Experimental oxygen potentials for $\text{U}_{1-y}\text{Pr}_y\text{O}_{2\pm x}$ and thermodynamic assessment of the U-Pr-O system

J.W. McMurray and C.M. Silva

*Materials Science and Technology Division,
Oak Ridge National Laboratory,
Oak Ridge, TN 37831-6063*

ABSTRACT

Thermogravimetric analysis (TGA) was used to determine the oxygen potentials of fluorite urania-praseodymia ($\text{U}_{1-y}\text{Pr}_y\text{O}_{2\pm x}$) solid solutions for $y = 0.10$ and 0.20 between 1000 and 1500°C . A thermodynamic assessment of U-Pr-O system was performed using the CALPHAD (CALculation of PHase Diagrams) method. The models well reproduce the TGA measurements and the computed phase relations are in good agreement with those proposed from an X-ray diffraction investigation.

Keywords: $\text{UO}_{2\pm x}$, uranium, praseodymium, oxygen, compound energy formalism, CALPHAD, oxygen potential, phase equilibria

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

*Corresponding author: Jacob W. McMurray email: mcmurrayjw1@ornl.gov phone: 865-574-6852

1. Introduction

In recent years, increases in computing power have facilitated advances in multi-physics based fuel performance simulations. Key components of this approach, such as the modeling of transport phenomena and phase transformations, rely on thermodynamics for inputs. Since the Ln (lanthanide) elements and Y are high yield fission products that dissolve extensively in fluorite urania, they affect many of the properties of nuclear fuel. Therefore, many experimental studies are devoted to the U-Ln-O ternaries. Particular emphasis is placed on heat capacity measurements and determining the oxygen potential (μ_{O_2}) of the fluorite $U_{1-y}Ln_yO_{2\pm x}$ solid solution as well as understanding the phase relations in the integral system. Further, there is an international effort to model the phases in U-Ln-O ternaries using the CALPHAD (CALculation of PHase Diagrams) method whereby the individual subsystems can be used to develop a global multicomponent description, e.g. to represent nuclear fuel with burn-up. Thermodynamic assessments that can be used within this framework for U-Pu-O [1], U-Ce-O [2], U-La-O [3], U-Y-O[4], and U-Nd-O [5] already exist. However, Pr is also a high yield fission product (FP) but CALPHAD models for the phases in the U-Pr-O system have yet to be developed. Therefore, this work aims to perform a thermodynamic assessment of U-Pr-O system using the CALPHAD approach.

The CALPHAD method uses both thermochemical and phase equilibria data for model development. Unfortunately, experimental investigations reporting both types of this information for U-Pr-O are scarce compared to some of the other U-Ln-O systems. A literature survey revealed only one study authored by Yamashita et al. [6] reporting limited equilibrium oxygen potentials (μ_{O_2}) at 1350°C in air, He, and under vacuum. Therefore, the μ_{O_2} -composition-temperature relationship for $U_{1-y}Pr_yO_{2\pm x}$ was measured by thermogravimetric analysis (TGA) to accumulate sufficient thermochemical data necessary to develop a compound energy formalism (CEF) representation for the fluorite $U_{1-y}Pr_yO_{2\pm x}$ solution. These TGA results and the phase relations shown in Figure 1, taken from [7] and based on the work of De Alleluia et al. [8], were used to perform the integral U-Pr-O assessment.

2. Experimental

2.1 Sample preparation

Areva UO_{2+x} powder (>99.85 mass % uranium oxide) and Pr_6O_{11} from American Elements (>99.995 mass % Rare Earth oxide) were mechanically mixed in ratios corresponding to 1/10 and 1/5 Pr to U. These compositions were pressed into a disc (5mm in diameter and 1mm in height) that was then conditioned at 1350°C for 17 hrs in an oxygen atmosphere corresponding to $\log p_{O_2} = -13$ to both sinter and form a single phase solid solution with an approximate O/M = 2. A SPEX mill was then used to reform the powder for an additional mixing, pressing, and conditioning step as described above. An X-ray diffraction (XRD) analysis revealed only the presence of a single phase solution corresponding to the fluorite crystal structure. As can be seen in Fig. 2, the lattice parameters obey Vegard's law and are well represented by the relation given by Ohmichi et al. [9] for $U_{1-y}Ln_yO_2$ where Ln is a fixed trivalent cation.

2.2 Thermogravimetric technique

The oxygen potential-temperature-composition relationship for $U_{1-y}Pr_yO_{2\pm x}$ was determined by TGA using a Netzsch STA 449 F1 Jupiter for $y = 0.10$ and 0.20 from 1000 to 1500°C . Feed gases were procured from Air Liquide S.A. and oxygen potentials were fixed by mixing $\text{Ar-3\%H}_2$ and $\text{Ar-2\%O}_2$ in appropriate ratios determined from thermodynamic calculations.

The details of the particular experimental technique used here are described in detail in Refs. [10, 11]. In brief, a $U_{1-y}Pr_yO_{2\pm x}$ sample of approximately 1 gram was conditioned to an O/M of 2. A change in oxygen potential results in a weight gain (or loss) that can be correlated to a new O/M using the relation:

$$O/M = 2 + \frac{mw_s \times \Delta m}{16 \frac{\text{g}}{\text{mol}} \times mass_s} \quad \mathbf{1}$$

where mw_s is the molecular weight of $U_{1-y}Pr_yO_{2.00}$, Δm is the change in mass due to uptake or release of oxygen and $mass_s$ is the sample mass at room temperature. A precise value of $mass_s$ for $U_{1-y}Pr_yO_{2\pm x}$ at the operating temperature of the measurement cannot be known since cooling from the conditioning step in $\text{Ar-3\% H}_2$ likely causes the sample to become hypo-stoichiometric. Changes in the microbalance signal due to gas buoyancy are well documented in TGA. Therefore, the $mass_s$ during conditioning cannot be directly compared to the $mass_s$ reading at room temperature, i.e the change in stoichiometry from O/M = 2.00 during cooling in $\text{Ar-3\% H}_2$ cannot be easily determined. Fortunately, using the error propagation approach in [10, 11] allows the uncertainty to be quantified. The mass difference between the nominal and actual stoichiometry is very conservatively estimated at 10 mg. While the error in determining $mass_s$ represents the most significant contribution to the total uncertainty in O/M, the total uncertainty is still acceptably small and of the same magnitude as other TGA $U_{1-y}Ln_yO_{2.00}$ measurements [12, 13]. The estimated uncertainties in O/M are given alongside the experimental results in Table 1.

3. Modeling

3.1 The vapor phase

The gas phase is considered to be an ideal mixture of O, O_2 , O_3 , U, UO , UO_2 , UO_3 , Pr, and PrO . The references from which the thermodynamic data for each of these vapor species are taken are given in Table 2.

3.2 Pure elements and stoichiometric phases

The references from which the thermodynamic data for U_4O_9 , U_3O_8 , UO_3 , Pr_2O_3 , Pr_6O_{11} , Pr_7O_{12} , Pr_9O_{16} , $\text{Pr}_{11}\text{O}_{20}$, $\text{Pr}_{40}\text{O}_{72}$, and elemental U are taken are given in Table 2. While a homogeneity range may exist for rhombohedral $\text{UPr}_6\text{O}_{12}$ [8], due to insufficient data the phase was considered to be stoichiometric. As was done for UY_6O_{12} [4] and $\text{UGd}_6\text{O}_{12}$ [14], the heat capacity for $\text{UPr}_6\text{O}_{12}$ was calculated from the Neumann-Kopp rule while the standard state enthalpy (H^{SER}) and entropy (S^{SER}) were determined using phase relations from [8]. Due to a lack of calorimetric data, the values for H^{SER} and S^{SER} should be considered tentative.

3.3 The liquid phase

The TSLM is described in [15] and many examples of its use can be found in [1, 3, 14, 15]. The sublattice representation for the TSLM describing the U-Pr-O melt is:

The molar Gibbs energy of the liquid phase is:

$$\begin{aligned} G^{liq} = & y_{\text{Pr}^{3+}} y_{\text{O}^{2-}} {}^{\circ}G_{\text{Pr}_2\text{O}_3}^{liq} + y_{\text{Pr}^{4+}} y_{\text{O}^{2-}} 2 {}^{\circ}G_{\text{PrO}_2}^{liq} + y_{\text{U}^{4+}} y_{\text{O}^{2-}} 2 {}^{\circ}G_{\text{UO}_2}^{liq} \\ & + Q \left[y_{\text{Va}^{\text{Q-}}} \left(y_{\text{Pr}^{3+}} {}^{\circ}G_{\text{Pr}^{3+}, \text{Va}^{\text{Q-}}}^{liq} + y_{\text{Pr}^{4+}} {}^{\circ}G_{\text{Pr}^{4+}, \text{Va}^{\text{Q-}}}^{liq} + y_{\text{U}^{4+}} {}^{\circ}G_{\text{U}^{4+}, \text{Va}^{\text{Q-}}}^{liq} \right) + y_{\text{O}} {}^{\circ}G_{\text{O}}^{liq} \right] \\ & + RTP \left(y_{\text{Pr}^{3+}} \ln y_{\text{Pr}^{3+}} + y_{\text{Pr}^{4+}} \ln y_{\text{Pr}^{4+}} + y_{\text{U}^{4+}} \ln y_{\text{U}^{4+}} \right) \\ & + RTQ \left(y_{\text{O}^{2-}} \ln y_{\text{O}^{2-}} + y_{\text{Va}^{\text{Q-}}} \ln y_{\text{Va}^{\text{Q-}}} + y_{\text{O}} \ln y_{\text{O}} \right) \\ & + {}^{xs}G^{liq} \end{aligned} \quad 2$$

where T is the absolute temperature and R is the ideal gas constant. The coefficients P and Q are defined by Eqns. 3 and 4 respectively.

$$P = \sum_A \nu_A y_A + Q y_{\text{Va}} \quad 3$$

$$Q = \sum_C \nu_C y_C \quad 4$$

The symbols ν_i and y_i are the charge and site fractions and the subscripts A and C represent the species on the anion and cation sublattices respectively while Va denotes a vacancy.

The Gibbs functions, ${}^{\circ}G_i^{liq}$, for the Pr containing end-members were taken from the Pr-O assessment performed by McMurray [16] while the neutral O and those with U cations come from [17].

The molar excess Gibbs energy term, ${}^{xs}G^{liq}$, is described with the zeroth, first and second order interaction parameters from a Redlich-Kister [18] polynomial expansion:

$$\begin{aligned}
{}^{xs}G^{liq} = & y_{Pr^{3+}}^i y_{Pr^{4+}}^i y_{O^{2-}}^{ii} \left[{}^0L_{Pr^{3+},Pr^{4+},O^{2-}}^{liq} + \left(y_{Pr^{3+}}^i - y_{Pr^{4+}}^i \right) \left({}^1L_{Pr^{3+},Pr^{4+},O^{2-}}^{liq} \right) \right] \\
& + y_{Pr^{3+}}^i y_{O^{2-}}^{ii} y_{Va}^{ii} {}^0L_{Pr^{3+},O^{2-},Va}^{liq} \\
& + y_{U^{4+}}^i y_{O^{2-}}^{ii} y_{Va}^{ii} \left[{}^0L_{U^{4+},O^{2-},Va}^{liq} + \left(y_{O^{2-}}^{ii} - y_{Va}^{ii} \right) \left({}^1L_{U^{4+},O^{2-},Va}^{liq} \right) + \left(y_{O^{2-}}^{ii} - y_{Va}^{ii} \right)^2 \left({}^2L_{U^{4+},O^{2-},Va}^{liq} \right) \right] \\
& + y_{Pr^{3+}}^i y_{U^{4+}}^i y_{O^{2-}}^{ii} {}^0L_{Pr^{3+},U^{4+},O^{2-}}^{liq} + y_{Pr^{4+}}^i y_{U^{4+}}^i y_{O^{2-}}^{ii} {}^0L_{Pr^{4+},U^{4+},O^{2-}}^{liq}
\end{aligned} \tag{5}$$

The lack of melting data for U-Pr-O does not permit the TSLM to be confidently developed, therefore the interaction parameters ${}^0L_{Pr^{3+},U^{4+},O^{2-}}^{liq}$ and ${}^0L_{Pr^{4+},U^{4+},O^{2-}}^{liq}$ are assumed to be the same as ${}^0L_{Ce^{3+},U^{4+},O^{2-}}^{liq}$ and ${}^0L_{Ce^{4+},U^{4+},O^{2-}}^{liq}$ from the U-Ce-O assessment[ref] due to the similar behavior of Pr and Ce in the U-O system, The remainder of the adjustable terms are adopted from the assessments of U-O [1] and Pr-O [16].

3.4 The fluorite $U_{1-y}Pr_yO_{2\pm x}$ phase

The CEF for $U_{1-y}Pr_yO_{2\pm x}$ is represented with three sublattices as follows:

The CEF Gibbs energy for the $U_{1-y}Pr_yO_{2\pm x}$ solid solution can be written as:

$$\begin{aligned}
G^F = & y_{U^{3+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{3+},O^{2-}}^F + y_{U^{3+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{U^{3+},O^{2-},Va}^F + y_{U^{3+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{3+},Va,O^{2-}}^F + y_{U^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{U^{3+},Va,Va}^F \\
& + y_{U^{4+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{4+},O^{2-}}^F + y_{U^{4+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{U^{4+},O^{2-},Va}^F + y_{U^{4+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{4+},Va,O^{2-}}^F + y_{U^{4+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{U^{4+},Va,Va}^F \\
& + y_{U^{5+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{5+},O^{2-}}^F + y_{U^{5+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{U^{5+},O^{2-},Va}^F + y_{U^{5+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{5+},Va,O^{2-}}^F + y_{U^{5+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{U^{5+},Va,Va}^F \\
& + y_{U^{6+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{6+},O^{2-}}^F + y_{U^{6+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{U^{6+},O^{2-},Va}^F + y_{U^{6+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{U^{6+},Va,O^{2-}}^F + y_{U^{6+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{U^{6+},Va,Va}^F \\
& + y_{Pr^{3+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{Pr^{3+},O^{2-}}^F + y_{Pr^{3+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{Pr^{3+},O^{2-},Va}^F + y_{Pr^{3+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{Pr^{3+},Va,O^{2-}}^F + y_{Pr^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{Pr^{3+},Va,Va}^F \\
& + y_{Pr^{4+}}^i y_{O^{2-}}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{Pr^{4+},O^{2-}}^F + y_{Pr^{4+}}^i y_{O^{2-}}^{ii} y_{Va}^{iii} {}^\circ G_{Pr^{4+},O^{2-},Va}^F + y_{Pr^{4+}}^i y_{Va}^{ii} y_{O^{2-}}^{iii} {}^\circ G_{Pr^{4+},Va,O^{2-}}^F + y_{Pr^{4+}}^i y_{Va}^{ii} y_{Va}^{iii} {}^\circ G_{Pr^{4+},Va,Va}^F \\
& + RT \left[\left(y_{U^{3+}}^i \ln y_{U^{3+}}^i + y_{U^{4+}}^i \ln y_{U^{4+}}^i + y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i + y_{Pr^{3+}}^i \ln y_{Pr^{3+}}^i + y_{Pr^{4+}}^i \ln y_{Pr^{4+}}^i \right) \right. \\
& \left. + 2 \left(y_{O^{2-}}^{ii} \ln y_{O^{2-}}^{ii} + y_{Va}^{ii} \ln y_{Va}^{ii} \right) + \left(y_{O^{2-}}^{iii} \ln y_{O^{2-}}^{iii} + y_{Va}^{iii} \ln y_{Va}^{iii} \right) \right] \\
& + {}^{xs}G^F
\end{aligned} \tag{6}$$

The CEF for the $U_{1-y}Pr_yO_{2\pm x}$ phase from this work combines the models for the $UO_{2\pm x}$ from [17] with that of $PrO_{2\pm x}$ developed by McMurray [16] along with the thermodynamic functions for the U^{6+} containing end-member additions from [14]. The excess molar Gibbs energy uses the Redlich-Kister [18] expansion and is given as:

$$\begin{aligned}
{}^{xs}G^F = & y_{Va}^{ii} y_{Va}^{iii} \left(\begin{aligned} & y_{U^{4+}}^i y_{Pr^{3+}}^i {}^0L_{U^{4+},Pr^{3+},Va:Va}^F + y_{U^{4+}}^i y_{Pr^{3+}}^i (y_{U^{4+}}^i - y_{Pr^{3+}}^i) {}^1L_{U^{4+},Pr^{3+},Va:Va}^F \\ & + y_{U^{4+}}^i y_{Pr^{4+}}^i {}^0L_{U^{4+},Pr^{4+},Va:Va}^F + y_{U^{4+}}^i y_{Pr^{4+}}^i (y_{U^{4+}}^i - y_{Pr^{4+}}^i) {}^1L_{U^{4+},Pr^{4+},Va:Va}^F \\ & + y_{U^{5+}}^i y_{Pr^{4+}}^i {}^0L_{U^{5+},Pr^{4+},Va:Va}^F + y_{U^{5+}}^i y_{Pr^{4+}}^i (y_{U^{5+}}^i - y_{Pr^{4+}}^i) {}^1L_{U^{5+},Pr^{4+},Va:Va}^F \\ & + y_{Pr^{3+}}^i y_{Pr^{4+}}^i {}^0L_{Pr^{3+},Pr^{4+},Va:Va}^F + y_{Pr^{3+}}^i y_{Pr^{4+}}^i (y_{Pr^{3+}}^i - y_{Pr^{4+}}^i) {}^1L_{Pr^{3+},Pr^{4+},Va:Va}^F \end{aligned} \right) \\
& + y_O^{ii} y_{Va}^{iii} \left(\begin{aligned} & y_{U^{3+}}^i y_{U^{4+}}^i {}^0L_{U^{3+},U^{4+},O:Va}^F + y_{U^{3+}}^i y_{U^{4+}}^i (y_{U^{3+}}^i - y_{U^{4+}}^i) {}^1L_{U^{3+},U^{4+},O:Va}^F \\ & + y_{U^{3+}}^i y_{Pr^{3+}}^i {}^0L_{U^{3+},Pr^{3+},O:Va}^F + y_{U^{4+}}^i y_{Pr^{4+}}^i {}^0L_{U^{4+},Pr^{4+},O:Va}^F + y_{U^{5+}}^i y_{Pr^{4+}}^i {}^0L_{U^{5+},Pr^{4+},O:Va}^F \\ & + y_{Pr^{3+}}^i y_{Pr^{4+}}^i {}^0L_{Pr^{3+},Pr^{4+},O:Va}^F + y_{Pr^{3+}}^i y_{Pr^{4+}}^i (y_{Pr^{3+}}^i - y_{Pr^{4+}}^i) {}^1L_{Pr^{3+},Pr^{4+},O:Va}^F \end{aligned} \right) \\
& + y_{U^{4+}}^i y_{U^{5+}}^i y_O^{ii} y_O^{iii} {}^0L_{U^{4+},U^{5+},O:O}^F + y_O^{ii} y_O^{iii} (y_{U^{5+}}^i y_{Pr^{4+}}^i {}^0L_{U^{4+},Pr^{4+},O:O}^F)
\end{aligned} \tag{7}$$

3.5 Parameter optimization

An iteration scheme within the Optisage module of FactSage [19] software was used to simultaneously optimize all adjustable parameters of the CALPHAD models in order to achieve a self-consistent set of values that gave a best fit to μ_{O_2} and phase equilibria measurements for the U-Pr-O system. The resulting thermodynamic functions are given in Table 2 along with those for the U-O[17] [14] and Pr-O assessments.

4. Results and discussion

The models with the optimized adjustable parameters are compared to the experimental thermodynamic data. The tentative U-Pr binary diagram was computed and is shown in Fig. 3. For simplicity during the optimization, complete immiscibility in the condensed phases was assumed for the U-Pr subsystem. This is based on the observation by Haeffling and Dane [20] of very limited mutual solubility U and Pr as a liquid. Therefore, a large positive binary interaction parameter was introduced in the TSLM to reproduce that behavior and solid U and Pr phases were treated as pure metals as was done for the U-Gd [14], U-La [3], and U-Y [4] systems.

The parameters of the ${}^{xs}G^F$ term of the model for fluorite $U_{1-y}Pr_yO_{2\pm x}$ given by Eqn. 7 that contain both U and Pr cations were adjusted to reproduce the phase relations in Fig. 1 and equilibrium oxygen pressures measured by TGA given in Table 1. Figure 4 plots the experimental and the CEF derived p_{O_2} values for $U_{1-y}Pr_yO_{2\pm x}$. Figure 5 shows the calculated ternary isotherm at 1250°C for comparison to the phase diagram proposed by Alleluia et al. [8] in Fig. 1a. Computed defect fractions for $U_{0.831}Pr_{0.169}O_{2\pm x}$ at 1500°C as a function of O/M and $\log p_{O_2}$ in Fig. 6 shows oxidation results in primarily promoting Pr^{3+} to Pr^{4+} and U^{4+} to U^{5+} to maintain charge neutrality while O^{2-} anions fill the vacant octahedrally coordinated interstitial sites.

While Figs. 4 and 5 show good agreement between observed and computed thermodynamic behavior, there are some discrepancies in the broader U-Pr-O system. For example, the U_3O_8 - $U_{1-y}Pr_yO_{2\pm x}$ biphasic region is too narrow in Fig. 6 compared to that of Fig. 1b. This could be explained by Pr dissolution in U_3O_8 since Ce is chemically similar to Pr and has been observed to substitute for U in U_3O_8 [21, 22]. For simplicity, U_3O_8 is not modeled as a ternary solution phase in this work. Including a CEF representation of orthorhombic $(U,Pr)_3O_8$ might bring the computed F – U_3O_8 boundary into better agreement with Fig. 1b. However, it should be pointed out that Fig. 1b is based on XRD analysis of quenched samples. Another possible interpretation of the differences between Fig. 5 and Fig. 1a is that hyperstoichiometric fluorite urania is known to precipitate out higher oxide phases upon rapid cooling [23]. Therefore, there does not appear to be sufficient experimental evidence at this time to definitively model the U_3O_8 phase with a homogeneity range in the U-Pr-O system.

Many oxides of Pr are isostructural with those of Ce since both elements are known to exhibit 3+ and 4+ oxidation states. This is also likely due to their comparable ionic radii [24]. It is therefore reasonable to expect Pr to behave similarly to Ce in the U-Ln-O ternary. However, Pr dissolution in fluorite $U_{1-y}Pr_yO_{2\pm x}$ does not persist to $y = 1$ at 1250°C in contrast to Ce in $U_{1-y}Ce_yO_{2\pm x}$. Praseodymium even shows less solubility as an Ln in fluorite $U_{1-y}Ln_yO_{2\pm x}$ at 1250°C than does La [3, 25] despite the fact that La is not known to exhibit a 4+ valence state. This behavior is perplexing since one criterion for a high degree of mutual solubility is that the end-members be isostructural. Fluorite PrO_{2-x} has been observed to be stable for Pr but not for La, i.e. LaO_{2-x} does not exist. Either the phase relations reported in [8] are in error or some other phenomena are affecting Pr dissolution in $U_{1-y}Pr_yO_{2\pm x}$, e.g. defect cluster formation or lattice strain as suggested by Aizenshtein [26] and Alexandrov et al. [27] respectively. The $U_{1-y}Pr_yO_{2\pm x}$ solution does show similar μ_{O_2} behavior compared to $U_{1-y}Ce_yO_{2\pm x}$ [2] and the $U_{1-y}Ln_yO_{2\pm x}$ [3-5, 14] solutions in general, i.e. increasing μ_{O_2} with temperature, x and y .

5. Summary and Conclusions

This report calls for the phase relations in the vicinity of $U_{1-y}Pr_yO_{2\pm x}$ to be re-examined to verify the results reported in [8]. Since H^{SER} and S^{SER} for UPr_6O_{12} determined in this work are only tentative, these values should be confirmed by an appropriate calorimetric technique. Further, melting data for the U-Pr-O system is needed to best develop the TSLM. The equilibrium oxygen pressures over $U_{1-y}Pr_yO_{2\pm x}$ as a function of temperature and composition were characterized using TGA and are added to the thermochemical database for the U-Pr-O system. These measurements were used along with reported phase relations to perform a thermodynamic assessment of the U-Pr-O ternary. The CALPHAD models for U-Pr-O from this work can be extended for higher order descriptions of U-O with FPs, part of the larger multicomponent thermodynamic database effort for nuclear fuel material [28].

Acknowledgements

The authors would like to thank Dongwon Shin and Brian Jolly of Oak Ridge National Laboratory for helpful comments. The work was supported by the US Department of Energy, Office of Nuclear Energy Fuel Cycle Technology Program.

References

- [1] C. Guéneau, C. Chatillon, B. Sundman, *J. Nucl. Mater.*, 378 (Thermodynamic modelling of the plutonium–oxygen system) (2008) 257-72.
- [2] J. W. McMurray, S. Hirooka, T. Murakami, K. Suzuki, J. T. White, S. L. Voit, A. T. Nelson, B. W. Slone, T. Besmann, K. J. McClellan, M. Kato, Thermodynamic assessment of the U-Ce-O system, *Journal of Nuclear Materials*; submitted for publication.
- [3] J. McMurray, D. Shin, T. Besmann, *J. Nucl. Mater.*, 456 (2015) 142-50.
- [4] R. Brese, J. McMurray, D. Shin, T. Besmann, *J. Nucl. Mater.*, 460 (2015) 5-12.
- [5] S. M. Lee, T. W. Knight, J. W. McMurray, T. Besmann, Thermochemical modeling of the U-Nd-O system; submitted for publication.
- [6] T. Yamashita, T. Fujino, H. Tagawa, *J. Nucl. Mater.*, 132 (2) (1985) 192-201.
- [7] ACerS-NIST PHASE EQUILIBRIA DIAGRAMS Version 4.0; 2013.
- [8] I. B. De Alleluia, M. Hoshi, W. G. Jocher, C. Keller, *Journal of Inorganic and Nuclear Chemistry*, 43 (8) (1981) 1831-4.
- [9] T. Ohmichi, S. Fukushima, A. Maeda, H. Watanabe, *J. Nucl. Mater.*, 102 (1) (1981) 40-6.
- [10] J. W. McMurray, *Thermodynamic Modeling of Uranium and Oxygen Containing Ternary Systems with Gadolinium, Lanthanum, and Thorium*, PhD Thesis, University of Tennessee, Knoxville, 2014.
- [11] J. W. McMurray, S. L. Voit, T. Besmann, A combined experimental and computational thermodynamic investigation of the U-Th-O system, *Journal of the American Ceramic Society*; submitted for publication.
- [12] T. B. Lindemer, A. L. Sutton Jr., *J. Am. Ceram. Soc.*, 71 (7) (1988) 553-61.
- [13] K. Yoshida, T. Arima, Y. Inagaki, K. Idemitsu, M. Osaka, S. Miwa, *J. Nucl. Mater.*, 418 (1–3) (2011) 22-6.
- [14] J. W. McMurray, D. Shin, B. W. Slone, T. M. Besmann, *J. Nucl. Mater.*, 452 (1–3) (2014) 397-406.
- [15] M. Hillert, B. Jansson, B. Sundman, *Metall. Trans. A*, 16 (1) (1985) 261-6.
- [16] J. W. McMurray, Thermodynamic assessment of the Pr-O system, *Journal of the American Ceramic Society*; submitted for publication.
- [17] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J. C. Dumas, S. Gosse, S. Chatain, F. De Bruycker, D. Manara, R. J. M. Konings, *J. Nucl. Mater.*, 419 (2011) 145-67.
- [18] O. Redlich, A. T. Kister, *Industrial and Engineering Chemistry*, 40 (2) (1948) 345-8.
- [19] C. W. Bale, P. Chartrand, S. A. Degterov, S. Eriksson, K. Hack, R. B. Mahfoud, J. Melancon, A. D. Pelton, S. Petersen, *CALPHAD*, 26 (2002) 189.
- [20] J. Haefling, A. Daane, *Trans. Met. Soc. AIME*, 215 (1959)
- [21] T. Markin, R. Street, E. Crouch, *Journal of Inorganic and Nuclear Chemistry*, 32 (1) (1970) 59-75.
- [22] H. P. Nawada, P. Sriramamurti, K. V. G. Kutty, S. Rajagopalan, R. B. Yadav, P. R. V. Rao, C. K. Mathews, *J. Nucl. Mater.*, 139 (1) (1986) 19-26.
- [23] F. Grønvold, *Journal of Inorganic and Nuclear Chemistry*, 1 (6) (1955) 357-70.
- [24] R. Shannon, *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 32 (5) (1976) 751-67.
- [25] H. G. Diehl, C. Keller, *J. Solid State Chem.*, 3 (4) (1971) 621-36.
- [26] M. Aizenshtein, T. Y. Shvareva, A. Navrotsky, *J. Am. Ceram. Soc.*, 93 (12) (2010) 4142-7.
- [27] V. Alexandrov, N. Grønbech-Jensen, A. Navrotsky, M. Asta, *J. Nucl. Mater.*, 444 (1–3) (2014) 292-7.
- [28] Thermodynamics of Advanced Fuels – International Database (TAF-ID) Project, <https://www.oecd-neo.org/science/taf-id/>
- [29] SGTE Substances Database Version 2, <http://www.thermocalc.com/TCDATA.htm>
- [30] R. J. Konings, O. Beneš, *J. Phys. Chem. Ref. Data*, 39 (2010) 043102.
- [31] M. Zinkevich, D. Djurovic, F. Aldinger, *Solid State Ionics*, 177 (11) (2006) 989-1001.
- [32] M. Zinkevich, *Progress in Materials Science*, 52 (4) (2007) 597-647.

Table 1.

Equilibrium oxygen pressures versus O/M for $\text{U}_{1-y}\text{Pr}_y\text{O}_{2\pm x}$ from thermogravimetry.

y	Temperature (°C)	O/M	Error in O/M	$\log p_{\text{O}_2}$	Error in $\log p_{\text{O}_2}$
0.1	1000	1.999	0.0010	-18.0	0.079
0.1	1000	2.000	0.0010	-16.0	0.079
0.1	1000	2.000	0.0010	-14.0	0.128
0.1	1000	2.227	0.0028	-4.0	0.767
0.1	1300	2.000	0.0030	-14.0	0.055
0.1	1300	2.002	0.0030	-12.0	0.055
0.1	1300	2.003	0.0030	-10.0	0.057
0.1	1300	2.112	0.0033	-4.0	0.226
0.1	1300	2.192	0.0039	-3.0	0.059
0.1	1500	1.998	0.0020	-12.0	0.041
0.1	1500	2.000	0.0020	-10.0	0.041
0.1	1500	2.002	0.0020	-8.0	0.041
0.1	1500	2.010	0.0020	-6.0	0.135
0.1	1500	2.218	0.0035	-2.0	0.041
0.2	1000	1.997	0.0034	-18.0	0.079
0.2	1000	2.000	0.0034	-14.4	0.079
0.2	1000	1.999	0.0034	-16.0	0.079
0.2	1000	2.000	0.0034	-14.0	0.128
0.2	1000	2.216	0.0038	-4.0	0.767
0.2	1285	1.995	0.0060	-14.2	0.055
0.2	1285	1.998	0.0060	-12.2	0.055
0.2	1285	2.001	0.0060	-10.2	0.057
0.2	1285	2.105	0.0061	-4.0	0.226
0.2	1285	2.175	0.0062	-3.0	0.059
0.2	1500	1.995	0.0050	-12.0	0.041
0.2	1500	1.999	0.0050	-10.0	0.041
0.2	1500	2.001	0.0050	-8.0	0.041
0.2	1500	2.003	0.0050	-6.0	0.135
0.2	1500	2.026	0.0050	-4.0	0.223
0.2	1500	2.167	0.0052	-2.0	0.041

Table 2.

Gibbs functions for the models constituting the U-Pr-O assessment.

Thermodynamic parameters (J/mole)	Reference
Gas phase	
$^{\circ}G_{O_2}^{gas}$	[29]
$^{\circ}G_{O_3}^{gas}$	[29]
$^{\circ}G_O^{gas}$	[29]
$^{\circ}G_{Pr}^{gas}$	[29]
$^{\circ}G_{PrO}^{gas}$	[29]
$^{\circ}G_U^{gas}$	[30]
$^{\circ}G_{UO_3}^{gas}$	[30]
$^{\circ}G_{UO_2}^{gas}$	[30]
$^{\circ}G_{UO}^{gas}$	[30]
Pure elements and stoichiometric compounds	
$^{\circ}G_U^{\alpha}$	[29]
$^{\circ}G_U^{\beta}$	[29]
$^{\circ}G_U^{\gamma}$	[29]
$^{\circ}G_{UO_3}^{solid}$	[17]
$^{\circ}G_{U_3O_8}^{\alpha}$	[17]
$^{\circ}G_{U_3O_8}^{\beta}$	[17]
$^{\circ}G_{U_3O_8}^{\gamma}$	[17]
$^{\circ}G_{U_3O_8}^{\delta}$	[17]
$^{\circ}G_{U_4O_9}^{\alpha}$	[17]
$^{\circ}G_{U_4O_9}^{\beta}$	[17]
$^{\circ}G_{U_4O_9}^{\gamma}$	[17]
$^{\circ}G_{Pr_2O_3}^A$	
$^{\circ}G_{Pr_2O_3}^H$	
$^{\circ}G_{Pr_2O_3}^X$	
$^{\circ}G_{Pr_7O_{12}}$	[31]
$^{\circ}G_{Pr_9O_{16}}$	[31]

$$^{\circ}G_{Pr_{40}O_{72}} \quad [31]$$

$$^{\circ}G_{Pr_{11}O_{20}} \quad [31]$$

$$^{\circ}G_{Pr_6O_{11}} \quad [31]$$

Fluorite solution ($U^{3+}, U^{4+}, U^{5+}, U^{6+}, Pr^{3+}, Pr^{4+}$)₁(O^{2-}, Va^0)₂(O^{2-}, Va^0)

$$^{\circ}G_{UO_2}^F \quad [29]$$

$$^{\circ}G_{PrO_2}^F \quad [31]$$

$$^{\circ}G_{Pr_2O_3}^F \quad [31]$$

$$^{\circ}G_{U^{3+}:O^{2-}:O^{2-}}^F = ^{\circ}G_{U^{3+}:O^{2-}:Va}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [17]$$

$$^{\circ}G_{U^{3+}:O^{2-}:Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{U^{4+}:Va:Va}^F + ^{\circ}G_{U^{3+}:Va:Va}^F \quad [17]$$

$$^{\circ}G_{U^{3+}:Va:Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{O_2}^{gas} + 747127 - 70.23T - 2RT[0.75\ln(0.75) + 0.25\ln(0.25)] \quad [17]$$

$$^{\circ}G_{U^{3+}:Va:O^{2-}}^F = 100000 \quad [17]$$

$$^{\circ}G_{U^{4+}:O^{2-}:O^{2-}}^F = ^{\circ}G_{UO_2}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [17]$$

$$^{\circ}G_{U^{4+}:O^{2-}:Va}^F = ^{\circ}G_{UO_2}^F \quad [17]$$

$$^{\circ}G_{U^{4+}:Va:Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{O_2}^{gas} + 545210.5 \quad [17]$$

$$^{\circ}G_{U^{4+}:Va:O^{2-}}^F = 100000 \quad [17]$$

$$^{\circ}G_{U^{5+}:O^{2-}:O^{2-}}^F = ^{\circ}G_{U^{5+}:O^{2-}:Va}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [17]$$

$$^{\circ}G_{U^{5+}:O^{2-}:Va}^F = ^{\circ}G_{UO_2}^F - 58351.62 + 39.68T - RT\ln(0.5) \quad [17]$$

$$^{\circ}G_{U^{5+}:Va:Va}^F = ^{\circ}G_{U^{5+}:O^{2-}:Va}^F - ^{\circ}G_{O_2}^{gas} + 700000 \quad [17]$$

$$^{\circ}G_{U^{5+}:Va:O^{2-}}^F = 100000 \quad [17]$$

$$^{\circ}G_{U^{6+}:O^{2-}:O^{2-}}^F = ^{\circ}G_{U^{5+}:O^{2-}:O^{2-}}^F + 31961.2 + 0.498T \quad [14]$$

$$^{\circ}G_{U^{6+}:O^{2-}:Va}^F = ^{\circ}G_{U^{5+}:O^{2-}:Va}^F + 31961.3 + 0.978T \quad [14]$$

$$^{\circ}G_{U^{6+}:Va:Va}^F = ^{\circ}G_{U^{5+}:Va:Va}^F - 668038.4 - 2.062T \quad [14]$$

$$^{\circ}G_{U^{6+}:Va:O}^F = 100000 \quad [14]$$

$$^{\circ}G_{Pr^{3+}:O^{2-}:Va}^F = ^{\circ}G_{Pr_2O_3}^F + \frac{1}{2}^{\circ}G_{O_2} + 18.702165T \quad [31]$$

$$^{\circ}G_{Pr^{3+}:O^{2-}:O^{2-}}^F = ^{\circ}G_{Pr^{3+}:O^{2-}:Va}^F + \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^{\circ}G_{Pr^{3+}:Va:Va}^F = ^{\circ}G_{Pr_2O_3}^F - \frac{1}{2}^{\circ}G_{O_2} + 18.702165T \quad [31]$$

$$^{\circ}G_{Pr^{3+}.Va.O^{2-}}^F = ^{\circ}G_{Pr^{3+}.Va.Va}^F - \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^{\circ}G_{Pr^{4+}.O^{2-}.O^{2-}}^F = ^{\circ}G_{PrO_2}^F + \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^{\circ}G_{Pr^{4+}.O^{2-}.Va}^F = ^{\circ}G_{PrO_2}^F \quad [31]$$

$$^{\circ}G_{Pr^{4+}.Va.Va}^F = ^{\circ}G_{PrO_2}^F - ^{\circ}G_{O_2} \quad [31]$$

$$^{\circ}G_{Pr^{4+}.Va.O^{2-}}^F = ^{\circ}G_{Pr^{4+}.Va.Va}^F - \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^FL_{U^{4+}.U^{5+}.O^{2-}.O^{2-}}^0 = -124936 - 21.68T \quad [17]$$

$$^FL_{U^{3+}.U^{4+}.O^{2-}.Va}^0 = 40133.7 \quad [17]$$

$$^FL_{U^{3+}.U^{4+}.O^{2-}.Va}^1 = 1076.4 \quad [17]$$

$$^FL_{Pr^{3+}.Pr^{4+}.O^{2-}.Va}^0 = ^FL_{Pr^{3+}.Pr^{4+}.Va.Va}^0 = -58786 + 12.98725T \quad [31]$$

$$^FL_{Pr^{3+}.Pr^{4+}.O^{2-}.Va}^1 = ^FL_{Pr^{3+}.Pr^{4+}.Va.Va}^1 = -57516.5 + 15.5513T \quad [31]$$

$$^FL_{U^{4+}.Pr^{3+}.O^{2-}.O^{2-}}^0 = ^FL_{U^{4+}.Pr^{4+}.O^{2-}.O^{2-}}^0 = -200000 \quad \text{This work}$$

$$^FL_{U^{4+}.Pr^{3+}.O^{2-}.Va}^0 = -310000 \quad \text{This work}$$

$$^FL_{U^{4+}.Pr^{3+}.Va.Va}^0 = ^FL_{U^{4+}.Pr^{4+}.Va.Va}^0 = -750000 \quad \text{This work}$$

$$^FL_{U^{4+}.Pr^{4+}.O^{2-}.Va}^0 = -365920 \quad \text{This work}$$

$$^FL_{U^{5+}.Pr^{3+}.O^{2-}.O^{2-}}^0 = ^FL_{U^{5+}.Pr^{4+}.O^{2-}.O^{2-}}^0 = -400000 \quad \text{This work}$$

$$^FL_{U^{5+}.Pr^{3+}.O^{2-}.O^{2-}}^1 = ^FL_{U^{5+}.Pr^{4+}.O^{2-}.O^{2-}}^1 = -250000 \quad \text{This work}$$

$$^FL_{U^{5+}.Pr^{3+}.O^{2-}.Va}^0 = ^FL_{U^{5+}.Pr^{4+}.O^{2-}.Va}^0 = -350000 \quad \text{This work}$$

Liquid $(Pr^{3+}, Pr^{4+}, U^{4+})_R(O^{2-}, Va^{Q-}, O)_Q$

$$^{\circ}G_U^{liq} \quad [29]$$

$$^{\circ}G_O^{liq} \quad [17]$$

$$^{\circ}G_{Pr}^{liq} \quad [31]$$

$$^{\circ}G_{UO_2}^{liq} \quad [17]$$

$$^{\circ}G_{PrO_2}^{liq} \quad [31]$$

$$^{\circ}G_{Pr_2O_3}^{liq} \quad [31]$$

$$^{\circ}G_{U^{4+}.O^{2-}}^{liq} = ^{\circ}G_{UO_2}^{liq} \quad [17]$$

$$^{\circ}G_{U^{4+}.Va}^{liq} = ^{\circ}G_U^{liq} \quad [17]$$

$$^{\circ}G_{Pr^{3+}.Va}^{liq} = ^{\circ}G_{Pr}^{liq} \quad [31]$$

$$\circ G_{Pr^{3+};O^{2-}}^{liq} = \circ G_{Pr_2O_3}^{liq} \quad [31]$$

$$\circ G_{Pr^{4+};Va}^{liq} = 2\circ G_{Pr}^{liq} + 3\circ G_{PrO_2}^{liq} - 2\circ G_{Pr_2O_3}^{liq} \quad [31]$$

$$\circ G_{Pr^{4+};O^{2-}}^{liq} = \circ G_{PrO_2}^{liq} \quad [31]$$

$$^{liq}L_{U^{4+};O^{2-};Va}^0 = 1773475.9 - 516T \quad [17]$$

$$^{liq}L_{U^{4+};O^{2-};Va}^1 = 46774.9 - 120.3789T \quad [17]$$

$$^{liq}L_{U^{4+};O^{2-};Va}^2 = -500000 \quad [17]$$

$$^{liq}L_{U^{4+};O^{2-};O^{2-}}^0 = -370000 \quad [17]$$

$$^{liq}L_{Pr^{3+};Pr^{4+};O^{2-}}^0 = -105398 \quad [31]$$

$$^{liq}L_{Pr^{3+};Pr^{4+};O^{2-}}^1 = -35158 \quad [31]$$

$$^{liq}L_{Pr^{3+};O^{2-};Va}^0 = 114250 \quad [31]$$

$$^{liq}L_{Pr^{4+};U^{4+};O^{2-}}^0 = -10000 - 12.5T \quad \text{This work}$$

$$^{liq}L_{Pr^{3+};U^{4+};O^{2-}}^0 = -105000 - 35 \quad \text{This work}$$

C-Pr₃O_{5±x} (Pr³⁺, Pr⁴⁺)₂(O²⁻, Va⁰)₃(O²⁻, Va⁰)₁

$$\circ G_{Pr_2O_3}^C \quad [32]$$

$$\circ G_{Pr^{3+};O^{2-};Va}^C = \circ G_{Pr_2O_3}^C \quad [31]$$

$$\circ G_{Pr^{3+};O^{2-};O^{2-}}^C = \circ G_{Pr_2O_3}^C + \frac{1}{2}\circ G_{O_2}^{gas} \quad [31]$$

$$\circ G_{Pr^{4+};O^{2-};Va}^C = 19140 + 2\circ G_{Pr_2O_3}^C - \frac{1}{2}\circ G_{O_2}^{gas} \quad [31]$$

$$\circ G_{Pr^{4+};O^{2-};O^{2-}}^C = 19140 + 2\circ G_{Pr_2O_3}^C \quad [31]$$

$$^CL_{Pr^{3+};Pr^{2+};O^{2-};O^{2-}}^0 = ^CL_{Pr^{3+};Pr^{2+};O^{2-};Va}^0 = -7178 - 17.7264T \quad [31]$$

$$^CL_{Pr^{3+};Pr^{2+};O^{2-};O^{2-}}^1 = ^CL_{Pr^{3+};Pr^{2+};O^{2-};Va}^1 = -25591 + 22.2801T \quad [31]$$

Figure 1. Experimentally determined phase relations from De Alleluia et al. [8] for (a) the U-Pr-O ternary at 1250°C and (b) at 1 atm O_2 pressure. Reprinted with permission of The American Ceramic Society (www.ceramics.org).

Figure 3. Lattice parameters for fluorite structure $U_{1-y}Pr_yO_2$ as a function of Pr content. The experimental values (symbols) are compared to those computed (dashed line) using the relation proposed by Ohmichi et al. [9].

Figure 3. Computed phase diagram for the U-Pr binary system.

Figure 4. Computed (lines) and experimental (symbols) equilibrium oxygen pressures over $\text{U}_{0.9}\text{Pr}_{0.10}\text{O}_{2\pm x}$ (a) and $\text{U}_{0.80}\text{Pr}_{0.20}\text{O}_{2\pm x}$ (b).

Figure 5. (a) Computed U-Pr-O ternary isotherm at 1250°C and (b) section of that isotherm in the vicinity of the single phase fluorite solution region.

Figure 6. Computed phase relations in the U-Pr-O system at 1 atm O₂ pressures for comparison to Fig. 1(b).

Figure 7. CEF computed sublattice site fractions as a function of O/M **(a)** and $\log p_{O_2}$ **(b)** at 1500°C and $y = 0.169$ for fluorite $U_{1-y}Pr_yO_{2\pm x}$.