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Standard Enthalpies of Formation of Cesium Fluoroxysulfate ($CsSO_4F$) and Cesium Peroxydisulfate ($Cs_2S_2O_8$)[1a]

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The enthalpies of reaction of cesium fluoroxysulfate, $CsSO_4F$, and cesium peroxydisulfate, $Cs_2S_2O_8$, with HI(aq) have been measured by solution calorimetry, and the following standard enthalpies of formation at 298.15 K have been derived: $\Delta H_f°(CsSO_4F(c)) = -1004.9 \pm 1.6$ kJ mol^{-1} and $\Delta H_f°(Cs_2S_2O_8(c)) = -1936.7$ [illegible] 2.8 kJ mol^{-1}. The enthalpy of solution of $Cs_2S_2O_8(c)$ in 5345 mol of water at 298.15 K has been determined to be 79.5 ± 1.9 kJ mol^{-1}. The Gibbs energy of solution of $CsSO_4F$ at 298.15 K has been determined from solubility measurements to be $\Delta G_{soln}°(CsSO_4F) = 6.15 \pm 0.40$ kJ mol^{-1}. The fluoroxysulfate results have been used in conjunction with an estimated entropy for solid $CsSO_4F$ to calculate a standard potential of 2.52 ± 0.05 V at 298.15 K for the half-reaction $SO_4F^-(aq) + 2H^+(aq) + 2e^- \rightarrow HSO_4^-(aq) + HF(aq)$.

Introduction

Salts of the fluoroxysulfate ion, SO_4F^-, have only recently been isolated.[2] Aqueous solutions of the ion are powerful oxidizers and can also act as fluorinating agents. The dry salts are fairly stable and are of considerable interest as potential synthetic and analytical reagents. For that reason, it is important to know the thermodynamic properties of these compounds. As a first step, we have determined the standard enthalpy of formation of cesium fluoroxysulfate, $\Delta H_f°(CsSO_4F(c))$, by calorimetric measurements of its enthalpy of reaction with aqueous HI. The reaction, which proceeds without the formation of significant quantities of SO_3F^-,[3] can be represented as

$$CsSO_4F(c) + 3HI(aq) = [Cs^+, H^+, I_3^-, HF, HSO_4^-](aq)$$

The cesium fluoroxysulfate that we used contained approximately 0.6 mass % cesium peroxydisulfate, $Cs_2S_2O_8$, as an impurity. It was therefore also necessary to determine the enthalpy of reaction of $Cs_2S_2O_8$ with aqueous HI, and this, in turn, led to the determination of $\Delta H_f°(Cs_2S_2O_8(c))$. Since there is a lack of agreement among the $\Delta H_f°$ data tabulated in the literature[4-7] for Cs_2SO_4 and $CsHSO_4$, we have made measurements of the enthalpies of solution of both salts in the aqueous HI reaction medium.

Experimental Section

Materials. $CsSO_4F(c)$. Cesium fluoroxysulfate was prepared by passing F_2 (20% in N_2) through a 2 M solution of cesium sulfate in water at −5 °C.[2] The precipitate was washed several times with ice water and dried first in a stream of argon and then under vacuum. When not in use, the sample was stored at −10 °C under dry nitrogen. The salt was analyzed by reaction with 0.2 M KI and titration with a thiosulfate solution that had been standardized against primary standard grade KIO_3. The peroxydisulfate impurity was determined by making the titrated solution 1 M in KI, saturating it with N_2, and letting it stand for 15 min before titrating again with thiosulfate.[8]

$Cs_2S_2O_8(c)$. Cesium peroxydisulfate was prepared by potentiometrically titrating an ammonium persulfate solution with CsOH. The precipitated salt was recrystallized and then dried first in an argon stream and finally under vacuum. The dry product was analyzed iodometrically by titration with thiosulfate after reaction with 1 M KI for 15 min. The analysis indicated a purity of 100.07 ± 0.16%.

$CsHSO_4(c)$. Cesium bisulfate was prepared by adding a stoichiometric quantity of H_2SO_4 solution (Baker Dilut-it) to a weighed amount of Merck Supra-Pur Cs_2SO_4. The solution was evaporated to dryness, and the residue was crushed and dried at 170 °C. Titration with base indicated a purity of 100.10 ± 0.20%.

$Cs_2SO_4(c)$. Cesium sulfate was Merck Supra-Pur. It was dried at 140 °C before use.

HI(aq). Constant-boiling hydriiodic acid was prepared by distillation of Merck Supra-Pur 48% HI from a slight excess of H_3PO_2, followed by dilution to the required concentration with argon-saturated, twice-distilled water. The distillation and dilution operations were carried out in an inert atmosphere and in subdued light to prevent oxidation of the HI. Three HI solutions were made, the concentrations of which were determined to be 0.1993, 0.2001, and 0.1770 M by titration with standardized NaOH. The H_2O:HI mole ratios for these solutions were calculated to be 274.76, 275.86, and 310.90, respectively, on the basis of the published densities.[9] The solutions were stored in amber-colored bottles in an inert atmosphere.

$I_2(c)$. Iodine crystals, part of a batch of high-purity (99.99%) material,[10,11] were pulverized in an agate mortar to facilitate dissolution and were then dissolved in the $HI{\cdot}310.90H_2O$ solution to give an I_2:HI ratio of 1:14.403. Care was taken to reproduce this ratio exactly, since it has been established that the enthalpy of solution of I_2 in HI(aq) is strongly concentration dependent.[12]

H_2SO_4(aq) and HF(aq). Solutions of these acids were prepared by dilution of analytical grade acids with water that had been distilled twice in an inert atmosphere.

Calorimetric System. The calorimetric measurements were carried out in a LKB-8700 Precision Calorimetric System. The 0.1-dm^3 glass reaction vessel was modified so that temperature measurements could be made with a quartz-crystal thermometer (Hewlett-Packard Model 2801-A). The stirrer–ampule holder assembly was constructed of Kel-F plastic, which is inert to iodine.

The overall performance of the calorimetric system was checked by measuring the enthalpy of reaction of Tris [tris(hydroxymethyl)aminomethane, National Bureau of Standards Sample 724] with excess 0.1 M hydrochloric acid. Five experiments at 298.15 K and a Tris concentration of 5 g dm^{-3} yielded a value and standard deviation of -245.51 ± 0.14 J g^{-1} for the enthalpy of reaction. This result is in excellent agreement with results previously obtained at this laboratory with different reaction vessels: -245.56 ± 0.10,[13] -245.56 ± 0.04,[11] and -245.51 ± 0.21[14] J g^{-1}, as well as with the results reported by Hill et al.[15] (-245.54 ± 0.02 J g^{-1}) and Gunn[16] (−245.47

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Table I. Reaction of $CsSO_4F$ with HI(aq)[a]

$m(CsSO_4F)$,[b] g	$\langle\varepsilon(\text{calor})\rangle$, J K^{-1}	$\Delta\theta_c$, K	$(-\Delta\theta_c) \times \langle\varepsilon(\text{calor})\rangle$, J	$\Delta H_r/M$, J g^{-1}
0.30761	447.08	0.97478	−435.81	−1416.9
0.29197	438.68	0.94184	−413.17	−1415.2
0.30835	438.47	0.99551	−436.50	−1415.7
0.29564	438.85	0.95141	−417.53	−1412.4
0.30683	438.93	0.98557	−432.60	−1410.0
0.30157	439.83_5	0.96963	−426.48	−1414.3

$\langle\Delta H_r/M\rangle = -1414.1 \pm 2.0^c$ J g^{-1}

[a] In each experiment 99.41 cm^3 of 0.2001 mol dm^{-3} HI solution was used. The reaction is represented by eq A in Table VI. Throughout $\Delta H_{vap} = -0.03$ J. [b] Analysis showed 99.16 ± 0.13 mass % $CsSO_4F$ and 0.60 ± 0.05 mass % $Cs_2S_2O_8$. [c] Uncertainty is twice the standard deviation of the mean.

Table II. Reaction of $Cs_2S_2O_8$ with HI(aq)[a]

$m(Cs_2S_2O_8)$, g	$\langle\varepsilon(\text{calor})\rangle$, J K^{-1}	$\Delta\theta_c$, K	$(-\Delta\theta_c) \times \langle\varepsilon(\text{calor})\rangle$, J	$\Delta H_r/M$, J g^{-1}
0.56902	438.46	0.70036	−307.08	−539.72
0.52806	439.30	0.64886	−285.04	−539.84
0.52020	438.37	0.64039	−280.73	−539.72
0.60514	438.82	0.74415	−326.55	−539.68

$\langle\Delta H_r/M\rangle = -539.74 \pm 0.12^b$ J g^{-1}
$\Delta H_r = -247.16 \pm 0.05^{b,c}$ kJ mol^{-1}

[a] In each experiment 99.41 cm^3 of 0.1993 mol dm^{-3} HI solution was used. The reaction is represented by eq A in Table VII. Throughout $\Delta H_{vap} = -0.03$ J. [b] Uncertainty is twice the standard deviation. [c] The molar mass, M, of $Cs_2S_2O_8$ was taken to be 457.926 g mol^{-1}.

Table III. Dissolution of $CsHSO_4$ in HI/I_3^-(aq)[a]

$m(CsHSO_4)$, g	$\Delta\theta_c$, K	$(-\Delta\theta_c) \times \langle\varepsilon(\text{calor})\rangle$,[b] J	ΔH_{elec}, J	$\Delta H_{soln}/M$, J g^{-1}
0.29582	0.03594	−15.778	25.034	31.19
0.25388	0.00384	−1.686	10.014	32.68
0.28798	0.00186	−0.817	10.014	31.83
0.28608	−0.00197	+0.865	9.012	34.42

$\langle\Delta H_{soln}/M\rangle = 32.53 \pm 2.40^c$ J g^{-1}
$\Delta H_{soln} = 7.48 \pm 0.55^{c,d}$ kJ mol^{-1}

[a] The dissolution is represented by eq C in Table VI. Throughout $\Delta H_{vap} = -0.03$ J. [b] A value of 439.0 J K^{-1} was used for $\langle\varepsilon(\text{calor})\rangle$ in these experiments. [c] Uncertainty is twice the standard deviation. [d] The molar mass, M, of $CsHSO_4$ was taken to be 229.971 g mol^{-1}.

± 0.05 J g^{-1}). Our result, though somewhat lower in numerical value, is also in agreement with the certified value,[17] −245.76 ± 0.26 J g^{-1}.

For the exothermic reactions, electrical calibration experiments were conducted before and after each reaction, and the average value was used for ε(calor), the energy equivalent of the calorimetric system. For the endothermic reactions, electrical energy was added to the calorimeter in an amount approximately equal to the expected enthalpy of dissolution. In these latter experiments, therefore, the corrected temperature change was very small. The mean temperature of the calorimetric system for all of the experiments was 298.15 ± 0.02 K.

In the $Cs_2S_2O_8$/HI measurements, the rate of reaction was low, and approximately 2 h was required to reach the final calorimetric drift rate. The $CsSO_4F$ reacted rapidly, but the overall reaction period was at least 1 h because of the $Cs_2S_2O_8$ impurity.

The solubility of $CsSO_4F$ in H_2O at 298.15 K was determined by rapid stirring of an aqueous slurry of the salt. Samples of the solution were withdrawn through a glass wool filter at 1-min intervals, and the SO_4F^- concentration was determined iodometrically. Correction was made for small amounts of decomposition, on the basis of kinetic and stoichiometric data in the literature.[3]

Table IV. Dissolution of Cs_2SO_4 in HI/I_3^- Solution[a]

$m(Cs_2SO_4)$, g	$\Delta\theta_c$, K	$(-\Delta\theta_c) \times \langle\varepsilon(\text{calor})\rangle$,[b] J	ΔH_{elec}, J	$\Delta H_{soln}/M$, J g^{-1}
0.43093	0.00846	−3.714	45.062	95.88
0.43092	0.00208	−0.913	42.558	96.57
0.44140	0.00140	−0.615	42.558	94.95
0.46509	0.00303	−1.330	45.062	93.96

$\langle\Delta H_{soln}/M\rangle = 95.34 \pm 1.97^c$ J g^{-1}
$\Delta H_{soln} = 34.50 \pm 0.71^{c,d}$ kJ mol^{-1}

[a] The dissolution is represented by eq C in Table VIII. Throughout $\Delta H_{vap} = -0.03$ J. [b] A value of 439.0 J K^{-1} was used for $\langle\varepsilon(\text{calor})\rangle$ in these experiments. [c] Uncertainty is twice the standard deviation. [d] The molar mass, M, of Cs_2SO_4 was taken to be 361.868 g mol^{-1}.

Table V. Dissolution of $H_2SO_4 \cdot 29H_2O$ in Reaction Mixture[a]

$m(H_2SO_4)$, g	$\Delta\theta_c$, K	$\langle\varepsilon(\text{calor})\rangle$, J K^{-1}	$(-\Delta\theta_c) \times \langle\varepsilon(\text{calor})\rangle$,[b] J	$\Delta H_{soln}/M$, J g^{-1}
0.77277	0.01888	440.88	−8.324	10.77
0.82289	0.02061	439.88	−9.066	11.02
0.73525	0.01825	441.93	−8.065	10.97
0.70127	0.01782	441.35	−7.865	11.22

$\langle\Delta H_{soln}/M\rangle = -10.99_5 \pm 0.32^b$ J g^{-1}
$\Delta H_{soln} = -6.82 \pm 0.20^{b,c}$ kJ mol^{-1}

[a] The dissolution is represented by eq D in Table VIII. [b] Uncertainty is twice the standard deviation. [c] A molar mass, M, of 620.514 g mol^{-1} was used for $H_2SO_4 \cdot 29H_2O$.

Table VI. Reaction Scheme for the Derivation of $\Delta H_f^\circ(CsSO_4F(c))$ at 298.15 K[a]

A $CsSO_4F(c) + 16.403[HI \cdot 275.86H_2O] = [Cs^+, HSO_4^-, HF, I_3^-, 14.403H^+, 13.403I^-] \cdot 4524.9H_2O$
$\Delta H = -352.90 \pm 0.73$ kJ mol^{-1} [b,c]

B $[I_3^-, 14.403H^+, 13.403I^-] \cdot 4477.90H_2O = I_2(c) + 14.403[HI \cdot 310.90H_2O]$
$\Delta H = -5.07_5 \pm 0.11_3$ kJ mol^{-1} [d]

C $[Cs^+, HSO_4^-, I_3^-, 14.403H^+, 13.403I^-] \cdot 4477.90H_2O = CsHSO_4(c) + [I_3^-, 14.403H^+, 13.403I^-] \cdot 4477.90H_2O$
$\Delta H = -7.48 \pm 0.55$ kJ mol^{-1} [b]

D $[Cs^+, HSO_4^-, I_3^-, HF, 14.403H^+, 13.403I^-] \cdot 4523.9H_2O = HF \cdot 47H_2O + [Cs^+, HSO_4^-, I_3^-, 14.403H^+, 13.403I^-] \cdot 4477.9H_2O$
$\Delta H = 2.34 \pm 0.08$ kJ mol^{-1} [e]

E $14.403[HI \cdot 310.90H_2O] + H_2(g) + I_2(c) + 47H_2O(l) = 16.403[HI \cdot 275.86H_2O]$
$\Delta H = -112.38 \pm 0.05$ kJ mol^{-1} [d,f]

F $HF \cdot 47H_2O = {}^1/_2H_2(g) + {}^1/_2F_2(g) + 47H_2O(l)$
$\Delta H = 322.29 \pm 0.30$ kJ mol^{-1} [e]

G $CsHSO_4(c) = Cs(c) + {}^1/_2H_2(g) + S(c,rh) + 2O_2(g)$
$\Delta H = 1158.1 \pm 1.3$ kJ mol^{-1} [g]

H $CsSO_4F(c) = Cs(c) + S(c,rh) + 2O_2(g) + {}^1/_2F_2(g)$
$\Delta H = -\Delta H_f^\circ(CsSO_4F(c)) = 1004.9 \pm 1.6$ kJ mol^{-1}

[a] Species in this table are aqueous unless designated otherwise. [b] This work. [c] Includes uncertainty due to impurity level. [d] References 11 and 12. [e] Reference 13. [f] Reference 18. [g] Reference 7.

Results

Calorimetric data for the oxidation of HI(aq) by $CsSO_4F$ and $Cs_2S_2O_8$ are given in Tables I and II, respectively. Calorimetric results for the dissolution of $CsHSO_4$, Cs_2SO_4, and $H_2SO_4 \cdot 29H_2O$ in aqueous HI are given in Tables III–V. In the tables m is the mass of sample; ⟨ε(calor)⟩ is the mean energy equivalent of the calorimetric system based on the electrical calibrations; ΔH_{vap} is the correction for saturating the air in the free volume of the ampule with water vapor, based on the enthalpy of vaporization of water,[6] 44.02 kJ mol^{-1}; ΔH_{elec} is the electrical energy added to the calorimeter to

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Table VII. Reaction Scheme for the Derivation of $\Delta H_f^\circ(Cs_2S_2O_8(c))$ at 298.15 K[a]

A $Cs_2S_2O_8(c) + 16.403[HI\cdot 274.76H_2O] = [2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4506.9H_2O$
$\Delta H = -247.16 \pm 0.05$ kJ mol^{-1} [b]

B $[I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O = I_2(c) + 14.403[HI\cdot 310.90H_2O]$
$\Delta H = -5.07_5 \pm 0.11_3$ kJ mol^{-1} [c]

C $[2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O = 2CsHSO_4(c) + [I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O$
$\Delta H = -14.96 \pm 1.10$ kJ mol^{-1} [b]

D $[2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4506.9H_2O = [2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O + 29H_2O(l)$
$\Delta H = 0.0 \pm 0.05$ kJ mol^{-1} [d]

E $14.403[HI\cdot 310.90H_2O] + H_2(g) + I_2(c) + 29H_2O(l) = 16.403[HI\cdot 274.76H_2O]$
$\Delta H = -112.34 \pm 0.05$ kJ mol^{-1} [c,d]

F $2CsHSO_4(c) = 2Cs(c) + H_2(g) + 2S(c,rh) + 4O_2(g)$
$\Delta H = +2316.2 \pm 2.6$ kJ mol^{-1} [e]

G $Cs_2S_2O_8(c) = 2Cs(c) + 2S(c,rh) + 4O_2(g)$
$\Delta H = -\Delta H_f^\circ(Cs_2S_2O_8(c)) = 1936.7 \pm 2.8$ kJ mol^{-1}

[a] Species in this table are aqueous unless designated otherwise. [b] This work. [c] References 11 and 12. [d] Reference 18. [e] Reference 7.

Table VIII. Reaction Scheme Interrelating $\Delta H_f^\circ(Cs_2SO_4(c))$ and $\Delta H_f^\circ(CsHSO_4(c))$[a]

A $[2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O = 2CsHSO_4(c) + [I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O$
$\Delta H = -14.96 \pm 1.10$ kJ mol^{-1} [b]

B $[2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4506.9H_2O = [2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O + 29H_2O(l)$
$\Delta H = 0.0 \pm 0.05$ kJ mol^{-1} [d]

C $Cs_2SO_4(c) + [I_3^-, 14.403H^+, 13.403I^-]\cdot 4477.9H_2O = [2Cs^+, HSO_4^-, I_3^-, 13.403H^+, 13.403I^-]\cdot 4477.9H_2O$
$\Delta H = +34.50 \pm 0.71$ kJ mol^{-1} [b]

D $H_2SO_4\cdot 29H_2O + [2Cs^+, HSO_4^-, I_3^-, 13.403H^+, 13.403I^-]\cdot 4477.9H_2O = [2Cs^+, 2HSO_4^-, I_3^-, 14.403H^+, 13.403I^-]\cdot 4506.9H_2O$
$\Delta H = -6.82 \pm 0.20$ kJ mol^{-1} [b]

E $H_2(g) + S(c,rh) + 2O_2(g) + 29H_2O(l) = H_2SO_4\cdot 29H_2O$
$\Delta H = -885.90 \pm 0.50$ kJ mol^{-1} [c]

F $Cs_2SO_4(c) + H_2(g) + S(c,rh) + 2O_2(g) = 2CsHSO_4(c)$
$\Delta H = -873.2 \pm 1.4$ kJ mol^{-1}

[a] Species in this table are aqueous unless designated otherwise. [b] This work. [c] Reference 19. [d] Reference 18.

approximately offset the effects of the endothermic dissolutions; and $\Delta H_r/M$ or $\Delta H_{soln}/M$ is the specific enthalpy of reaction or solution of the sample.

The thermochemical cycles used to derive $\Delta H_f^\circ(CsSO_4F(c))$ and $\Delta H_f^\circ(Cs_2S_2O_8(c))$ are given in Tables VI and VII, respectively. Table VIII gives the interrelationship between $\Delta H_f^\circ(CsHSO_4(c))$ and $\Delta H_f^\circ(Cs_2SO_4(c))$. The derived value for reaction F, Table VIII, of -873.2 ± 1.4 kJ mol^{-1} is in excellent agreement with that obtained by using the data in ref 7, i.e., -873.2 ± 1.3 kJ mol^{-1}.

The cesium fluoroxysulfate was found by iodometric analysis to be 99.15 ± 0.13 mass % $CsSO_4F$ and 0.60 ± 0.05 mass % $Cs_2S_2O_8$. The latter has an enthalpy of reaction of -539.7 J g^{-1} (Table II). The remaining 0.25 ± 0.15 mass % was probably a mixture of $CsHSO_4$, $CsSO_3F$, and Cs_2SO_4, for which we have estimated an enthalpy of solution in our medium of 100 ± 100 J g^{-1}. Correction of the results in Table I for these impurities and use of a molar mass, M, of 247.961 g mol^{-1} for $CsSO_4F$ give $\Delta H_r = -352.90 \pm 0.73$ kJ mol^{-1} for the reaction of pure $CsSO_4F$ (reaction A, Table VI).

Measurements were made of the enthalpy of solution of cesium peroxydisulfate in water to give a final solution of approximate composition $Cs_2S_2O_8\cdot 5345H_2O$. Three determinations gave the results 176.1, 170.9, and 173.5 J g^{-1}, corresponding to $\langle \Delta H_{soln}/M \rangle = 173.5 \pm 4.2$ J g^{-1} and $\Delta H_{soln} = 79.5 \pm 1.9$ kJ mol^{-1}, where the uncertainties are twice the standard deviation.

The solubility of $CsSO_4F$ in water at 298.15 K was found to be 0.535 ± 0.025 mol dm^{-3}.

Discussion

In the following discussion all thermodynamic quantities are quoted at 298.15 K.

Cesium Peroxydisulfate. The value obtained in this investigation for $\Delta H_f^\circ(Cs_2S_2O_8(c))$ is -1936.7 ± 2.8 kJ mol^{-1}. Combination of this value with $\Delta H_{soln}(Cs_2S_2O_8)$ yields $\Delta H_f^\circ(Cs_2S_2O_8(aq)) = -1857.2 \pm 3.4$ kJ mol^{-1}, in good agreement with the selected value,[7] -1855.6 ± 4.2 kJ mol^{-1}.

Cesium Fluoroxysulfate. We obtain a value of -1004.9 ± 1.6 kJ mol^{-1} for $\Delta H_f^\circ(CsSO_4F(c))$. Our results may also be used to derive an approximate value for the oxidation potential of the aqueous SO_4F^- ion. We estimate the standard entropy of $CsSO_4F(c)$ to be $S^\circ = 170 \pm 25$ J K^{-1} mol^{-1}.[20] Combining this value with S° values of 85.2, 205.0, 31.9, and 202.8 J K^{-1} mol^{-1} for Cs(c), $O_2(g)$, S(c,rh), and $F_2(g)$, respectively,[6,19] we obtain $\Delta S_f^\circ(CsSO_4F(c)) = -458 \pm 30$ J K^{-1} mol^{-1} and $\Delta G_f^\circ(CsSO_4F(c)) = -868 \pm 9$ kJ mol^{-1}. We may combine the measured solubility of $CsSO_4F$ with an estimated activity coefficient[20] $\gamma_\pm = 0.54 \pm 0.04$ to obtain an ideal solubility product of 0.0835 ± 0.015 mol^2 dm^{-6}, corresponding to $\Delta G_{soln}^\circ(CsSO_4F) = 6.15 \pm 0.4$ kJ mol^{-1}. We may then calculate for the half-reaction

$$SO_4F^-(aq) + 2H^+(aq) + 2e^- = HSO_4^-(aq) + HF(aq)$$

a standard electrode potential of 2.52 ± 0.05 V.[21] This implies that fluoroxysulfate is one of the most potent oxidants known. Only F_2, XeF_2, and OF_2 are known to have higher electrode potentials. This high thermodynamic oxidizing power is quite in accord with the remarkable oxidizing and fluorinating behavior of the fluoroxysulfate ion.[2,3]

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Registry No. $CsSO_4F$, 70806-67-6; $Cs_2S_2O_8$, 29287-69-2; HI, 10034-85-2; $CsHSO_4$, 7789-16-4; Cs_2SO_4, 10294-54-9; H_2SO_4, 7664-93-9.

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