*Presented at IUPAC Conference on Chemical Thermodynamics, Hamilton, Ontario, Canada, August 13-17, 1984.
To be published in Journal of Nuclear Materials.*

CONF-840807--5

ENTHALPY OF FORMATION OF AMERICIUM SESQUIOXIDE; SYSTEMATICS OF ACTINIDE SESQUIOXIDE THERMOCHEMISTRY

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CONF-840807--5
DE85 000081

The enthalpy of formation of hexagonal Am_2O_3 at 298.15 K has been determined to be -1690.4 ± 7.9 kJ mol^{-1} by solution microcalorimetry. Systematic comparison of the measured enthalpies of formation of hexagonal Pu_2O_3 and Am_2O_3, monoclinic Cm_2O_3, and all lanthanide sesquioxides has been utilized to develop a predictive understanding of stability relationships among all actinide sesquioxides and other actinide species.

1. INTRODUCTION

As part of a systematic study of actinide oxide thermochemistry, and of structure-stability relationships in actinide compounds, we decided to determine the enthalpy of formation of Am_2O_3. This compound is one of only three actinide sesquioxides (the other two are Cm_2O_3 and Cf_2O_3) that can be prepared stoichiometrically at moderate temperature in order for solution calorimetry to be carried out efficiently. These data can then be used to predict similar properties for other actinide sesquioxides.

2. EXPERIMENTAL

Beginning with a stock solution of 50 mg of isotopically pure (>99.9 atom percent) ^{243}Am (half life 7370 y) as its trivalent aqueous ion, we purified it in two batches from all common cationic impurities by cation exchange using ultrapure reagents. For each batch, americium(III) oxalate was precipitated, calcined to AmO_2 at 625°C in oxygen, and reduced to Am_2O_3 in a H_2-N_2 gas mixture at 630 to 665°C. Complete reduction was assured by monitoring the weight loss and by handling the tan-colored sesquioxide only in a dry box with oxygen content ~ 5 ppm.

Both reduced oxide samples were found to be hexagonal Am_2O_3 by X-ray powder diffraction films taken 3 hr after completion of reduction; least-squares refinement yielded lattice parameters $a_0 = 3.818 \pm 0.001$ and $c_0 = 5.972 \pm 0.002$ Å. The best literature values, from $^{241}Am_2O_3$ films taken 1 hr after reduction, are $a_0 = 3.8155 \pm 0.0006$ and $c_0 = 5.975 \pm 0.002$ Å.[4] We note that previous studies of the phase transitions of Am_2O_3 (all of which used the shorter-lived isotope ^{241}Am, for which the half life is 433 y) suggest that at 675°C the body-centered cubic isomorph should be stable and that the bcc-hexagonal transition occurs between 700°C and 800°C.[1-4]

Calorimeter samples were weighed in the dry box on a Cahn 27 microbalance and sealed in thin-walled borosilicate-glass ampoules kindly furnished by Professor J. Fuger (University of Liege, Belgium).

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*Work performed under auspices of U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-ENG-38.

Solution calorimetry was carried out in a new vacuum-jacketed tantalum isoperibol microcalorimeter modeled upon established designs.[5-7] This instrument has a liquid capacity of 5 cm^3, a thermal leakage modulus of 0.006 min^{-1}, and a temperature noise level of 1 x 10^{-5} K (resulting in a thermal sensitivity of 4 x 10^{-4} J). Calibrations of the enthalpy of solution of Mg metal in 1 mol dm^{-3} HCl(aq) and of KCl in water agreed with literature values to better than ± 0.5 per cent. The enthalpies of solution of seven Am_2O_3 samples (each ~ 2 mg) in 6.0 mol dm^{-3} HCl(aq) at 298.15 K are reported in Table 1. These measurements and auxiliary data lead to $\Delta_f H_m^\circ(Am_2O_3,cr,hexag,298.15\ K)$ = -1690.4 ± 7.9 kJ mol^{-1} (Table 2).

3. CONCLUSIONS

Although the trivalent ions of all the actinides uranium through lawrencium have been observed in aqueous solution, only the sesquioxides of plutonium through einsteinium have been prepared. Enthalpies of formation of hexagonal Pu_2O_3, from high-temperature thermodynamic measurements,[8,9] and of monoclinic Cm_2O_3, from solution calorimetry,[10] have been reported. The results of this research permit us to assess and to predict the thermochemical properties

Table 1

Enthalpies of solution of Am_2O_3(cr,hexag) in 6.0 mol dm^{-3} HCl(aq) at 298.15 K.

Prep.	m(solute)/mg	$\Delta H/J^{k}$	$\Delta_{sol}H_m/(kJ\ mol^{-1}k)$
A	2.137	1.526	-381.4
A	2.029	1.529	-402.2
A	2.918	2.198	-402.2
A	2.472	1.807	-390.4
B	2.658	1.940	-389.8
B	3.426	2.567	-400.2
B	3.852	2.878	-399.0
		Mean	-395.0 ± 7.4 (95% confidence)

Table 2

Reaction scheme for enthalpy of formation of Am_2O_3 at 298.15 K

Am_2O_3(cr,hexag) + 6 HCl(6 mol dm^{-3}) = 2 $AmCl_3$(in 6 mol dm^{-3} HCl) + 3 H_2O(in 6 mol dm^{-3} HCl)	$\Delta H_1 = -395.4 \pm 7.4$ kJ[a]
Am(cr) + 3 HCl(6 mol dm^{-3}) = $AmCl_3$(in 6 mol dm^{-3} HCl)	$\Delta H_2 = -613.0 \pm 1.3$ kJ[b]
H_2(g) + 1/2 O_2(g) = H_2O(in 6 mol dm^{-3} HCl)	$\Delta H_3 = -286.6 \pm 0.4$ kJ[c]
2 Am(cr) + 3/2 O_2(g) = Am_2O_3(cr,hexag)	$\Delta_f H_m^\circ(Am_2O_3,\text{cr,hexag}) = -\Delta H_1 + 2\,\Delta H_2 + 3\Delta H_3 = -1690.4 \pm 7.9$ kJ mol^{-1} (95% confidence)

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[a] This research.

[b] J. Fuger and F. L. Oetting, The Chemical Thermodynamics of Actinide Elements and Compounds (IAEA, Vienna, 1976) Part 2.

[c] V. B. Parker, D. D. Wagman, and D. Garvin, U.S. Nat. Bur. Stand. Tech. Rep. NBSIR-75-968 (1976).

of actinide sesquioxides in comparison with the lanthanide sesquioxides.

Table 3 and Figure 1 show enthalpies of solution in dilute acid (calculated at infinite dilution) of all lanthanide sesquioxides as well as of $PuO_{1.5}$, $AmO_{1.5}$, and $CmO_{1.5}$. For comparison, enthalpies of solution in water of trichlorides are also shown in Figure 1. It is seen that the values for the actinides are significantly

Table 3

Thermochemical and Structural Data for Figure 1

	$\Delta_f H_m^\circ(M^{3+},aq)$	$\Delta_f H_m^\circ(MO_{1.5},cr)$	$\Delta_{soln} H_m^\circ(MO_{1.5})^g$	Molar Vol/cm^3 ^{f,h}
Y	-715 ± 15^a	-952.8 ± 1.1(cubic)^{d,f}	-191 ± 15	44.9
La	-709.4 ± 1.6^a	-897.1 ± 0.4(hexag)^{d,e,f}	-241 ± 2	49.6
Ce	-700.4 ± 2.1^a	-898.1 ± 1.4(hexag)^{d,e}	-231 ± 2	47.9
Pr	-706.2 ± 1.6^a	-913.8 ± 3.2(cubic)^f	-221 ± 4	52.2
		-911.7 ± 3.2(hexag)^{d,f}	-223 ± 4	46.7
Nd	-696.6 ± 1.7^a	-904.0 ± 0.5(hexag)^{d,e,f}	-221 ± 2	45.9
Pm		(hexag)		44.9
Sm	-691.1 ± 1.7^a	-911.8 ± 0.9(monocl)^{d,e}	-208 ± 2	45.0
		-913.7 ± 1.5(cubic)^{d,f}	-206 ± 2	49.2
Eu	-605.6 ± 2.3^a	-825.7 ± 1.7(monocl)^{d,e}	-209 ± 3	44.0
		-831.4 ± 1.9(cubic)^{d,e}	-203 ± 3	48.4
Gd	-687.0 ± 2.1^a	-907.8 ± 1.8(monocl)^{d,f}	-208 ± 3	43.3
		-913.4 ± 3.1(cubic)^d	-202 ± 4	47.6
Tb	-698 ± 6^a	-932.6 ± 3.8(cubic)^{d,e}	-194 ± 7	46.5
Dy	-696 ± 5^b	-931.6 ± 1.8(cubic)^{d,e,f}	-193 ± 5	45.6
Ho	-707 ± 8^a	-940.5 ± 2.4(cubic)^{d,e,f}	-195 ± 8	44.9
Er	-708.7 ± 1.8^c	-948.9 ± 0.9(cubic)^{d,e,f}	-189 ± 2	44.1
Tm	-705.2 ± 3.0^a	-944.3 ± 2.9(cubic)^{d,e,f}	-190 ± 4	43.4
Yb	-674.5 ± 3.0^a	-907.3 ± 1.1(cubic)^{d,e,f}	-196 ± 3	42.8
Lu	-702.6 ± 2.6^a	-939.1 ± 3.8(cubic)^{d,e,f}	-192 ± 5	42.2
U	-489.1 ± 3.8^i	-728(hexag)^j	-190^k	
Np	-527.2 ± 2.1^i	-761(hexag)^j	-195^k	
Pu	-592.0 ± 2.1^i	-842 ± 10(hexag)^l	-179 ± 10	45.6^m
		-828(hexag)^n	-193	45.6^m
Am	-616.7 ± 1.3^i	-845 ± 4(hexag)^p	-200 ± 4	45.4^p
Cm	-615.0 ± 5.0^i	-841 ± 6(monocl)^q	-203 ± 6	45.8^q

Table 3 (continued)

[a] L. R. Morss, Chem. Revs. 76 (1976) 827.

[b] Reassessed from L. R. Morss, Chem. Revs. 76 (1976) 827 and L. R. Morss and J. A. Fahey, Proc. 12th Rare-Earth Res. Conf., Vol. 1 (1976) 443.

[c] J. Fuger, L. R.Morss, and D. Brown, J. Chem. Soc. Dalton (1980) 1076.

[d] K. A. Gschneidner, Jr., N. Kippenhan, and O. D. McMasters, IS-RIC-6, Institute for Atomic Research, Iowa State University, Ames, Iowa (1973).

[e] R. H. Schumm, D. D. Wagman, S. Bailey, W. H. Evans, and V. B. Parker, U. S. Nat. Bur. Stand. Tech. Note 270-7, Washington, D. C., 1973.

[f] Gmelin Handbuch der Anorg. Chemie, Seltenerdelemente, Teil C1, pp. 118-122 and 131-133, Springer-Verlag, Berlin, 1974.

[g] For the reaction $MO_{1.5}(cr) + 3H^+(aq) \rightarrow M^{3+}(aq) + 1.5\ H_2O(\ell)$, $\Delta_{soln}H_m^\circ = \Delta_f H_m^\circ(M^{3+},aq) + 1.5\ \Delta_f H_m^\circ(H_2O,\ell) - \Delta_f H_m^\circ(MO_{1.5},cr)$.

[h] L. Eyring, The Rare Earth Oxides, in Handbook on the Physics and Chemistry of Rare Earths, ed. K. A. Gschneidner, Jr. and L. Eyring, Vol. 3, Ch. 27, North-Holland, Amsterdam (1978).

[i] J. Fuger and F. L. Oetting, The Chemical Thermodynamics of Actinide Elements and Compounds (IAEA, Vienna, 1976) Part 2.

[j] Calculated from $\Delta_f H_m^\circ(M^{3+},aq) + 1.5\ \Delta_f H_m^\circ(H_2O,\ell) - \Delta_{soln}H_m^\circ$.

[k] Estimated from Figure 1.

[l] Reference 9.

[m] H. E. Flotow and M. Tetenbaum, J. Chem. Phys. 74 (1981) 5269.

[n] Reference 11.

[p] This research.

[q] Reference 10.

less exothermic than the values for the corresponding lanthanides. The result of an independent assessment of $\Delta H_f^\circ(PuO_{1.5},cr)$[11] by Besmann and Lindemer is also plotted in Figure 1 and is seen to be much more consistent with the $AmO_{1.5}$ and $CmO_{1.5}$ data than is the $PuO_{1.5}$ data point from the work of Chereau et al.[9] We conclude that the actinide sesquioxides are slightly more stable than the lanthanide sesquioxides in comparison with their aqueous ions. The right side of Figure 1 shows that similar behavior is observed in the hexagonal trichlorides. These systematics allow us to predict $\Delta_f H_m^\circ(UO_{1.5},cr,hexag) = -728$ and $\Delta_f H_m^\circ(NpO_{1.5},cr,hexag) = -761$ kJ mol^{-1} (Table 3).

In Figure 2 the trivalent correlation function P(M) is plotted for lanthanide and actinide aqueous ions, sesquioxides, and trichlorides.[12,13] This figure has been updated by inclusion of a new measurement of $\Delta_f H_m^\circ(Cf^{3+},aq) = -577 \pm 5$ kJ mol^{-1}[14] and by newly assessed energy levels of Am(g)f^6ds^2, $^8H_{3/2}$, at 10684 cm^{-1}, and Bk(g)f^8ds^2, $^8G_{13/2}$, at 9141 cm^{-1}.[15] The P(M) points for the actinides are shifted systematically from those of the lanthanides and appear to fall nearly on a single straight line rather than a V-shaped line. Our $\Delta_f H_m^\circ(Am_2O_3,cr)$

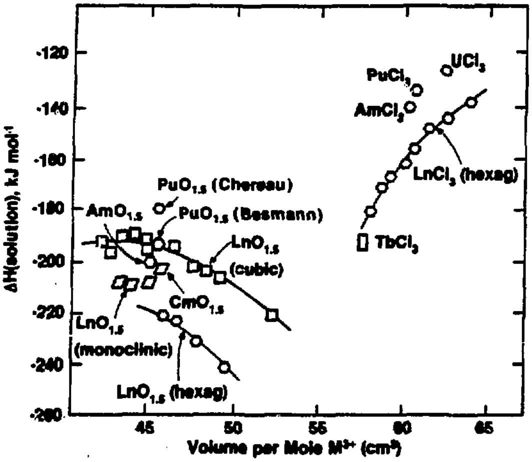

FIGURE 1
Enthalpies of solution of lanthanide and actinide sesquioxides and trichlorides in water as a function of molar volume.

and the new energy level assignments yield more consistent P(M) plots for actinides than did earlier studies.[12,13]

It is possible to extend the correlations of Figures 1 and 2 by measuring the enthalpy of solution of Cf_2O_3, using milligram quantities of ^{249}Cf isolated from ^{249}Bk produced at Oak Ridge National Laboratory. This project has been initiated in our laboratory. It is unlikely that solution calorimetry can be employed for determination of $\Delta_f H^\circ_m(Pu_2O_3)$ or $\Delta H_f H^\circ_m(Bk_2O_3)$ because of the extremely high temperatures required for reduction of their dioxides. Since classical methods cannot be used for thermodynamic measurements on compounds of elements beyond Cf, the measurements on Am_2O_3, Cm_2O_3, and Cf_2O_3 will be useful in predicting thermochemical properties for trivalent compounds of heavier elements as well as predicting $\Delta_f H^\circ_m$ for U, Np, and Bk sesquioxides.

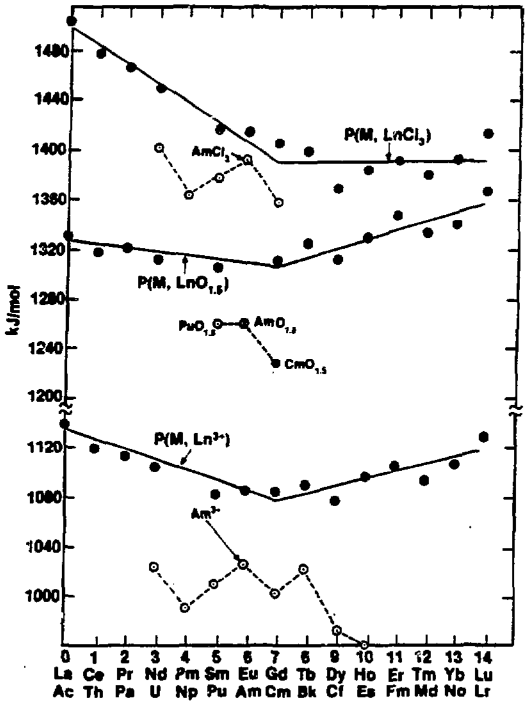

FIGURE 2
Correlation function P(M) for lanthanide and actinide trivalent species.

The estimated values of $\Delta_f H^\circ_m$ for U_2O_3 and Np_2O_3 lead, as expected, to highly positive free energies for any possible syntheses of these oxides and to highly negative free energies for their disproportionation, e.g.[16]

$$2\ Np_2O_3(s) \rightarrow 3\ NpO_2(s) + Np(s) \qquad \Delta G^\circ = -169\ kJ$$

The instability of these sesquioxides is confirmed by their impossibility of preparation. Since Figure 1 shows essentially constant differences between enthalpies of

Table 4

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

M	$M^{3+}(aq)$[a]	Diff.	$MO_{1.5}(s)$[a]	Diff.	$MCl_3(cr,hexag)$[b]
U	-489	-239	-728	-138	-866
Np	-527	-234	-761	-137	-898
Pu	-592	-236	-828[c]	-132	-960
Am	-617	-228	-845	-133	-978
Cm	-615	-226	-841	-133	-974

[a] Same references as Table 3.

[b] J. Fuger, V. B. Parker, W. N. Hubbard and F. L. Oetting, The Chemical Thermodynamics of Actinide Elements and Compounds (IAEA, Vienna, 1983), Part 8.

[c] Recommended by Reference 11 and consistent with our results.

solution of actinide sesquioxides and trichlorides, we compare the differences between enthalpies of formation in Table 4. The constancy of these differences confirms our confidence in our estimates of $\Delta_f H_m^\circ$ for U_2O_3 and Np_2O_3 as well as Besmann's[11] estimate for Pu_2O_3.

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