MASTER

April 15, 1980

Technical Progress Report
1 September 1979 to 1 April 1980

CHEMISTRY OF GASEOUS LOWER HALIDES OF URANIUM

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Prepared for:

DEPARTMENT OF ENERGY
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Washington, D.C. 20545

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Contract DE-AT0-3-79ER10414
SRI Project 8864

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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 $UF_5(g)$,[1] the gaseous reaction equilibrium

$$UF_5(g) + Ag(g) = UF_4(g) + AgF(g) \tag{1}$$

was investigated, in which the thermochemical properties of the uranium species are determined by reference to silver monofluoride, AgF. Although the thermochemistry of AgF was not firmly established, it proved to be one of the few suitable reference standards for the relatively weak F_4U-F bond. We have now completed measurements of the gaseous equilibrium

$$Ag(g) + CuF(g) = AgF(g) + Cu(g) \tag{2}$$

by mass spectrometry and determined $\Delta H^\circ_{298} = D^\circ_{298}(CuF) - D^\circ_{298}(AgF) = 18.5 \pm 1$ kcal/mol by second and third law analysis, leading to $\Delta_f H^\circ_{298}(AgF,g) = 1.8 \pm 1$ kcal/mol and $D^\circ_{298}(AgF) = 85.1$ kcal/mol. This firms up the thermochemistry of $UF_5(g)$.

By passing BaF_2 vapor over UC(s) in a graphite effusion cell, it was possible to generate beams containing UF_3, UF_2, UF, and U, in addition to the reaction partners Ba and BaF. The uranium species were positively identified from the threshold appearance potentials of the corresponding ions: UF_3^+(7.0 eV); UF_2^+(6.2 eV); UF^+(6.0 eV); U^+(6.2 eV). With this arrangement it was possible to study the reaction equilibria

$$U(g) + BaF(g) = UF(g) + Ba(g) \tag{3}$$

$$UF(g) + BaF(g) = UF_2(g) + Ba(g) \tag{4}$$

$$UF_2(g) + BaF(g) = UF_3(g) + Ba(g) \tag{5}$$

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

$$UF_3(g) + CaF(g) = UF_4(g) + Ca(g) \tag{6}$$

was investigated by reacting UF_4 vapor with 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 UF_5 and UF_4 obtained in earlier work.[1] 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, UF_2, and 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 UF_6(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 UF_4 vapor

$$UF_4 + e \rightarrow UF_3^+ + F + 2e \tag{7}$$

was determined as 13.28 ± 0.10 eV, and the ionization potential of UF_3 was measured at 6.97 ± 0.10 eV. Combination of these two results yields $D(F_3U-F) = 13.28-6.97 = 6.31$ eV = 145.5 kcal/mol, in close agreement with the equilibrium value.

The experimental (expt) entropies of gaseous UF, UF_2, and 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 UF, S°_{2300}(expt) = 83.1 cal/deg mole, and S°_{2300}(trv) = 76.3 cal/deg mol; for UF_2, S°_{2200}(expt) = 108.6 cal/deg mol, and S°_{2200} (trv) = 96.9 cal/deg mol; and for UF_3, S°_{2200}(expt) = 125.3 cal/deg mol, and S°_{2200}(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 UF, UF_2, and 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 UF, UF_2, and UF_3.

B. Sublimation/Decomposition of UO_2F_2

The vaporization chemistry of uranyl fluoride, UO_2F_2(s), is being investigated in order to characterize the thermochemistry of UO_2F_2(g) and to clarify the mechanism of the thermal decompositon of UO_2F_2(s). Previous investigators[2,3] have identified the solid product as U_3O_8(s) and have inferred that the gaseous decomposition products are UF_6 and O_2. On vaporizing UO_2F_2(s) from a platinum effusion cell, we have identified gaseous UO_2F_2, UOF_4, UF_5 and a small amount of UF_4 in the saturated vapor, but definitely no UF_6 or O_2. These latter experiments were done by means of modulated beam mass spectrometry, and should be quite reliable. Contrary to previous results,[2,3] UO_2F_2(g) appears to be the major species in the saturated vapor, several determinations of the enthalpy of sublimation of $UO_2F_2(g)$ 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 CuCl and CuBr

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

$$Ag(g) + CuCl(g) = AgCl(g) + Cu(g) \qquad (8)$$

and

$$Ag(g) + CuBr(g) = AgBr(g) + Cu(g) \qquad (9)$$

with the results $\Delta H^\circ_{298}(8) = 15.1 \pm 1$ kcal/mol and $\Delta H^\circ_{298}(9) = 12.8 \pm 1$ kcal/mol. These data yield $D^\circ_{298}(CuCl) = 90.1$ kcal/mol and $D^\circ_{298}(CuBr) = 79.5$ 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

Gaseous Reaction	Range, K	ΔH°_T(II) kcal/mol	Derived Result
$U + BaF = UF + Ba$	2222-2505	-17.8 ± 0.7	D(U-F) = 156 kcal/mol
$UF + BaF = UF_2 + Ba$	2034-2466	4.8 ± 0.6	D(FU-F) = 134
$UF_2 + BaF = UF_3 + Ba$	2034-2466	- 8.3 ± 0.4	$D(F_2U\text{-}F)$ = 147
$UF_3 + CaF = UF_4 + Ca$	1533-1745	-19.5 ± 0.6	$D(F_3U\text{-}F)$ = 146

Table II

DERIVED THERMOCHEMICAL PROPERTIES OF GASEOUS URANIUM FLUORIDES[a]

Gaseous Species	$\Delta_f H^\circ_{298}$	Bond	D°_{298}
UF	-10.1	U-F	156
UF_2	-125.2	FU-F	134
UF_3	-253.3	F_2U-F	147
UF_4	-379.3	F_3U-F	146
UF_5	-462.1	F_4U-F	102
		F_5U-F	69
		Sum =	754
		$D^\circ_{298}(UF_6)$ =	753.7

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[a] All in kcal/mol.