Measurement of the Oxygen Partial Pressure and Thermodynamic Modeling of the U-Nd-O System

SeungMin Lee ^a, Travis W. Knight^{a*}, Jacob W. McMurray ^b, and Theodore M. Besmann^a

^aUniversity of South Carolina, 300 Main Street, Columbia, SC 29208

^bMaterials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Abstract

Fission products greatly impact the properties of fuel necessitating a thorough understanding of the thermochemical properties of oxide fuels with fission products. However, thermochemical data for the U-Nd-O system is insufficient even though neodymium is a major fission product. As neodymium will likely be present as a solute in UO₂, this research focuses on the study of (U_{1-y}Nd_y)O_{2±x}. Experimental measurements and analyses of the oxygen partial pressure (pO₂)-temperature-oxygen to metal ratio (O/M ratio) relationships were performed using a thermogravimetric analyzer (TGA) and an oxygen analyzer. Thermodynamic computational modeling was performed using the CALPHAD (CALculation of PHase Diagrams) method with the FactSage software. The Gibbs energy of the (U_{1-y}Nd_y)O_{2±x} solid solution was described by the compound energy formalism (CEF), which is based on earlier thermodynamic modeling data of the binary U-O system from Guéneau et al.. The thermodynamic and phase diagram data of the U-Nd-O system produced in this work show good agreement with the experimental data.

*Corresponding author. Tel.: +1 803 777 1465.
Email: knighttw@cec.sc.edu

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1. Introduction

High burnup oxide fuel will undergo fission for a longer period at high temperature and fuel properties will be influenced by the increasing concentration of fission products in the fuel. It is therefore necessary to understand the properties and characteristics of the fuel with the added influence of fission products to appropriately represent fuel behavior [1,2]. Several previous investigations have been performed on uranium-rare earth oxide systems. This research focuses specifically on experimental work and computational modeling for the U-Nd-O system because Nd is a dominant fission product in the fluorite oxide [1, 3, 4]. It is also important to understand the oxidation of fission products in the oxide fuel because oxygen potential is an important parameter in fuel behavior. Oxygen potential is affected by impurities such as fission products which can cause phase transformation in the fuel and influence its characteristics, and also affect oxidation of the cladding. Oxygen potential and O/M ratio can be measured and are dependent on the temperature and concentration of fission products in the uranium dioxide fuel. In the case of neodymium, the Nd^{3+} valence in the uranium oxide fuel increases the oxygen potential of UO_{2+x} due to the higher affinity for oxygen [1, 3].

This research included TGA experimental measurements and computational modeling performed to establish a thermodynamic understanding of the U-Nd-O system using the CALPHAD approach [7, 21, 22]. In this work a complete thermochemical database for the U-Nd-O system is developed from experiments together with earlier thermodynamic modeling data of the binary U-O system from Guéneau et al. [7] and data for the binary Nd-O system from the

literature. This work provides suitable experimental procedures and thermodynamic modeling methods useful for other oxide systems, especially uranium-rare earth oxide systems.

2. Experiment and Modeling

2.1. Sample preparation

Four oxide powder compositions were prepared at Oak Ridge National Laboratory (ORNL): 5.6%, 15.5%, 29.5%, and 53.0% (atomic) Nd concentration by the Modified Direct Denitration (MDD) process [8, 9]. Auranyl nitrate solution was prepared by dissolving a known weight of UO_2 in nitric acid and the neodymium nitrate solution was prepared by dissolving a known weight of neodymium nitrate hexahydrate in water. Mixtures of the U-Nd parent batch were then prepared by weighing the solutions, and ammonium nitrate was added to the U-Nd weak nitric acid solution in a 2:1 molar ratio of NH_4 to metal. The mixed metal nitrate double salt was passed through a perforated center tube and allowed it to drip onto the inner wall of a heated rotating pipe where it dehydrated and began to decompose as it traveled down the heated pipe. The decomposition product was an amorphous solid oxide which was sieved and calcined in a furnace at 823 K to ensure complete conversion and to transform the product from an amorphous to a crystalline solid. The decomposition atmosphere is oxygen rich so the oxide that is formed is a two-phase mixture and each phase is in the highest oxidation state (i.e., UO_3 and Nd_2O_3). This highest oxidation state was substantiated using X-ray diffraction (XRD) and TGA/DTA at ORNL [8, 9]. When the product is heated at high temperature (>1473 K) during sintering, the two-phase mixture readily forms a single fluorite phase solid solution under the reducing atmosphere needed to achieve an oxygen stoichiometry of 2.0 [8-10]. Each powder sample was pressed at 280 MPa for 5 minutes into a pellet which was 13 mm in diameter and

2mm in thickness. After pressing, it was heated at 723K for 5 hours to evaporate all moisture in the pellet and sintered in a 4% H₂ – 96% Ar mixture gas at 1873K for 5 hours to produce stoichiometric (U_{1-y}Nd_y)O₂. To verify a single fluorite phase solid solution of (U_{1-y}Nd_y)O₂ XRD measurements were performed and the results showed good agreement with earlier work[10].

2.2. Measurement of the oxygen partial pressure and O/M ratio for the (U_{1-y}Nd_y)O_{2±x} solid solution

A TGA (NETZSCH STA-409CD) was employed to adjust stoichiometry and perform measurements for (U_{1-y}Nd_y)O_{2±x}. Calibration tests of the TGA thermocouple were carried out using melting point standards of indium, gold and nickel. The uncertainty was found to be about ±3 K. Experiments in the TGA were performed at 1281K, 1586K, 1790K and 1944K. All samples were equilibrated at a given temperature and specific pO₂ to obtain the desired hyper- or hypo-stoichiometric (U_{1-y}Nd_y)O_{2±x}. The O/M ratio was typically set to 2.0, and experiments proceed to the desired non-stoichiometric (U_{1-y}Nd_y)O_{2±x} equilibrium state by adjusting temperature and oxygen pressure. At each equilibrium the sample mass change from the stoichiometric condition was measured and the equilibrium O/M ratio calculated.

An oxygen analyzer was employed to measure oxygen partial pressure and confirm values expected from the gas composition. The oxygen analyzer (Cambridge-sensotec Rapidox3100) was connected to the exhaust line from the TGA and determined the oxygen concentration in the gas. Calibration tests of the oxygen analyzer were carried out using various gas flow rates (mixtures of UHP Ar and 5% H₂ – Ar were used). The measurements indicated an uncertainty within 5%, so that no adjustment of the oxygen analyzer was needed.

A total of 151 experiments were conducted for the four temperatures used to determine pO₂ and O/M ratio at a fixed temperature.

2.3. Thermochemical modeling

The considered U-Nd-O system consists of a gas phase, liquid phase, solid phases of the metals and their oxides, which include a fluorite solid solution phase and a rhombohedral oxide phase according to the surveyed literature [7, 11-17]. Thermodynamic values and models for all phases in the U-Nd-O system were defined using the Gibbs energy approach determined by CALPHAD method [7, 21-22]. Specifically, the CEF model for the fluorite solid solution phase and oxide rhombohedral phase was employed in this work. The CEF model for the U-O system has been established by Guéneau et al. [7] and the U-Nd-O system described herein is an extension of their multi-sublattice representation of the U-O system.

The gas phase can be described by an ideal gas mixture and the following species are considered: Nd, NdO, NdO₂, O, O₂, O₃, U, UO, UO₂, and UO₃. The Gibbs energy of the gas phase can be expressed by:

$$G^{gas} = \sum_i x_i [\circ G_i^{gas} - \sum_j b_{ij} H_j^{SER} + RT \ln x_i] + RT \ln \left(\frac{P}{P_0} \right) \quad \text{Eq. (1)}$$

where x_i is the mole fraction of gaseous species i , b_{ij} is the number of atoms j in the species i , P_0 is the standard pressure of 1 atm, P is the total pressure, $\circ G_i^{gas}$ is the standard Gibbs energy of species i , H_j^{SER} is the enthalpy of the atom j in the species i at 298.15 K and 1 atm, R is the ideal gas constant, and T is the absolute temperature. The Gibbs energy of the gaseous species were taken from the FACT database in FactSage [20].

The liquid phase can be described by the ionic two-sublattice model [7, 22] and expressed by:

$$P = \sum_j v_j y_{Aj} + Q y_{Va}$$

$$Q = \sum_i v_i y_{Ci}$$

Eq. (2)

where P and Q are equal to the average charge on the opposite sublattice, y_i is the site fraction and v_i is the charge of the constituent i, A is an anion, C is a cation, and Vais a vacancy [7, 22].
The molar Gibbs energy for the liquid phase is defined in this treatment by:

$$\begin{aligned} G^{liquid} = & \cancel{y_{U^{4+}} y_{O^{2-}} G_{U^{4+}, O^{2-}}^0 + y_{Nd^{3+}} y_{O^{2-}} G_{Nd^{3+}, O^{2-}}^0 + Q y_{Va} G_{U^{4+}, Va}^0 + Q y_{Va} G_{Nd^{3+}, Va}^0 + Q y_O G_O^0} \\ & + \cancel{PRT(y_{U^{4+}} \ln y_{U^{4+}} + y_{Nd^{3+}} \ln y_{Nd^{3+}})} \\ & + \cancel{QRT(y_{O^{2-}} \ln y_{O^{2-}} + y_{Va} \ln y_{Va} + y_O \ln y_O)} \\ & + \cancel{y_{Nd^{3+}} y_{U^{4+}} y_{O^{2-}} [L_{Nd^{3+}, U^{4+}, O^{2-}}^0 + (y_{Nd^{3+}} - y_{U^{4+}}) L_{Nd^{3+}, U^{4+}, O^{2-}}^1} \\ & + (y_{Nd^{3+}} - y_{U^{4+}}) L_{Nd^{3+}, U^{4+}, O^{2-}}^2]} \\ & + \cancel{y_{Nd^{3+}} y_{U^{4+}} y_{Va} [L_{Nd^{3+}, U^{4+}, Va}^0 + (y_{Nd^{3+}} - y_{U^{4+}}) L_{Nd^{3+}, U^{4+}, Va}^1}]} \\ & + \cancel{y_{U^{4+}} y_{O^{2-}} y_{Va} [L_{U^{4+}, O^{2-}, Va}^0 + (y_{O^{2-}} - y_{Va}) L_{U^{4+}, O^{2-}, Va}^1} \\ & + (y_{O^{2-}} - y_{Va}) L_{U^{4+}, O^{2-}, Va}^2]} \\ & + \cancel{y_{Nd^{3+}} y_{O^{2-}} y_{Va} [L_{Nd^{3+}, O^{2-}, Va}^0 + (y_{O^{2-}} - y_{Va}) L_{Nd^{3+}, O^{2-}, Va}^1}]} \\ & + \cancel{y_{U^{4+}} y_{O^{2-}} y_O (L_{U^{4+}, O^{2-}, O}^0)} \end{aligned}$$

Eq. (3)

where L is an interaction parameter which is obtained from the optimization of tunable parameters. Nd^{3+} was added to the first sub-lattice of the ionic liquid model developed by Guéneau et al. [7].

The stoichiometric phases, Nd, Nd₂O₃, U, UO₃, U₃O₈ and U₄O₉, have temperature dependent Gibbs energies [7, 11] with the form:

$$G^\phi - \sum_i n_i^\phi H_i^{SER} = a + bT + cT \ln T + \sum_n d_n T^n$$

Eq. (4)

where n_i^ϕ is the stoichiometric coefficient of element i in ϕ and H_i^{SER} is the enthalpy of the element i in its stable state at the temperature of 298.15 K and 1 atm.

For the variable composition (U_{1-y}Nd_y)O_{2+x}, a three sub-lattice model is employed which is described by (U³⁺, U⁴⁺, U⁵⁺, U⁶⁺, Nd³⁺)₁(O²⁻, Va)₂(O²⁻, Va)₁. The Gibbs energies for the end members containing U³⁺, U⁴⁺ and U⁵⁺ constituents are defined by Guéneau et al. [7] with the addition of end members containing U⁶⁺ defined by McMurray et al. [12]. The Nd³⁺ containing end members were defined in this work. The Gibbs energy for the fluorite solid solutions can be expressed by Eq. (5) through Eq. (7).

$$G_{fluorite}^{CEF} = \sum_i G_i^\circ \prod_s y_i^s + RT \left(\sum_s n^s \sum_i y_i^s \ln y_i^s \right) + G_{fluorite}^E$$

Eq. (5)

where $G_{fluorite}^E$ is the excess Gibbs energy of the fluorite solid solution.

$$\begin{aligned}
G_{(U,Nd)O_2}^{CEF} = & \cancel{y_{U^{3+}}^1 y_{O^{2-}}^2 y_{O^{2-}}^3 G_{U^{3+}:O^{2-}:O^{2-}}^\circ} + \cancel{y_{U^{3+}}^1 y_{O^{2-}}^2 y_{Va}^3 G_{U^{3+}:O^{2-}:Va}^\circ} + \cancel{y_{U^{3+}}^1 y_{Va}^2 y_{O^{2-}}^3 G_{U^{3+}:Va:O^{2-}}^\circ} \\
& + \cancel{y_{U^{3+}}^1 y_{Va}^2 y_{Va}^3 G_{U^{3+}:Va:Va}^\circ} + \cancel{y_{U^{4+}}^1 y_{O^{2-}}^2 y_{O^{2-}}^3 G_{U^{4+}:O^{2-}:O^{2-}}^\circ} + \cancel{y_{U^{4+}}^1 y_{O^{2-}}^2 y_{Va}^3 G_{U^{4+}:O^{2-}:Va}^\circ} \\
& + \cancel{y_{U^{4+}}^1 y_{Va}^2 y_{O^{2-}}^3 G_{U^{4+}:Va:O^{2-}}^\circ} + \cancel{y_{U^{4+}}^1 y_{Va}^2 y_{Va}^3 G_{U^{4+}:Va:Va}^\circ} + \cancel{y_{U^{5+}}^1 y_{O^{2-}}^2 y_{O^{2-}}^3 G_{U^{5+}:O^{2-}:O^{2-}}^\circ} \\
& + \cancel{y_{U^{5+}}^1 y_{O^{2-}}^2 y_{Va}^3 G_{U^{5+}:O^{2-}:Va}^\circ} + \cancel{y_{U^{5+}}^1 y_{Va}^2 y_{O^{2-}}^3 G_{U^{5+}:Va:O^{2-}}^\circ} + \cancel{y_{U^{5+}}^1 y_{Va}^2 y_{Va}^3 G_{U^{5+}:Va:Va}^\circ} \\
& + \cancel{y_{U^{6+}}^1 y_{O^{2-}}^2 y_{O^{2-}}^3 G_{U^{6+}:O^{2-}:O^{2-}}^\circ} + \cancel{y_{U^{6+}}^1 y_{O^{2-}}^2 y_{Va}^3 G_{U^{6+}:O^{2-}:Va}^\circ} + \cancel{y_{U^{6+}}^1 y_{Va}^2 y_{O^{2-}}^3 G_{U^{6+}:Va:O^{2-}}^\circ} \\
& + \cancel{y_{U^{6+}}^1 y_{Va}^2 y_{Va}^3 G_{U^{6+}:Va:Va}^\circ} + \cancel{y_{Nd^{3+}}^1 y_{O^{2-}}^2 y_{O^{2-}}^3 G_{Nd^{3+}:O^{2-}:O^{2-}}^\circ} + \cancel{y_{Nd^{3+}}^1 y_{O^{2-}}^2 y_{Va}^3 G_{Nd^{3+}:O^{2-}:Va}^\circ} \\
& + \cancel{y_{Nd^{3+}}^1 y_{Va}^2 y_{O^{2-}}^3 G_{Nd^{3+}:Va:O^{2-}}^\circ} + \cancel{y_{Nd^{3+}}^1 y_{Va}^2 y_{Va}^3 G_{Nd^{3+}:Va:Va}^\circ} \\
& + RT \left(\cancel{y_{U^{3+}}^1 \ln y_{U^{3+}}^1} + \cancel{y_{U^{4+}}^1 \ln y_{U^{4+}}^1} + \cancel{y_{U^{5+}}^1 \ln y_{U^{5+}}^1} + \cancel{y_{U^{6+}}^1 \ln y_{U^{6+}}^1} + \cancel{y_{Nd^{3+}}^1 \ln y_{Nd^{3+}}^1} \right) \\
& + 2RT \left(\cancel{y_{O^{2-}}^2 \ln y_{O^{2-}}^2} + \cancel{y_{Va}^2 \ln y_{Va}^2} \right) + RT \left(\cancel{y_{O^{2-}}^3 \ln y_{O^{2-}}^3} + \cancel{y_{Va}^3 \ln y_{Va}^3} \right) + G^E
\end{aligned}$$

Eq. (6)

$$\begin{aligned}
G_{(U,Nd)O_2}^E = & \cancel{y_{U^{3+}}y_{U^{4+}}y_{O^{2-}}y_{Va} \left[L_{(U^{3+},U^{4+})(O^{2-})(Va)}^{(U,Nd)O_2} + (y_{U^{3+}} - y_{U^{4+}})L_{(U^{3+},U^{4+})(O^{2-})(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{4+}}y_{U^{5+}}y_{O^{2-}}y_{O^{2-}} \left[L_{(U^{4+},U^{5+})(O^{2-})(O^{2-})}^{(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{3+}}y_{Nd^{3+}}y_{O^{2-}}y_{O^{2-}} \left[L_{(U^{3+},Nd^{3+})(O^{2-})(O^{2-})}^{(U,Nd)O_2} + (y_{U^{3+}} - y_{Nd^{3+}})L_{(U^{3+},Nd^{3+})(O^{2-})(O^{2-})}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{3+}}y_{Nd^{3+}}y_{O^{2-}}y_{Va} \left[L_{(U^{3+},Nd^{3+})(O^{2-})(Va)}^{(U,Nd)O_2} + (y_{U^{3+}} - y_{Nd^{3+}})L_{(U^{3+},Nd^{3+})(O^{2-})(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{3+}}y_{Nd^{3+}}y_{Va}y_{Va} \left[L_{(U^{3+},Nd^{3+})(Va)(Va)}^{(U,Nd)O_2} + (y_{U^{3+}} - y_{Nd^{3+}})L_{(U^{3+},Nd^{3+})(Va)(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{4+}}y_{Nd^{3+}}y_{O^{2-}}y_{O^{2-}} \left[L_{(U^{4+},Nd^{3+})(O^{2-})(O^{2-})}^{(U,Nd)O_2} + (y_{U^{4+}} - y_{Nd^{3+}})L_{(U^{4+},Nd^{3+})(O^{2-})(O^{2-})}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{4+}}y_{Nd^{3+}}y_{O^{2-}}y_{Va} \left[L_{(U^{4+},Nd^{3+})(O^{2-})(Va)}^{(U,Nd)O_2} + (y_{U^{4+}} - y_{Nd^{3+}})L_{(U^{4+},Nd^{3+})(O^{2-})(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{4+}}y_{Nd^{3+}}y_{Va}y_{Va} \left[L_{(U^{4+},Nd^{3+})(Va)(Va)}^{(U,Nd)O_2} + (y_{U^{4+}} - y_{Nd^{3+}})L_{(U^{4+},Nd^{3+})(Va)(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{5+}}y_{Nd^{3+}}y_{O^{2-}}y_{O^{2-}} \left[L_{(U^{5+},Nd^{3+})(O^{2-})(O^{2-})}^{(U,Nd)O_2} + (y_{U^{5+}} - y_{Nd^{3+}})L_{(U^{5+},Nd^{3+})(O^{2-})(O^{2-})}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{5+}}y_{Nd^{3+}}y_{O^{2-}}y_{Va} \left[L_{(U^{5+},Nd^{3+})(O^{2-})(Va)}^{(U,Nd)O_2} + (y_{U^{5+}} - y_{Nd^{3+}})L_{(U^{5+},Nd^{3+})(O^{2-})(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{5+}}y_{Nd^{3+}}y_{Va}y_{Va} \left[L_{(U^{5+},Nd^{3+})(Va)(Va)}^{(U,Nd)O_2} + (y_{U^{5+}} - y_{Nd^{3+}})L_{(U^{5+},Nd^{3+})(Va)(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{6+}}y_{Nd^{3+}}y_{O^{2-}}y_{O^{2-}} \left[L_{(U^{6+},Nd^{3+})(O^{2-})(O^{2-})}^{(U,Nd)O_2} + (y_{U^{6+}} - y_{Nd^{3+}})L_{(U^{6+},Nd^{3+})(O^{2-})(O^{2-})}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{6+}}y_{Nd^{3+}}y_{O^{2-}}y_{Va} \left[L_{(U^{6+},Nd^{3+})(O^{2-})(Va)}^{(U,Nd)O_2} + (y_{U^{6+}} - y_{Nd^{3+}})L_{(U^{6+},Nd^{3+})(O^{2-})(Va)}^{1(U,Nd)O_2} \right]} \\
& \cancel{+ y_{U^{6+}}y_{Nd^{3+}}y_{Va}y_{Va} \left[L_{(U^{6+},Nd^{3+})(Va)(Va)}^{(U,Nd)O_2} + (y_{U^{6+}} - y_{Nd^{3+}})L_{(U^{6+},Nd^{3+})(Va)(Va)}^{1(U,Nd)O_2} \right]}
\end{aligned}$$

Eq. (7)

where y is the fraction of ionic species in the sub-lattice and L is a set of interaction parameters defined by Redlich-Kister expansion [23].

The rhombohedral phase ULa_6O_{12} from McMurray et al. was used with the end members modified to replace La with Nd in this work [12]. Thus the rhombohedral phase can be described by $(U^{4+}, U^{5+}, U^{6+})_1(Nd^{3+})_6(O^{2-}, Va)_{12}$ and the Gibbs energy is defined by Eq. (8).

$$\begin{aligned}
 G^{UNd_6O_{12}} = & \cancel{y_{U^{4+}}^1 y_{Nd^{3+}}^2 y_{O^{2-}}^3 G_{U^{4+}:Nd^{3+}:O^{2-}}^\circ} + \cancel{y_{U^{4+}}^1 y_{Nd^{3+}}^2 y_{Va}^3 G_{U^{4+}:Nd^{3+}:Va}^\circ} + \cancel{y_{U^{5+}}^1 y_{Nd^{3+}}^2 y_{O^{2-}}^3 G_{U^{5+}:Nd^{3+}:O^{2-}}^\circ} \\
 & + \cancel{y_{U^{5+}}^1 y_{Nd^{3+}}^2 y_{Va}^3 G_{U^{5+}:Nd^{3+}:Va}^\circ} + \cancel{y_{U^{6+}}^1 y_{Nd^{3+}}^2 y_{O^{2-}}^3 G_{U^{6+}:Nd^{3+}:O^{2-}}^\circ} \\
 & + \cancel{y_{U^{6+}}^1 y_{Nd^{3+}}^2 y_{Va}^3 G_{U^{6+}:Nd^{3+}:Va}^\circ} + RT \left(\cancel{y_{U^{4+}}^1 \ln y_{U^{4+}}^1} + \cancel{y_{U^{5+}}^1 \ln y_{U^{5+}}^1} + \cancel{y_{U^{6+}}^1 \ln y_{U^{6+}}^1} \right) \\
 & + 12RT \left(\cancel{y_{O^{2-}}^3 \ln y_{O^{2-}}^3} + \cancel{y_{Va}^3 \ln y_{Va}^3} \right)
 \end{aligned}$$

Eq. (8)

For the optimization process the Optisage module of FactSage was utilized and all available thermodynamic data such as oxygen potential versus O/M ratio and temperature, phase equilibria, heat capacity, and enthalpy increment were used. The Gibbs energy of end members and interaction parameters for the excess Gibbs energy term were adjusted in the optimization process to obtain the best representation of the data.

3. Results and Discussion

3.1. Oxygen partial pressure vs. O/M ratio vs. temperature

Table 1 is a summary of the experimental results from this work (detailed measurement data used in the optimization are tabulated in Appendix B). The experimental results show the typical sigmoidal curve with oxygen partial pressure versus O/M ratio (Plots with the experimental results are shown in section 3.2). In addition, the oxygen partial pressure of the U-Nd-O system is influenced by temperature and Nd concentration. For example, the oxygen

partial pressure increased as the Nd concentration increased as noted above. Oxygen partial pressure also increased with temperature at a given Nd concentration as would be expected.

Nd concentration	Temp. (K)	O/M ratio	-Log(pO ₂)
5.6%	1281-1944	1.9850-2.0162	19.059-7.434
15.5%	1281-1944	1.9629-2.0011	17.068-7.021
29.5%	1281-1944	1.9354-2.0066	17.000-4.979
53.0%	1281-1944	1.8215-2.0000	16.863-0.000

Table 1. Summary of the experimental results from this work.

3.2. Optimization of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution

To optimize the interaction parameters of the liquid phase and solid solution phase, available data from both this work and the literature were used. In addition, adjusting Gibbs energies for the Nd containing end members was necessary to overcome the tendency to indicate a miscibility gap at high temperatures when in fact it is only observed at relatively low temperatures. Figures 1-4 show the comparison between the calculated pO₂(solid line) and measured pO₂ with the different Nd concentration sample groups at different temperatures.

Figure 1. Comparison between computed and experimental oxygen partial pressure values for 5.6%Nd at 1281K, 1586K, 1790K, and 1944K.

Figure 2. Comparison between computed and experimental oxygen partial pressure values for 14% and 15.5% Nd at various temperatures.

Figure 3. Comparison between computed and experimental oxygen partial pressure values for 27% and 29.5% Nd at various temperatures.

Figure 4. Comparison between computed and experimental oxygen partial pressure values for 53%Nd at 1281K, 1586K, 1790K, and 1944K.

The measured data are in good agreement with the calculated values. Wadier[14] measured oxygen potentials at 20%, 30%, 40%, and 50%Nd at 1123K, however his experimental data showed a greater residual than data from this work or that of Une and Oguma[13]. Therefore, the oxygen partial pressure data from Wadier[14] was excluded in the optimization. In addition, the oxygen partial pressure data for 53%Nd concentration from this work showed higher residuals than did that for lower Nd concentrations. This is due to the difficulty in obtaining a standard O/M ratio of 2.0 at this high concentration of Nd. To resolve this difficulty the XRD lattice parameter data was employed assuming a linear relationship between lattice parameter and O/M ratio. After a sample reached an arbitrary equilibrium state at a given pO_2 in

the TGA, the lattice parameter was determined by XRD. The O/M ratio was then derived from the linear relationship and was used as a standard point. While this can provide reasonably good values, they are inferior to those obtained by fixing the O/M at 2.0 using the wide oxygen potential range at O/M=2 present at the lower Nd concentrations.

The site fractions of the ionic species and vacancies derived from the CEF model for $(U_{1-y}Nd_y)O_{2\pm x}$ vary predictably depending on Nd concentration and O/M ratio as shown in Figure 5.

Figure 5. Calculated site fractions of the ionic species and vacancies in the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution phase at 1573K for different Nd concentrations.

3.3. Computed phase diagrams

Phase diagrams for the U-Nd-O system were computed (Figs. 6-8) and compared to those in the literature [15-18] and are in good agreement with the experimental data of Keller et al [15] and Lambertson et al [16].

Figure 6. Calculated ternary phase diagram of the U-Nd-O system at 1523K. Source of data points: Keller et al. [15].

Figure 7. Calculated pseudo-binary phase diagram of the $\text{UO}_2\text{-NdO}_{1.5}$ system. Source of data points: Lambertson et al. [16].

Figure 8. Calculated binary phase diagram of the U-Nd under 1 atm of pO_2 . Source of data points: Keller et al. [15].

Figure 9 is a computed binary phase diagram of the Nd-O system which compares well with that computed by Lysenko[17].

Figure 9. Calculated binary phase diagram of the Nd-Osystem (Nd-Nd₂O₃).

Figure 10 shows the binary phase diagram of the U-Nd system and Fig. 11 shows the ternary phase diagram of the U-Nd-O system at low temperature. A miscibility gap at low temperature was predicted in Dottavio et al. [18] which is reproduced in the current computed diagram.

Figure 10. Calculated tentative binary phase diagram of the U-Nd system.

Figure 11. Calculated ternary phase diagram of the U-Nd-O system showing a miscibility gap at 800K.

3.4. Heat Capacity, Enthalpy and Entropy

Results from the current assessment for heat capacity, enthalpy, and entropy of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution were compared to the experimental data from Krishnan et al. [19](Figs. 12-14). The measured thermodynamic data for the solid solution are seen to be in good agreement with the calculated values from this work.

Figure 12. Comparison of the calculated heat capacity (lines) and measurements (points) of Krishnan et al. [19].

Figure 13. Comparison of the computed enthalpy (lines) and measurements (points) of Krishnan et al. [19].

Figure 14. Comparison of the computed entropy (lines) and measurements (points) of Krishnan et al. [19].

4. Conclusions

Oxygen partial pressure measurements over the single phase $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution were performed, and experimental pO_2 data, phase equilibria, heat capacity, and enthalpy increment were used to optimize thermodynamic interaction parameters and end member Gibbs energies for the U-Nd-O system using the CALPHAD method. For modeling the U-Nd-O system, the sub-systems of U-O and Nd-O were combined, and the thermodynamic data for all end members were calculated using FactSage [20, 21]. The U-O system assessment by Guéneau et al. [7] was used as a basis, and the Nd-O system was integrated to assess the U-Nd-O system. Very good agreement between the experimental data and calculated relations was obtained for oxygen

partial pressures, phase equilibria, heat capacity, enthalpy and entropy. As a result of this work, a useful thermodynamic database for the U-Nd-O system has been developed that is also suitable for use in expanded models of urania with multiple dissolved fission products and additives.

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