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Letter to the Editors

An estimate of the high temperature, metal rich phase boundary of plutonium sesquioxide

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Abstract

The composition of the metal rich phase boundary of plutonium sesquioxide has been estimated at 1400 K by comparing the calculated, equilibrium pressure of Pu(g) over the solid solution range of the sesquioxide with the reported Pu(g) pressure over the mutually saturated system, $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{Pu_2O_{3-x}} \rangle_{\mathrm{hex}}$. The Pu($g$) pressure at the previously recommended metal rich phase boundary is shown to be low by a factor of nearly 3000. The newly estimated metal rich phase boundary results in a homogeneity range for the sesquioxide that is larger by a factor of 1.8. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a prelude to planned experiments on liquid plutonium, the optical properties of liquid cerium were recently measured using rotating analyzer ellipsometry [1]. The chemically reactive cerium was inductively melted and levitated so that the specimen could be studied in a containerless environment. Pressure–composition phase diagrams for the Ce–O and Ce–N systems were calculated at a fixed temperature to characterize the vaporization behavior of cerium containing small amounts of oxygen and nitrogen. In the case of the Ce–O system, Ackermann and Rauh [2] measured the composition of the metal rich, sesquioxide phase boundary and the equilibrium vapor pressures of Ce(g) and CeO(g) over the mutually saturated system, $\mathrm{Ce(liquid, O_2\ saturated)} + \mathrm{Ce_2O_{3-x}}(s)$. Using their measurements and the assumption of ideal behavior for the dilute liquid metal phase, it was possible to construct the pressure–composition diagram extending from the pure metal to the sesquioxide.

In an attempt to perform similar calculations for the Pu–O system, it became apparent that the available data for metal rich compositions are even more uncertain than for Ce–O. Wriedt [3] has reviewed the phase behavior and thermodynamic properties for the Pu–O system. The sesquioxide has been reported as both a line compound and also as exhibiting a broad range of composition. However, based on experimental work by Besmann [4] for the temperature range 1400–1610 K, Wriedt recommended a composition range 59.3–60.5 at.% O. At low temperatures this range was presumed to taper to a narrow span near 60 at.% O. The metal rich phase boundary of the sesquioxide at high temperature suggested by Wriedt is not consistent with the reported thermodynamics for the Pu–O system as described below. Specifically, the pressure of Pu(g) calculated at the composition corresponding to the suggested metal rich phase boundary is too low by a factor of ≈ 3000 at 1400 K.

2. Plutonium sesquioxide partial pressures

The partial pressures of the gaseous species in equilibrium with plutonium sesquioxide may be calculated as a function of composition from existing thermodynamic data. At a fixed temperature and a fixed composition within the sesquioxide solid solution range, the system is invariant when both the condensed and gas phases are in equilibrium. The hexagonal, sesquioxide phase will be denoted $\langle \mathrm{PuO_{2-x}} \rangle_{\mathrm{hex}}$ and the components will be chosen

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as Pu and O_2. At a given temperature, if the integral free energy of mixing is known at one composition and the equilibrium pressure of oxygen, $p(O_2)$, is known as a function of composition, then the plutonium pressure, $p(\mathrm{Pu})$, may be calculated as a function of composition using a Gibbs–Duhem integration.

The integral free energy of mixing, $\Delta G_\mathrm{T}(\langle \mathrm{PuO}_{2-x}\rangle_\mathrm{hex})$, is the free energy change for reaction (1), which is written here for one mole of Pu. The reactants are in their chosen standard states, assuming the temperature is above the melting point of Pu.

$$\mathrm{Pu(liquid)} + \frac{2-x}{2}\mathrm{O}_2(g, 0.1013\ \mathrm{MPa}) = \langle \mathrm{PuO}_{2-x}\rangle_\mathrm{hex}. \tag{1}$$

The integral free energies corresponding to the two compositions, x' and x'', are related by a Gibbs–Duhem integration, Eq. (2), where x' has been taken as the stoichiometric composition, 0.5, corresponding to '$\mathrm{Pu_2O_3}$'.

$$\Delta G_\mathrm{T}(\langle \mathrm{PuO}_{2-x''}\rangle_\mathrm{hex}) = \Delta G_\mathrm{T}(\langle \mathrm{PuO}_{1.5}\rangle_\mathrm{hex}) - \frac{\mathrm{RT}}{2}\int_{x'=0.5}^{x''} \ln p(\mathrm{O}_2)\,\mathrm{d}x. \tag{2}$$

The relative partial molar free energy of Pu is the free energy change for the reaction in which one mole of Pu in its standard state is added to a solid solution, $\langle \mathrm{PuO}_{2-x}\rangle_\mathrm{hex}$ in this case. The amount of solution is assumed to be large enough that addition of one mole of Pu does not significantly change its composition. The relative partial molar free energy of O_2 is similarly defined. The relative partial molar free energies are related to their activities in Eqs. (3) and (4), where $p^\circ(\mathrm{Pu})$ is the vapor pressure of pure Pu.

$$\Delta\bar{G}_\mathrm{Pu} = \bar{G}_\mathrm{Pu} - G^\circ(\mathrm{Pu}) = \mathrm{RT}\ln(a_\mathrm{Pu}) \cong \mathrm{RT}\ln\left(\frac{p(\mathrm{Pu})}{p^\circ(\mathrm{Pu})}\right), \tag{3}$$

$$\Delta\bar{G}_{\mathrm{O}_2} = \bar{G}_{\mathrm{O}_2} - G^\circ(\mathrm{O}_2) = \mathrm{RT}\ln(a_{\mathrm{O}_2}) \cong \mathrm{RT}\ln\left(\frac{p(\mathrm{O}_2)}{0.1013\ \mathrm{MPa}}\right). \tag{4}$$

The approximation of the activities by the pressure ratios assumes that the gas in equilibrium with the sesquioxide behaves ideally and that the thermodynamic properties of the solid solution are independent of modest pressure changes. The relation between the integral and partial molar free energies is given in Eq. (5) and follows from the fact that the free energy is an extensive property.

$$\Delta G_\mathrm{T}(\langle \mathrm{PuO}_{2-x}\rangle_\mathrm{hex}) = \Delta\bar{G}_\mathrm{Pu} + \frac{2-x}{2}\Delta\bar{G}_{\mathrm{O}_2} \cong \mathrm{RT}\left[\ln\left(\frac{p(\mathrm{Pu})}{p^\circ(\mathrm{Pu})}\right) + \frac{2-x}{2}\ln\left(\frac{p(\mathrm{O}_2)}{0.1013\ \mathrm{MPa}}\right)\right]. \tag{5}$$

Besmann [4] has reported $\Delta G_\mathrm{T}(\langle \mathrm{PuO}_{1.5}\rangle_\mathrm{hex})$ and $p(\mathrm{O}_2)$ at 1400, 1500 and 1610 K, which may be used in Eqs. (2) and (5) to obtain $p(\mathrm{Pu})$ as a function of composition. For completeness, the partial pressures of the other known vapor species, $\mathrm{O}(g)$, $\mathrm{PuO}(g)$ and $\mathrm{PuO}_2(g)$, may be calculated from the following gaseous equilibria and the standard free energies of formations given by Green et al. [5]:

$$\mathrm{O}_2(g) = 2\mathrm{O}(g), \tag{6}$$

$$\mathrm{Pu(g)} + \frac{1}{2}\mathrm{O}_2(g) = \mathrm{PuO}(g), \tag{7}$$

$$\mathrm{Pu(g)} + \mathrm{O}_2(g) = \mathrm{PuO}_2(g). \tag{8}$$

Fig. 1 shows the partial pressures calculated at 1400 K as a function of composition. Besmann's value of $\Delta G_{1400}(\langle \mathrm{PuO}_{1.5}\rangle_\mathrm{hex})$ is −639.1 kJ/mol and a fit of his O_2 pressures at 1400 K is given in Eq. (9). The fit is based on data in Besmann's Table 1, but limited to the range $1.457 < \mathrm{O/Pu} < 1.522$ to ensure that the O_2 pressures correspond to the single sesquioxide phase.

$$\ln\left(\frac{p(\mathrm{O}_2)}{0.1013\ \mathrm{MPa}}\right) = -185.16 + 603.11x - 694.97x^2. \tag{9}$$

In Fig. 1, the oxygen rich phase boundary is taken as O/Pu = 1.532 or 60.5 at.% O, but the metal rich boundary has been extended beyond that recommended by Wriedt for reasons discussed below. This extension of the metal rich phase boundary required a significant extrapolation of the measured O_2 pressures.

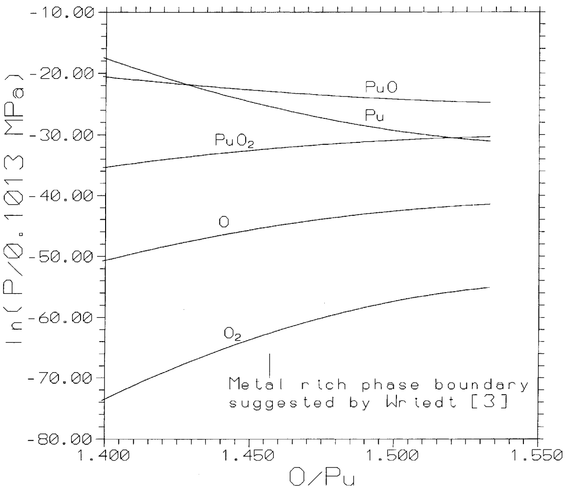

Fig. 1. Natural logarithm of the pressures (relative to the standard pressure, 0.1013 MPa) of gaseous species over plutonium sesquioxide, $\langle \mathrm{PuO}_{2-x}\rangle_\mathrm{hex}$, as a function of composition at 1400 K.

3. Plutonium sesquioxide metal rich phase boundary

At fixed temperature, the equilibrium, partial pressures are invariant over the system consisting of the two condensed phases, $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$, where x corresponds to the composition of the metal rich boundary. Such a system is an ideal candidate for a vaporization study because it is not necessary to know the overall composition. As vaporization proceeds, the overall composition of the condensed system changes because the relative amounts of the metal and sesquioxide change, but the pressures remain constant at constant temperature. Only one such vaporization study has been reported [6] for the Pu–O system. Unfortunately, the details of this mass spectrometric investigation are sketchy, but are presumably similar to work done on the cerium oxygen system [2]. From this study, the $\mathrm{Pu}(g)$ pressure calculated over $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$ is 2.78×10^{-3} Pa at 1400 K. This calculation probably involves an extrapolation of as much as 100–200 K, although the experimental temperature range was not quoted in the Argonne report [6].

The composition of the metal rich, sesquioxide phase boundary may be estimated from the composition in Fig. 1 where the $\mathrm{Pu}(g)$ pressure equals 2.78×10^{-3} Pa. The estimated phase boundary is O/Pu = 1.40, which is more metal rich than the value recommended by Wriedt, O/Pu = 1.457. In fact, this new estimate of the phase boundary, O/Pu = 1.40, results in a wider solid solution range for the sesquioxide by a factor of 1.8.

It is interesting that the $\mathrm{Pu}(g)$ pressure, 2.78×10^{-3} Pa, over the mutually saturated system, $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$, is only slightly lower than the pressure over pure Pu(liquid), 2.87×10^{-3} Pa at 1400 K [5]. A similar situation was found [2,7] in the case of the Ce–O system where the $\mathrm{Ce}(g)$ pressures over the mutually saturated system and the pure liquid are 7.81×10^{-4} and 9.04×10^{-4} Pa, respectively, at 1555 K. The temperatures chosen for this comparison, 1400 and 1555 K, are ≈ 490 K above the melting points of Pu and Ce, respectively. A better comparison would choose temperatures where the oxygen solubility was the same in Pu and Ce, but the solubilities are largely unknown. The estimated plutonium sesquioxide phase boundary from Fig. 1 is insensitive to whether the pressure of pure Pu(liquid) or the pressure over the mutually saturated system is used. In analogy with the lanthanide sesquioxides, Potter and Rand [8] estimated the high temperature, lower phase boundary of $\langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$ to be $\mathrm{O/Pu} \leqslant 1.4$ in agreement with the present estimate.

In his review, Wriedt [3] fails to point out that the lower O/Pu limit quoted by Besmann [4] for $\langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$ actually represents an upper bound to the metal rich phase boundary. As correctly noted by Besmann, this is because the equilibrium which he studied was $\langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}} - \langle \mathrm{PuC}_{1.5}\rangle - \langle \mathrm{C}\rangle$ and the equilibrium, $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$, may lead to a lower value for the metal rich phase boundary. Besmann's upper bound does not contradict the estimate made here, but the metal rich phase boundary, O/Pu = 1.427, from the micro-calorimetry work of Chereau [9] falls between the present estimate and the upper bound given by Besmann.

In the present case, the uncertainty in the estimated, metal rich phase boundary depends on the uncertainties in the $\mathrm{O}_2(g)$ pressure as a function of composition over $\langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$, the integral free energy of mixing of stoichiometric $\langle \mathrm{PuO}_{1.5}\rangle_{\mathrm{hex}}$, and the $\mathrm{Pu}(g)$ pressure over $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$. It is difficult to determine the uncertainty in the oxygen pressure because of the long extrapolation required beyond the measured range. However, even a variation of ±50% in the pressure calculated from Eq. (9) leads to a variation of less than ±0.005 in O/Pu of the metal rich phase boundary. A 10 kJ uncertainty in the integral free energy of mixing leads to a similar uncertainty in the phase boundary. It is impossible to estimate the uncertainty in the $\mathrm{Pu}(g)$ pressure over $\mathrm{Pu(liquid, O_2\ saturated)} + \langle \mathrm{PuO}_{2-x}\rangle_{\mathrm{hex}}$ because no experimental details were given in the Argonne report [6]. However, as noted above, even using the vapor pressure of pure Pu liquid, assuming similar behavior with the Ce–O system, does not significantly change the estimated phase boundary.

No attempt was made to repeat the above calculations at 1500 and 1610 K because the measured oxygen pressures [4] at these temperatures show significantly more scatter than at 1400 K.

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