

## Trends and anomalies in the thermodynamics of gaseous thorium and uranium halides

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**ABSTRACT** - Reaction enthalpies derived from mass spectrometric studies of high temperature gaseous equilibria were used to evaluate the individual bond dissociation energies (BDE) in the thorium and uranium fluorides, chlorides, and bromides  $\text{ThX}_n$  and  $\text{UX}_m$  where  $n = 1$  to 4 and  $m = 1$  to 5. The resulting BDE patterns do not follow regular or predictable trends, and the reasons for this are not clear. Reaction entropy data also give broad information about electronic level contributions. In addition, the sublimation pressures of all the crystalline thorium and uranium tetrahalides (except  $\text{UI}_4$ ) were determined by the torsion-effusion method. Both the sublimation entropies and absolute entropies calculated from them indicate that  $\text{ThF}_4$  and  $\text{ThCl}_4$  have regular tetrahedral structures, while those of  $\text{UF}_4$ ,  $\text{UCl}_4$ ,  $\text{UBr}_4$ ,  $\text{ThBr}_4$  and  $\text{ThI}_4$  are probably of lower symmetry, possibly  $\text{C}_{2v}$ . Results are discussed in terms of other relevant information in the literature.

### INTRODUCTION

In attempting to predict the thermodynamic properties of the halides and other compounds of the heavier transuranium elements, which will be very difficult to study experimentally, one could use the behavior of the initial members of the series, thorium and uranium, as a guide. Many factors such as electronic structure and inner shell effects would have to be taken into account in extrapolating to the heavier members, but a modeling approach of this type has merit.

Over the last decade, we have been studying the chemical thermodynamics of the gaseous thorium and uranium halides and related compounds, as a first step in obtaining a reliable data base for future modeling applications. Such information will also be useful in refining various approaches to molecular theory that should ultimately have strong predictive capabilities for molecular energy and structural quantities.

Since very little is known about the spectroscopic and molecular constants of these halide species needed in third law calculations, we have focused on careful equilibrium measurements over wide temperature ranges so that thermochemical quantities can be derived solely from second law analysis. Two types of experimental studies were made. In the first instance, gaseous reaction equilibria involving the various halide species were studied by effusion-beam mass spectrometry; all of the halides  $\text{ThX}$  through  $\text{ThX}_4$  and  $\text{UX}$  through  $\text{UX}_5$  were observed and the reaction thermodynamics were evaluated (ref. 1-8). Secondly, the sublimation pressures of the crystalline Th and U tetrahalides (except  $\text{UI}_4$ ) were determined by the torsion-effusion method, and the sublimation thermodynamics were evaluated by the second law method (ref. 9). From this information, enthalpy and entropy data were derived for the various species, and the results were examined for meaningful trends that might aid in developing predictive models. The outcome of these investigations is described here.

### EXPERIMENTAL

All mass spectrometric measurements were made with the magnetic sector instrument and experimental technique described in publications dealing with the thorium and uranium halides; details regarding the experimental arrangements, data interpretation, and uncertainties in derived thermochemical quantities are given therein (ref. 1-8). Following our usual practice, ion intensities used in second law enthalpy determinations were measured a few volts above the various ionization thresholds to eliminate overlapping fragmentation contributions at higher energies. For use in estimating absolute equilibrium constants and reaction entropies, however, fragment contributions and total ion yields were evaluated in most instances.

The accuracy of second law slope determinations, estimated as  $\pm 6 \text{ kJ mol}^{-1}$ , is checked frequently with lab standards such as tin and gold.

Total sublimation pressures of the thorium and uranium tetrahalides were determined by the torsion-effusion technique described earlier (ref. 10). Details of the measurements are given in the papers on  $\text{UF}_4$  (ref. 1),  $\text{ThF}_4$  (ref. 5),  $\text{ThCl}_4$  (ref. 6),  $\text{ThBr}_4$  (ref. 7) and on  $\text{UCl}_4$ ,  $\text{UBr}_4$  and  $\text{ThI}_4$  (ref. 9). Torsion pressures are estimated to be accurate within 5 percent, and slope enthalpies within 2 to 4  $\text{kJ mol}^{-1}$ .

### BOND DISSOCIATION ENERGIES

The individual bond dissociation energies (BDE) of the thorium and uranium halides, evaluated from the second law reaction enthalpies, are summarized in Table 1, and are plotted in Figs. 1 and 2 as a function of the ligand number in the molecule. In the uranium halides, the U-F system shows a distinctly different behavior than the U-Cl and U-Br systems in that  $D(\text{U-F}) \gg D(\text{FU-F})$ , while just the opposite holds for the chlorides and bromides. This difference is manifested directly in the enthalpy changes for the gaseous reaction



where X is a halogen, and which gives a direct measure of  $D(\text{XU-X}) - D(\text{U-X})$ . The measured second law values of  $\Delta H^\circ_{298}$  are -80.3, 40.2, and 57.7  $\text{kJ mol}^{-1}$  when  $X = \text{F}$ , Cl, and Br, respectively, clearly emphasizing the different behavior of the fluoride system. Similarly,  $D(\text{FU-F}) \ll D(\text{F}_2\text{U-F})$ , while the corresponding BDE values in the U-Cl and U-Br systems are nearly equal. And lastly,  $D(\text{X}_2\text{U-X}) \gg D(\text{X}_3\text{U-X})$  where  $X = \text{Cl}$  and Br, while  $D(\text{F}_2\text{U-F})$  and  $D(\text{F}_3\text{U-F})$  are nearly equivalent. Although the BDE patterns in the U-Cl and U-Br systems show roughly parallel behavior, the deviations from the U-F

TABLE 1. Bond Dissociation Energies of Uranium and Thorium Halides

Bond	$D^\circ_{298}, \text{kJ mol}^{-1}$					
	U-F	U-Cl	U-Br	Th-F	Th-Cl	Th-Br
(M-X)	648	439	377	652	489	364
(XM-X)	565	481	435	702	545	439
(X <sub>2</sub> M-X)	619	485	430	653	507	477
(X <sub>3</sub> M-X)	615	420	348	666	504	510
(X <sub>4</sub> M-X)	410	209	166			

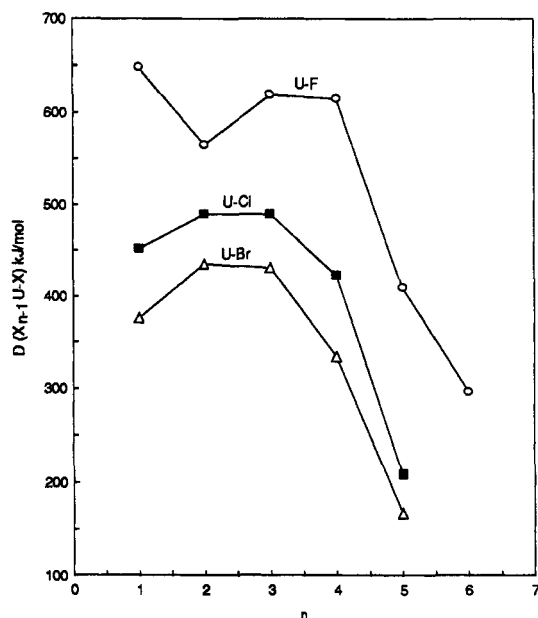


Figure 1. BDE of uranium halides as a function of halogen ligands.

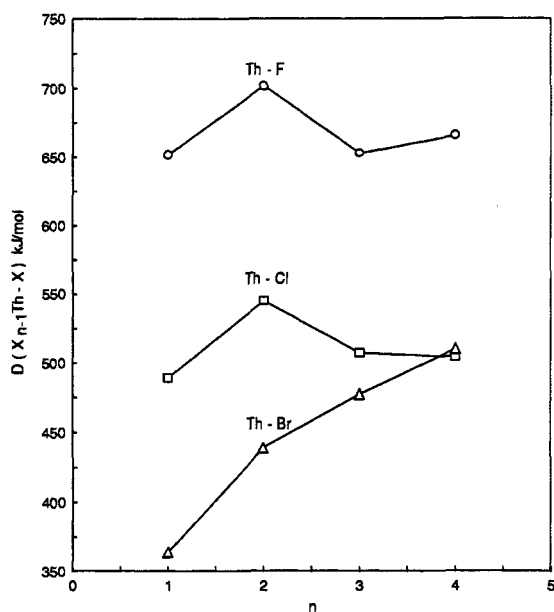


Figure 2. BDE of Thorium halides as a function of halogen ligands.

pattern are very large and far outside experimental error. The one concordant note in all three BDE patterns is that  $D(X_3U-X) \gg D(X_4U-X)$ , which one expects from the high stability of the tetravalent state, and the energy penalty for valence promotion to the pentavalent state.

In the thorium halides, the BDE situation is rather different in that the Th-F and Th-Cl patterns are quite similar, while that of the Th-Br system differs sharply. In contrast to the fluorides and chlorides, the Th-Br BDE values show a monotonic increase from  $D(\text{Th-Br})$  to  $D(\text{Br}_3\text{Th-Br})$ , with the surprising result that  $D(\text{Br}_3\text{Th-Br}) \sim D(\text{Cl}_3\text{Th-Cl})$ . In other U and Th halides there has been a significant difference between the metal-halogen bond strengths as the halogen is varied, with the fluoride, chloride, and bromide BDE values decreasing in that order. This latter point is in accord with the increased atomic size and longer metal-halogen bond lengths associated with the heavier halogens. However, the near equality of the  $(\text{Br}_3\text{Th-Br})$  and  $(\text{Cl}_3\text{Th-Cl})$  bond strengths is quite unexpected.

### ENTROPIES OF LOWER VALENT HALIDES

A summary of the experimental total entropies of the mono-, di- and trihalides in the U-F, U-Cl, U-Br, Th-F, and Th-Cl systems was presented in an earlier publication (ref. 11). Similar entropy data have since been obtained for the Th-Br system (ref. 7). For essentially all of these species, the major uncertainty in evaluating thermal functions stems from the unknown electronic level contributions. A striking feature of the results is that the calculated translational-rotational-vibrational entropies of the diatomic metal halides are uniformly lower than the experimental values at 2000 to 2300 K by  $31 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$  for the uranium species, and by  $18 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$  for the thorium species. These are very close to the electronic entropies of atomic U and Th at these temperatures, 33 and  $25 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, and indicate that there is probably only a minimal splitting of the atomic electronic levels due to the approach of the halogen as the first M-X bond is formed. In first approximation, therefore, one can assume that the diatomic actinide halides will have electronic level structures close to those of the actinide atoms.

For the di- and trihalides, the comparison of experimental and calculated translational-rotational-vibrational entropies indicates generally smaller electronic entropies, as one would naturally expect from further splitting of the atomic levels, plus an apparent decrease in electronic entropy with increasing atomic number of the halogen (ref. 11). For the polyatomic molecules, however, one cannot push the analysis too far because of increasing uncertainties in the experimental total entropies. Nevertheless, the entropy data give a reasonably consistent picture that will be helpful in predicting compatible spectroscopic constants needed for calculating thermal functions.

### THORIUM AND URANIUM TETRAHALIDES

The sublimation pressures of the thorium and uranium tetrahalides, except for  $\text{UI}_4$  which sublimes by decomposition, were determined by the torsion-effusion method and the derived results have been summarized (ref. 9). There are other determinations in the literature of variable accuracy, which cover different temperature and pressure ranges. In order to eliminate systematic differences and to obtain results of high internal consistency and demonstrated accuracy, however, selected values of the sublimation entropies and enthalpies were derived by second law analysis from the torsion pressure determinations made in this laboratory.

Table 2 shows the derived sublimation entropies of  $\text{UF}_4$ ,  $\text{UCl}_4$ ,  $\text{UBr}_4$ ,  $\text{ThF}_4$ ,  $\text{ThCl}_4$ ,  $\text{ThBr}_4$ , and  $\text{ThI}_4$ . For ease of comparison, values of  $\Delta S^\circ_T$  for the fluorides were corrected to 1100 K with the aid of estimated thermal functions (ref. 9), and all others were corrected to 700 K. All values are for sublimation to the ideal gas at 1 atm pressure. From frequent measurements on laboratory vapor pressure standards, we estimate that the second law slope values of  $\Delta S^\circ_T$  are accurate to within  $\pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Included in Table 2 are the crystal symmetries of the tetrahalides. The comparison shows that the  $\Delta S^\circ_T$  values for  $\text{UF}_4$  and  $\text{UCl}_4$  are distinctly higher than those of their isomorphous Th counterparts by 12 to 13  $\text{J K}^{-1} \text{ mol}^{-1}$ . Significantly perhaps, this value is close to the calculated rotational entropy difference of  $R \ln 12/2 = 14.9 \text{ J K}^{-1} \text{ mol}^{-1}$  between  $T_d$  and  $C_{2v}$  molecular symmetries. For isomorphous solid phases of the Th and U tetrahalides, the  $\Delta S^\circ_T$  values should reflect to a first approximation any changes in the entropies of the gaseous molecules. Thus the sublimation data alone suggest significantly higher entropies and perhaps lower symmetries for  $\text{UF}_4$  and  $\text{UCl}_4$ , as compared to  $\text{ThF}_4$  and  $\text{ThCl}_4$ .

For  $\text{UBr}_4$  and  $\text{ThBr}_4$ , however, the sublimation entropies at 700 K are essentially identical, and close in magnitude to those of  $\text{UF}_4$  and  $\text{UCl}_4$ , suggesting a possible lower symmetry for  $\text{ThBr}_4$ . Although the bromide solid phases are not isomorphous, the monoclinic and tetragonal structures are somewhat similar, so that the identical values of  $\Delta S^\circ_{700}$  indicate the possibility of similar molecular constants and configurations for  $\text{UBr}_4$  and  $\text{ThBr}_4$ . The magnitude of the sublimation entropy of  $\text{ThI}_4$  likewise suggests a behavior similar to that of  $\text{ThBr}_4$  and the uranium tetrahalides.

TABLE 2. Sublimation Entropies of Thorium and Uranium Tetrahalides

MX <sub>4</sub>	ΔS° <sub>T</sub>		Crystal Symmetry
	T/K	(J K <sup>-1</sup> mol <sup>-1</sup> )	
UF <sub>4</sub>	1100	188.3	Monoclinic
ThF <sub>4</sub>	1100	176.7	Monoclinic
UCl <sub>4</sub>	700	194.1	Tetragonal
ThCl <sub>4</sub>	700	181.2	Tetragonal
UBr <sub>4</sub>	700	194.6	Monoclinic
ThBr <sub>4</sub>	700	195.0	Tetragonal
ThI <sub>4</sub>	700	202.9	Monoclinic

TABLE 3. Experimental Entropies and Calculated Values for Tetrahedral Structure

MX <sub>4</sub>	T/K	S° <sub>T(g)</sub> (J K <sup>-1</sup> mol <sup>-1</sup> )	
		Exptl.	Calc. T <sub>d</sub>
ThF <sub>4</sub>	1100	478 ± 2	475
ThCl <sub>4</sub>	700	476 ± 8	476
ThBr <sub>4</sub>	700	535 ± 8	520
ThI <sub>4</sub>	700	571 ± 8	552
UF <sub>4</sub>	1100	504 ± 2	487
UCl <sub>4</sub>	700	502 ± 2	488
UBr <sub>4</sub>	700	547 ± 8	538

In Table 3 are listed the experimental total entropies of the gaseous tetrahalides derived from the sublimation entropies and data for the solid phases, and corresponding entropies of the gases calculated by statistical methods for a T<sub>d</sub> molecular symmetry. The sources of the solid phase data and the assigned molecular constants are described in ref. (9). Aside from the structural considerations, a major uncertainty in the calculated entropies results from the vibrational frequency assignments, because of the very limited amount of experimental spectroscopic data. However, it appears possible to derive consistent vibrational assignments that are reliable to within 4 J K<sup>-1</sup> mol<sup>-1</sup> in the vibrational entropy at the selected temperatures. For the uranium tetrahalides, a substantial electronic entropy is also expected, but this can be evaluated from the assigned electronic levels in UCl<sub>4</sub>; no significant electronic contribution is expected for the closed-shell thorium tetrahalides.

For UF<sub>4</sub>, UCl<sub>4</sub>, and ThF<sub>4</sub>, where accurate solid-phase entropies are available from calorimetric measurements, the experimental entropies of the gaseous tetrahalides are estimated to be reliable to within 2 J K<sup>-1</sup> mol<sup>-1</sup>, and the calculated entropies to within 4 J K<sup>-1</sup> mol<sup>-1</sup>. The comparison in Table 3 shows clearly that although the experimental entropy of ThF<sub>4</sub> is in complete accord with T<sub>d</sub> symmetry, those of UF<sub>4</sub> and UCl<sub>4</sub> are higher by 14 to 17 kJ mol<sup>-1</sup> and are therefore incompatible with T<sub>d</sub> symmetry. Without the electronic level contributions, the calculated T<sub>d</sub> entropies of UF<sub>4</sub> and UCl<sub>4</sub> would differ even more from the experimental values.

For the other thorium tetrahalides and for UBr<sub>4</sub>, where the experimental entropies have larger uncertainties of 8 J K<sup>-1</sup> mol<sup>-1</sup>, only ThCl<sub>4</sub> is seen to be compatible with T<sub>d</sub> symmetry. However, the experimental entropies of ThBr<sub>4</sub>, ThI<sub>4</sub> and UBr<sub>4</sub> are again 9 to 19 kJ mol<sup>-1</sup> higher than the calculated T<sub>d</sub> values and are therefore in conflict with regular tetrahedral symmetry. For UBr<sub>4</sub>, the estimated electronic entropy based on the UCl<sub>4</sub> levels is probably slightly high, since experience indicates a progressive lowering of the metal ion levels with increasing mass of the halogen ligand; thus the calculated T<sub>d</sub> entropy of UBr<sub>4</sub> in Table 3 is slightly too large and the correct value is even more out of line with the experimental result.

## DISCUSSION

We have no explanation for the irregular BDE patterns in the U and Th halides. The sums of the individual BDE values are consistent with the more-accurately known enthalpies of atomization of the gaseous tetrahalides, and the deviations of the U-F and Th-Br patterns are well beyond any reasonable experimental errors. Furthermore, the relationship between D(U-F) and D(FU-F) was checked by two independent reaction equilibria, with highly concordant results (ref. 8). Therefore, we must accept these experimental BDE patterns, even though we do not understand the underlying factors governing them.

One would expect a substantial change in ionic-covalent bonding character in passing from the relatively ionic fluorides to the more covalent bromides, and this could lead to a change in bonding that would influence the BDE patterns. Even so, the classical Rittner electrostatic model does reasonably well in predicting the dissociation energies (BDE's) of the diatomic U and Th halides (ref. 2-7), with certain assumptions about the  $U^+$  and  $Th^+$  dipole polarizabilities. At present, the calculational models and molecular input data for the polyatomic species are not sufficiently well developed to yield meaningful BDE values, but it seems unlikely from the nature of the interactions that electrostatic effects alone could account for the distinctly different behavior of the U-F and Th-Br BDE patterns. It is possible, though, that energetics associated with metal valence-state promotion could play a role, but this is difficult to quantify. Detailed ab initio calculations might shed some insight here, especially if relativistic configuration interaction is taken into account. In any event, the prediction of actinide halide BDE patterns is presently one of the more difficult and uncertain tasks.

All of the thermodynamic evidence presented here suggests strongly that there are two distinctly different structural configurations among the thorium and uranium tetrahalides. The entropy data for the starting members of the actinide series,  $ThF_4$  and  $ThCl_4$ , are completely consistent with regular tetrahedral configurations, while the results for  $ThBr_4$ ,  $ThI_4$ ,  $UF_4$ ,  $UCl_4$  and  $UBr_4$  are definitely more compatible with structures of lower symmetry, most likely distorted tetrahedra of  $C_{2v}$  symmetry.

If the molecular symmetries were actually  $C_{2v}$  rather than  $T_d$ , as suggested by some of the structural studies (ref. 12-15), the fundamental frequencies would shift somewhat and become non-degenerate but the total vibrational entropies of the two configurations would probably not differ by more than a few  $J K^{-1} mol^{-1}$  at the experimental temperatures. For example, the vibrational entropy of  $UF_4$  at 1500 K calculated from frequencies derived by a force constant treatment for a  $T_d$  configuration (ref. 16) is only  $4 J K^{-1} mol^{-1}$  lower than that calculated from an alternate assignment for a  $C_{2v}$  structure (ref. 17). Therefore, the major difference between the statistical entropies of the two structures will result from the change in rotational symmetry number, equivalent to  $\Delta S^\circ = R \ln 12/2 = 14.9 J K^{-1} mol^{-1}$ . As can be seen in Table VI, the experimental entropies of  $ThBr_4$ ,  $ThI_4$ ,  $UF_4$ ,  $UCl_4$  and  $UBr_4$  range from 9 to  $19 J K^{-1} mol^{-1}$  higher than the calculated  $T_d$  values, and are thus more compatible with  $C_{2v}$  configurations for those tetrahalides.

Certainly, the thermodynamic evidence does not provide any kind of a proof of structure, but it does put limits on what types of structures are reasonable. On the other hand, the structural and spectroscopic evidence (ref. 12, 13, 18, 19) is conflicting and, on the whole, inconclusive. The original electron diffraction results imply that all of the Th and U tetrafluorides, -chlorides, and -bromides have  $C_{2v}$  symmetry, but the large amplitudes of vibration at the experimental vaporization temperatures make interpretation difficult. Another electron diffraction study (ref. 20) on  $UF_4$  was interpreted in terms of either  $D_{2d}$  or  $C_{2v}$  symmetry. And although a more recent electron diffraction result (ref. 13) on  $UCl_4$  vapor was interpreted in terms of  $C_{2v}$  symmetry with two different U-Cl internuclear distances of 0.2475 and 0.2558 nm, a subsequent re-evaluation of the data (ref. 14) retained the lower symmetry but gave a somewhat different set of structural parameters. However, the interpretation is strongly dependent on fitting observed diffraction patterns to those calculated for different structural models, and the delineations are not sharp. In one other study supporting the thermodynamic conclusions, the deflection of a molecular beam of  $UF_4$  in an inhomogeneous magnetic field was reported (ref. 15), suggesting a small dipole moment and therefore a non- $T_d$  geometry.

The band structures of the photoelectron spectra of  $UF_4$ ,  $UCl_4$ ,  $ThF_4$  and  $ThCl_4$ , however, were found to be compatible with regular tetrahedral geometries (ref. 18), but the bands were broad and heavily overlapped, so that small distortions away from  $T_d$  symmetry could not be ruled out. And although krypton matrix IR studies on  $ThCl_4$  and  $UCl_4$  indicated  $C_{2v}$  symmetry for the two species under those conditions (ref. 21), subsequent studies (ref. 22) showed the molecules to have  $T_d$  symmetry in neon matrices. It would seem that matrix interaction effects cast doubt on structural conclusions derived from matrix IR spectroscopy.

At this stage, the question of the equilibrium molecular geometries of the Th and U tetrahalides remains unresolved, but the thermodynamic data provide a strong stimulus for attacking the problem with newer and sharper tools.

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