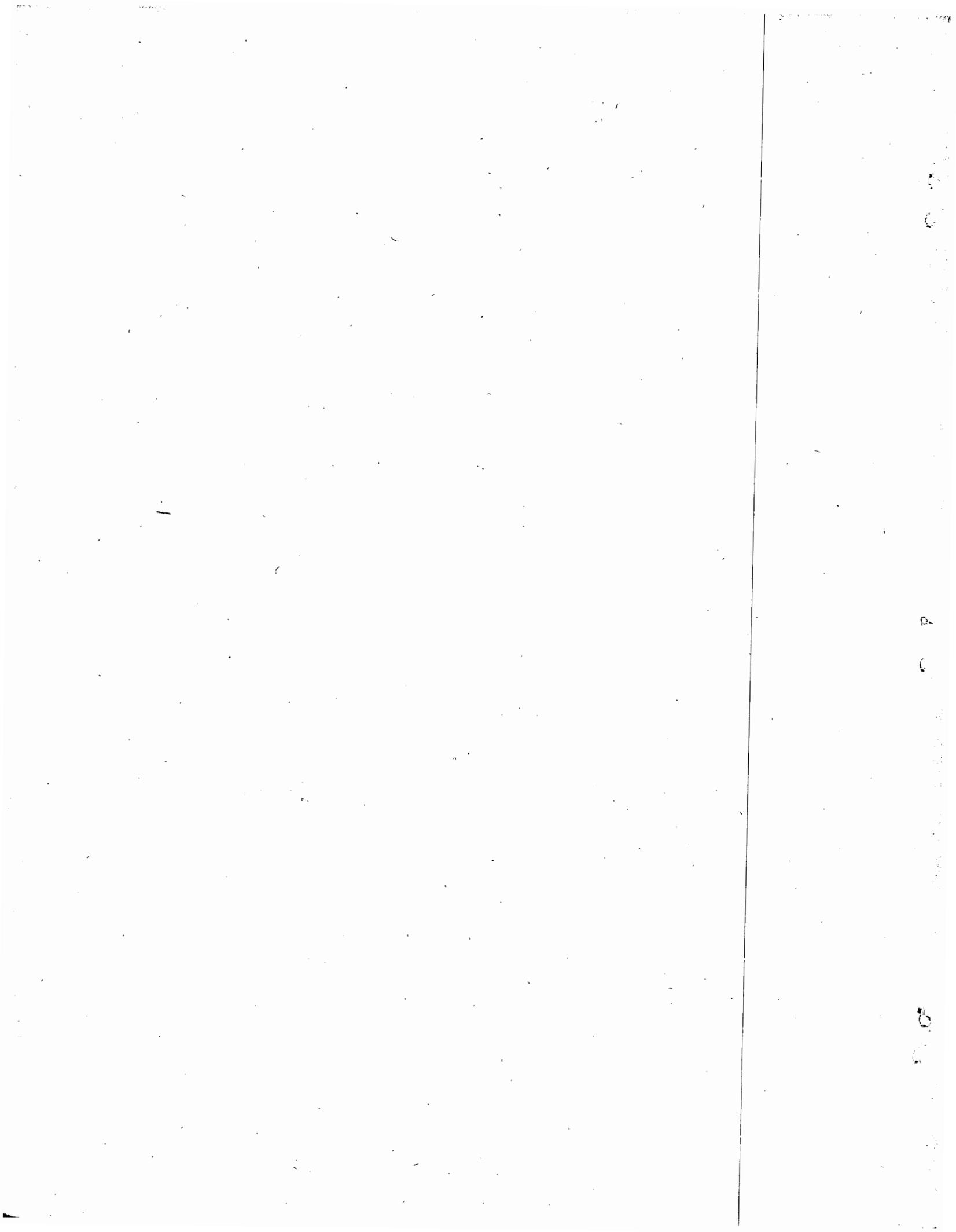
## ACKNOWLEDGMENTS

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Finally, the authors are grateful to W. H. Warwick for aiding in the experimental investigation.

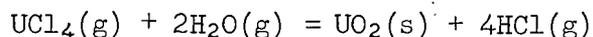
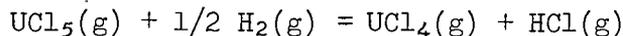


APPENDIX



## APPENDIX

Calculation Procedure for Thermodynamic Feasibility  
Consideration of Reaction Sequence



The thermodynamic properties of the compounds involved will be given for a pressure of 1 atm. In the temperature range of interest here (600 to 900°C), all of the reactants and intermediate products are gaseous at 1 atm except  $\text{UCl}_4$ , which is solid.

The free energy of formation of the gaseous species are estimated from values for the solid and the vapor pressure over the solid by the equation

$$\Delta F^\circ_g = \Delta F^\circ_s + \Delta F^\circ_{\text{vap}}$$

$$\Delta F^\circ_{\text{vap}} = -RT \ln VP$$

$\Delta F^\circ_g$  = standard free energy of formation of the gaseous species,

$\Delta F^\circ_s$  = standard free energy of formation of the solid species,

$\Delta F^\circ_{\text{vap}}$  = standard free energy of vaporization,

R = gas constant,

T = temperature in °K, and

VP = vapor pressure of compound in atmospheres.

For example, the  $\text{UCl}_4$  vapor pressure is given<sup>10</sup> as

$$\log VP_{\text{mm}} = +23.21 - 11,350/T - 3.02 \log T$$

Since

$$\Delta F^\circ_{\text{vap}} = -RT \ln VP$$

substitution yields

$$\Delta F^\circ_{\text{vap}} = 52,000 + 13.81T \log T - 92.95T$$

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<sup>10</sup>R. K. Steunenberg and R. C. Vogel, Chap. 6 in Reactor Handbook, 2nd ed., vol 2, Fuel Reprocessing, ed. by S. M. Stoller and R. B. Richards, Interscience, New York, 1961.

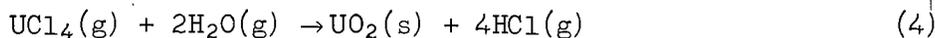
Addition of this to the equation for  $\Delta F^\circ_s$  produces the equation for  $\Delta F^\circ_g$  for  $UCl_4$  at 1 atm. Since the equations for the free energy of the rest of the compounds involved have been tabulated for the same state as that in which they appear in the reactions, the standard free energy changes of the reactions can now be calculated from

$$\Delta F^\circ = \sum \Delta F^\circ_{\text{products}} - \sum \Delta F^\circ_{\text{reactants}}$$

This would represent the free energy of reaction assuming that each gaseous product has a 1-atm pressure. The free energies of reaction given in the tables have been corrected with the assumption that each gaseous product has a 2-torr pressure to approximate the actual pressure in the system.

#### Analysis of Probable Intermediate Steps in Reaction (4)

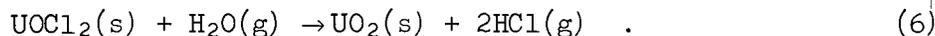
The compound  $UOCl_2(s)$  has been identified, which immediately suggests that



could proceed according to the reactions



and



These reactions are almost prohibited from being the actual process, because in every existing thermochemical deposition system to our knowledge the formation of a solid product in an intermediate reaction has precluded completion of the reaction. In this sequence, the solid product  $UOCl_2$  is formed and must subsequently react with  $H_2O(g)$  according to Reaction (6). However,  $UOCl_2(s)$  does not appear to vaporize but decomposes via the reaction

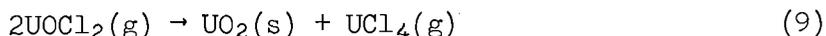


according to Shchukarev.<sup>11</sup> Therefore, in the event of the nucleation of  $\text{UOCl}_2(\text{s})$ , the fact that Reaction (7) proceeds under the conditions of this process indicates that the decomposition of  $\text{UOCl}_2$  would not have to proceed according to Reaction (6) but could occur via Reaction (7) to produce a  $\text{UO}_2$  product.

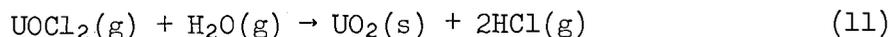
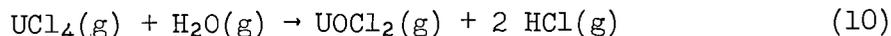
The free energy change for the vaporization process,



may be expected to be more positive than that for Reaction (7). It should be noted, however, that Reaction (7) is not a true disproportionation reaction. In the gaseous state



would require a bimolecular collision of  $\text{UOCl}_2(\text{g})$ , a species that is likely to be present in low concentrations. As a result, molecular  $\text{UOCl}_2$  might exist as a gas in the vapor-plating system. If it exists in this system, then the reactions



would be the probable stepwise procedure for Reaction (4). This sequence, with no solid intermediate, could form a continuous  $\text{UO}_2$  solid deposit as observed by Heestand.<sup>12</sup>

In order to evaluate the standard free energies of Reactions (10) and (11), the standard free energy of Reaction (8) must be known. This

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<sup>11</sup>S. A. Shchukarev *et al.*, Zh. Neorgan. Khim. 1, 2272-77 (1956).

<sup>12</sup>R. L. Heestand and C. F. Leitten, Jr., "Thermochemical Reduction of Uranium Hexafluoride for the Direct Fabrication of Uranium Dioxide Ceramic Fuels," Nucl. Appl. 1, 584-88 (1965).

free energy can be related to the standard free energy of Reaction (7) in the following manner

$$-\Delta F_7^\circ = RT \ln K_7 \cong RT \ln X_{\text{UCl}_4} \pi, \quad (\text{I})$$

where

$K_7$  = equilibrium constant of dissociation at temperature of solid,

$\pi$  = total pressure of system,

$X_{\text{UCl}_4}$  = mole fraction of  $\text{UCl}_4$  in vapor .

Likewise,

$$-\Delta F_8^\circ = RT \ln K_8 \cong RT \ln X_{\text{UOCl}_2} \pi, \quad (\text{II})$$

which gives

$$\Delta F_8^\circ = \Delta F_7^\circ + RT \ln \frac{X_{\text{UCl}_4(\text{g})}}{X_{\text{UOCl}_2(\text{g})}} \quad (\text{III})$$

where  $X_{\text{UCl}_4(\text{g})}$  and  $X_{\text{UOCl}_2(\text{g})}$  are the mole fractions of  $\text{UCl}_4$  and  $\text{UOCl}_2$  in the vapor above  $\text{UOCl}_2(\text{s})$ .

Shchukarev did not detect any  $\text{UOCl}_2$  in his vapor condensate. He examined the condensate by x-ray diffraction, which would not reveal a component present in small concentrations. His chlorine-to-uranium ratio in the condensate was 3.98. Assuming that the  $\text{UCl}_4$  was contaminated by  $\text{UOCl}_2$  and that his limit of detection of  $\text{UOCl}_2$  was 1% of the total, then one can assume that the vapor concentration of  $\text{UOCl}_2(\text{g})$  over the solid is 1% of that of  $\text{UCl}_4(\text{g})$ . This is the number indicated by a chlorine-to-uranium ratio of 3.98 if  $\text{UOCl}_2$  was his contaminant. This value can be substituted into Eq. (III) for calculation of  $\Delta F_8^\circ$ . From Shchukarev's data  $\Delta F_7^\circ$  is calculated utilizing his equation for the pressure of  $\text{UCl}_4(\text{g})$  over  $\text{UOCl}_2(\text{s})$ . Addition of Reaction (8) to (5) yields Reaction (10). Subtraction of Reaction (10) from Reaction (4) yields Reaction (11).

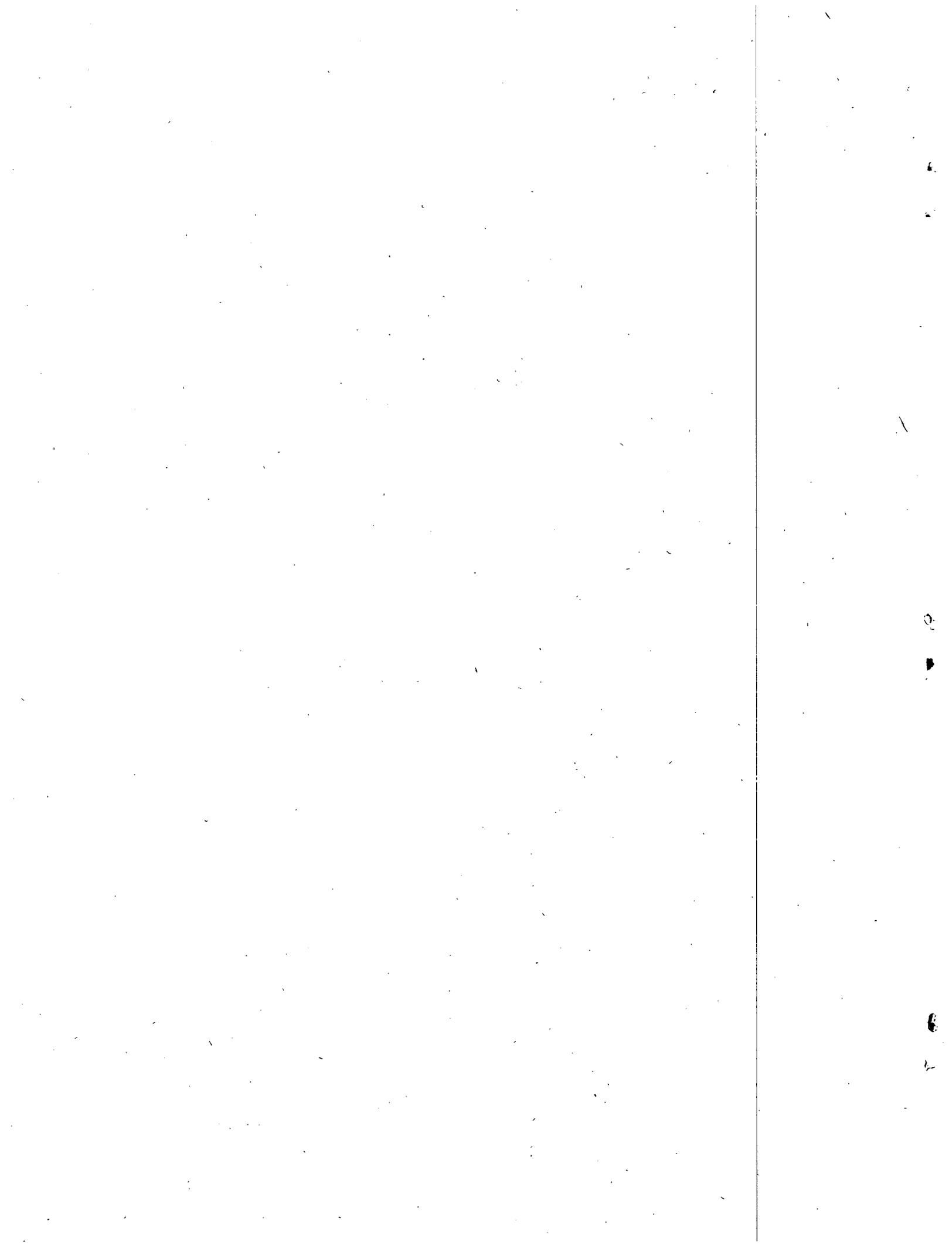
Table 6 lists the standard free energies of Reactions (5) and (7) at 2 torrs as a function of temperature. These values indicate the feasibility of the deposition of a powdered  $\text{UO}_2$  product above 950°K. Table 6 also lists the free energy changes of Reaction (10)

for  $X_{\text{UCl}_4(\text{g})}/X_{\text{UOCl}_2(\text{g})}$  ratios of  $10^2$  and  $10^4$ . All of these reactions exhibited a negative free energy, with none of them having a larger negative number than that of Reaction (4). This indicates that Reaction (11), to effect the complete conversion to  $\text{UO}_2$ , will also be negative. These values indicate that Reaction (4) has a possibility of forming solid  $\text{UO}_2$  even if the vapor pressure of  $\text{UOCl}_2(\text{g})$  is two orders of magnitude below the probable detection limit of the techniques used by the Russians.

There is no more reliable way to estimate the vapor pressure of  $\text{UOCl}_2(\text{g})$  over  $\text{UOCl}_2(\text{s})$ . Similar compounds,  $\text{UOBr}_2$  and  $\text{ThOF}_2$ , also dissociate instead of vaporizing, hence we cannot use data from these reactions to estimate the vapor pressure of  $\text{UOCl}_2(\text{s})$ . However, the calculations indicated that uranium oxide powder could be formed via this process, so the experiments were performed. The production of a solid deposit in the experiments indicates that the vapor pressure of  $\text{UOCl}_2(\text{g})$  over  $\text{UOCl}_2(\text{s})$  is not much less than  $10^{-4}$  times the pressure of  $\text{UCl}_4$ .

Table 6. Calculated Free Energies of Reactions  
at 2 torrs per Gaseous Phase

Temperature (°K)	$\Delta F_5$ (cal)	$\Delta F_7$ (cal)	$\Delta F_{10}$ (cal)	
			$P_{\text{UCl}_4}/P_{\text{UOCl}_2} = 10^2$	$P_{\text{UCl}_4}/P_{\text{UOCl}_2} = 10^4$
850	-26,700	+5,020	-13,900	-6,100
900	-25,600	+2,160	-15,200	-7,000
950	-24,900	-700	-16,900	-8,200
1000	-23,900	-3,550	-18,300	-9,150
1050	-23,100	-6,400	-19,900	-10,300
1100	-22,200	-9,300	-21,200	-11,100
1150	-21,500	-12,100	-23,200	-12,600



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