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OXYGEN DISSOCIATION PRESSURES AND PHASE
BEHAVIOR IN THE TRANSPLUTONIUM OXIDES^(a)

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Oxygen Dissociation Pressures and Phase Behavior in the Transplutonium Oxides

T. D. Chikalla and R. P. Turcotte

Abstract

The results of recent oxygen vapor pressure measurements over nonstoichiometric AmO_x , CmO_x , and BkO_x are presented. These include derived information concerning the phase relations and partial thermodynamics of oxygen solution over the range $1.5 < x < 2.0$ and $300 < T < 1200^\circ\text{C}$.

The americium - oxygen system has been examined by thermogravimetric techniques in the single phase α region for $1.80 < x < 2.00$ to yield relative partial molar heat and entropy data. Supporting information obtained by quench methods and x-ray diffraction analysis extend the results to lower compositions and, additionally, demonstrate the existence of a bcc σ phase over a wide composition range. Phase relations in the curium - oxygen system have been defined by a series of isobars in the pressure range $2 < p_{\text{O}_2} \text{ (mm)} < 730$. In addition to α and σ phases, compounds of more narrow compositional width are seen at $\text{CmO}_{1.72}$ and $\text{CmO}_{1.82}$, and a plausible phase diagram is constructed. Differences obtained on two curium isotopes of greatly different radioactivity are discussed. The berkelium - oxygen system has been examined using a

novel capacitance manometer system and a 1.2 mg sample. A set of five isotherms was obtained over the range $852 < T (^{\circ}\text{C}) < 1150$. The isotherms show a regular variation across α and σ regions separated by a diphasic field at $x \sim 1.79$. In addition, a narrow two-phase region exists between $\text{BkO}_{1.91}$ and $\text{BkO}_{1.93}$. Certain similarities are shown to exist between this and certain other fluorite related ternary oxide systems.

In addition, melting behavior of the di- and sesquioxides and polymorphism in the sesquioxide is described over the entire actinide series.

Key Words

Actinide oxides, actinide sesquioxides, americium oxides, berkelium oxides, curium oxides, melting points of actinide oxides, nonstoichiometry, oxides, thermodynamics.

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1. Introduction

The recent investigations of transplutonium oxides in this laboratory and others have progressed to the point at which compilation of the existing information is of value. Indeed, understanding of the actinide oxide systems in the $M^{3+} - M^{4+}$ regime is yet primitive by comparison to other areas of solid state science. In detail, the behavior in each of the systems for $1.5 < x < 2.0$ in MO_x (where $M = Am, Cm, Bk$) is markedly different and we observed the systematic trends ascribed to these elements as a family only in a coarse comparison.

At the end member compositions ($x = 1.500$ and $x = 2.000$), the behavior through the series is more regular, and phase relations (polymorphism) in the sesquioxide are now well documented for both the actinide and lanthanide series [1,2].¹ It is our primary interest to consider the phase behavior in what would normally be considered the nonstoichiometric field where $1.5 < x < 2.0$ and the

¹ Figures in brackets indicate the literature references at the end of this paper.

sesquioxide is of the fluorite related C-type structure. In an effort toward completeness, the high temperature phase diagram and melting behavior of the stoichiometric end member oxides is discussed in the first section. We call attention to a previous discussion of the fluorite related actinide oxide systems that serves as a basis in some respects for the extension presented here [3].

2. M_2O_3 and MO_2

The melting behavior of the actinide dioxides and sesquioxides has recently been reviewed [2]. In addition, polymorphism in the sesquioxide has been correlated with ionic radii for both the actinide and lanthanide series.

There are no melting point data for oxides higher than curium. As shown in figure 1, a reasonably linear decrease in the melting point of the dioxides with increasing Z is observed, while the opposite trend is true for the sesquioxides. The heats of formation of the actinide dioxides decrease in a similar manner which reflects the lowering of bond energies with increasing atomic number. The increasing stability of the sesquioxides with increasing Z parallels behavior in the lanthanides, where the melting point increases to a maximum at Gd_2O_3 , whereafter it remains essentially constant [1]. If the same behavior occurs in the actinides, this maximum may exist at Cm_2O_3 , which, based on electronic configuration, is the actinide homologue of Gd_2O_3 .

Phase transformation behavior for both lanthanide and actinide sesquioxides shows a good correlation of the thermal stability domains of the various polymorphs and ionic radii (figure 2). The five crystallographic modifications for the sesquioxide include A (hexagonal), B (monoclinic), C (cubic), H (hexagonal), and X (unknown) forms. It is interesting to note that the high temperature H-form sesquioxide is probably the only crystal structure common to all of the lanthanide and actinides with the exception of Lutetium. Relevant to later discussion, the metastability of the C-type structure relative to $C \rightarrow B$ or $C \rightarrow A$ transitions in the $< 1000^\circ\text{C}$ temperature range should be pointed out. This is really to be expected at these temperatures, where necessary cation movement is slow.

3. AmO_x

The early dissociation pressure measurements of Asprey and Cunningham [4] with a milligram-size sample demonstrated the existence of an AmO_{2-x} (α) phase to at least $x = 0.15$. More recent work at lower temperatures by Chikalla and Eyring [5] by a tensimetric method agreed with the early measurements and allowed accurate determination of the partial thermodynamic quantities. The isotherms (figure 3) are smooth curves over the entire measured range $1.80 < \text{O/Am} < 2.00$. Thermodynamic equilibrium was demonstrated at all but the lowest temperature where data were taken in reduction only. There is a notable change in slope

in the isotherms at $O/Am = 1.98-1.96$, reflecting a change in defect structure, at this time undefined. The partial molar entropy and enthalpy obtained by the relations

$$\Delta \bar{S}_{O_2} = - \partial (\Delta \bar{G}_{O_2}) / \partial T \quad (1)$$

$$\Delta \bar{H}_{O_2} = R \partial (\ln p_{O_2}) / \partial (1/T) \quad (2)$$

are given in figure 4, again indicating a larger rate of change at the high composition end of the α field.

An x-ray diffraction analysis of quenched samples was made across the entire compositional width $1.50 < O/Am < 2.00$ [6]. These show the formation of a bcc phase (σ) in the range $1.50 < O/Am < 1.67$. Samples annealed in the α region could not be quenched but always gave a two-phase mixture of $AmO_{2.00}$ and a phase of estimated composition $AmO_{1.8}$. By implication, it was suggested that another diphasic region must exist in the interval $1.67 < O/Am < 1.8$.

These results may be compared to a recent investigation of the system by ceramographic and DTA methods by Sari and Zamorani [7]. A phase diagram is suggested which closely parallels that for the PuO_x system but which is at some variance with these earlier data. A miscibility gap of two α phases shows closure at $1000^\circ C$. The low composition phase intersects the σ field at $O/Am \approx 1.68$, while the high composition phase approaches $O/Am \approx 1.98$ at a temperature of $\sim 850^\circ C$.

As discussed above, the x-ray work [6] would suggest a greater complexity in the 1.67-1.80 region and that the σ field extends to the 1.50 composition rather than to 1.63 as indicated by Sari and Zamorani [7]. Clearly, these differences can be resolved only by equilibrium studies over the full range of composition, most importantly by high temperature diffraction methods.

4. CmO_x

Posey et al. [8] reported the first thermograms for the decomposition of CmO_2 , followed shortly after by Mosley [9], whose effort concentrated on the sesquioxide as a candidate isotopic fuel. Chikalla and Eyring [10] published results of a detailed study of dissociation pressure - composition - temperature relations obtained using a thermobalance technique. Most recently, a similar study of $^{248}\text{CmO}_x$ has been completed on a sub-milligram sample using an automated capacitance manometer system [11]. All previous studies were made on ^{244}Cm , which is an alpha emitter with a half life of 18.1 years compared to 4.7×10^5 years for the ^{248}Cm isotope. It was the objective of this study to assess possible differences in the chemical nature of the Cm-O system due to radiation damage.

Since only one milligram of ^{248}Cm oxide was available, classical microbalance methods for studying dissociation behavior could not be used. The differential capacitance manometer system employed (figure 5) is capable of detecting gaseous uptake or

evolution of $< 10^{-10}$ moles of gas. The major problem in realizing an accuracy approaching this sensitivity level is the elimination of system effects either due to physical or chemical changes. The capabilities of the system and detailed information concerning its construction and reduction of data have been reported [12].

For the $^{248}\text{CmO}_x$ sample, isobaric traces were recorded with a sensitivity which allowed composition to be estimated to 0.001 in x . In the present case, the assumption of three (P-T-x) points ($x = 1.500, 1.714, 2.000$) was used to fix correction curves (ΔP_{system} versus T) for each isobar independently of any other run. The corrections were very small at lower pressures (< 50 mm Hg), but at 760 mm Hg, approached values as high as 30% of the pressure change due to complete sample reaction. Analysis of the data suggests an uncertainty of ± 0.003 in O/Cm for the stoichiometry measurement.

The $^{244}\text{CmO}_x$ results [10] demonstrated the existence of a number of intermediate phases in close parallel to the behavior of the rare earth systems CeO_x , PrO_x , and TbO_x , now well established. (See [3] for references.) Representative isobars are given in figure 6. The decomposition is seen to proceed through a narrow region of CmO_{2-x} (α), to phases $\text{CmO}_{1.82+x}$ (δ) and $\text{CmO}_{1.72}$ (ϵ) and finally $\text{CmO}_{1.5+x}$ (σ). Complete reduction to the sesquioxide was not achieved even in a H_2 atmosphere.

These results may be compared to isobars of the $^{248}\text{CmO}_2$ decomposition at an oxygen pressure of 735 mm Hg in figure 7. The similarities are evident. The major apparent differences are the shift of composition for the δ phase to $\text{CmO}_{1.80+x}$ and the ease of reduction to the sesquioxide at $\sim 865^\circ\text{C}$. The three isobars shown demonstrate that the degree of completion of the $\sigma \rightarrow \text{Cm}_2\text{O}_3$ decomposition relates directly to the subsequent oxidizability of the product. The oxidation resistance of the B-form sesquioxide has been discussed by Mosley [9], where no oxidation was observed in 1 atm O_2 except for $250 < T < 520^\circ\text{C}$. Thus, we interpret the break from σ to lower compositions as a $\sigma \rightarrow \text{B} - \text{Cm}_2\text{O}_3$ decomposition. This interpretation is, however, not consistent with the kinetic data [9] for the transformation $\text{C} \rightarrow \text{B}$ since no conversion occurred below 900°C and 1280°C was required for completion. We ascribe this difference to impurity or crystallite size differences and note the long history of different temperatures reported for the rare earth oxide polymorphic phase transformations.

The ^{244}Cm and ^{248}Cm results may be more completely compared by the phase boundary plot of figure 7. There are marked temperature shifts for several of the reactions and differences in entropy values (slopes of the $RT \ln p_{\text{O}_2}$ versus T lines). The vertical lines obtained in the low temperature region of the α - δ boundary and the $\sigma \rightarrow \text{B}$ boundary are taken to indicate non-thermodynamic behavior (kinetic limitations), while the remaining reaction boundaries give reasonable changes in entropy of ~ 40 - 60 eu. It is remarkable that the $^{244}\text{CmO}_x$ data for $\alpha \rightarrow \delta$ do show an acceptable

temperature dependence even though occurring at temperatures $\sim 30^\circ\text{C}$ lower. We ascribe this increased oxygen mobility to self-radiation, and point out the recent observation of Noe and Fuger [13] that $^{244}\text{CmO}_2$ may release oxygen even at room temperature when in vacuum.

The large temperature shift in the $\sigma \rightarrow \alpha$ boundary to higher values in $^{248}\text{CmO}_x$ and the marked change in slope of the $\alpha \rightarrow \sigma$ reduction are not well understood. It is to be expected that effects due to radiation damage are much reduced at these temperatures due to annealing. Sample purity of the $^{248}\text{CmO}_x$ at 99.9 mole% was higher than for the $^{244}\text{CmO}_x$ sample which contained 2.5 mole% AmO_2 and approximately 0.4% other impurities, mainly Fe and Si. Purity and other physical differences must play some role in these types of reaction, at a level, however, which is unknown.

The phase diagram for the CmO_x system (figure 8) has not been altered from that given previously [10]. The $^{248}\text{CmO}_x$ results suggest only minor changes and any significant revision will require a detailed high temperature x-ray diffraction examination of the system under controlled oxygen pressures.

5. BkO_x

With the exception of a few x-ray diffraction studies on Bk_2O_3 and BkO_2 , the only work on the BkO_x system was by Turcotte, Chikalla, and Eyring [14]. The paucity of data is readily attributable to its scaracity and short (314 day) half life. The decay mechanism predominantly involves a 114 KeV beta, introducing californium-249 ($t_{1/2} = 360$ yrs) at the rate of about 1.5%/week.

Since only milligram samples of this element were available and the weight loss for a $\text{BkO}_2 \rightarrow \text{BkO}_{1.5}$ decomposition is 34.2 μg per milligram of BkO_2 , balance techniques were ruled out and the capacitance manometer system was developed as described earlier. The 1.22 mg sample was investigated in the temperature interval 852-1150°C and oxygen partial pressures from 10^{-7} to 10^{-20} atm.

The low oxygen pressures required to attain equilibrium with various nonstoichiometric BkO_x compositions were set by appropriate CO_2/CO mixtures. The equilibration of a given gas mixture with the sample was made isothermally followed by cooling to 500°C in vacuum. At this point, the reduced sample was quantitatively oxidized to $\text{BkO}_{2.00}$. Repetition of this procedure with various CO_2/CO ratios and with appropriate evacuations and flushings resulted in the isotherms shown in figure 9. The data shown are grouped according to ^{249}Cf content which varied from 3 to 13% during the course of the experiment. The conditions of oxidation of the substoichiometric BkO_x preparations (7 mm O_2 and 500°C) were not sufficient to oxidize the Cf present significantly above $\text{O/Cf} = 1.50$. The ingrowing californium was thus treated as an inert impurity in correlating the raw data and O/Bk values. Structurally, it is virtually certain that the Cf^{+3} was fully incorporated in solid solution and the data obtained refer to the ternary $(\text{Bk}_y, \text{Cf}_{1-y})\text{O}_x$. It is likely, however, that the dissociation pressures are little different for the pure BkO_x system as suggested by the present results and by the small changes observed in other studies as in $\text{U}_{1-z}\text{Ce}_z\text{O}_{2-x}$ [15] relative to CeO_x and in $\text{U}_y\text{Th}_{1-y}\text{O}_{2+x}$ [16] relative to UO_{2+x} .

The interpretation of the plateau regions shown in figure 9 and by the derived thermodynamic quantities (figure 10) is complicated by a variety of possibilities suggested by phase relations in other binary and ternary fluorite related oxide systems. Without x-ray diffraction analysis, we can only speculate as follows: a single phase $\text{BkO}_{1.5+x}(\sigma)$ region extends from low compositions up to a maximum O/Bk which is a function of temperature (1.73 at 1150°C and 1.78 at 852°C). A two-phase region separates σ from the $\text{BkO}_{2-x}(\alpha)$ region which extends to near the dioxide composition unperturbed at 1075 and 1150°C but which is broken into α and α' regions at the lower temperatures.

Alternatively, the observed plateaus (figure 9) at $\text{O/Bk} \sim 1.92$ may be related to recent observations of several phases of narrow composition width in the ternary systems $(\text{U,Ce})\text{O}_x$ [15], $(\text{Zr,Sc})\text{O}_x$ [17], $(\text{Hf,Sc})\text{O}_x$ [18], and $(\text{Hf,Y})\text{O}_x$ [19]. We note in these systems also that, in general, the major intermediate formed is not $\text{MO}_{1.714}$ (as for the pure Ce, Pr, Tb, and Cm oxide systems), but the nonstoichiometric pyrochlore phase (mean $\text{O/M} = 1.75$) predominates. Although unobserved in any of the binary systems, radii considerations relative to Roth's data [20] do not rule out this possibility as explaining the mid-field plateau observed at $\text{O/Bk} 1.73 - 1.82$ in the $(\text{Bk,Cf})\text{O}_x$ system.

6. CfO_x and Higher Z Oxides

The isotopes including californium and all those of higher atomic number, have not been examined tensimetrically. Baybarz et al [21], however, have prepared $^{249}\text{CfO}_2$ by oxidation of Cf_2O_3 in approximately 100 atm O_2 or by use of atomic oxygen. During the course of these preparations, samples of intermediate compositions were obtained which tended to cluster about compositions $\text{O/Cf} = 1.56, 1.70, \text{ and } 1.90$ as estimated by lattice parameter considerations. By analogy to the rare earth systems, the better crystallized preparations of the 1.7-1.8 compositions showed rhombohedral distortion.

The heavier actinides offer isotopes of increasingly lower half-lives. Einsteinium-253 ($t_{1/2} = 20$ days) and fermium-257 ($t_{1/2} = .94$ days) will likely be the last elements amenable to solid state studies (excluding possible stable super-heavy elements) if and when they become available in suitable quantities.

7. Summary

In summary, the chemical behavior of the transplutonium actinide elements as seen through the behavior of the ($\text{M}^{3+}, \text{M}^{4+}$) oxides supports the concept that they should be generally similar, but in detail they are clearly individual. Of this series, berkelium would seem anomalous if indeed curium and californium are as similar as indicated. This is perhaps related to the half-filled 5f subshell of Bk (IV) or to perturbation by the ingrowing

Cf in the sample studied. On the other hand, AmO_x does not appear to form the ordered intermediate phases suggested for CmO_x and CfO_x .

The thermodynamics obtained from these studies have no general theory to which they can be compared and the influence of impurities on entropy changes, for example, have not been adequately investigated. The structural details to which correlation must be made are not available, particularly in the grossly nonstoichiometric regions.

For the actinide oxides, the question of future studies is related to both the stability and very small quantities in existence as already noted and to the oxygen pressure range and temperatures experimentally accessible. In figure 11, we have compared oxidation-reduction potentials for the $\text{M}^{\text{III}}-\text{M}^{\text{IV}}$ couple [22] with dissociation pressures over $\text{MO}_{1.90}$ at 900°C using the known data for Pu, Bk, and Am oxides. Error bars for the redox potentials of ± 0.2 V are high and the very excellent fit of the three points should not be taken as too meaningful. The data do predict correctly, however, that the Cf higher oxide requires greater O_2 pressures for formation than Cm. It is clear that measurement of oxidation of Es^{3+} and the heavier elements will be virtually impossible even considering the reduction in dissociation pressures of approximately 15 units in $\log p_{\text{O}_2}$ for a temperature reduction to 400°C and another approximately 8 units if one considers a composition $\text{MO}_{1.51}$. More clearly stated, the dissociation pressure over a hypothetical $\text{EsO}_{1.51}$ oxide at 400°C

would be on the order of 10^{15} atmospheres of oxygen. It is worth pointing out here that a consideration of the lanthanide III-IV potentials reveals that all but Ce, Pr, and Tb have similar or lower values than Es and indeed none have been prepared in the +4 state.

A summary of the known phases in the (III-IV) field is given in Table I for all of the actinides. The progression from high stability for the +4 ion at Th proceeds with increasing Z through a crossover to the case of a highly stable +3 oxidation state as already indicated. It is the intermediate group from Np through Cf which offers the formation of compounds of mixed valence as the pure oxides and a host of ternary systems all showing behavior which in detail we are only now beginning to examine at a level necessary for full understanding and possible utilization.

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9. Captions

Table

- I Fluorite related phases in the actinide oxides.

Figure

- 1 Melting points of actinide di- and sesquioxides.
- 2 Stability diagram of polymorphic forms of lanthanide and actinide sesquioxides.
- 3 Dissociation pressure isotherms for AmO_x .
- 4 Partial molar entropy and enthalpy for AmO_x .
- 5 Capacitance manometer system.
- 6 Selected $^{244}\text{CmO}_x$ isobars.
- 7 Isobars for $^{248}\text{CmO}_x$ at 735 mm Hg O_2 .
- 8 Partial molar free energy versus T at phase boundaries in CmO_x .
- 9 Phase relations for CmO_x .
- 10 Dissociation pressure isotherms for BkO_x .
- 11 Partial molar entropy and enthalpy for BkO_x .
- 12 $\text{M}^{\text{III-IV}}$ redox potentials versus dissociation pressures over $\text{MO}_{1.90}$ at 900°C .

OBSERVED PHASES $(M^{+3}, M^{+4})O_x$

M	$MO_{1.500}$ C	$MO_{1.5+x}$ σ	$MO_{1.714}$ i	$MO_{1.82\pm x}$ δ	MO_{2-x} α	$MO_{2.000}$ F
Th					✓	✓
Pa						✓
U					✓	✓
Np					✓	✓
Pu	✓	✓			✓	✓
Am	✓	✓			✓	✓
Cm	✓	✓	✓	✓	✓	✓
Bk	✓	✓			✓	✓
Cf	✓	✓	✓(?)	✓(?)	✓	✓
Es	✓(?)

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