Molar enthalpies of formation of BaCmO$_3$ and BaCfO$_3$*

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Abstract

The enthalpies of solution of BaCmO$_3$ and BaCfO$_3$ in 1.00 mol dm^{-3} HClO$_4$ were measured at 298.15 ± 0.05 K and $p° = 101.325$ kPa as $-(345.3 \pm 4.7)$ and $-(347.2 \pm 1.9)$ kJ mol^{-1}, respectively. The resulting standard molar enthalpies of formation, $\Delta_f H_m^\circ(\text{BaCmO}_3, \text{cr}) = -(1517.8 \pm 7.1)$ kJ mol^{-1} and $\Delta_f H_m^\circ(\text{BaCfO}_3, \text{cr}) = -(1477.9 \pm 5.6)$ kJ mol^{-1}, together with other corresponding experimental values for several lanthanide, actinide and transition metal complex oxides with barium and strontium, are used to estimate the molar enthalpies of formation of a number of homologous actinide compounds. The present results also provide additional information on the standard molar enthalpy of formation of CfO$_2$ and on the Cf^{4+}/Cf^{3+} standard potential.

1. Introduction

Studies of the thermodynamic properties of perovskite-related complex (ternary) oxides of several quadrivalent lanthanides and actinides with barium and strontium have been published in recent years. Quantitative data on the molar enthalpies of formation of such compounds exist for BaCeO$_3$ [1, 2], BaPrO$_3$ [1], BaTbO$_3$ [1, 2], BaUO$_3$ [3], BaPuO$_3$ [4], BaAmO$_3$ [2], SrCeO$_3$ [2], SrTbO$_3$ [2] and SrAmO$_3$ [2]. Morss and coworkers [1, 3, 4] showed that, for a number of barium compounds with the general formula BaM'O$_3$ (M' = Ti, Mo, Hf, Zr, Tb, Pr, U or Pu), the enthalpy change, $\Delta_f H_m^\circ(\text{complex})$, corresponding to the formation of these compounds from the binary oxides according to reaction (1).

$$\text{BaO(cr)} + \text{M'O}_2(\text{cr}) = \text{BaM'O}_3(\text{cr})$$
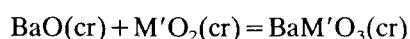
$$\Delta_f H_m^\circ(\text{complex}) \qquad (1)$$

becomes less favorable as the Goldschmidt tolerance factor, t, [5] decreases. This factor t is expressed as $t = (T_{\text{Ba}} + R_{\text{O}})/(2^{1/2})(R_{\text{M'}} + R_{\text{O}})$, where R represents the ionic radius of Ba, O or M' [6]. The value of t describes the size (ideal for $t = 1$) of the octahedral holes for accommodating the M' ions in the close-packed BaO$_3$ layers. In fact, it was shown recently [2] that a linear relationship exists between $\Delta_f H_m^\circ(\text{complex})$ and t which could be extended to analogous strontium compounds, especially those composed of cerium, terbium and americium, which exhibit a distorted perovskite structure. The only known exceptions to this linear relationship are found with BaPrO$_3$ and BaMoO$_3$; tentative explanations have been offered for their deviations from this linear relationship [1, 3 4].

One of the purposes of the present study was to determine if the above correlation extended to BaCmO$_3$ and BaCfO$_3$, i.e. to the heaviest actinides for which such compounds can be prepared. With a broader base of experimental values, we would be able to provide better estimations of the molar enthalpies of formation

of other, some of them yet to be prepared, homologous actinide $MM'O_3$ compounds (e.g. M = Ba or Sr, M' = Th, Pa, Np or Bk).

In addition, with adequate auxiliary thermodynamic data, the present results on $BaCfO_3$ permit the derivations of the molar enthalpy of formation of stoichiometric CfO_2 and the standard potential of the Cf^{4+}/Cf^{3+} couple.

2. Experimental details

The ternary oxides, $BaCmO_3$ and $BaCfO_3$, were prepared by calcining residues obtained by evaporating mixtures of approximately stoichiometric quantities of $Ba(NO_3)_2$ (2–3 mol.% excess) and the trivalent actinide nitrate salts. These preparations were carried out on the 5–10 mg scale. These intimately mixed nitrate salts provided better control of the stoichiometries and a more reactive oxide mixture at lower temperatures than could be achieved by weighing and then calcining mixtures of the separately formed oxide powders.

The solid, mixed nitrate salts were calcined first at 600 °C to decompose the nitrates and form oxides, and then heated to 1200 °C to form the desired ternary oxide. This product was homogenized, pelletized and reheated at 1200 °C for eight hours in oxygen. The final step of the preparations involved cooling to 400 °C, after which a stepwise "cool and hold in oxygen" sequence was used to acquire the desired oxygen content.

Two different preparations of $BaCmO_3$ (I and II) and a single preparation of $BaCfO_3$ were made in this manner.

The barium and actinide contents of the various preparations were analyzed using aliquots from solutions following the calorimetry. Inductively coupled plasma techniques (Analytical Chemistry Division, ORNL) and standard radioactive counting techniques ($2\,\pi$ alpha) were used for the barium and actinide analysis, respectively.

For $BaCmO_3$ the curium content was found to be 56.8 ± 0.4 mass % (calc. 57.22 mass %) and the barium content 31.6 ± 0.2 mass % (calc. 31.70 mass %). In the case of $BaCfO_3$, the analytical results were 57.1 ± 1.6 mass % (calc. 57.33 mass %) for californium and for barium, 31.6 ± 0.5 mass% (calc. 31.62 mass %). These mass percentages are the averages (95% confidence) of individual analyses of six separate calorimetric solutions from each of the two compounds.

X-ray powder diffraction was used to ensure that the proper compounds had been obtained and to ascertain that separate phases were not present (e.g. BaO, actinide oxide, etc.). Characterization by X-ray diffraction was made with a Rigaku rotating anode X-ray generator using filtered MoK$_\alpha$ radiation. De-

bye–Scherrer powder cameras (114.6 mm, Straumanis mounting) with Kodak DEF-392 film were employed.

All samples were handled in a gloved box whose helium atmosphere contained less than 1 p.p.m. water (as measured by a Parametrics Model 2000 hygrometer) and 10–100 p.p.m. oxygen and nitrogen (as measured with a Varian quadrupole gas analyzer).

The techniques used for handling and weighing the samples for calorimetry have been described [7]. In each calorimetric run one to three pieces, cut from the bulk sample, were used. The isoperibolic calorimeter, having a nominal capacity of 5 cm³, has also been described [8], and the details of the verification of its performance have been published [8–10].

The selected dissolution medium was 1 mol dm⁻³ $HClO_4$ because, based on similar experiments [3] with $BaTbO_3$ and $SrTbO_3$, this medium dissolves such compounds rapidly (few minutes) and because the non-complexing nature of the ClO_4^- ion simplifies the extrapolation of data to infinite dilution. Hydrochloric acid solutions were not used so as to avoid potential oxidation of Cl^- to $Cl°$ by the Cm^{4+} or Cf^{4+}, which would complicate the overall reaction scheme.
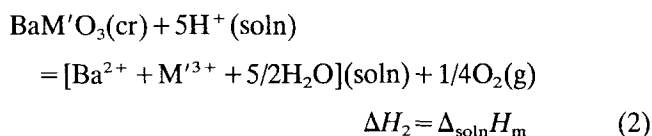
The concentration of the $HClO_4$ solution was verified to be 1.000 ± 0.005 mol dm⁻³ just prior to calorimetry by titration against a 1 mol dm⁻³ NaOH solution which itself had been titrated against a $1,000 \pm 0.005$ mol dm⁻³ Merck certified HCl solution.

The atomic mass of curium was taken as 247.9 (from the known isotopic composition) and that of californium as 249.07, based on the ¹²C scale of atomic masses. Uncertainty limits on the mean of several calorimetric measurements are based on the Student t 95% confidence level. All measurements are reported for 298.15 ± 0.05 K and $p° = 101.325$ kPa. Unless otherwise specified, auxiliary thermodynamic data are those recommended by CODATA [11].

3. Results and discussion

The X-ray powder patterns of both $BaCmO_3$ preparations and the $BaCfO_3$ preparation exhibited only lines which were indexable in cubic symmetry, although it is well known from neutron powder diffraction and high resolution X-ray powder diffraction analysis that these 4f- and 5f-element barium perovskites are often rhombohedrically or orthorhombically distorted [12–16]. The average lattice parameter (pseudo b.c.c.) obtained for the $BaCmO_3$ preparations was $a_0 = 0.4364$ nm, and that for the one $BaCfO_3$ preparation was $a_0 = 0.4356$ nm. These values are in agreement with the parameters previously obtained [17] for these compounds.

The results of the dissolution of the two compounds, according to eqn. (2):

$$BaM'O_3(cr) + 5H^+(soln)$$

$$= [Ba^{2+} + M'^{3+} + 5/2H_2O](soln) + 1/4O_2(g)$$

$$\Delta H_2 = \Delta_{soln}H_m \qquad (2)$$

where (soln) stands for 1.000 mol dm^{-3} HClO$_4$ and M' = Cm or Cf, are given in Table 1. As can be deduced from these data, the actinide concentration in the calorimetric solutions was $\leq 10^{-3}$ dm^{-3}. Heat evolution upon dissolution of the compounds was complete (within 99.9%) within 9–12 minutes in the case of the BaCmO$_3$ samples and within 5 minutes in the case of the BaCfO$_3$ samples. This difference in solution behavior, which is unexplained, leads to larger uncertainties in the calculation of the heat effect in the BaCmO$_3$ case, which is reflected in the larger uncertainty of the $\Delta_f H_m^\circ$(BaCmO$_3$, cr), as compared to that for BaCfO$_3$.
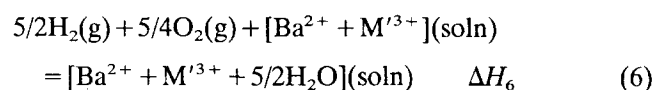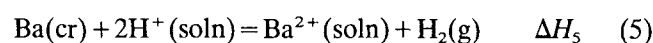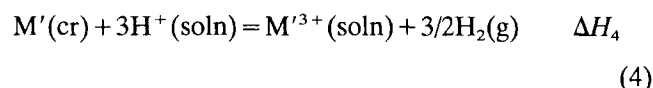
Although the evolution of gas (O$_2$), as expected from reaction (2), was observed through a microscope from the dissolution of a piece of BaCmO$_3$ in a small quantity of 1.000 mol dm^{-3} HClO$_4$, we have no proof that, under the actual experimental conditions in the calorimeter chamber, this oxygen evolution was quantitative. Quantitative evolution of O$_2$(g) would correspond to a small endothermic effect of 0.3 kJ mol^{-1} of dissolved oxide, due to the saturation of the gas by the water vapor at its equilibrium pressure [18] over 1.000 mol dm^{-3} HClO$_4$. On the other hand, dissolution of 20% of the oxygen released in reaction (2) would correspond to an exothermic effect of 0.55 kJ mol^{-1} of dissolved

TABLE 1. Molar enthalpy of solution of BaCmO$_3$ and BaCfO$_3$ in 5.00 cm^3 of 1.000 mol dm^{-3} HClO$_4$ at 298.15 ± 0.05 K and p° = 101.325 kPa

Sample and preparation number	Sample mass (μg)	ΔH^a (J)	$\Delta_{soln}H_m$ (kJ mol^{-1})
BaCmO$_3$			
I	568.0	0.4563	−348.2
I	532.0	0.4184	−340.9
II	1144	0.9312	−352.8
II	1463	1.1539	−342.1
II	2112	1.6734	−343.3
II	1402	1.1148	−344.6
		Mean	−(345.3 ± 4.7)^b
BaCfO$_3$			
I	869.7	0.6934	−346.3
I	566.7	0.4539	−347.9
I	908.3	0.7249	−346.7
I	622.0	0.5020	−350.6
I	753.0	0.6005	−346.4
I	1001.9	0.7969	−345.5
		Mean	−(347.2 ± 1.9)^b

^{a}Corrected for ampoule breaking and evaporation of solvent into the helium gas in the ampoule.
^{b}95% confidence level.

oxide [19, 20]. No correction was applied for these effects, which, in any case, lead to an uncertainty which is much smaller than the uncertainty limits reported on the mean of $\Delta_f H_m^\circ$ calculated from multiple experimental runs.

From the enthalpy of solution according to eqn. (2), the molar enthalpy of formation according to reaction (3)

$$Ba(cr) + M'(cr) + 3/2O_2(g) = BaM'O_3(cr)$$
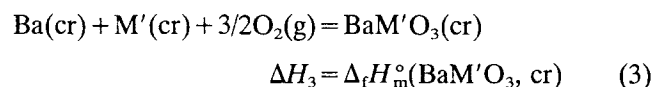
$$\Delta H_3 = \Delta_f H_m^\circ(BaM'O_3, cr) \qquad (3)$$

can be obtained through the use of the following reactions, all in 1.000 mol dm^{-3} HClO$_4$ (referred to as soln),

$$M'(cr) + 3H^+(soln) = M'^{3+}(soln) + 3/2H_2(g) \qquad \Delta H_4$$

$$(4)$$

$$Ba(cr) + 2H^+(soln) = Ba^{2+}(soln) + H_2(g) \qquad \Delta H_5 \qquad (5)$$

$$5/2H_2(g) + 5/4O_2(g) + [Ba^{2+} + M'^{3+}](soln)$$

$$= [Ba^{2+} + M'^{3+} + 5/2H_2O](soln) \qquad \Delta H_6 \qquad (6)$$

Thus,

$$\Delta H_3 = \Delta_f H_m^\circ(BaM'O_3, cr) = \Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_2 \qquad (7)$$

The standard molar enthalpies of formation of Cm^{3+}(aq) and Cf^{3+}(aq) have been reported as −(615 ± 5) kJ mol^{-1} [21] and −(577 ± 5) kJ mol^{-1} [10], respectively. These values were obtained from enthalpy of solution measurements of the metals in 1.000 mol dm^{-3} HCl at final actinide concentrations lower than 10^{-3} mol dm^{-3}, which yielded (−614.5 ± 4.5) kJ mol^{-1} and −(576.1 ± 3.1) kJ mol^{-1} for curium and californium, respectively. Making the reasonable assumption that these enthalpies change negligibly between 1.000 mol dm^{-3} HClO$_4$ (denoted soln) and standard conditions, we have, for ΔH_4 $\Delta_f H_m$(Cm^{3+}, soln) = −(615 ± 5) kJ mol^{-1} and $\Delta_f H_m$(Cf^{3+}, soln) = −(577 ± 5) kJ mol^{-1}.

Similarly, we take $\Delta H_5 = \Delta_f H_m$(Ba^{2+}, soln) = −(533.5 ± 1.7) kJ mol^{-1}, a value identical to that accepted for standard conditions [22]. Finally we take $\Delta H_6 = -5/2(285.84 ± 0.04)$ kJ mol^{-1} from the standard molar enthalpy of formation of water [11] and the relative partial molar enthalpy of water [23] in 1.000 mol dm^{-3} HClO$_4$, assuming that the influence of small (< 10^{-3} mol dm^{-3}) concentrations of Ba^{2+} and trivalent actinides is negligible.

Thus, we obtain:

$$\Delta_f H_m^\circ(BaCmO_3, cr) = -(1517.8 ± 7.1) \text{ kJ mol}^{-1}$$

and

$$\Delta_f H_m^\circ(BaCfO_3, cr) = -(1477.9 ± 5.6) \text{ kJ mol}^{-1}$$

TABLE 2. Estimated molar enthalpies of formation for a number of barium and strontium ternary oxides with tetravalent actinides

M'	$\Delta_f H^\circ_m(M'O_2, cr)$ (kJ mol^{-1}) from ref. 25	t		$\Delta_f H^\circ_m$(complex)[a] (kJ mol^{-1}) from eqn. (8)		$\Delta_f H^\circ_m$(BaM'O$_3$, cr) (kJ mol^{-1})	
		BaM'O$_3$(cr)	SrM'O$_3$(cr)	BaM'O$_3$(cr)	SrM'O$_3$(cr)	BaM'O$_3$(cr)	SrM'O$_3$(cr)
Th	$-(1226.7 \pm 1.7)$	0.831	0.780	-31.0	$+20.0$	$-(1805.7 \pm 8.9)$	
Pa	$-(1109 \pm 15)$	0.845	0.793	-45.0	$+7.0$	$-(1702 \pm 17)$	
U	$-(1084.9 \pm 0.8)$		0.797		$+3.0$		
Np	$-(1074.0 \pm 2.5)$	0.857	0.804	-57.0	-4.0	$-(1679.0 \pm 9.1)$	$-(1668.5 \pm 8.9)$
Pu	$-(1056.2 \pm 0.7)$		0.807		-7.0		$-(1653.7 \pm 8.9)$
Cm	$-(911 \pm 6)$		0.811		-11.0		$-(1513 \pm 10)$
Bk	$-(1026 \pm 9)$	0.872	0.818	-72.0	-18.0	$-(1646 \pm 13)$	$-(1635 \pm 12)$

[a]$\Delta_f H^\circ_m$(complex) refers to values from binary oxides

From the experimental values: $\Delta_f H^\circ_m$(BaO, cr) = $-(548.0 \pm 2.0)$ kJ mol^{-1} [24] and $\Delta_f H^\circ_m$(CmO$_2$, cr) = $-(911 \pm 6)$ kJ mol^{-1} [25], we can calculate, as we have done [2] for analogous compounds, $\Delta_f H^\circ_m$(complex) according to reaction (1). We obtain for BaCmO$_3$, $\Delta_f H^\circ_m$(complex) = $-(58.8 \pm 9.5)$ kJ mol^{-1}. Use of this result together with the corresponding values listed in ref. 2 for various MM'O$_3$ compounds (M = Ba and M' = Ti, Hf, Zr, Tb, Am, Pu, Ce, U; M = Sr and M' = Ti, Mo, Zr, Tb, Am, Ce), in conjunction with the Goldschmidt tolerance factor t calculated from the ionic radii (CN = 6) from Shannon [6], leads to relationship (8)

$$\Delta_f H^\circ_m(\text{complex}) = 800.4 - 1000.5t \text{ (kJ mol}^{-1}) \qquad (8)$$

which, over the range $0.8 < t < 1$, fits the experimental results for all the above-listed compounds with an average standard deviation of 8.5 kJ mol^{-1}. This result is quite satisfactory given the uncertainties in the ionic radii and the variation in the crystal structures of the complex oxides.

From relationship (8), the Shannon ionic radii [6] and the standard molar enthalpies of formation of the various actinide dioxides and of BaO [24], given above, and of SrO as $-(590.53 \pm 1.00)$ kJ mol^{-1} [26], we can estimate the molar enthalpies of formation of several complex oxides (some of which remain to be prepared) for which no thermochemical data exist; these values are given in Table 2. The value we obtain for $\Delta_f H^\circ_m$(complex) in the case of BaThO$_3$ is distinctly more negative than that of -20 kJ mol^{-1}, estimated by Williams et al. [3]. Because SrCeO$_3$ with a $\Delta_f H^\circ_m$(complex) as small as $-(6 \pm 11)$ kJ mol^{-1} has been synthesized [2], it appears probable that the difficulties encountered [27] in the preparation of BaThO$_3$ free of impurities may be due in part to the very refractory nature of ThO$_2$. It also appears from our estimates that there is little hope of obtaining in pure form any SrM'O$_3$ compounds with actinides lighter than nep-

tunium, although the existence of these compounds (Pa–Pu) has been reported [28].

Equation (8) can be used to estimate $\Delta_f H^\circ_m$(CfO$_2$, cr) based on our $\Delta_f H^\circ_m$(BaCfO$_3$, cr) = $-(1477.9 \pm 5.6)$ kJ mol^{-1}. With $r_{Cf^{4+}} = 0.0821$ nm, $t = 0.876$ and $\Delta_f H^\circ_m$(complex) = $-(76.0 \pm 8.5)$ kJ mol^{-1}, we obtain $\Delta_f H^\circ_m$(CfO$_2$, cr) = $-(854 \pm 10)$ kJ mol^{-1}. This value is in very good agreement with that of -858 kJ mol^{-1}, estimated by Morss [29] based on the empirical interrelationship between the molar volumes of the lanthanide and actinide dioxides and their standard molar enthalpies of solution.

An extrapolation to californium of the plot $\{\Delta_f H^\circ_m(M'O_2, cr) - \Delta_f H^\circ_m(M'^{4+}, aq)\}$ versus M'^{4+} ionic radius [25] leads to $\{\Delta_f H^\circ_m(CfO_2, cr) - \Delta_f H^\circ_m(Cf^{4+}, aq)\} = -(549 \pm 5)$ kJ mol^{-1} and yields $\Delta_f H^\circ_m(Cf^{4+}, aq) = -(305 \pm 11)$ kJ mol^{-1}, which compare favorably with -313 kJ mol^{-1} estimated by Morss [29]. Finally, using the entropy values listed by this latter author, namely, $S^\circ_m(Cf^{4+}, aq) = -412$ J K^{-1} mol^{-1}, $S^\circ_m(Cf^{3+}, aq) = -197$ J K^{-1} mol^{-1}, accepting an uncertainty of ± 20 J K^{-1} mol^{-1} for the difference $\{S^\circ(Cf^{4+}, aq) - S^\circ(Cf^3, aq)\}$, and $S^\circ(H_2, g) = 130.571 \pm 0.005$ J K^{-1} mol^{-1} [11], we obtain $E^\circ(Cf^{4+}/Cf^{3+}) = 3.28 \pm 0.14$ V for the standard potential of the Cf^{4+}/Cf^{3+} couple. Our value is virtually identical to that of 3.2 V given by Morss [29], but is based on the first experimental thermochemical data from a solid tetravalent californium compound.

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