Thermodynamic assessment of the U-La-O system

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Abstract

The CALPHAD methodology was used to develop a thermodynamic assessment of the U-La-O system. The solid solution and liquid phases are described with the compound energy formalism (CEF) and the partially ionic two-sublattice liquid model, respectively. Experimental thermodynamic and phase equilibria data published in the open literature were then used in optimizations to develop representations of the phases in the system that can be extended to include other actinide and fission products for multi-component models. The models that comprise this assessment very well reproduce experimentally determined oxygen potentials and the observed phase relations for the U-La-O system.

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

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1. Introduction

The objective of the current work is to develop a thermodynamic assessment of the U-La-O ternary from 298 K to 3500 K to support physics-based fuel performance simulation efforts. Lanthanum is a high yield fission product making the U-La-O a fundamental subsystem needed to understand the chemistry of nuclear fuel undergoing burn-up. A comprehensive review and critical assessment of the available thermodynamic studies is used along with the CALPHAD (Calculation of Phase Diagrams) methodology to develop robust models that may be extrapolated into areas of little or no data to allow high confidence predictions of the chemical behavior in those regions. Furthermore, the approach allows for multi-component thermodynamic descriptions to be constructed from binary and ternary fundamental subsystems assuming only two and three body interactions. This is significant for nuclear fuel assessments for two reasons. First, there exists a significant body of work characterizing the phase equilibria, thermochemical and thermophysical properties of urania with the rare earth (RE) elements, many of which, like La, are high yield fission products (FPs). Second, these FPs exist in relatively low concentrations, even at high burn-up, so the effect of their interactions with one another in solution can be assumed to be negligible. This means these U-RE-O ternaries can be assessed independently and then subsequently combined for a useful thermodynamic representation of multi-component U-O bearing systems relevant to oxide nuclear fuels.

2. Literature review

The U-La-O and U-Nd-O ternaries are among the most extensively studied U-RE-O systems. The fully oxidized U-La-O phase relations along with a section of the isotherm at 1250°C in the vicinity of the $U_{1-y}La_yO_{2\pm x}$ solid solution have been well characterized by Diehl and Keller using high temperature x-ray diffraction (HTXRD) [1]. Another study reports solubility limits of the RE elements in uranium liquid and vice-versa [2], however the melting temperatures were not determined. Oxygen potential-composition-temperature measurements were critically assessed in [3] and the reported self-consistent data [4-7] are summarized in Table 1. However, there are no solidus/liquidus measurements or pseudo-binary phase diagrams for UO_2 - $LaO_{1.5}$ as there are for the UO_2 - $GdO_{1.5}$ [8-12], UO_2 - $NdO_{1.5}$ [13], and UO_2 - $YO_{1.5}$ [14] systems. Given the chemical similarity of the trivalent RE elements, the phase relations near melting along the UO_2 - $REO_{1.5}$ isopleths in the U-Gd-O, U-Nd-O, and U-Y-O systems were used as guides to inform approximate solidus/liquidus boundaries for the UO_2 - $LaO_{1.5}$ pseudo-binary and therefore allow the development of a model for the liquid phase in the U-La-O ternary.

3. Modeling

This work uses the approach of Guéneau et al. [15] and extends the U-O binary assessment to include La. As such, much of the details concerning the base models for fluorite $UO_{2\pm x}$ phase and U-O liquid can be found in references [15-18]. In the current effort, the Gibbs energy of all condensed phases is assumed to be pressure independent and all species are referred to the enthalpy and entropy of formation from their stable elements at standard state conditions of 298.15 K and 1 atm. The FactSage computational thermodynamic software [19] was used for equilibrium calculations and parameter optimizations.

3.1 The gas phase

The major gaseous species in the U-La-O system are considered to be O₂, U, UO, UO₂, UO₃, La₂, LaO, La₂O, and La₂O₂. The reference molar Gibbs energy functions for U, O, O₃ and O₂ are taken from the SGTE Substances Database Version 2 [20], those for La₂, LaO, La₂O, and La₂O₂ come from the Factsage 6.4 database [19], and the functions for UO, UO₂ and UO₃ are taken from the work of Konings et al. [21].

3.2 Pure elements and stoichiometric phases

The compounds U₄O₉, U₃O₈, and UO₃ are treated as stoichiometric phases after Guéneau et al. [15, 16] and the La₂O₃ Gibbs energy functions are from the assessment by Zinkevich [22]. Elemental U and La values are from the SGTE database [20].

3.3 The liquid phase

The partially ionic two sublattice model [23] for U-O from Guéneau et al. [15] is extended to include La³⁺ in the cation sublattice, which becomes:

where “O” is a neutral oxygen constituent and Va^{Q-} is a vacancy having a charge of Q-.

Charge neutrality necessitates that P and Q vary such that:

$$P = \sum_A \nu_A y_A + Q y_{\text{Va}} \quad 1$$

$$Q = \sum_C \nu_C y_C \quad 2$$

where ν_A and y_A are the charge and site fraction of the anion species and ν_C and y_C are the charge and site fraction of the cation C, respectively; y_{Va} is the site fraction for a vacancy of charge Q-.

The molar Gibbs energy of the liquid phase is defined by:

$$G^{\text{liq}} = \sum_C \sum_A y_C y_A {}^\circ G_{\text{C:A}} + Q y_{\text{Va}} \sum_C y_C {}^\circ G_C + Q y_{\text{O}} {}^\circ G_{\text{O}} - T S^{\text{liq}} + {}^{\text{xs}} G^{\text{liq}} \quad 3$$

where T is the absolute temperature, ${}^\circ G_{\text{C:A}}$ is the Gibbs energy of the liquid constituent corresponding to the formula $\text{C}_{\nu_A} \text{A}_{\nu_C}$ and ${}^\circ G_C$ is the Gibbs energy of cation C (either liquid Gd or U). The symbols y_{O} and ${}^\circ G_{\text{O}}$ correspond to the site fraction and the Gibbs energy of neutral “O”, respectively.

The configurational entropy term S^{liq} is given by:

$$S^{liq} = -R \left[P \sum_C y_C \ln y_C + Q \left(\sum_A y_A \ln y_A + y_{Va} \ln y_{Va} + y_O \ln y_O \right) \right] \quad 4$$

where R is the ideal gas constant and the molar excess Gibbs energy, $^{xs}G^{liq}$, term is described with the zeroth, first and second order interaction parameters from a Redlich-Kister [24] polynomial expansion:

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

The adjustable parameters are the interaction terms and the standard enthalpy and entropy of the La_2O_3 liquid.

3.4 The rhombohedral ULa_6O_{12-x} phase

The compound energy formalism (CEF) [25] can describe long range ordering by proper selection of the sublattice representation. For example, Grundy et al. [26] modeled the perovskite $LaMnO_3$ phase by subdividing the cation sublattices since the La and Mn atoms occupy distinctly different crystallographic sites. This is indeed the case for the rhombohedral δ -phase (RI) represented by the general formula URE_6O_{12} . It can be viewed as a fluorite derivative structure belonging to the $R\bar{3}$ space group with ordering of both RE and U on the cation sublattice and O and Va on the anion sublattice [27]. Diehl and Keller [1] report the δ -phase in the U-La-O system exhibits hypostoichiometric behavior with a very narrow cation homogeneity range. Due to the minimal concentrations of either cation interstitials or vacancies, the RI phase can be adequately represented as ULa_6O_{12-x} and modeled using the CEF with the following sublattice description:

The CEF is given in general form after Hillert [25] as:

$$G^{SS} = \sum_k {}^oG_k \prod_s y_J^s + RT \left(\sum_s \sum_J n^s y_J^s \ln y_J^s \right) + ^{xs}G \quad 6$$

where oG_k is the molar Gibbs energy for the end-member k , y_J^s is the site fraction of constituent J on sublattice s , R is the ideal gas constant, T is the absolute temperature, and ^{xs}G is the excess Gibbs energy due to interactions between components in the same sublattice. The $\prod_s y_J^s$ terms account for all the sublattices that contain components of end-member k , the end member being operated on by the summation. The excess Gibbs energy is expressed as an expansion of the Redlich-Kister [24] polynomial in terms of site fractions.

Using Eqn. 6, the Gibbs energy of the RI phase is adequately represented without an ^{xs}G term and is thus defined as:

$$G^{\delta} = y_{U^{4+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{U^{4+}:La^{3+}:O}^{\delta} + y_{U^{4+}}^i y_{La^{3+}}^{ii} y_{Va}^{iii} \circ G_{U^{4+}:La^{3+}:Va}^{\delta} + y_{U^{5+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{U^{5+}:La^{3+}:O}^{\delta} + y_{U^{5+}}^i y_{La^{3+}}^{ii} y_{Va}^{iii} \circ G_{U^{5+}:La^{3+}:Va}^{\delta} + y_{U^{6+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{U^{6+}:La^{3+}:O}^{\delta} + y_{U^{6+}}^i y_{La^{3+}}^{ii} y_{Va}^{iii} \circ G_{U^{6+}:La^{3+}:Va}^{\delta} + RT \left[\left(y_{U^{4+}}^i \ln y_{U^{4+}}^i + y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i \right) + 12 \left(y_O^{iii} \ln y_O^{iii} + y_{Va}^{iii} \ln y_{Va}^{iii} \right) \right] \quad 7$$

Here $^{\circ}G$ is the Gibbs energy for the subscripted end-member and y_J^s is the site fraction of constituent J on sublattice s .

The heat capacity relation was taken from Venkata et al. [28] and assumed to be the same for each end member for simplicity. The standard state enthalpy and entropy values were selected as adjustable parameters and determined using phase relations from Diehl and Keller [1] to formulate the reference molar Gibbs energy functions for the end-members.

3.5 The rhombohedral $U_2La_6O_{15}$ phase

The rhombohedral $U_2La_6O_{15}$ (RII) phase was observed by Diehl and Keller [1] to exhibit a narrow cation homogeneity range and to deviate very little in oxygen stoichiometry. The reflections for RII from HTXRD from Diehl and Keller [1] are reportedly the same as those for the RI phase and are in agreement with the study by Aitken et al. [29] of the analogous structures in the U-Y-O system. Due to the similarities between the fluorite parent structure and the small observed departures from stoichiometry, it is quite likely that the observed homogeneity range is within the limits of experimental error; therefore, this phase is treated as a stoichiometric compound. The heat capacity was calculated using the Neumann-Kopp rule while the standard state enthalpy and entropy were determined using phase relations from Diehl and Keller [1]. The entropy at 298 K of $316 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$ determined from a fit of phase equilibria data is in contrast to that computed from the Neumann-Kopp rule of $547 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$.

3.6 The rhombohedral $(U,L a)_8O_{16}$ phase

Diehl and Keller [1] report a third rhombohedral (RIII) structure but failed to determine the space group. The RIII phase was observed to be stoichiometric with respect to oxygen with a La compositional range between 55 and 67 at. %. The proposed formula from Diehl and Keller [1] is $(U,L a)_8O_{16}$; therefore, the CEF sublattice model chosen to represent this phase is:

where the molar Gibbs energy, again with no ^{xs}G term, is defined as:

$$G^{RIII} = y_{La^{3+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{La^{3+}:La^{3+}:O}^{RIII} + y_{U^{5+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{U^{5+}:La^{3+}:O}^{RIII} + y_{U^{6+}}^i y_{La^{3+}}^{ii} y_O^{iii} \circ G_{U^{6+}:La^{3+}:O}^{RIII} + RT \left[4 \left(y_{La^{3+}}^i \ln y_{La^{3+}}^i + y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i \right) \right] \quad 8$$

As with the RII phase, the heat capacity was calculated using the Neumann-Kopp rule. The adjustable parameters were the standard state enthalpy and entropy, and therefore the reference molar Gibbs energy functions for the end-members, were determined using phase relations from Diehl and Keller [1].

3.7 The fluorite $U_{1-y}La_yO_{2\pm x}$ phase

The fluorite $U_{1-y}La_yO_{2\pm x}$ phase is modeled using the same approach as that for $U_{1-y}Gd_yO_{2\pm x}$ from McMurray et al. [18] and much of the details of the procedure can be seen in that report. In brief, the CEF model developed for $UO_{2\pm x}$ by Guéneau et al. [16] was extended to include the La^{3+} and U^{6+} species such that the sublattice representation becomes:

The CEF Gibbs energy for the $U_{1-y}La_yO_{2\pm x}$ solid solution is thus:

$$\begin{aligned} G^F = & y_{U^{3+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{3+}:O:O}^F + y_{U^{3+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{3+}:O:Va}^F + y_{U^{3+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{3+}:Va:O}^F + y_{U^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{3+}:Va:Va}^F + \\ & y_{U^{4+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{4+}:O:O}^F + y_{U^{4+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{4+}:O:Va}^F + y_{U^{4+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{4+}:Va:O}^F + y_{U^{4+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{4+}:Va:Va}^F + \\ & y_{U^{5+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{5+}:O:O}^F + y_{U^{5+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{5+}:O:Va}^F + y_{U^{5+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{5+}:Va:O}^F + y_{U^{5+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{5+}:Va:Va}^F + \\ & y_{U^{6+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{6+}:O:O}^F + y_{U^{6+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{6+}:O:Va}^F + y_{U^{6+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{6+}:Va:O}^F + y_{U^{6+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{6+}:Va:Va}^F + \\ & y_{La^{3+}}^i y_O^{ii} y_O^{iii} \circ G_{La^{3+}:O:O}^F + y_{La^{3+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{La^{3+}:O:Va}^F + y_{La^{3+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{La^{3+}:Va:O}^F + y_{La^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{La^{3+}:Va:Va}^F + \\ & RT \left[\left(y_{U^{3+}}^i \ln y_{U^{3+}}^i + y_{U^{4+}}^i \ln y_{U^{4+}}^i + y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i + y_{La^{3+}}^i \ln y_{La^{3+}}^i \right) + \right. \\ & \left. 2 \left(y_O^{ii} \ln y_O^{ii} + y_{Va}^{ii} \ln y_{Va}^{ii} \right) + \left(y_O^{iii} \ln y_O^{iii} + y_{Va}^{iii} \ln y_{Va}^{iii} \right) \right] + \\ & {}^{xs}G^F \end{aligned} \quad 9$$

The model for the $U_{1-y}La_yO_{2\pm x}$ phase from this work uses the thermodynamic functions for the $UO_{2\pm x}$ CEF representation developed by Guéneau et al. [15] and those for the U^{6+} containing end-member additions from [18]. The excess molar Gibbs energy, expressed as an expansion of the Redlich-Kister [24] polynomial in terms of site fractions, is represented as:

$$\begin{aligned} {}^{xs}G^F = & y_{Va}^{ii} y_{Va}^{iii} \left(y_{U^{4+}}^i y_{La^{3+}}^i {}^0L_{U^{4+}:La^{3+}:Va:Va}^F + y_{U^{5+}}^i y_{La^{3+}}^i {}^0L_{U^{5+}:La^{3+}:Va:Va}^F \right) + \\ & y_O^{ii} y_{Va}^{iii} \left(y_{U^{3+}}^i y_{La^{3+}}^i {}^0L_{U^{3+}:La^{3+}:O:Va}^F + y_{U^{3+}}^i y_{La^{3+}}^i \left(y_{U^{3+}}^i - y_{La^{3+}}^i \right) L_{U^{3+}:La^{3+}:O:Va}^F + \right. \\ & \left. y_{U^{4+}}^i y_{La^{3+}}^i {}^0L_{U^{4+}:La^{3+}:O:Va}^F + y_{U^{4+}}^i y_{La^{3+}}^i \left(y_{U^{4+}}^i - y_{La^{3+}}^i \right) L_{U^{4+}:La^{3+}:O:Va}^F + \right. \\ & \left. y_{U^{5+}}^i y_{La^{3+}}^i {}^0L_{U^{5+}:La^{3+}:O:Va}^F + y_{U^{5+}}^i y_{La^{3+}}^i \left(y_{U^{5+}}^i - y_{La^{3+}}^i \right) L_{U^{5+}:La^{3+}:O:Va}^F \right) + \\ & y_O^{ii} y_O^{iii} \left(y_{U^{4+}}^i y_{La^{3+}}^i {}^0L_{U^{4+}:La^{3+}:O:O}^F + y_{U^{5+}}^i y_{La^{3+}}^i {}^0L_{U^{5+}:La^{3+}:O:O}^F \right) + \\ & y_O^{ii} y_{Va}^{iii} \left(y_{U^{3+}}^i y_{U^{4+}}^i {}^0L_{U^{3+}:La^{3+}:O:Va}^F + y_{U^{3+}}^i y_{U^{4+}}^i \left(y_{U^{3+}}^i - y_{U^{4+}}^i \right) L_{U^{3+}:La^{3+}:O:Va}^F \right) + \\ & y_{U^{4+}}^i y_{U^{5+}}^i y_O^{ii} y_O^{iii} {}^0L_{U^{4+}:U^{5+}:O:O}^F \end{aligned} \quad 10$$

It can be seen from Eqn. 10, magnitude of the effect of interactions between constituents scales with the product of their respective site fractions. This means when FPs exist in low concentrations in the fluorite phase, as is the case for nuclear fuel, Eqn. 10, and therefore Eqn. 6, is insensitive to FP-FP interactions.

The La-containing end-members were calculated using the following relations:

$$^{\circ}G_{La^{3+}:O:O} = \frac{1}{2}^{\circ}G_{La_2O_3}^A + \frac{3}{4}^{\circ}G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow LaO_2} \quad 11$$

$$^{\circ}G_{La^{3+}:O:Va} = \frac{1}{2}^{\circ}G_{La_2O_3}^A + \frac{1}{4}^{\circ}G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow LaO_2} \quad 12$$

$$^{\circ}G_{La^{3+}:Va:Va} = \frac{1}{2}^{\circ}G_{La_2O_3}^A - \frac{3}{4}^{\circ}G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow LaO_2} \quad 13$$

where $^{\circ}G_{La_2O_3}^A$ is the Gibbs energy of the hexagonal A-form La_2O_3 ($P32/m$ space group) [30]. Given the very low likelihood of its stability, the value for $^{\circ}G_{La^{3+}:Va:O}$ was arbitrarily set to +100,000 J/mol after Guéneau et al. [15]. To a first approximation, the Gibbs energies of the La end-members were estimated using $^{\circ}G_{La_2O_3}^A$ plus the lattice stability, $\Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow LaO_2}$, calculated by Shin and Besmann [3] from DFT simulations and addition and subtraction of oxygen as noted above. Eqns. 11 – 13 were subsequently adjusted by optimizing the standard state enthalpy and entropy terms along with the interaction parameters from Eqn. 10, in order to best reproduce both phase equilibria and oxygen potential data.

3.8 Parameter optimization

The Optisage module of FactSage [19] was used to find the best fit to the experimental oxygen potential and phase equilibria measurements for the La-O and U-La-O systems using the models described above. The thermodynamic functions in Table 2 were used along with those for the U-O assessment taken from Guéneau et al. [15] and McMurray et al. [18]. The solidus and liquidus temperatures along the UO_2 - $LaO_{1.5}$ isopleth were inferred and based on those for the UO_2 - $GdO_{1.5}$, UO_2 - $NdO_{1.5}$, and UO_2 - $YO_{1.5}$ pseudo-binary diagrams. An iterative procedure was employed to simultaneously optimize all adjustable parameters for all the models in order to achieve a self-consistent set of values that sufficiently describes the oxygen potential and phase equilibria of the La-O and U-La-O systems. The results from the optimization are given in Table 2.

4. La-O system

A computed phase diagram for the La-O system is shown in Fig. 1(a). The liquid phase represented by Eqns. 1-5 for this binary contains no interaction parameters between La and O but follows from the optimization discussed in Section 3.8. The phase relations determined from a study assessing the La- La_2O_3 binary space [31] is given in Fig. 1(b) for comparison; both diagrams are tentative due to a lack of experimental data but both agree at least qualitatively. The major difference lies in the fact that [31] used a sublattice model to describe the solubility of oxygen in the metallic and sesquioxide phases. Although,

combining the La-La₂O₃ assessment from [31] with this work was considered, it was ultimately decided to use the models for La from [20], and sesquioxides from [22], for three reasons. First, it was consistent with the previous work assessing the U-Gd-O system [18]. Second, La is only considered to exhibit a 3+ oxidation state in this work; the assessment from Grundy et al. [31] allows for both La³⁺ and La²⁺ in the sublattice models for the La₂O₃ phases. Third, there is a lack of sufficient experimental data to confidently validate the models from Grundy et al. [31]. Thus the La allotropes and the La₂O₃ polymorphs are represented as pure elements and stoichiometric compounds, respectively.

5. U-La system

All condensed phases were assumed to be immiscible for this assessment based on the extremely limited inter-solubilities of La and U in the metallic and liquid phases from Haeffling [2]. A tentative diagram of the U-La binary is shown in Fig. 2.

6. U-La-O system

6.1 Oxygen potential

The phase representations fairly well reproduce critically assessed oxygen pressure measurements from Shin and Besmann [3] as seen in Fig. 3. Most of the data are reported over single phase U_{1-y}La_yO_{2±}. However, in Fig. 3(c), there is invariant oxygen potential for O/M ≥ 2.25, a consequence of a three phase region. Indeed, at T ≤ 1073 K and O/M ≥ 2.25, U₃O₈-U₄O₉- U_{1-y}La_yO_{2±x} coexist and thus the oxygen pressure does not vary with composition. However, at T > 1173 K, the p_{O₂} only appears to be constant; in reality, a very small increase in p_{O₂} with O/M change can be discerned and the models predict that this region corresponds to a U_{1-y}La_yO_{2±x}- U₃O₈ two-phase field. The plateau in p_{O₂} for 2.15 < x < 2.20 may be indicative of a phase transition. Indeed, the computed equilibria from this work shows U_{1-y}La_yO_{2±x}- U₄O₉ coexistence up to 1073 K for y = 0.05. The data presented in Fig. 3(c) suggest this two phase region may persist to higher temperatures in contrast to the computed equilibria from this work; therefore, further investigation is needed to determine whether this is the case, or simply an artifact of the measurements is the cause of the plateaus for 2.15 < x < 2.20 and T > 1073 K.

6.2 Ternary phase equilibria

The computed isothermal section of U-La-O at 1250°C shown in Fig. 4 agrees remarkably well with the reported phase relations from [1] with a few exceptions. The authors claim to observe a U-La homogeneity range in both the RI and RII phases; however, as mentioned above, this range is very small and it is likely to lie within the experimental error since some of the data for the U_{1-y}La_yO_{2±x}-RI and U_{1-y}La_yO_{2±x}-RII phase fields appear contradictory. Figure 5 shows the computed fully oxidized U-La-O phase equilibria as a function of temperature and composition. The agreement between the computed phase diagram and the experimental data is good, but again, there are a few exceptions. First, Diehl and Keller [1] report single phase U_{1-y}La_yO_{2±x} at 1200°C and 1100°C at ~50 mole % LaO_{1.5}, whereas the models show a two-phase U_{1-y}La_yO_{2±x}- RIII region. One explanation is that the RIII phase was not observed by Diehl and Keller [1] because the crystal structures are very similar and only around 0.3 and 0.17 mole fraction of RIII is predicted to be present at 1200°C and 1100°C, respectively. The computed equilibrium concentrations of U_{1-y}La_yO_{2±x} and RIII approach parity at 50 mole % LaO_{1.5} and 1000°C, but

sluggish equilibration may account for incomplete transformation of $U_{1-y}La_yO_{2\pm x} \rightarrow RIII$. The situation may be similar with respect to the discrepancy between reported observations and the predicted coexistence of $U_{1-y}La_yO_{2\pm x}$ -RI. In this case, however, the evidence is stronger that the RI phase was missed due to contradictory data at 1250°C showing both single $U_{1-y}La_yO_{2\pm x}$ and biphasic $U_{1-y}La_yO_{2\pm x}$ -RI at the same composition. Finally, Diehl and Keller [1] observed that long annealing times (~240 hours) were needed to obtain the $U_{1-y}La_yO_{2\pm x} \rightarrow RII$ transition; therefore sluggish equilibration could explain the discrepancy between the computed RII-RIII equilibrium and the observed $U_{1-y}La_yO_{2\pm x}$ - RII coexistence below 1250°C.

As noted above, the phase relations along the UO_2 - $GdO_{1.5}$ isopleth from [18] were used as a guide for inferring a reasonable solidus and liquidus for UO_2 - $LaO_{1.5}$ due to the lack of data for the system containing La; therefore the pseudo-binary UO_2 - $LaO_{1.5}$ diagram shown in Fig. 6 is only tentative.

6.3 $U_{1-y}La_yO_{2\pm x}$ defect chemistry

Computed oxygen defect and cation site fractions as a function of $\log_{10} p_{O_2}$ and O/M at 1773 K and $y = 0.169$ are shown in Fig. 7 and are compared to those for $U_{1-y}Gd_yO_{2\pm x}$ under the same conditions. As with the $U_{1-y}Gd_yO_{2\pm x}$, the U^{6+} concentration is minimal and only becomes noticeable for very high O/M values, consistent with U^{5+} as the predominant oxidation state [32, 33]. Unlike the U-Gd-O system however, the phase relations for U-La-O determined by Diehl and Keller [1] at high La compositions show $U_{1-y}La_yO_{2\pm x}$ exists at O/M values that must include U^{6+} to achieve electro-neutrality, as can be seen in Fig. 4. The inclusion of U^{6+} is also necessary in the U-Nd-O system. The defect behavior for $U_{1-y}La_yO_{2\pm x}$ and $U_{1-y}Gd_yO_{2\pm x}$ are very similar; however, it is worth noting that $U_{1-y}La_yO_{2\pm x}$ shows a slightly higher U^{6+} concentration at high O/M values.

7. Conclusions

The thermodynamic assessment of the U-La-O ternary has resulted in self-consistent thermodynamic values and models that well reproduce the oxygen potential measurements and experimentally determined phase relations for this system. Both the CEF for the $UO_{2\pm x}$ and the liquid model for U-O [15] were extended to incorporate La^{3+} in the cation sublattice. There is good agreement between the computed phase diagram and the major phases in the vicinity of the fluorite region with the phase equilibria determination of Diehl and Keller [1]. A Gibbs energy function for the RII $U_2La_6O_{15}$ compound and CEF models of the RI and RIII phases were determined by fitting phase equilibria data and using the Neumann-Kopp rule for heat capacity. The La_2O_3 polymorphs were treated as stoichiometric compounds after Zinkevich [22] but limited evidence suggests some degree of oxygen content variability. Grundy et al. [31] assessed the La-O system and included a sublattice description of the La and La_2O_3 phases to represent the oxygen homogeneity range; however there is insufficient data to validate the compositions. These models developed in this work can be further extended to include other fission and activation products for multicomponent thermodynamic representations essential for understanding the chemical behavior of high burn-up fuel.

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List of Figures

Figure 1 Reported phase diagrams for La-O **(a)** from [31](Reprinted with permission of The American Ceramic Society, www.ceramics.org All rights reserved.) and **(b)** the computed diagram from this work (A=low temperature hexagonal, H=high temperature hexagonal, X=high temperature cubic, L=liquid).

Figure 2 U-La binary phase diagram computed using the partially ionic two-sublattice liquid model.

Figure 3 Equilibrium oxygen partial pressures over $U_{1-y}La_yO_{2\pm x}$ vs. O/M. Individual measurements are the points shown for **(a)** $y = 0.025$ from [6], **(b)** $y = 0.05$ from [6], **(c)** $y = 0.05$ from [7], **(d)** and $y = 0.20$ from [5]. The computed results are the solid lines with the dashed lines in **(c)** representing $UO_{2\pm x}$ for reference.

Figure 4 Computed phase equilibria at 1250°C. The expanded section shows the phases in the vicinity of the single phase fluorite region together with points from experimentally observed phase equilibria [1]. The red dashed line shows the extent of maximum oxygen composition for single phase fluorite $U_{1-y}La_yO_{2\pm x}$ using U^{5+} as the highest uranium oxidation state. (F=fluorite solid solution, RI=rhombohedral $U_2La_6O_{15}$, RII= rhombohedral $U_2La_6O_{15}$, A=hexagonal La_2O_3 , O=orthorhombic U_3O_8 , L1=liquid phase, L2=second liquid phase)

Figure 5 Computed pseudo-binary diagram (lines) of fully oxidized U-La with the experimentally determined phase relations from [1] (points) shown as well. (F=fluorite solid solution, RI=rhombohedral $U_2La_6O_{15}$, RII= rhombohedral $U_2La_6O_{15}$, A=hexagonal La_2O_3 , O=orthorhombic U_3O_8)

Figure 6 Computed phase diagram along the UO_2 - $LaO_{1.5}$ isopleth. (A=low temperature hexagonal, H=high temperature hexagonal, X=high temperature cubic, L=liquid, F=fluorite solid solution)

Figure 7 Computed sublattice site fractions as a function of O/M **(a)** and $\log p_{O_2}$ **(b)** at 1773 K and $y = 0.169$ for $U_{1-y}La_yO_{2\pm x}$ from the CEF representation of the phase. The results from similar calculations at the same conditions are shown in **(c)** and **(d)** for $U_{1-y}Gd_yO_{2\pm x}$ [18] for comparison. The tetrahedral and octahedral sublattices are distinguished by the (ii) and (iii) symbols, respectively.

Table 1

Table 1 Selected oxygen potential measurements for $\text{U}_{1-y}\text{La}_y\text{O}_{2+x}$ from the critical assessment by Shin and Besmann [3] used in the current assessment.

[illegible]

Table 2

Table 2 Thermodynamic functions and parameters for the U-La-O assessment.

Thermodynamic parameters (J/mole)	Reference
Gas phase	
$^{\circ}G_{O_2}$	[20]
$^{\circ}G_{O_3}$	[20]
$^{\circ}G_O$	[20]
$^{\circ}G_{LaO}$	[20]
$^{\circ}G_{La_2}$	[20]
$^{\circ}G_{La_2O}$	[20]
$^{\circ}G_{La_2O_2}$	[20]
$^{\circ}G_U$	[20]
$^{\circ}G_{UO_3}$	[21]
$^{\circ}G_{UO_2}$	[21]
$^{\circ}G_{UO}$	[21]
Stoichiometric compounds	
$^{\circ}G_{La}^{dhcp}$	[20]
$^{\circ}G_{La}^{fcc}$	[20]
$^{\circ}G_{La}^{bcc}$	[20]
$^{\circ}G_{La_2O_3}^A$	[22]
$^{\circ}G_{La_2O_3}^H$	[22]
$^{\circ}G_{La_2O_3}^X$	[22]
$^{\circ}G_U^{\alpha}$	[20]
$^{\circ}G_U^{\beta}$	[20]
$^{\circ}G_U^{\gamma}$	[20]
$^{\circ}G_{UO_3}$	[15]
$^{\circ}G_{U_3O_8}^{\alpha}$	[15]
$^{\circ}G_{U_3O_8}^{\beta}$	[15]
$^{\circ}G_{U_3O_8}^{\gamma}$	[15]
$^{\circ}G_{U_3O_8}^{\delta}$	[15]
$^{\circ}G_{U_4O_9}^{\alpha}$	[15]
$^{\circ}G_{U_4O_9}^{\beta}$	[15]
$^{\circ}G_{U_4O_9}^{\gamma}$	[15]

$$\begin{aligned} {}^\circ G_{U_2La_6O_{15}} = & -8975017.608 + 3570.35355T - 573.361T \ln T \\ & + 2.928000E-04T^2 - 6.361983E-06T^3 + \\ & 4.161472E+06T^{-1} - 30000000T^{-2} \end{aligned}$$

This work

Fluorite SS: $(U^{3+}, U^{4+}, U^{5+}, U^{6+}, La^{3+})_1(O^{2-}, Va^0)_2(O^{2-}, Va^0)$

$$\begin{aligned} {}^\circ G_{La_2O_3} = & -1834559.8 + 686.41611T - 119.72939 T \ln T \\ & - 0.007115T^2 + 675024.4700T^{-1} \end{aligned}$$

[19]

$$\Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow CaF_2} = 8739$$

This work

$${}^\circ G_{La^{3+}:O:O} = \frac{1}{2} {}^\circ G_{La_2O_3} + \frac{3}{4} {}^\circ G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow CaF_2} - 173551.98 + 107.52T$$

This work

$${}^\circ G_{La^{3+}:O:Va} = \frac{1}{2} {}^\circ G_{La_2O_3} + \frac{1}{4} {}^\circ G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow CaF_2} - 140021.83 + 14.94T$$

This work

$${}^\circ G_{La^{3+}:Va:Va} = \frac{1}{2} {}^\circ G_{La_2O_3} - \frac{3}{4} {}^\circ G_{O_2} + \Delta E_{LaO_{1.5}}^{LaO_{1.5} \rightarrow CaF_2} + 387211.19 + 9.80T$$

This work

$${}^\circ G_{La^{3+}:Va:O} = 100000$$

This work

$$L_{U^{3+}.La^{3+}:O:Va}^0 = -50000$$

This work

$$L_{U^{3+}.La^{3+}:O:Va}^1 = 500000$$

This work

$$L_{U^{4+}.La^{3+}:Va:Va}^0 = -472248.79$$

This work

$$L_{U^{4+}.La^{3+}:O:Va}^0 = -48198.701$$

This work

$$L_{U^{5+}.La^{3+}:O:O}^0 = -427681.07$$

This work

$$L_{U^{5+}.La^{3+}:O:Va}^0 = -9350 - 50T$$

This work

$$L_{U^{5+}.La^{3+}:Va:Va}^0 = -786023.31 - 217.00T$$

This work

$$L_{U^{6+}.La^{3+}:O:Va}^0 = -75000$$

This work

Liquid: $(La^{3+}, U^{4+})_p(O^{2-}, Va^0, O)_Q$

$$\begin{aligned} {}^\circ G_{La^{3+}:Va} = & 5332.6530 + 18.230120 T - 11.018819T \ln T \\ & - 0.20171603E-01T^2 + 0.29377500E-05T^3 \\ & - 133541.00T^{-1} \end{aligned}$$

298<T<1134
[20]

$${}^\circ G_{La^{3+}:Va} = -3942.0031 + 171.01844T - 34.308800T \ln T$$

1134<T<4000

$$\begin{aligned} {}^\circ G_{La^{3+}:O^{2-}} = & -1691745.0 + 636.34440T - 120.62900T \ln T \\ & - 0.68540000E-02T^2 + 808000.00T^{-1} - 10000000T^{-2} \end{aligned}$$

[22]

$${}^{liq} L_{La^{3+}.U^{4+}:O^{2-}}^0 = 770000.00 - 320.00T$$

This work

$${}^{liq} L_{La^{3+}.U^{4+}:O^{2-}}^1 = 720000.00 - 276.00T$$

This work

$${}^{liq} L_{La^{3+}.U^{4+}:O^{2-}}^2 = 10000.0 - 29.997T$$

This work

$${}^{liq} L_{La^{3+}.U^{4+}:Va} = +1E6$$

This work

RI: $(U^{4+}, U^{5+}, U^{6+})_1(La^{3+})_6(O^{2-}, Va^0)_{12}$

$^{\circ}G_{U^{4+};La^{3+};O} = -6594442.10 + 19.7705140T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
$^{\circ}G_{U^{4+};La^{3+};Va} = -6624442.1 + 19.7705140T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
$^{\circ}G_{U^{5+};La^{3+};O} = -6390467.3 - 250.229T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
$^{\circ}G_{U^{5+};La^{3+};Va} = -6390467.3 - 250.2294T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
$^{\circ}G_{U^{6+};La^{3+};O} = -7283192.1 + 269.77051T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
$^{\circ}G_{U^{6+};La^{3+};Va} = -7339342.1 + 269.77051T - 119.7340T \ln T -$ $7.1130E-03T^2 + 675500T^{-1}$	This work
RIII: (La ³⁺ ,U ⁵⁺ ,U ⁶⁺) ₄ (La ³⁺) ₄ (O ²⁻) ₁₆	This work
$^{\circ}G_{La^{3+};La^{3+};O^{2-}} = -9171306.753 + 3686.43212T - 603.642T \ln T$ $+ 9.529E-03T^2 - 8.483E-06T^3 + 4471296T^{-1}$ $- 26666666.667T^{-2}$	This work
$^{\circ}G_{U^{5+};La^{3+};O^{2-}} = -9139089.753 + 3556.43212T - 603.642T \ln T$ $+ 9.529E-03T^2 - 8.483E-06T^3 + 4471296T^{-1}$ $- 26666666.667T^{-2}$	This work
$^{\circ}G_{U^{6+};La^{3+};O^{2-}} = -9109173.753 + 3686.43212T - 603.642T \ln T$ $+ 9.529E-03T^2 - 8.483E-06T^3 + 4471296T^{-1}$ $- 26666666.667T^{-2}$	This work

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7