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Enthalpy of solution of californium oxychloride; calculation of the standard enthalpy of formation of CfOCl

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Abstract

The enthalpy of solution of CfOCl in 1.022 $\mathrm{mol\,dm^{-3}}$ HCl was measured on the 0.4–1.5 mg scale, and the standard enthalpy of formation at 298 K for this compound was calculated. The CfOCl was prepared by heating in air at 280–320°C the solid hydrated trichloride, obtained by slow evaporation of Cf(III) in HCl solution. X-ray powder diffraction analysis confirmed the material to be the expected oxychloride, which exhibits the PbFCl-type tetragonal structure. Dissolutions of the oxychloride were made at 25.0°C in an isoperibol solution microcalorimeter. Enthalpy of solution values were calculated according to the equation: $\mathrm{CfOCl_{(cr)}}+\mathrm{2HCl_{(sln)}}\rightarrow\mathrm{CfCl_{3(sln)}}+\mathrm{H_2O_{(sln)}}$. The $\Delta_f H^0$ ($\mathrm{CfOCl_{(cr)}}$) was determined to be -920 ± 7 $\mathrm{kJ\,mol^{-1}}$. Interpolation within $\Delta_f H^0$ ($\mathrm{AnOCl_{(cr)}}$), where An=U, Pu, Am, Cm, and Cf, as a function of An(III) ionic radius yielded $\Delta_f H^0$ ($\mathrm{BkOCl_{(cr)}}$)$=-944\pm10$ $\mathrm{kJ\,mol^{-1}}$. © 1998 Elsevier Science S.A.

Keywords: Californium; Oxychloride; Enthalpy; Berkelium

1. Introduction

Solution calorimetry is a well-known route to the determination of standard enthalpies of formation of compounds and has been used for several transplutonium materials. Californium is likely to be the actinide with the highest atomic number that can be studied by such calorimetry, even when using a microcalorimeter. Thus, californium oxychloride was studied in this work to extend the range of experimental thermodynamic data to the heavier elements, which will permit better extrapolations to the higher actinides through systematic relationships. Specifically, the data obtained were used to establish more well-defined trends in the standard enthalpies of formation for these oxychlorides.

These experiments were performed using ^{249}Cf, selected due to its relatively long half-life and availability of milligram quantities. This isotope is an α-emitter (main $E_a=5.812$ MeV, 84.4% branching) with a half-life of 351 years and decays to Cm-245. The 4 mg of Cf-249 used in this study was equivalent to ~16 mCi, which could be handled in a gloved box. Cf-252, although available in larger quantities, has a spontaneous fission decay branch, and the associated neutron field limits gloved box operations to only a few micrograms.

The preparation of CfOCl followed the approach used successfully by us for preparing selected lanthanide oxychlorides for similar calorimetry studies [1]. The CfOCl product was confirmed by X-ray powder diffraction analysis and exhibited the expected PbFCl-type tetragonal structure, common to the lanthanide oxychlorides through erbium [2]. All of the known actinide (An) oxychlorides of formula AnOCl exhibit this same tetragonal structure [2].

The f-element oxychlorides are essentially insoluble in water and stable in air at room temperature. For the solution calorimetry, we used nominally 1 $\mathrm{mol\,dm^{-3}}$ HCl as the dissolution medium and the isoperibol microcalorimeter used previously in our laboratory for studies of selected lanthanide oxychlorides [1] and actinide metals [3]. The dissolutions were performed at 25°C and yielded

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data for the enthalpy of solution of CfOCl, from which we calculated the standard enthalpy of formation at 298 K for this compound. From a plot of the standard enthalpy of formation of the oxychlorides of U, Pu, Am, Cm, and the present value for Cf versus the corresponding trivalent actinide ionic radius, we predicted by interpolation the standard enthalpy of formation for BkOCl. We report here the results of experimental studies on CfOCl and the interpolated enthalpy of formation for BkOCl.

2. Experimental

2.1. Oxychloride synthesis

The method of synthesis selected for making CfOCl was modeled after that which proved successful for GdOCl and EuOCl [1]. On the basis of their comparable trivalent ionic radii (Gd(III), 93.8 pm; Eu(III), 94.8 pm; and Cf(III), 95 pm [4]), Gd and Eu should be similar to Cf in their oxychloride chemistries and structures (PbFCl-type tetragonal structure; space group D_{4h}^{7}-$P4/nmm$). While several methods exist for preparing oxychlorides, we found in earlier work [1] that heating carefully the solid trichloride hydrates in air was a successful route, and we have used this approach for the production of CfOCl. Thus,

$$\mathrm{CfCl_3 \cdot {\it x}H_2O_{(s)} \rightarrow CfOCl_{(s)} + ({\it x}-1)H_2O_{(g)} + 2HCl_{(g)}} \quad (1)$$

Two possible complicating factors in this reaction in air are formation of the sesquioxide and oxidization of some Cf(III) to produce Cf_7O_{12}. This latter oxide is similar to that exhibited by terbium under similar conditions [5]. The IV/III reduction potentials of Tb and Cf (aqueous, acid) are very similar [6,7], so we perfected our preparative techniques using terbium as a stand-in for preparing californium oxychloride on the 2–4 mg scale. Two important parameters in this preparation route are the temperature and time of heating. We found that 280–320°C for ~10 min after obtaining the solid trichloride hydrate was best. This produced a pale green solid without any brown coloration (such a coloration would indicate that partial oxidation of the Cf(III) had occurred).

2.2. X-ray diffraction analysis

X-ray powder diffraction was the primary technique for sample characterization and employed Debye–Scherrer cameras, Mo Kα radiation, and Kodak DEF-392 film. The powder patterns were read to ±0.05 mm on a Phillips–Norelco film reader. Product identifications were made by comparing observed line positions and intensities to those reported for the compounds in the JCPDS Powder Diffraction File.

2.3. Solution microcalorimetry

All dissolutions were performed using the isoperibol solution microcalorimeter whose operation has been described previously [1]; all measurements were made at 25.0°C, and all thermodynamic values are reported at 298 K. Samples were weighed in air at ambient conditions using a Perkin-Elmer (model AZ-2D) electrobalance with a nominal sensitivity of 0.1 μg. All calorimetry bulbs (supplied by Prof. J. Fuger, University of Liège) were loaded with CfOCl (383 to 1470 μg) to yield a total dissolution heat in excess of 0.1 J. The 1.022 $\mathrm{mol\,dm^{-3}}$ HCl (Aldrich, volumetric standard) was used as the dissolving medium (denoted herein as sln). The calorimeter employed a tantalum vessel of 5 ml capacity for the dissolutions.

The pertinent thermodynamic cycle for the calculation of the standard enthalpy of formation of $CfOCl_{(cr)}$ is:

$$\begin{array}{llllllll}
\mathrm{Cf_{(cr)}} & + & \mathrm{3HCl_{(sln)}} & \rightarrow & \mathrm{CfCl_{3(sln)}} & + & \mathrm{3/2H_{2(g)}}; & \Delta H_1 \\
\mathrm{1/2H_{2(g)}} & + & \mathrm{1/2Cl_{2(g)}} & \rightarrow & \mathrm{HCl_{(sln)}}; & & & \Delta H_2 \\
\mathrm{H_{2(g)}} & + & \mathrm{1/2O_{2(g)}} & \rightarrow & \mathrm{H_2O_{(sln)}}; & & & \Delta H_3 \\
\mathrm{CfOCl_{(cr)}} & + & \mathrm{2HCl_{(sln)}} & \rightarrow & \mathrm{CfCl_{3(sln)}} & + & \mathrm{H_2O_{(sln)}}; & \Delta_{\mathrm{sln}} H \\
\hline
\mathrm{Cf_{(cr)}} & + & \mathrm{1/2O_{2(g)}} & + & \mathrm{1/2Cl_{2(g)}} & \rightarrow & \mathrm{CfOCl_{(cr)}} & \Delta_{\mathrm{f}} H^0
\end{array}$$

By Hess's law, $\Delta_{\mathrm{f}} H^0$ $(\mathrm{CfOCl_{(cr)}}) = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta_{\mathrm{sln}} H$. ΔH_1, the dissolution enthalpy of elemental Cf in 1 $\mathrm{mol\,dm^{-3}}$ HCl, has been reported as -576.1 ± 3.1 $\mathrm{kJ\,mol^{-1}}$ [3]. ΔH_2, the partial molal enthalpy of formation of HCl into $HCl_{(sln)}$, is -164.364 ± 0.040 $\mathrm{kJ\,mol^{-1}}$, calculated from $\Delta_{\mathrm{f}} H^0$ $(\mathrm{HCl_{(aq)}})$ at an HCl:H_2O ratio of 1:54.41 [8]. ΔH_3, the enthalpy of formation of water into $HCl_{(sln)}$, is taken as -285.830 ± 0.042 $\mathrm{kJ\,mol^{-1}}$ $(= \Delta_{\mathrm{f}} H^0$ $(\mathrm{H_2O})$ [8,9]), because it has been shown [10] that this value is nearly constant up to 2.00 $\mathrm{mol\,dm^{-3}}$ $HCl_{(sln)}$. Therefore,

$$\Delta_{\mathrm{f}} H^0(\mathrm{CfOCl_{(cr)}}) = (-576.1 \pm 3.1) + (-164.364 \pm 0.040) + (-285.830 \pm 0.042) - \Delta_{\mathrm{sln}} H, \quad (2)$$

where the latter quantity was determined in this work.

The observed heat effects were corrected for the small heat generated by the breakage of the sample bulb. No attempt was made to correct final californium ion concentrations to infinite dilution. The Cf(III) ion concentrations were 10^{-3} M and below, which have been accepted (in lanthanide studies) as sufficiently dilute to make concentration corrections unnecessary [11]. Inclusion of such a correction would have made the $\Delta_{\mathrm{f}} H^0$ $(\mathrm{CfOCl_{(cr)}})$ value reported here slightly more negative.

Chemical and thermal interactions of the sample's radiation with the solution were also considered. Prior to bulb breakage, energy from the α-emissions of Cf is absorbed by the glass bulb, and the heat generated diffuses into the solution. Following bulb breakage, the emitted α-particles react with the surrounding solution, principally water molecules. This has the potential of creating an extraneous heat effect (at the moment of dissolution), and as alpha radiation can oxidize water, this may also yield soluble peroxide and oxygen and helium gases. As the amount of energy dissipated remains the same before and after bulb breakage, any effect on the measurement must be attributed to the generation of helium and oxygen gases, and any heat they carry away by volatilization. An assessment of the oxidation of water by α-particles indicated a total generation of less than one picomole of gaseous species during the time span of the calorimetry experiments. Aberration to the heat flow diagram and damage to the structural integrity of the thin glass membrane of the sample bulb were not observed in this work.

Error limits reported for the enthalpy of solution measurements given here are one standard deviation (σ). The uncertainty given for the enthalpy of formation is estimated based on both experimental errors in the present work and on the precisions reported in published work.

3. Results and discussion

Studies to determine the enthalpy of solution of CfOCl were preceded by comparable work on EuOCl, GdOCl and LuOCl [1]. In the CfOCl work, in contrast to our earlier lanthanide efforts, there were two complicating factors. One was the limited quantity of Cf available (4 mg), and the second was the potential for Cf to be partially oxidized during the preparation of the CfOCl. To address these issues, techniques for CfOCl preparations were developed using $TbCl_3$ as a stand-in for $CfCl_3$, as both elements display similar behavior with regard to formation of their oxides and/or oxidation to higher oxides (e.g., M_7O_{12}) [5].

We were successful in preparing the desired TbOCl product on the mg scale and used similar conditions for the preparation of CfOCl. Evidence for the formation of Tb_4O_7 or Tb_7O_{12} in the TbOCl preparations was noted in X-ray diffraction patterns and also visually by a dark coloration of portions of the products. These observations were made when the oxychloride products were heated above 400°C or for extended periods at lower temperatures. The upper limit for formation of pure TbOCl, and CfOCl, by this method was therefore assumed to be 400°C. Consequently, a more conservative approach was chosen for the preparation of CfOCl, wherein the preparation temperature was kept below 320°C. The CfOCl products were all a uniformly light green color and yielded diffraction patterns consistent with that expected for CfOCl, except in one case where a minor temperature excursion was encountered. In the latter case, a dark coloration was noted in portions of the 'CfOCl' sample, and it was not used for calorimetry.

The sample preparation procedure consisted of first obtaining hydrated californium trichloride by evaporating hydrochloric acid solutions of Cf(III). The resulting trichloride hydrate solid was then heated in a platinum boat in air up to 280–320°C for approximately 10 min, held at this temperature for an additional 5–10 min, and then cooled to room temperature. Single pieces from two different preparations were chosen for calorimetry, and smaller portions of each preparation were taken for X-ray powder diffraction analysis. Sample dissolutions were carried out as soon as possible (<2 days) after bulb loading to minimize damage to the bulb membrane or alteration of the sample's composition via α-particle irradiation. There was no X-ray or visual evidence for oxidation or hydration of the CfOCl products used in the calorimetry studies.

Although there was a limited number of diffraction lines (nominally five), all lines observed corresponded to those reported for CfOCl [12]. It is likely that the limited crystallinity arose due to the lower temperatures employed in the preparations. Even though the number of lines was limited, lattice parameters were calculated ($a_0 = 0.3958(5)$; $c_0 = 0.6678(7)$ nm) and found to be in reasonably good agreement with the literature values ($a_0 = 0.3956(2)$; $c_0 = 0.6662(9)$ nm). Our lattice parameters generated a unit cell volume for CfOCl that was 2% greater than that calculated using the literature data. Analysis of the CfOCl products by Raman spectroscopy was attempted, but a definitive signal could not be obtained from either CfOCl preparation.

Enthalpy data obtained are presented in Table 1. Contamination of the oxychloride product with oxide should yield an enthalpy of solution value more negative than that of the pure oxychloride, which would generate a less-negative calculated enthalpy of formation. Remnants of trichloride in the oxychloride product should yield a less-negative enthalpy of solution, and therefore a more negative enthalpy of formation for CfOCl. The presence of small amounts of either unreacted trichloride or oxide could account for the differences noted in our lattice parameter values and the literature values, even though there was no evidence for the presence of these materials in the products. Therefore, it was not possible to make corrections to our observed enthalpies of solution for these potential impurities.

A prediction of the value of $\Delta_f H^0$ ($BkOCl_{(cr)}$) was made from interpolation in a second-order-fitted plot of $\Delta_f H^0$

Table 1
Enthalpy data—californium oxychloride (300.527 g mol^{-1})

Heat effect (J)	Powder sample mass (μg)	$\Delta_{sln}H$ (kJ mol^{-1})
−0.4917	1470	−101
−0.1617	461	−105
−0.3107	810	−115
−0.1300	383	−102
−0.1701	484	−106
		mean (σ) = −106 (6)

Inserting this mean value into Eqn. (2) yields $\Delta_f H^0$ ($CfOCl_{(cr)}$) = −920±7 kJ mol^{-1}.

($AnOCl_{(cr)}$) versus the corresponding trivalent ionic radius (CN=6) [4] for U, Pu, Am, Cm, and Cf. The value obtained at the Bk(III) radius was -944 ± 10 kJ mol^{-1}.

4. Summary

The enthalpy of solution of PbFCl-type tetragonal CfOCl in 1.022 mol dm^{-3} HCl at 298 K was measured as -106 ± 6 kJ mol^{-1}, which yielded a standard enthalpy of formation for CfOCl of -920 ± 7 kJ mol^{-1}. Interpolating in a plot of the standard enthalpy of formation of the oxychlorides of U, Pu, Am, Cm, and Cf versus their corresponding trivalent ionic radius, the standard enthalpy of formation of BkOCl was predicted to be -944 ± 10 kJ mol^{-1}.

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