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New Calorimetric Studies of Inorganic Fluorine Compounds*

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New Calorimetric Studies of Inorganic Fluorine Compounds*

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In this paper, recently determined thermodynamic quantities will be presented for two fluorides, namely, silver(I)uranium(V)fluoride, $AgUF_6$, and cesium fluoroxysulfate, $CsSO_4F$.

$AgUF_6$. The ability of UF_5 to form complexes with other metallic fluorides has been well documented in the literature. However, no thermochemical studies have been reported for those complexes, apart from the investigation of MUF_6 (M = Na, K, Rb, Cs) by Kudryashov et al.[1] As part of our continuing research on volatile compounds of uranium, we have performed solution calorimetric measurements on the complex with AgF. The sample was prepared from solutions of AgF and UF_5 in anhydrous HF. The following enthalpies of reaction at 298.15 K were determined:

$$UF_5(c,\beta) + \text{soln A} = \text{soln B}, \qquad \Delta H = -(190.25 \pm 0.45)\ \text{kJ mol}^{-1} \tag{1}$$

$$AgF(c) + \text{soln B} = \text{soln C}, \qquad \Delta H = -(24.73 \pm 0.32)\ \text{kJ mol}^{-1} \tag{2}$$

$$\text{soln C} = AgUF_6(c) + \text{soln A}, \qquad \Delta H = (162.34 \pm 2.02)\ \text{kJ mol}^{-1} \tag{3}$$

Combination of the above reactions gives:

$$AgF(c) + UF_5(c,\beta) = AgUF_6(c), \qquad \Delta H = -(52.64 \pm 2.09)\ \text{kJ mol}^{-1} \tag{4}$$

and, thus, $\Delta H_f^\circ(AgUF_6, c) = -(2341 \pm 7)$ kJ mol^{-1}

The implications of the result vis-a-vis the thermal stability of $AgUF_6$ will be discussed.

$CsSO_4F$. Cesium fluoroxysulfate which has recently been synthesized for the first time,[2] has considerable potential for use as a synthetic and analytical reagent, and aqueous solutions of it are powerful oxidizers that can also act as fluorinating agents. Indeed, our preliminary thermodynamic estimates[3] suggested that $CsSO_4F$ was one of the most potent oxidizing agents known--only slightly less powerful than F_2, XeF_2, and OF_2.

We have recently reported[3] the standard enthalpy of formation, $\Delta H_f^\circ(CsSO_4F)$, at 298.15 K. The present report is concerned with low-temperature (5-310 K) measurements on $CsSO_4F$ and the derivation of the standard entropy, S°, at 298.15 K. This result yields ΔG_f° which, when combined with the solubility and auxiliary thermochemical data, leads to the standard electrode potential, E°, for the half-reaction:

$$SO_4F^-(aq) + 2H^+(aq) + 2e^- = HSO_4^-(aq) + HF(aq) \tag{5}$$

The preliminary value is $E^\circ = (2.40 \pm 0.01)$ V. This result will be compared with the electrode potentials for other oxidizing agents.

*Work performed under the auspices of the United States Department of Energy.

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2. Appelman, E. H.; Basile, L. J.; Thompson, R. C. J. Amer. Chem. Soc. 1979, 101, 3384.

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