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THERMODYNAMIC SYSTEMATICS OF OXIDES OF AMERICIUM, CURIUM, AND NEIGHBORING ELEMENTS

CONF-841210--22

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CONF-841210--22

DE85 009704

ABSTRACT. Recently-obtained calorimetric data on the sesquioxides and dioxides of americium and curium are summarized. These data are combined with other properties of the actinide elements to elucidate the stability relationships among these oxides and to predict the behavior of neighboring actinide oxides.

1. INTRODUCTION

The solid-state chemistry of metallic elements is centered on their oxides. For the transuranium elements, the oxides were the first well-characterized substances to be prepared and have been the most thoroughly studied class of compounds. For the elements beyond plutonium, however, inaccessibility of adequate amounts of long-lived isotopes inhibited the study of their solid-state properties until recently.

Thermodynamic measurements on transplutonium oxides before 1980 were limited to thermogravimetric and manometric studies (1-8) and one solution-calorimetry investigation (9). This paper summarizes more recent results and places these results in the perspective of other relevant thermodynamic data for these and adjacent elements.

Table I shows the known binary actinide oxides, arranged by increasing atomic numbers and oxidation states. Measured enthalpies of formation and standard entropies at 298 K are shown to indicate those oxides which have been thermodynamically well characterized. (Some MO_{2-x} phases have been omitted for clarity.)

Although this paper focuses only on oxides $MO_{1.5}$ and MO_2 , it should be noted that there is a rich chemistry of higher actinide oxidation states in complex oxides of protactinium through americium (10). These complex oxides fill many of the blank regions in the lower right region of Table I, and allow the study of spectroscopic, magnetic, electronic, and thermodynamic properties of these oxidation states.

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TABLE I.

Well-Characterized Binary Actinide Oxides. Measured enthalpies of formation (kJ mol^{-1}) and standard entropies ($\text{J mol}^{-1}\text{K}^{-1}$) are shown beneath corresponding formulas.

An(III)		An(IV)		An(V)		An(VI)
AcO _{1.5}		ThO ₂ -1226.4 ± 3.5 65.23 ± 0.20				
		PaO ₂		PaO _{2.5}		
		UO ₂ -1085.0 ± 1.0 77.03 ± 0.20	UO _{2.25} -1127.6 ± 1.2 83.53 ± 0.18	UO _{2.33} -1142.4 ± 0.9 83.51	UO _{2.67} -1191.6 ± 0.8 94.18 ± 0.17	UO ₃ (γ) -1223.8 ± 2.0 96.11 ± 0.40
		NpO ₂ -1074.0 ± 2.5 80.3 ± 0.4		NpO _{2.5}		
PuO _{1.5} (-828) 81.51 ± 0.32	PuO _{1.61} -884.5 ± 16.7	PuO ₂ -1056.2 ± 0.7 66.13 ± 0.26				
AmO _{1.5} -845 ± 8	AmO _{1.6} (?)	AmO ₂ -932.2 ± 2.7				
CmO _{1.5} -841.5 ± 6.6	CmO _{1.714}	CmO ₂ -911 ± 6				
BkO _{1.5}	BkO _{1.8}	BkO ₂				
CfO _{1.5} -826 ± 5	CfO _{1.714}	CfO ₂				

References for Table I: References 10, 11, and Morss, L. R.; Fuger, J. to be published (CfO_{1.5}).

2. AMERICIUM OXIDES

The enthalpy of formation of hexagonal Am₂O₃ was determined recently by solution microcalorimetry (11). Although this measurement was not the first thermodynamic property of an actinide sesquioxide to be reported (12-14), Am₂O₃ represents the lightest actinide sesquioxide suitable for solution calorimetry. (Although a large sample of plutonium sesquioxide has been prepared (13) and still exists, its high temperature of synthesis renders it so refractory that it is probably unsuitable either for solution or combustion calorimetry. Lighter actinide sesquioxides such as U₂O₃ and Np₂O₃ are unknown.) Since Am₂O₃ readily oxidizes in air, it had to be handled in an oxygen-free dry box. Fortunately, its reactivity facilitated solution calorimetry in 6M hydrochloric acid, in which it readily dissolves.

Unsuccessful efforts were made by this author to prepare multi-milligram samples of monoclinic Am₂O₃, which may (3) have a narrow stability range (figure 1) or may be observed only when stabilized by a lanthanide impurity (15). The hexagonal sesquioxide was observed upon reduction of the dioxide in hydrogen at temperatures above 625°C, with rapid or slow cooling; lower reduction temperatures yielded only the body-centered cubic sesquioxide. Because of concern that the bcc sesquioxide might not be stoichiometric (3), solution-calorimetry measurements were not undertaken on the bcc phase.

A few years earlier, the enthalpy of formation of AmO₂ was redetermined (16). Although Am sesquioxide, as well as those of Cm, Cf, and

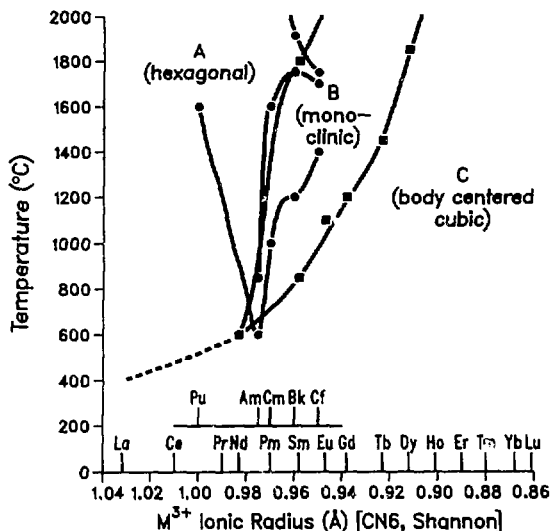


Figure 1. Phase diagram for ■ lanthanide and ● actinide sesquioxides (region above 2000°C omitted).

the lanthanides, dissolves readily in dilute hydrochloric acid (11) (the most convenient calorimetric solvent), the dioxide requires stronger acid to dissolve it. AmO_2 also has been observed to disproportionate partially and nonreproducibly when dissolved in acid (16). Therefore, it was necessary to carry out the solution calorimetry in a complexing acid (H_2SO_4) with a reductant (I^-) to achieve adequate dissolution rates and a well-defined reaction. An important result obtained from this study was a thermochemical estimate of the standard aqueous electrode potential $E^\circ(\text{Am}^{4+}/\text{Am}^{3+}) = 2.62 \pm 0.09 \text{ V}$ (16).

Ackermann and Chandrasekharaiah (17) correlated the behavior of these oxides with other sesquioxides and dioxides and with the aqueous ions. More recent investigators have refined such correlations in terms of the functional dependence of enthalpy of solution upon ionic size and crystal structure (11,16,18) and in terms of the energetics of gaseous atoms in different electron configurations (18). Even more recently Brewer's reassignment of the energy levels of Am I (neutral Am) (19) has led to a much more consistent comparison (11) of the energetics of Am metal, vapor, and trivalent species with other f elements (by means of the correlation function $P(M)$) than had earlier been calculated (20,21). A refined treatment of the systematics of lanthanide atomic energy levels (22) should further improve actinide metal/oxide/aquo-ion systematics when it is applied to the 5f elements.

3. CURIUM OXIDES

Curium sesquioxide was the first actinide sesquioxide to be studied by solution calorimetry (14). The determination of $\Delta_f H_m^\circ(\text{Cm}_2\text{O}_3)$ was

facilitated by the availability of multimilligram amounts of ^{248}Cm , a long-lived (half-life 3×10^5 y) isotope purified from its radiochemical parent ^{252}Cf in the transplutonium production program at Oak Ridge National Laboratory, by the ease of reduction of CmO_{2-x} to $\text{CmO}_{1.5}$, by the relative stability of stoichiometric monoclinic sesquioxide (figure 1) above 700°C , and by its rapid dissolution in hydrochloric acid.

Curium dioxide, on the other hand, has proved to be much more intractable than AmO_2 . Early studies with ^{244}Cm (half-life 18.1 y) showed significant substoichiometry (4,5,23), especially as a function of time, due to alpha-particle lattice damage. Despite the more recent availability of ^{248}Cm , which appeared from thermogravimetric measurements and X-ray powder diffraction lattice parameter to yield stoichiometric $\text{CmO}_{2.00}$ in oxygen at 1 atm pressure, recent magnetic susceptibility determinations infer significant hypostoichiometry (x near 0.2 in CmO_{2-x}) (24-27). Very careful annealing in pure oxygen for several days at 1 atm pressure and even at 100 atm pressure (25,26) failed to eliminate Curie-Weiss paramagnetism attributable to Cm(III) . Since annealed dioxide dissolves very slowly in acidic media, calorimetric solvents required complexing (HSO_4^- , BF_4^-) and reducing (I^-) agents to accelerate dissolution of CmO_2 . Typical data (24) (table II) show significant scatter.

TABLE II.

CmO_2 THERMOCHEMISTRY
Solution calorimetry in 0.5 M H_2SO_4 - 0.1 M KI:
$\text{CmO}_2(\text{cr}) + 4 \text{H}^+(\text{aq}) + 3/2 \text{I}^- \rightarrow \text{Cm}^{3+} + 1/2 \text{I}_3^- + 2 \text{H}_2\text{O}(\text{aq})$
Sample A($\text{CmO}_{2.00}$): $\Delta\text{H} = -223.6 \pm 2.1 \text{ kJ mol}^{-1}$ (5 experiments, 95% confidence)
Sample B($\text{CmO}_{1.93}$): $\Delta\text{H} = -225 \pm 6 \text{ kJ mol}^{-1}$ (3 experiments, 95% confidence, corrected to $\text{CmO}_{2.00}$)
Solution calorimetry in 6M HNO_3 - 0.1 M NaBF_4 :
$\text{CmO}_2(\text{cr}) + 3 \text{H}^+(\text{aq}) \rightarrow \text{Cm}^{3+} + 3/2 \text{H}_2\text{O}(\text{aq}) + 1/4 \text{O}_2(\text{g})$
Sample C($\text{CmO}_{1.986}$): $\Delta\text{H} = -160.5 \text{ kJ mol}^{-1}$ (1 experiment)
Sample D($\text{CmO}_{1.982}$): $\Delta\text{H} = -153.0 \text{ kJ mol}^{-1}$ (2 experiments)
These experimental data, combined with currently accepted auxiliary data and small corrections to standard states, yield $\Delta_f\text{H}^\circ(\text{CmO}_2, \text{cr}) = -911 \pm 6 \text{ kJ mol}^{-1}$ (95% confidence).

The thermochemical measurements on curium oxides have been utilized systematically in a manner parallel to those on americium oxides: correlation of enthalpies of solution with ionic size (18,22), correlation (P(M)) with energetics of gaseous atoms (18), and thermochemical estimation (24) of the aqueous $E^\circ(\text{Cm}^{4+}/\text{Cm}^{3+}) = 3.0 \pm 0.1$ V. The steps in the latter calculation are shown in table III. Similar thermodynamic behavior is found in the lanthanides praseodymium (aqueous $E^\circ(\text{Pr}^{4+}/\text{Pr}^{3+}) = 3.2 \pm 0.2$ V) and terbium (aqueous $E^\circ(\text{Tb}^{4+}/\text{Tb}^{3+}) = 3.1 \pm 0.5$ V (28) or 3.3-3.4 V, see below). These tetravalent lanthanides have been stabilized in complexed form in carbonate solutions (29), but, unexpectedly, Cm(IV) has not yet been stabilized in this medium (30).

TABLE III.

<p>Estimation of $E^\circ(\text{Cm}^{4+}/\text{Cm}^{3+})$</p> <p>For the reaction $\text{CmO}_2(\text{cr}) + 4\text{H}^+(\text{aq}) \rightarrow \text{Cm}^{4+}(\text{aq}) + 2\text{H}_2\text{O}(\ell)$</p> <p>we predict $\Delta H^\circ = -40 \pm 7$ kJ mol⁻¹ from data on other MO_2 and M^{4+} (see fig. 3).</p> <p>Since we have calculated $\Delta_f H^\circ(\text{CmO}_2, \text{cr}) = -911 \pm 6$ kJ mol⁻¹, we may calculate $\Delta_f H^\circ(\text{Cm}^{4+}, \text{aq})$ from the above data:</p> $\Delta_f H^\circ(\text{Cm}^{4+}, \text{aq}) = \Delta_f H^\circ(\text{CmO}_2, \text{cr}) - 2 \Delta_f H^\circ(\text{H}_2\text{O}) + (-40 \pm 7)$ $= -911 \pm 6 - 2(-285.83) - 40 \pm 7 = -379 \pm 9 \text{ kJ mol}^{-1}.$ <p>Thus for the reaction</p> $\text{Cm}^{4+}(\text{aq}) + \frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{Cm}^{3+}(\text{aq}) + \text{H}^+(\text{aq})$ $\Delta H^\circ = -615 \pm 5 - (-379 \pm 9) = -236 \pm 10 \text{ kJ mol}^{-1}.$ <p>From estimated entropies</p> $\Delta S^\circ = 170 \pm 21 \text{ J K}^{-1} \text{ mol}^{-1}$ <p>Thus $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -287 \pm 12$ kJ mol⁻¹.</p> <p>Hence $E^\circ(\text{Cm}^{4+}/\text{Cm}^{3+}) = -\Delta G^\circ/nF = +2.96 \pm 0.12$ V (compared with literature estimates of 3.1 and 3.2 V).</p>

4. RELATIONSHIPS TO OTHER THERMODYNAMIC MEASUREMENTS

There are high-temperature calorimetric measurements on the incremental oxidation of cerium (31) and plutonium (12) oxides. For cerium (32), praseodymium (33), terbium (34), and all actinides thorium through

californium (2,5-8,35) there are oxygen-pressure dissociation data as a function of temperature and composition. Each of these methods leads to $\bar{H}(O_2)$, the partial molal enthalpy of oxygen in these systems. High-temperature solid-state EMF measurements also yield thermodynamic information on these oxides (36).

Chikalla and Turcotte (37) compared $\log P(O_2)$ data at 1173 K for the composition $MO_{1.9}$ with the aqueous $E^\circ(M^{4+}/M^{3+})$, since both of these parameters are proportional to the free energy change of $M(IV)-M(III)$ species. They predicted $P(O_2)$ for other oxides $MO_{1.9}$. The $E^\circ(Am^{4+}/Am^{3+})$ has been reassessed as 2.62 V (16) and a data point for $CeO_{1.9}$ is available; the revised plot (figure 2) still predicts only slightly more stability for $CmO_{1.9}$ than for $CfO_{1.9}$. Isobars for $^{248}CmO_{2-x}$ show $P(O_2) = 0.72$ atm for $CmO_{1.9}$ at 723 K (6); measurements are lacking for the CfO_x system above $x = 1.72$. Nevertheless, CmO_x and CfO_x isobars ($6,8$) ($1.50 < x < 1.72$) show CmO_x to lose oxygen at lower temperatures than CfO_x . These contradictory interpretations need to be reconciled.

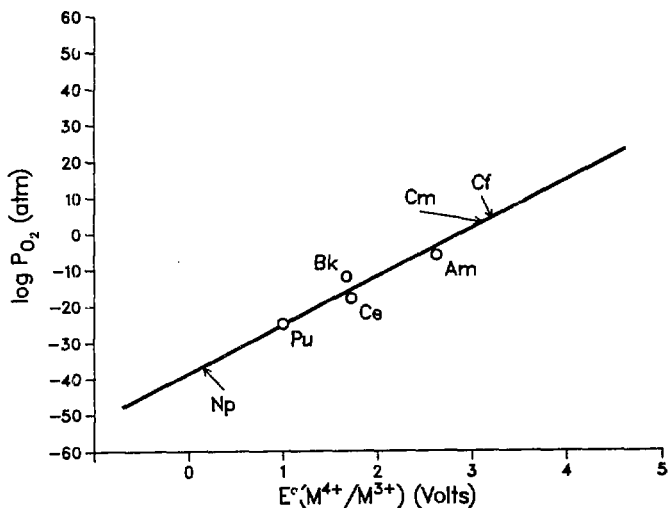


Figure 2. Correlation of $\log P(O_2)$ for $MO_{1.90}$ at 1173 K (refs. 32,35, and 37) with aqueous $E^\circ(M^{4+}/M^{3+})$ (ref. 28).

Ackermann and Rauh (35) tabulated $\bar{G}(O_2)$ for $MO_{1.96}$ ($M = Th-Am$) at 1875 K. There are insufficient data to extrapolate $\bar{G}(O_2)$ for $CmO_{1.90}$ at 1173 K for comparison with Chikalla and Turcotte's plot (37). The stoichiometry of CmO_2 must still be established by new thermogravimetric or analytical measurements.

Enthalpy-of-solution correlations of sesquioxides and dioxides as a function of ionic size lead to interesting conclusions. Such a plot for lanthanide and actinide dioxides shows a single straight line with the

exception of terbium (figure 3). This plot permits the prediction of the enthalpies of formation of BkO_2 (-1020 kJ/mol) and of CfO_2 (-858 kJ/mol) using accepted $E^\circ(\text{An}^{4+}/\text{An}^{3+})$, estimated entropies, and new thermochemical data on $\text{Cf}^{3+}(\text{aq})$ (38). Since there is no reason to doubt the reliably determined enthalpy of formation of TbO_2 , we must suspect that the estimated (28) enthalpy of formation of Tb^{4+} is too exothermic by ca. 20-30 kJ/mol. Consequently, the estimated aqueous potential $E^\circ(\text{Tb}^{4+}/\text{Tb}^{3+})$ must be revised from 3.1 (28) to 3.3-3.4 V.

A more practical conclusion that may be reached from figure 3 is that the tetravalent lanthanides and actinides in eightfold oxide coordination are similarly stable with respect to the tetravalent aquo-ions. Thus Ce(IV) is a good model for either Pu(IV) or Np(IV) in nuclear waste isolation studies.

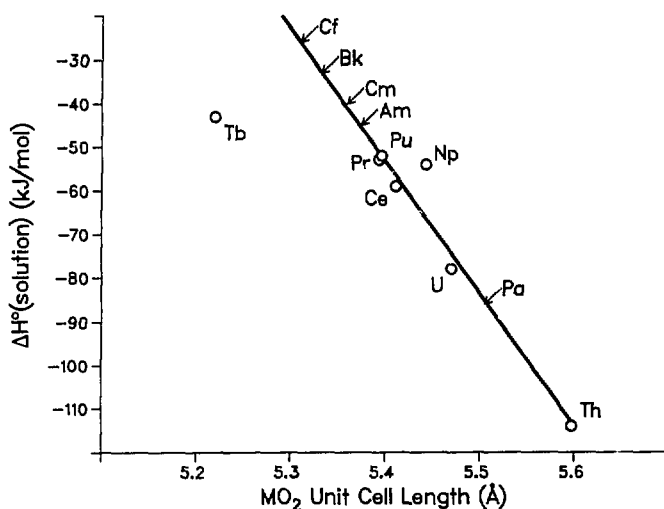


Figure 3. Enthalpy of solution of MO_2 as function of unit cell size.

When a similar plot (figure 4) is examined for the sesquioxides, which have three structure types, it is noted that the enthalpies of solution of actinide sesquioxides of each structure type are ca. 20 kJ/mol less exothermic than those of structurally similar lanthanide sesquioxides. Similar differences are seen for structurally similar hexagonal trichlorides. These systematic trends permit one to predict enthalpies of formation for unstable sesquioxides (for U and Np) as well as for Pu_2O_3 and Bk_2O_3 (table IV). Carrying the comparison one step farther, we have calculated free energies of solution from enthalpy differences and from measured entropies for a lanthanide and actinide ion of similar size in table IV. Not only do figure 4 and table IV show that lanthanides may be used to model trivalent actinide behavior in nuclear waste matrices, but that the lanthanide models provide a conservative safety margin — the actinide(III) ions in sixfold oxide

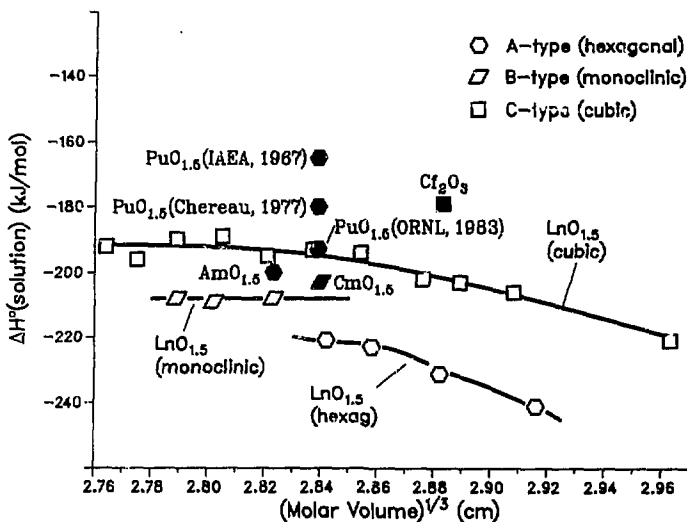


Figure 4. Enthalpy of solution of lanthanide (open symbols) and actinide (filled symbols) sesquioxides as function of interatomic distance. Data from reference 11; data point for $CfO_{1.5}$ from Morss, L.; Fuger, J., to be published.

TABLE IV.

Differences in Enthalpies of Formation of Trivalent Actinide Species (kJ mol^{-1}).

M	$M^{3+}(\text{aq})^a$	$MO_{1.5}-M^{3+}$		MCl_3-M^{3+}	
		Diff.	$MO_{1.5}(s)^a$	Diff.	$MCl_3(\text{cr, hexag})^a$
U	-489	(-239)	(-728)[hexag]	-377	-866
Np	-527	(-234)	(-761)[hexag]	-371	-898
Pu	-592	(-236)	(-828)[hexag]	-368	-960
Am	-617	-228	-845[hexag]	-361	-978
Cm	-615	-226	-841[monocl]	-355	(-970)
Bk	-601	(-246)	(-847)[cubic]	(-350)	(-951)
Cf	-577	-249	-826[cubic]	(-345)	(-922)

^aFrom solution calorimetry; entries in parentheses are estimates.

Lanthanide-Actinide Comparison (kJ mol^{-1})

	$\Delta H(\text{soln})$	$\Delta G(\text{soln})$
$NdO_{1.5}(s) + 3H^+(\text{aq}) + Nd^{3+}(\text{aq}) + 3/2 H_2O(l)$	-221	-169
$PuO_{1.5}(s) + 3H^+(\text{aq}) + Pu^{3+}(\text{aq}) + 3/2 H_2O(l)$	-193	-145

coordination are ca. 20 kJ/mol more stable than structurally similar lanthanides in comparison with aqueous ions.

Enthalpies of solution represent differences between lattice enthalpies and hydration enthalpies. We hypothesize that actinide sesquioxides have enhanced covalent stabilization compared to lanthanide sesquioxides because of their more extended 5f orbitals, whereas the actinide dioxides do not manifest a significant stabilization. This conclusion can be conveniently tested (39) for the trivalent ions by comparing enthalpies of solution of similar hydrated salts; fortunately, a suitable pair is available in the trichloride hexahydrates. The enthalpy of solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (corrected to infinite dilution) is -38 kJ/mol (28), and the enthalpy of solution of $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$ is -35 kJ/mol (40). These nearly identical values reflect the similar coordination in the hydrated salts and hydrated aquo-ions: In the trichloride hexahydrates, the trivalent ion is coordinated to six water molecules and two chloride ions (41) and in the aquo ions the coordination is believed to be ninefold (42).

TABLE V.

Americium and Curium Oxides ^a	
<u>Trivalent</u>	
$\text{AmO}_{1.5}$	$\text{CmO}_{1.5}$
LiAmO_2	
$\text{SrAm}_2\text{O}_4, \text{BaAm}_2\text{O}_4$	
$\text{Ba}_2\text{Am}(\text{Nb}, \text{Ta}, \text{Pa})\text{O}_6$	
AmVO_4	
AmNbO_4	CmNbO_4
AmTaO_4	CmTaO_4
AmPaO_4	CmPaO_4
AmAlO_3	CmAlO_3
<u>Tetravalent</u>	
AmO_2	CmO_{2-x}
Na_2AmO_3	
SrAmO_3	
BaAmO_3	BaCmO_3

^aSee also paper by F. Weigel, this volume.

5. COMPLEX OXIDES OF AMERICIUM AND CURIUM

There are known complex oxides of Am(III), Am(IV), Am(V), and Am(VI) (table V) (10). As is the case with the lighter actinides U-Pu, the higher oxidation states are stabilized in complex oxides. There are no quantitative values for this stabilization, even in the case of BaAmO₃ (or even for BaPuO₃) (43). As of the time of writing, only a few complex oxides of Cm(III) and one of Cm(IV) are known (table V). [Note added in proof: see paper by F. Weigel, this symposium.] Although the perovskites BaMO₃ are significantly more stable than the binary oxides (43), the perovskite BaCmO₃ still showed significant Cm(III) from magnetic measurements (27). Quantitative results on the enthalpy of stabilization of numerous uranium, neptunium, and most recently plutonium complex oxides should guide efforts to synthesize new complex oxides of Am and Cm (44,45).

6. ACKNOWLEDGEMENT

This work was carried out under the auspices of the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract number W-31-109-ENG-38.

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