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High-temperature vaporization of transplutonium oxides

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Abstract

A systematic evaluation of the vaporization–decomposition behavior of the actinide oxides as a function of atomic number has been initiated. This work has provided important clues for understanding the underlying roles played by the actinide's f-electrons in this process. Studies of the actinide sesquioxides have determined that the major factor in determining their primary mode of vaporization is the magnitude of dissociation energies of the monoxides. It has been shown that the dissociation energy of the monoxide is linked to the promotion energy of the actinide element's f-electrons. Establishing this relationship has now provided both a predictive and a correlative approach to understanding the vaporization processes of the actinide sesquioxides. Results from our initial vaporization studies of selected transplutonium sesquioxides were found to be in accord with these predicted processes. This systematic correlation, recent information about the melting points of berkelium and californium sesquioxides, and a summary of the initial high-temperature vaporization behaviors of several transplutonium sesquioxides are presented here.

1. Introduction

A variety of oxidation states is observed in actinide oxides with the highest oxygen stoichiometry for a binary oxide in the series achieved with UO_3. This variation in oxidation states results from the close proximity of the 7s, 6d and 5f electrons in the actinides and the changing electronic nature of the elements across the series. With actinide metals, the largest number of electrons used in bonding occurs for the protactinium–plutonium group, where there is significant overlap of the 5f-orbitals with the valence electrons. This electronic complexity carries over to the oxide systems of protactinium, uranium and neptunium, which display binary oxides with greater oxygen stoichiometries than do higher members of the series. After neptunium, the highest binary oxide formed is the dioxide and this stoichiometry is known for all of the actinides from thorium through californium. However, the sesquioxide tends to become the primary oxide of the transplutonium elements, and is probably the highest binary oxide that will form for the elements beyond californium in the series (nobelium, element 102, may only form a monoxide).

If actinium is excluded from consideration, the first actinide sesquioxide is experienced at plutonium when progressing across the actinide series. With the possible exception of berkelium dioxide, the dioxides of the transplutonium elements are unstable at the elevated temperatures where vaporization would be encountered. In comparison with the lanthanide oxides, essentially only cerium, praseodymium and terbium form dioxides, and the thermal stabilities of the latter two are insufficient to study their vaporization behavior (*e.g.* terbium dioxide begins to decompose at 300 °C). As many of the lanthanide and actinide sesquioxides have physicochemical similarities, it is useful to compare their high-temperature vaporization–decomposition behavior.

The thermodynamic properties of the actinide oxides are not as well established as are those for the lanthanides, with the possible exceptions of the uranium and plutonium systems. Most of the studies concerning vaporization of actinide oxides have been on the thorium to plutonium oxides; only very limited experimental data are available for transplutonium oxides. The vaporization behaviors of the dioxides of thorium through neptunium [1], the dioxide and lower oxides (*e.g.* $PuO_{1.5}$, $PuO_{1.61}$, $PuO_{1.92}$) of plutonium [1, 2] and oxides of protactinium [3] have all been studied thoroughly. Vaporization of their dioxides generates gaseous metal atoms, monoxides and at times dioxides (especially in the cases of UO_2 and PaO_2) but the monoxides are frequently the major vapor species. With the lanthanide and actinide sesquioxides, the most probable vapor species are the monoxide and/or atomic atoms, although other species as M_2O, M_2O_2, M_2, etc., have been observed with the more extensively studied lanthanide oxides [4].

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The stabilities of the lanthanide and actinide sesquioxides are manifested by very large negative standard free energies of formation [5], often being more negative than for most other known oxides (*e.g.* CaO). In general, the lanthanide sesquioxides have more negative enthalpies of formation than do the actinide sesquioxides. Lower valence states are expected to increase in stability at higher temperatures, which accounts for the fact that it is the sesquioxide which is commonly encountered in high-temperature vaporization studies of these elements' oxides. From vaporization studies it is possible to determine enthalpies of decomposition and formation for the oxides, which are important thermodynamic parameters in the overall systematic understanding of actinide chemistry. Through the use of a correlation [1] it is possible to obtain indirectly enthalpies of solution of the An^{3+} aquo ions from the enthalpies of formation of the oxides. Because of scarcity and high specific radioactivity, it is not feasible to obtain the enthalpies of solution directly for oxides of the elements higher in the series than californium, although enthalpies of formation can be acquired for einsteinium and fermium oxides via special vaporization techniques. Thus, using this correlation it is possible to extrapolate enthalpies of solution for einsteinium and fermium from the experimental enthalpies of formation determined in vaporization studies.

The most complete report to date regarding vaporization of transplutonium oxides concerns curium sesquioxide [6]; however, the primary vaporizing species reported, CmO, was not determined directly by mass spectroscopic identification but rather inferred from thermochemical assessments. We have recently initiated vaporization studies of several transplutonium oxides and report here the initial results obtained for californium, berkelium and einsteinium sesquioxides. These studies have employed target collection techniques together with Knudsen effusion mass spectrometry, which allowed direct identification of the vapor species. Data from our studies, together with the published results from curium [6] and the lighter actinide oxides [1–3], are used to develop systematic rules for predicting the main vaporization behavior for the actinide oxides.

2. Experimental details

2.1. Materials

The transplutonium elements used in this work were obtained from isolation campaigns using products formed in the High Flux Isotope Reactor at Oak Ridge National Laboratory. The sesquioxides were prepared from chloride solutions of the actinides by precipitating their oxalates and calcining these air-dried salts to 1000 °C in air. The oxide products were then heated in vacuum, or hydrogen in the cases of americium and berkelium, to form their stoichiometric sesquioxides. X-ray analyses of the latter materials confirmed that the products were the desired sesquioxides. Approximately 5 mg of the actinide oxide (a mixture of einsteinium–californium sesquioxides was used for the einsteinium work) were transferred to a thorium dioxide cell (3 mm diameter, 6 mm long) for each of the Knudsen effusion experiments.

2.2. Instrumentation

A 1000 AMU Balzers quadrupole mass spectrometer (OMG 511) together with various associated vacuum and Knudsen cell components are installed in a helium-filled glove box for carrying out high-temperature studies with the actinides. The helium atmosphere allows air–moisture materials to be handled and was not necessary for these oxide studies, although it avoided contamination of the vacuum system with moisture during loading–unloading operations. The Knudsen cell system is also equipped with a target collection device and an on-line, solid-state-surface detector for alpha counting and energy analysis. This allows the collection of a condensed sample of the effusing product(s) together with *in situ* alpha radioanalysis; the targets may also be analyzed subsequently outside the vacuum system by various conventional radioassay techniques. The mass spectrometer is coupled to a PC (486/50 MHz) via a Teknivent Vector Two interface for data collection and analysis.

2.3. Analysis of the vaporization data

The rates of evaporation of the vapor species from the congruently vaporizing sesquioxides over the temperature range 1400–2275 K were measured by the effusion method, which employed either the target collection method, the mass spectrometer signals, or both. The cell temperatures were measured by two calibrated, independent, micro-optical pyrometers. The vapor pressures of the condensed-phase products were calculated using the standard effusion formula, $P_{atm} = \text{constant}(m/t)(1/A)(T/M)^{1/2}(1/CG)$, where m/t is the measured effusion rate ($\mu g\ s^{-1}$) of a molecular weight M at a temperature T (K); CG is the collection geometry and A is the office orifice area. The method of Freeman and Searcy [7] was used to define the fraction of effusing atoms that struck the collection targets under our experimental conditions. Targets were employed for determining the mass of the vaporized material that transferred per unit time and for calibrating the mass spectrometer outputs. The effusion cell holder was constructed of tantalum but the sample cell was of high-density thorium dioxide. Visual examinations of the sample cells and products after the vaporization studies did not indicate any reaction had taken place between the actinide sesquioxides and the thorium dioxide crucible. The tantalum components likewise did not show evidence of reaction or corrosion.

3. Discussion and results

3.1. General

In examining the vaporization–decomposition behavior of the transneptunium sesquioxides it is informative to consider the comparable behavior of the lanthanide sesquioxides, which have been studied more extensively. This is appropriate as there are several types of comparable behavior (*e.g.* phase behavior) between the sesquioxides of the two series. Major differences are known to exist between the trend in melting points with Z, as well as the melting temperatures, for the second-half members of each series. The melting points of the transcurium sesquioxides are lower and decrease in temperature when progressing to members with a higher atomic number [8]. Differences are also known to exist between the phase behaviors of these sesquioxides [8]. However, these differences in phase behavior and melting points do not affect appreciably the vaporization behavior of the oxides, as the changes in enthalpy between polymorphic forms, or when progressing from the solid to the liquid states, are expected to be relatively small (few kilojoules per mole).

It is worthwhile to comment here about the nature of the californium and berkelium residues following the vaporization studies, given the apparent low melting points that have been reported for these oxides [8]. Visual inspection of these oxide residues showed that the original powdered materials had melted, or at least sintered, to a single mass at or below the maximum temperature (2275 K) reached in the studies. Melting points of 2193 K (berkelium sesquioxide) and 1923 K (californium sesquioxide) have been reported previously [8]. Although these new data do not define exact melting points, they do establish a maximum melting temperature and support the fact that the melting points of these actinide sesquioxides are significantly lower than the melting points for the comparable transgadolinium sesquioxides, which are greater than 2600 K.

3.2. Vaporization modes and monoxide dissociation energies

Two of the major vaporization processes for the lanthanide sesquioxides [9] are shown in reactions (1) and (2) (where Ln = lanthanide):

$$Ln_2O_3(s) \longrightarrow LnO(g) + O(g) \qquad (1)$$

$$Ln_2O_3(s) \longrightarrow 2Ln(g) + 3O(g) \qquad (2)$$

Reaction (1) is characteristic of the lighter lanthanides while reaction (2) tends to be favored with the heavier lanthanides and especially with europium and ytterbium. It is significant that the latter two lanthanide elements are divalent metals and there is a higher probability for these elements to attain a divalent state in compounds. The vaporization of europium and ytterbium sesquioxides by reaction (2) rather than reaction (1) is not due directly to the availability or stability of a divalent state for these lanthanides but arises because of the lower stability of their monoxides.

From correlations established with the lanthanide sesquioxides [10] it has been established that the generation of LnO from sesquioxides (reaction (1)) is associated with lanthanides whose monoxides have large dissociation energies, while the lanthanides whose monoxides have low dissociation energies tend to produce atomic vapor during the vaporization of their sesquioxides. The dissociation energies for the different gaseous LnO products have been shown to vary irregularly across the series [10] and parallel trends observed with the enthalpies of vaporization for the metals. This led to associating these variations, for both the monoxides and metals, to the electronic nature of the elements themselves. Given the significance of these systematic results, it was deemed useful to develop working values for monoxide dissociation energies for the transplutonium elements, which would be valuable in evaluating the vaporization behavior of their sesquioxides.

The nature of the bonding in the monoxides is not understood fully, which makes comparisons between the enthalpies of formation and stabilities of lanthanide and actinide monoxides more difficult. Ames *et al.* [10] adopted a simple ionic model for the lanthanide monoxides which involved $Ln^{2+}O^{2-}$ components; a slightly different but perhaps a more realistic model involving both ionic and covalent bonding was proposed by Murad and Hildenbrand [11]. In both models the non-monotonic variation in the monoxide dissociation energies across the lanthanide series was related to the electronic promotional energies ($4f^n \rightarrow 4f^{n-1}5d$) for the elements, which suggested that this excitation energy was an important factor in the energetics of the monoxide bonds. The rationale for this relationship is that the ionic structure (*e.g.* $M^{2+}O^{2-}$) predominates in the monoxides and involves ds-electrons (or d-electrons) rather than two s-electrons (that is, at least one 6s-electron is therefore non-bonding in the monoxides). One piece of supporting evidence for this concept is the very close similarity of the ionization potentials for the lanthanide metals and the monoxides, where both potentials reflect the loss of a 6s-electron [11].

A model emerged [10, 11] for the lanthanides where the dissociation energy of an individual monoxide should be the difference between some base energy $D_{0\ \mathrm{base}}$

and a ΔE value. As a ds-state (or a d-electron state) is expected for the monoxide bonding, the promotion of an f-electron to a d-state would be required; this energy becomes the ΔE value. The base energy value is defined by the elements whose configuration already had a d-electron (*e.g.* the trivalent lanthanide metal atoms, lanthanum, gadolinium and lutetium). Thus, one obtains the following relationship [10, 11]:

$$D_0^\circ{}_{\text{predicted}} = D_0^\circ{}_{\text{base}} - \Delta E \qquad (3)$$

We have applied the above concepts to the actinide sesquioxides to estimate monoxide dissociation energies for the transplutonium elements, which are difficult to obtain experimentally. Our estimated values and published values for the lanthanide monoxides [11] are given in Table 1. The actinide sesquioxides, or metal atoms which have a ground state d-electron level are actinium, curium and lawrencium and these elements are selected for establishing the dissociation base energies. Of these, the only available datum is for curium monoxide [6]. However, the couples, actinium–lanthanum and lutetium–lawrencium, are expected to have the same general configurations ($5d6s^2/6d7s^2$ and $4f^{14}5d6s^2/5f^{14}6d7s^2$; the latter configuration for lawrencium is probably a few tenths of an electronvolt above the relativistic ground state $5f^{14}7s^27p^{1/2}$), as well as having similar physical properties. Based on the above, the base energies (monoxide dissociation energies) of lanthanum and lutetium monoxides were substituted for the actinium and lawrencium monoxide base energies. A relationship of base energy as a function of atomic number was then created for the actinides, as had been done for the lanthanides [11].

The ΔE values for the actinides (their f-electron promotion energies) were selected from values given by Brooks *et al.* [13]. Substituting these values in eqn. (3) provides the predicted monoxide dissociation energies for the transplutonium elements shown in Table 1. These calculated values are also plotted in Fig. 1 together with the known dissociation energies for the lanthanide monoxides and the earlier actinide monoxides.

One can establish qualitatively the probable vaporization modes for the transplutonium sesquioxides using Fig. 1 together with the reported vaporization behaviors of the lanthanide sesquioxides [10, 14]; these modes can then be compared with the initial experimental data for the transplutonium oxides. For the lanthanide oxides it is known that europium and ytterbium sesquioxides vaporize mainly by generation of atomic vapor (reaction (2)); lanthanum, gadolinium and lutetium sesquioxides vaporize by generation of monoxides; and the sesquioxides from dysprosium to erbium vaporize by a mixture of atomic metal and monoxide (approx-

TABLE 1. Dissociation energies for the monoxides

Oxide	D_0° (kJ mol^{-1})[a]	Oxide	D_0° (kJ mol^{-1})
LaO	794	AcO	(794)
CeO	786	ThO	891[b]
PrO	736	PaO	788[c]
NdO	699	UO	774[b]
PmO	(711)	NpO	736[b]
SmO	569	PuO	703[b]
EuO	469	AmO	(550)
GdO	711	CmO	728[d]
TbO	690	BkO	(598)
DyO	611	CfO	(498)
HoO	602	EsO	(460)
ErO	602	FmO	(443)
TmO	510	MdO	(418)
YbO	397	NoO	(268)
LuO	665	LrO	(665)

[a] Ref. 11.
[b] Ref. 12.
[c] Ref. 3.
[d] Ref. 6.
(This work).

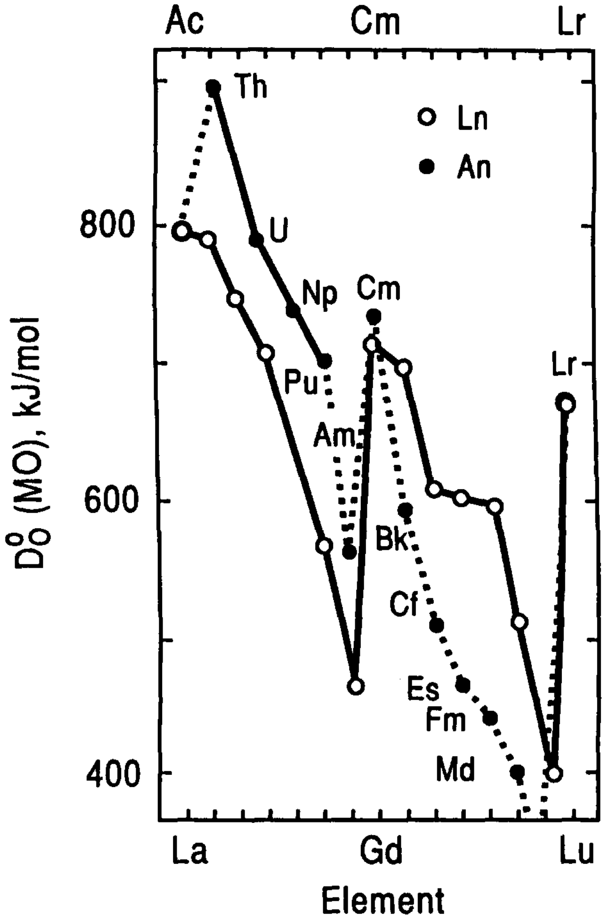

Fig. 1. Monoxide dissociation energies for the lanthanide and actinide oxides.

imately 1:2 metal:monoxide). Using the lanthanide sesquioxides' monoxide dissociation energies and vaporization behavior, assignments for probable vaporization behavior can be made by drawing arbitrary grid lines at 800, 700, etc. kJ mol^{-1} in Fig. 1. Thus, above a dissociation energy of 700 kJ mol^{-1}, the vaporization product would be expected to be a monoxide; below 600 kJ mol^{-1}, atomic vapor should become increasingly important (mixtures of atomic vapor and monoxide would be encountered); and with energies less than 500 kJ mol^{-1}, atomic vapor should be the main product. Using the calculated dissociation energies for the actinides in Table 1 in conjunction with Fig. 1, the projected vaporization modes for the transplutonium sesquioxides are as follows: berkelium sesquioxide, mixtures of atomic vapor and monoxide (like holmium sesquioxide); curium sesquioxide, monoxide; americium sesquioxide, mainly atomic vapor but also some monoxide; californium, einsteinium, fermium, mendelevium and nobelium sesquioxides, atomic vapor; lawrencium sesquioxide, monoxide. It is not likely that experiments involving the latter three oxides will be undertaken to confirm these predictions, owing to the scarcity and short half-lives of these elements, but these predictions can be compared with our initial findings for the other transplutonium sesquioxides.

3.3. *Vaporization of transplutonium sesquioxides*

Although actinium sesquioxide is known, vaporization data do not exist for it. The next known sesquioxide that forms in the series is plutonium sesquioxide and it has been well studied. For the beta-form of plutonium sesquioxide the vaporization process proceeds mainly via generation of plutonium monoxide [2, 15, 16]. Only limited work has been done on the americium sesquioxide's vaporization process [17–19] but experimental data indicate it vaporizes principally by the generation of americium atoms (reaction (2)). In contrast, curium sesquioxide vaporizes with the evolution of its monoxide [6], in accord with its higher monoxide dissociation energy. From our vaporization studies we have observed that californium and einsteinium sesquioxides vaporize via evolution of their atomic vapors. Our preliminary studies on berkelium sesquioxide show it produces a mixture of atomic vapor and its monoxide. The vaporization modes for these transneptunium sesquioxides and the approximate M-to-MO (metal-to-monoxide) ratios observed at a temperature of 1800 K are summarized in Table 2.

TABLE 2. Main vaporization modes for selected transneptunium sesquioxides

Oxide	Product	M-to-MO[a] ratio
Am_2O_3	Am	>10
Cm_2O_3	CmO	<0.1
Bk_2O_3	Bk, BkO	≈8
Cf_2O_3	Cf	>10
Es_2O_3	Es	>10
Fm_2O_3	(Fm)	–

[a]Ratio of metal to monoxide at a temperature of 1800 K.

Our data for the sesquioxides of californium, einsteinium, berkelium and the reported mode of vaporization for curium sesquioxide [6] are in good accord with our predicted modes based on the calculated monoxide dissociation energies. The preliminary experimental data for americium sesquioxide [17–19] differ in that only atomic vapor has been observed, while a mixture of atomic vapor and monoxide is predicted from Fig. 1. The predictions for the vaporization of the transeinsteinium sesquioxides are reasonable.

From the relationship of partial pressures of a species over a congruently vaporizing sesquioxide as a function of temperature, second law enthalpies of decomposition can be deduced for the mean temperature of the experiment. Standard free energies of formation can be calculated for each temperature studied, using thermodynamic values from the literature in conjunction with the experimental pressures. Enthalpies of formation can be calculated using these free energies and entropy values known for comparable sesquioxides; free energy functions allow enthalpies to be converted to a standard temperature (*e.g.* 298 or 0 K). Tentative values for the enthalpies of formation of berkelium, californium and einsteinium sesquioxides at 298 K obtained in our initial studies fall in the range −1650 to −1700 kJ mol^{-1} of sesquioxide. Finalized values will be published at a later date following additional experimental measurements. The only other experimental data known to have been reported is the enthalpy of formation of californium sesquioxide (−1653 kJ mol^{-1}) obtained from solution calorimetry experiments [20].

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