

Equilibrium measurements as a source of entropies and molecular constant information

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Abstract - The absolute entropies of a number of high temperature gaseous molecules with uncertain molecular constant assignments were derived from equilibrium measurements with accuracies of 1 to 2 cal·K⁻¹·mol⁻¹. These results were derived from measurement of reaction equilibrium constants over wide temperature ranges by application of second law analysis. The results give clear indications about the magnitudes of electronic level contributions of the lower-valent uranium and thorium halides, the symmetries and geometric structures of uranium and thorium tetrahalides, and about the low frequency vibrations of some M₂SO₄ metal sulfate species. The general usefulness of this approach is discussed.

INTRODUCTION

Satisfactory interpretation and analysis of all types of vaporization processes requires information about the spectroscopic and molecular constants of the vaporizing species. When these constants are known and reliable thermodynamic functions can be calculated, vaporization data at various temperatures can be analyzed for consistency, enthalpy data can be derived for the process, and the results can be accurately extrapolated to other temperatures. For many compounds of the transition, lanthanide, and actinide metals, however, where incomplete d and f electron shells complicate the bonding, the spectroscopic and structural analyses are complex and usually incomplete, leading to uncertain molecular constant assignments and inaccurate calculated thermodynamic functions. There are, of course, many other instances of uncertain vibrational and structural assignments, particularly involving the low-frequency deformation vibrations that are so thermodynamically important. Despite the clear need, experimental spectroscopic studies have been very limited and often unable to address the low-frequency modes lying at 200 cm⁻¹ and below.

An alternate method that yields broad-gauge information about molecular parameters is based on the comparison of experimentally determined total entropies with values calculated from assigned spectroscopic and molecular constants. Giauque and his co-workers (ref. 1-3) pioneered this approach more than half a century ago; vapor entropies derived from accurate calorimetric measurements were compared with values calculated from spectroscopic data and much useful information about the validity of assigned molecular parameters was obtained. In a more recent application, Weinstock (ref. 4) has described the way in which calorimetric entropy data were used to verify the regular octahedral O_h structure of UF₆, as opposed to a structure of lower symmetry suggested by electron diffraction measurements. The thermodynamic data were decisive in favor of the octahedral structure with rotational symmetry number $\sigma = 24$, since the less symmetrical structures with $\sigma = 8$ or 3 led to entropy differences of 2.2 and 4.1 cal·K⁻¹·mol⁻¹, well outside the experimental uncertainty of the results. In fact, the comparison ultimately led to a re-examination of the theory of electron diffraction for heavy atoms that resolved the discrepancy. So there is ample precedent for the use of entropy data in checking the compatibility of assigned molecular constants.

In the work described here, vapor entropy data derived from equilibrium measurements are compared with values calculated for certain molecular parameter assignments. Obviously, entropies derived from equilibrium data (second law entropies) are less accurate than calorimetric values, which are normally reliable to within 0.1 cal·K⁻¹·mol⁻¹. We believe that, with care, second law entropies may be derived with accuracies of 0.5 to 2 cal·K⁻¹·mol⁻¹. Some examples of the use of such results are described in this paper.

EXPERIMENTAL

Equilibrium measurements of some high temperature reactions were made both by mass spectrometry and by torsion-effusion vapor pressure techniques. Some of the results have been published elsewhere, and a description of experimental techniques and interpretive methods is given there (ref. 5-11). For these studies, special emphasis was placed on accurate measurement of reaction equilibrium constants over broad temperature ranges so that both enthalpy and entropy data could be determined with an established accuracy that was sufficiently high for the purposes at hand. Frequent checks with laboratory vapor pressure standards have shown that second law enthalpy changes can be determined regularly with accuracies of 0.7 to 1.4 kcal·mol⁻¹. For simple vaporization processes where absolute pressures are determined by the torsion-effusion method, the corresponding entropy changes have an estimated accuracy of 0.5 to 1 cal·K⁻¹·mol⁻¹, or better, while for gaseous reactions studied by mass spectrometry, the estimated accuracy is on the order of 1 to 2 cal·K⁻¹·mol⁻¹. The larger uncertainty in the latter arises primarily from uncertainties in ionization cross section ratios used in converting ion intensity data to absolute equilibrium constants. A further discussion of these factors is given in reference 7.

URANIUM HALIDES

In Table I are listed the experimental total entropies of some U-F, U-Cl, and U-Br gaseous species, obtained at the indicated average temperatures. Also shown for comparison are calculated entropies, based mostly on estimated molecular parameters, that involve only the translational, rotational, and vibrational contributions. Except for UCl₄(g), the electronic contributions are unknown but are expected to be significant; we have not attempted to estimate them here. The entropy comparisons will in fact give an indication as to their magnitudes. The estimated rotational and vibrational parameters are believed to be reliable within 1 cal·K⁻¹·mol⁻¹ in the temperature range of our measurements, with the exception of the tetrahalide species UX₄, where there is some question about the correct molecular geometry. Electron diffraction studies suggest a distorted tetrahedral arrangement of C_{2v} symmetry, while the band structures of the observed photoelectron spectra of UF₄ and UCl₄ (ref. 12) seem more in accord with regular tetrahedral T_d symmetry. Since the entropy difference between the two structures with rotational symmetry numbers of 12 and 2 is at least $R \ln 6 = 3.56 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, the experimental entropy data can assist in making a choice. On examining the experimental and calculated entropies in Table I and the difference values given there, several significant points emerge.

First, in all instances but UCl₅ and UBr₅, the experimental total entropies are appreciably larger than the calculated (trv) values, indicating that the electronic level contributions, which are excluded from the calculations, are indeed significant. For the gaseous monohalides UF, UCl and UBr, the deviation $\Delta = [S_T(\text{exptl}) - S_T(\text{calc, trv})]$ is in all cases, remarkably close to the electronic entropy of U(g) at the experimental temperatures, suggesting that the electronic levels of the gaseous uranium atom are not appreciably perturbed by addition of the first halogen ligand. It also appears that, on the whole, the electronic contributions for the polyatomic species tend to decrease with increasing mass of the halogen. Furthermore, the comparisons suggest that the electronic contributions are negligibly small for UCl₅ and UBr₅, a trend that is expected on approaching the valence-saturated UX₆ species.

Second, the comparisons strongly suggest that the tetrahalides UF₄, UCl₄ and UBr₄ have equilibrium structures of lower symmetry than the standard T_d symmetry associated with the regular tetrahedron. As seen in the table, the T_d structure shows entropy deficits of 6.5 to 8.7 cal·K⁻¹·mol⁻¹, which are considered to be much larger than the expected electronic contributions for the UX₄ species. In fact, the states deduced from the electronic spectrum of UCl₄(g) (ref. 13) yield electronic entropies of 2.9 and 4.0 cal·K⁻¹·mol⁻¹ at 650 and 2100 K, respectively. Thus, it seems that the calculated entropies of the tetrahedral configurations of UF₄, UCl₄, and UBr₄ are incompatible with the experimental values when a reasonable electronic entropy is included. For the less symmetrical C_{2v} structure suggested by electron diffraction, however, where the calculated (trv) entropy is higher by 3.6 cal·K⁻¹·mol⁻¹ as noted earlier, the entropy deficits are only 3 to 4 cal·K⁻¹·mol⁻¹, in close accord with the electronic entropies calculated from the electronic level assignments for UCl₄ (ref. 13). Actually, the calculated total entropy for the C_{2v} structure of UCl₄ using the molecular constants of reference 7 and the electronic state assignments of reference 13 is 116.7 cal·K⁻¹·mol⁻¹ at 650 K, compared to the experimental value of 117.8 cal·K⁻¹·mol⁻¹. More recent electron diffraction studies on UF₄(g) (ref. 14) indicate best agreement for D_{2d} and C_{3v} symmetries, still higher in entropy by 2.2 and 2.8 cal·K⁻¹·mol⁻¹ than the T_d configuration. We conclude that the experimental entropy data strongly favor a structure of lower effective symmetry than T_d for the three uranium tetrahalides, most likely C_{2v} or C_{3v}. This distinction has a significant effect on the analysis of vaporization data and other thermodynamic calculations.

TABLE 1. Comparison of Experimental and Calculated Entropies of U-X Molecular Species

Molecule	$S_T^\circ, \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		Δ	T/K
	Exptl.	Calc.(trv)		
UF	83.1 ± 2	76.3	6.8	2300
UF ₂	108.6 ± 2.8	97.8	10.8	2200
UF ₃	124.5 ± 3.4	117.2	7.3	2200
UF ₄	119.3 ± 1	110.6(T _d)	8.7	1050
UF ₄	119.3 ± 1	114.2(C _{2v})	5.1	1050
UCl	85.7 ± 2	78.8	6.9	2100
UCl ₂	108.2 ± 2.5	103.2	5.0	2100
UCl ₃	128.8 ± 3	123.8	5.0	2100
UCl ₄	117.8 ± 0.5	110.2(T _d)	7.6	650
UCl ₄	117.8 ± 0.5	113.8(C _{2v})	4.0	650
UCl ₅	128.5 ± 2.5	129.3	-0.8	740
UBr	89.4 ± 2	81.3	8.1	2000
UBr ₂	112.1 ± 2.5	109.0	3.1	2200
UBr ₃	134.3 ± 3	130.5	3.8	2200
UBr ₄	131.7 ± 1.5	125.2(T _d)	6.5	700
UBr ₄	131.7 ± 1.5	128.8(C _{2v})	2.9	700
UBr ₅	143.4 ± 2.5	143.2	0.2	700

$$S^\circ(\text{U,g, electronic}) = 7.6 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ at } 2000 \text{ K}$$

$$= 8.1 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ at } 2300 \text{ K}$$

TABLE 2. Comparison of Experimental and Calculated Entropies of Th-X Molecular Species

Molecule	$S_T^\circ, \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		Δ	T/K
	Exptl.	Calc.(trv)		
ThF	80.5 ± 2	76.2	4.3	2200
ThF ₂	98.3 ± 2.5	97.6	0.7	2200
ThF ₃	115.8 ± 3	113.0	2.8	1900
ThF ₄	114.0 ± 1	113.5(T _d)	0.5	1100
ThF ₄	114. ± 1	117.1(C _{2v})	-3.1	1110
ThCl	83.8 ± 2	79.6	4.2	2300
ThCl ₂	102.5 ± 2.5	103.2	-0.7	2200
ThCl ₃	124.7 ± 3	122.9	1.8	2100
ThCl ₄	--	111.9(T _d)		700
ThCl ₄	--	115.5(C _{2v})		700

$$S^\circ(\text{Th,g, electronic}) = 6.0 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ at } 2200 \text{ K}$$

$$= 6.2 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ at } 2300 \text{ K}$$

THORIUM HALIDES

Similar comparisons between experimental and calculated entropies are shown for the thorium fluorides and chlorides in Table 2. In this instance, molecular constants used in the calculations were taken from the estimates of Krasnov et al., (ref. 15) as reviewed and extended by Wagman et al. (ref. 16). Again, no electronic contributions were included in the calculated values, since these are unknown. For the valence-saturated species ThF₄ and ThCl₄, however, there should be no contributions from ground or excited electronic states at the temperatures of interest, so that the trv values will be sufficient.

Here, too, the comparisons indicate significant electronic contributions for ThF and ThCl, with the difference Δ approaching the electronic entropy of Th(g) at the experimental temperatures. With the dihalides ThF₂ and ThCl₂, however, the experimental and calculated (trv) entropies are reasonably close, suggesting singlet electronic ground states and no low-lying excited states for these even-electron species. However, the calculated (trv) entropies of the trihalides ThF₃ and ThCl₃ are low by 1.8 to 2.8 cal·K⁻¹·mol⁻¹, possibly suggesting doublet ground states which would increase the calculated values by 1.4 cal·K⁻¹·mol⁻¹.

Only for ThF₄(g) can a reliable experimental entropy be established at present, but there the results are clearly in accord with the regular tetrahedral T_d structure. This contrasts sharply with the results for the UX₄ species and points to a fundamental structural difference that needs further spectroscopic investigation to resolve the issue.

TABLE 3. M-O Vibration Frequencies and Entropies of Alkali Sulfates

	Na ₂ SO ₄	K ₂ SO ₄	Rb ₂ SO ₄	Cs ₂ SO ₄
ω_i , cm ⁻¹ (1)	280 (170)	200 (150)	130	100
(2)	360 (280)	262 (240)	215	196
(2)	295 (240)	230 (220)	195	160
(2)	75 (60)	62 (50)	40	30
T/K	1200	1200	1100	1100
S _T [°] (calc) ^a	127.4 (130.2)	132.2 (134.1)	135.5	140.3
S _T [°] (exptl) ^a	131.2	135.8	135.5	138.7

^a in cal·K⁻¹·mol⁻¹

ALKALI SULFATES

The vaporization of alkali sulfates yields molecular sulfate species M₂SO₄ as well as decomposition to gaseous M, SO₂, and O₂. Lau et al. (ref. 9,10) have studied the M₂SO₄ vaporization equilibria and derived entropy values for the gaseous sulfates accurate to within 1 cal·K⁻¹·mol⁻¹. Electron diffraction studies have established a structure of D_{2d} symmetry for these species and the fundamental vibrational frequencies of the central SO₄ group, which are nearly independent of the alkali ligand, are also known; the structural and spectroscopic studies are described in references 17 and 18. A major uncertainty, however, resides in the frequencies associated with the highly delocalized polytopic M-O bonds. These frequencies would be expected to lie in the far infrared, below about 200 cm⁻¹; for the most part, these have not been observed experimentally and available assignments are based largely on estimates from ionic model calculations. Since the electronic entropies of these closed-shell systems are expected to be insignificant, the six M-O frequencies (two are doubly degenerate) make up the main uncertainties in the calculated entropies.

In Table 3 are shown the selected M-O frequency assignments (ref. 18) for the gaseous Na, K, Rb, and Cs sulfates, the calculated entropies based on these assignments and the established molecular parameters, together with the experimental total entropies. For Rb₂SO₄ and Cs₂SO₄, the calculated values agree well with the corresponding experimental values, while for Na₂SO₄ and K₂SO₄, the calculated entropies are low by 3 to 4 cal·K⁻¹·mol⁻¹. An inspection of the trends suggests that the M-O frequencies of Na₂SO₄ and K₂SO₄ might lie lower, perhaps in the range of the adjusted frequencies shown in parenthesis. As can be seen, these adjusted values yield total entropies that are in much better agreement with the experimental data, suggesting that the low frequency M-O modes be given much closer scrutiny. In fact, the very nature of this delocalized polytopic bonding needs a great deal of clarification.

CONCLUSIONS

The examples discussed here illustrate that reliable experimental entropies can be quite helpful in resolving uncertain molecular constant assignments, particularly those involving structures of appreciably different symmetry, low-lying electronic states or multiplet ground states, and thermodynamically-significant low-frequency vibrations. In carrying out high temperature equilibrium studies, therefore, it seems worthwhile to devote the extra attention and effort required to obtain accurate entropy data. In the past, equilibrium studies were seen almost exclusively as a source of enthalpy data, but they deserve equal consideration as a source of entropy data.

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