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CHEMISTRY OF GASEOUS LOWER HALIDES OF URANIUM

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## Abstract

The gaseous uranium species  $UF$ ,  $UF_2$ ,  $UF_3$ , and  $UF_4$  were generated in effusion cell beams by vaporization of  $UF_4(s)$  under reducing conditions, and they were identified and studied by mass spectrometry. From extensive second-law studies of reaction equilibria involving these species and several reaction partners used as reference standards, the individual bond dissociation energies and standard enthalpies of formation of the U-F species were derived. Reaction entropies derived from the slope data indicate that the electronic entropies of the U-F species are substantial, and are comparable to or larger than that of atomic uranium. Additional thermochemical measurements were made to establish the properties of several Ag and Cu monohalides that have been or will be used as reference standards in the uranium halide measurements. From studies of the sublimation and decomposition of uranyl fluoride,  $UO_2F_2(s)$ , the enthalpy of sublimation of  $UO_2F_2(g)$  has been determined, and another gaseous oxyfluoride,  $UOF_4(g)$ , has been tentatively identified. The gaseous products of decomposition of  $UO_2F_2(s)$  observed by mass spectrometry differ from those postulated by other investigators, indicating that the mechanism of decomposition has not been clearly established. A search of the thermochemical literature on uranium halides has been completed.

## Introduction

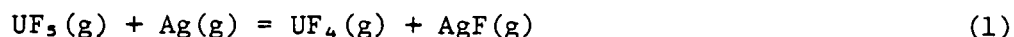
The program described here was undertaken to provide an accurate thermochemical characterization of the gaseous lower-valent halides and oxyhalides of uranium. Very little of this type of information is available in the literature, making it virtually impossible to carry out any meaningful thermodynamic equilibrium calculations on these systems or to evaluate the energetics of reactions involving these chemical species. Spectroscopic and molecular energy level data on the gaseous lower halides are also very sparse, so that heat capacity, entropy and

related thermodynamic functions cannot be calculated reliably by the usual statistical procedures. This precludes the analysis and modeling of many practical applications involving uranium chemistry.

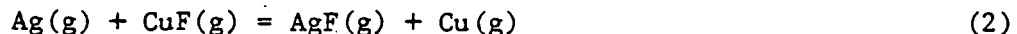
In this program, we are developing chemical techniques for generating the desired lower halide species, and are then utilizing mass spectrometric and effusion pressure techniques to study chemical reaction equilibria involving these species. From careful equilibrium measurements made over an extended temperature range, one can derive standard enthalpies of formation, entropies, and bond dissociation energies. We report here the results obtained in the first phase of the program, which is concerned with the uranium fluorides and oxyfluorides.

#### A. Lower-Valent Uranium Fluorides

In earlier studies on  $\text{UF}_3(\text{g})$ ,<sup>1</sup> the gaseous reaction equilibrium



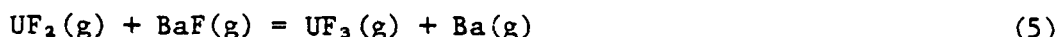
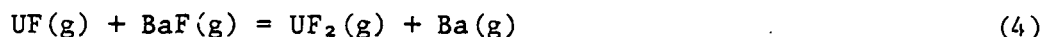
was investigated, in which the thermochemical properties of the uranium species are determined by reference to silver monofluoride,  $\text{AgF}$ . Although the thermochemistry of  $\text{AgF}$  was not firmly established, it proved to be one of the few suitable reference standards for the relatively weak  $\text{F}_4\text{U-F}$  bond. We have now completed measurements of the gaseous equilibrium



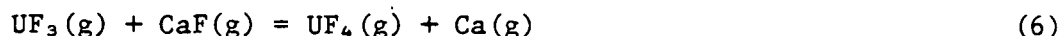
by mass spectrometry and determined  $\Delta H_{298}^\circ = D_{298}^\circ(\text{CuF}) - D_{298}^\circ(\text{AgF}) = 18.5 \pm 1$  kcal/mol by second and third law analysis, leading to  $\Delta_f H_{298}^\circ(\text{AgF}, \text{g}) = 1.8 \pm 1$  kcal/mol and  $D_{298}^\circ(\text{AgF}) = 85.1$  kcal/mol. This firms up the thermochemistry of  $\text{UF}_3(\text{g})$ .

By passing  $\text{BaF}_2$  vapor over  $\text{UC}(\text{s})$  in a graphite effusion cell, it was possible to generate beams containing  $\text{UF}_3$ ,  $\text{UF}_2$ ,  $\text{UF}$ , and  $\text{U}$ , in addition to the reaction partners  $\text{Ba}$  and  $\text{BaF}$ . The uranium species were positively identified from the threshold appearance potentials of the

corresponding ions:  $\text{UF}_3^+$  (7.0 eV);  $\text{UF}_2^+$  (6.2 eV);  $\text{UF}^+$  (6.0 eV);  $\text{U}^+$  (6.2 eV). With this arrangement it was possible to study the reaction equilibria

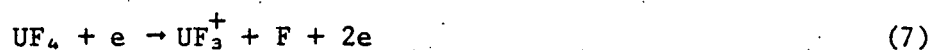


by mass spectrometry and to determine the reaction enthalpies by second law analysis alone. The results are shown in Table I. The additional equilibrium



was investigated by reacting  $\text{UF}_4$  vapor with  $\text{CaF}_2$  and B in a molybdenum effusion cell, with results shown in Table I.

Bond dissociation energies and standard enthalpies of formation of the U-F species derived from the results, based on the established thermochemical properties of BaF and CaF, are summarized in Table II. Included are data for  $\text{UF}_3$  and  $\text{UF}_4$  obtained in earlier work.<sup>1</sup> The individual bond dissociation energies are especially striking in showing the precipitous drop in thermodynamic stability in passing from the tetravalent to the pentavalent and hexavalent states of uranium. This is the first instance in which all of the individual bond dissociation energies in a hexavalent actinide compound have been determined, and the results should prove extremely helpful in evaluating the properties of other actinides. A good check on the internal consistency of the new results on UF,  $\text{UF}_2$ , and  $\text{UF}_3$  is provided by the fact that, as shown in Table II, the sum of the individual bond dissociation energies derived from the equilibrium studies agrees closely with the heat of atomization of  $\text{UF}_6(\text{g})$  evaluated from well established thermochemical data. As a further check on the equilibrium measurements, the threshold appearance potential for the dissociative ionization process in  $\text{UF}_4$  vapor



was determined as  $13.28 \pm 0.10$  eV, and the ionization potential of  $\text{UF}_3$  was measured at  $6.97 \pm 0.10$  eV. Combination of these two results yields  $D(\text{F}_3\text{U-F}) = 13.28 - 6.97 = 6.31$  eV = 145.5 kcal/mol, in close agreement with the equilibrium value.

The experimental (expt) entropies of gaseous  $\text{UF}$ ,  $\text{UF}_2$ , and  $\text{UF}_3$  were evaluated from the reaction equilibrium constants and their second law slopes, and were compared with values calculated by standard statistical methods taking into account the translational, rotational, and vibrational (trv) contributions only. The statistical calculations involve some estimated parameters, but are sufficiently accurate for present purposes. The comparisons are as follows: For  $\text{UF}$ ,  $S_{2300}^\circ(\text{expt}) = 83.1$  cal/deg mole, and  $S_{2300}^\circ(\text{trv}) = 76.3$  cal/deg mol; for  $\text{UF}_2$ ,  $S_{2200}^\circ(\text{expt}) = 108.6$  cal/deg mol, and  $S_{2200}^\circ(\text{trv}) = 96.9$  cal/deg mol; and for  $\text{UF}_3$ ,  $S_{2200}^\circ(\text{expt}) = 125.3$  cal/deg mol, and  $S_{2200}^\circ(\text{trv}) = 115.9$  cal/deg mol. In all instances, the experimental values are significantly higher than the trv calculated values, indicating that the electronic entropies of  $\text{UF}$ ,  $\text{UF}_2$ , and  $\text{UF}_3$  are substantial at the experimental temperatures and are comparable to or larger than that of atomic uranium (8.0 cal/deg mol at 2300 K). These will be useful in evaluating reliable thermodynamic functions for  $\text{UF}$ ,  $\text{UF}_2$ , and  $\text{UF}_3$ .

#### B. Sublimation/Decomposition of $\text{UO}_2\text{F}_2$

The vaporization chemistry of uranyl fluoride,  $\text{UO}_2\text{F}_2(\text{s})$ , is being investigated in order to characterize the thermochemistry of  $\text{UO}_2\text{F}_2(\text{g})$  and to clarify the mechanism of the thermal decomposition of  $\text{UO}_2\text{F}_2(\text{s})$ . Previous investigators<sup>2,3</sup> have identified the solid product as  $\text{U}_3\text{O}_8(\text{s})$  and have inferred that the gaseous decomposition products are  $\text{UF}_6$  and  $\text{O}_2$ . On vaporizing  $\text{UO}_2\text{F}_2(\text{s})$  from a platinum effusion cell, we have identified gaseous  $\text{UO}_2\text{F}_2$ ,  $\text{UOF}_4$ ,  $\text{UF}_3$ , and a small amount of  $\text{UF}_4$  in the saturated vapor, but definitely no  $\text{UF}_6$  or  $\text{O}_2$ . These latter experiments were done by means of modulated beam mass spectrometry, and should be quite reliable. Contrary to previous results,<sup>2,3</sup>  $\text{UO}_2\text{F}_2(\text{g})$  appears to be the major species in the saturated vapor, several determinations of the



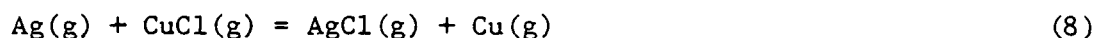
enthalpy of sublimation of  $\text{UO}_2\text{F}_2(\text{g})$  have been made, and the results are being evaluated. Further studies are in progress.

### C. Literature Search

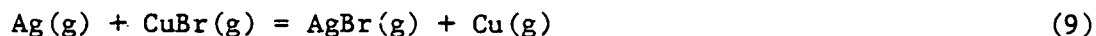
A computer-assisted search of the thermochemical literature on the halides and oxyhalides of uranium has been completed, and a number of pertinent references were uncovered. Copies of these papers were obtained and the material was evaluated.

### D. Gaseous $\text{CuCl}$ and $\text{CuBr}$

For use as potential reference standards and reaction partners in future studies of uranium chlorides and bromides, the thermochemical properties of gaseous  $\text{CuCl}$  and  $\text{CuBr}$  were determined by reference to  $\text{AgCl}$  and  $\text{AgBr}$ . The reactions studied were



and



with the results  $\Delta H_{298}^\circ(8) = 15.1 \pm 1 \text{ kcal/mol}$  and  $\Delta H_{298}^\circ(9) = 12.8 \pm 1 \text{ kcal/mol}$ . These data yield  $D_{298}^\circ(\text{CuCl}) = 90.1 \text{ kcal/mol}$  and  $D_{298}^\circ(\text{CuBr}) = 79.5 \text{ kcal/mol}$ . Results of this type are important since there are so few well established reference standards among the moderately stable chlorides and bromides.



#### REFERENCES

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2. L. M. Ferris and F. G. Baird, J. Electrochem. Soc. 107, 305 (1960).
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Table I

## REACTION THERMOCHEMISTRY OF URANIUM FLUORIDES

<u>Gaseous Reaction</u>	<u>Range, K</u>	$\Delta H_T^\circ(\text{II})$ <u>kcal/mol</u>	<u>Derived Result</u>
$\text{U} + \text{BaF} = \text{UF} + \text{Ba}$	2222-2505	$-17.8 \pm 0.7$	$D(\text{U-F}) = 156 \text{ kcal/mol}$
$\text{UF} + \text{BaF} = \text{UF}_2 + \text{Ba}$	2034-2466	$4.8 \pm 0.6$	$D(\text{FU-F}) = 134$
$\text{UF}_2 + \text{BaF} = \text{UF}_3 + \text{Ba}$	2034-2466	$-8.3 \pm 0.4$	$D(\text{F}_2\text{U-F}) = 147$
$\text{UF}_3 + \text{CaF} = \text{UF}_4 + \text{Ca}$	1533-1745	$-19.5 \pm 0.6$	$D(\text{F}_3\text{U-F}) = 146$

Table II

DERIVED THERMOCHEMICAL PROPERTIES OF  
GASEOUS URANIUM FLUORIDES<sup>a</sup>

<u>Gaseous Species</u>	<u><math>\Delta_f H_{298}^\circ</math></u>	<u>Bond</u>	<u><math>D_{298}^\circ</math></u>
UF	-10.1	U-F	156
UF <sub>2</sub>	-125.2	FU-F	134
UF <sub>3</sub>	-253.3	F <sub>2</sub> U-F	147
UF <sub>4</sub>	-379.3	F <sub>3</sub> U-F	146
UF <sub>5</sub>	-462.1	F <sub>4</sub> U-F	102
		F <sub>5</sub> U-F	<u>69</u>

Sum = 754

 $D_{298}^\circ(\text{UF}_6) = 753.7$ <sup>a</sup>All in kcal/mol.