Thermodynamic assessment of the U-Y-O system

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Abstract

A CALPHAD assessment of the U-Y-O system has been developed. To represent the YO_2 compound in the compound energy formalism (CEF) for $\text{U}_{1-y}\text{Y}_y\text{O}_{2\pm x}$, the lattice stability was calculated using density functional theory (DFT) while a partially ionic liquid sub-lattice model is used to describe the liquid phase. A Gibbs function for the stoichiometric rhombohedral UY_6O_{12} phase is proposed. Models representing the phases in the U-O and Y-O systems taken from the literature along with the phases that appear in the U-Y-O ternary are combined to form a complete assessment.

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

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1. Introduction

Modeling the behavior of a nuclear fuel element using a multi-physics approach is the subject of intense interest [1-3]. The use of thermodynamics plays an important role in this effort by providing inputs, such as chemical potentials and thermal properties, for phase transformation, microstructure evolution, and continuum transport simulations. Yttrium is a high-yield fission product that dissolves in $\text{UO}_{2\pm x}$ to form a solid solution given by the formula $\text{U}_{1-y}\text{Y}_y\text{O}_{2\pm x}$. Since fluorite structure urania is the dominant phase in reactor fuel, the chemistry of $\text{U}_{1-y}\text{Y}_y\text{O}_{2\pm x}$ plays an important role in the overall behavior of the system. In order to properly describe the complex urania fuel phase, a self-consistent thermodynamic description of the U-Y-O ternary needs to be included. Therefore, the objective of this work is the development an assessment of U-Y-O from 298 K to 3100 K.

2. Background

An accurate and inclusive model of fluorite structure urania with dissolved transuranics and fission products is necessary for representing the phase in oxide nuclear fuel, and it is being developed based on the recent assessment of $\text{UO}_{2\pm x}$ by Guéneau et al. [4]. For consideration of the Y-O system the assessment of Djurovic et al. [5] was utilized. The high-temperature phase relations in the U-Y-O ternary have been characterized in two separate studies [6, 7]. The phase diagrams of Bartram et al. [6] and Aitken and Joseph [7] however, partially disagree, with the fluorite phase in the latter containing significantly more yttrium than that of the former. Since there is a significant difference between the proposed phase regions, and Aitken and Joseph [7] only determined the presence of the fluorite and rhombohedral phases, the phase equilibria of Bartram et al. [6] were used in the current assessment. A limitation in the work of Bartram et al. [6] however, is that no three-phase regions appear in their proposed diagram, whereas that would be expected based on observations in similar systems containing rare earths (RE) [8]. The only other thermodynamic data for this system are from thermogravimetric determinations of oxygen potential vs O/M of Hagemark and Broli [9] and partial pressure determinations of U, UO, and UO_2 species from the Knudsen effusion mass spectrometry (KEMS) of Nakajima et al. [10].

3. Modeling

In the assessment the various phases are represented by thermochemical models which together with available property measurements, thermodynamic data, and phase equilibria allow description of the ternary U-Y-O system. The models of the phases and their thermodynamic functions are optimized with respect to observations [6, 7, 9] in the system to obtain a self-consistent description and are compared to the results of the KEMS of Nakajima et al. [10].

3.1 Gaseous phase

The predominant constituents of the gas phase in the U-Y-O system are O₂, O₃, YO, YO₂, Y₂O, Y₂O₂, UO, UO₂, and UO₃. The thermodynamic data for these vapor species comes from the SGTE Substance 1997 database [11].

3.2 Liquid Phase

Descriptions of Y-O [5] were used to extend the partially ionic two sub-lattice liquid model of U-O after Guéneau et al. [4, 12] to represent the U-Y-O melt by including Y³⁺, so that the sub-lattice description is defined as:

where Va^{Q-} is a charged vacancy, and O is a neutral oxygen species.

Charge neutrality is maintained by fixing the values of P and Q as follows:

$$P = 2y_{O^{2-}} + Qy_{Va} \quad (1)$$

$$Q = \sum_i v_i y_i \quad (2)$$

where v_i and y_i are the charge and site fraction of the constituent i , respectively.

The Gibbs energy of the system is defined by:

$$G^{liq} = \sum_C \sum_A y_C y_A {}^\circ G_{C:A} + Qy_{Va} \sum_C y_C {}^\circ G_C + Qy_O {}^\circ G_O - TS^{liq} + {}^{xs}G^{liq} \quad (3)$$

where ${}^\circ G_{C:A}$ corresponds to the standard free energy of the liquid with the formula $C_{v_A}A_{v_C}$ and ${}^\circ G_C$ is the Gibbs energy of the elemental cations corresponding to the pure liquid metal. The parameters y_O and ${}^\circ G_O$ represent the site fraction and Gibbs energy for the neutral oxygen atom, respectively. The ${}^{xs}G^{liq}$ term is an excess energy term described in this case by the zeroth, first, and second order interaction parameters, L^j , between the components in a Redlich-Kister polynomial expansion:

$$\begin{aligned}
{}^{XS}G^{liq} = & y_{Y^{3+}}y_{U^{4+}}y_{O^{2-}}[{}^{liq}L_{Y^{3+},U^{4+},O^{2-}}^0 \\
& + (y_{Y^{3+}} - y_{U^{4+}}){}^{liq}L_{Y^{3+},U^{4+},O^{2-}}^1 + (y_{Y^{3+}} - y_{U^{4+}})^2{}^{liq}L_{Y^{3+},U^{4+},O^{2-}}^2] \\
& + y_{Y^{3+}}y_{U^{4+}}y_{Va}{}^{liq}L_{Y^{3+},U^{4+},Va}^0 y_{U^{4+}}y_{O^{2-}}y_{Va}[{}^{liq}L_{U^{4+},O^{2-},Va}^0 \\
& + (y_{O^{2-}} - y_{Va}){}^{liq}L_{U^{4+},O^{2-},Va}^1 + (y_{O^{2-}} - y_{Va})^2{}^{liq}L_{U^{4+},O^{2-},Va}^1]
\end{aligned} \tag{4}$$

The configurational entropy of the system is given by:

$$S^{liq} = -R[P \sum_C y_C \ln y_C + Q(\sum_A y_A \ln y_A + y_{Va} \ln y_{Va} + y_0 \ln y_0)] \tag{5}$$

where R is the ideal gas law constant.

3.3 Pure Elements and stoichiometric phases

The compounds U_4O_9 , U_3O_8 , and UO_3 are treated as stoichiometric for consistency with the U-O assessment of Guéneau [4]. The Gibbs functions for the compounds and U metallic polymorphs come from the SGTE 1997 Substance database [11] while those for Y are from [5].

3.4 Rhombohedral phases

Aitken [13] was first to observe a rhombohedral (RI) structure belonging to the $R\bar{3}$ space group with RE and U atoms on distinct cation sub-lattices, and O on an anion sub-lattice. This phase was reported to exhibit variable stoichiometry and Aitken [13] chose to represent it using the formula $U_mY_{7-m}O_{12}$ where $1 \leq m \leq 3.4$. For simplicity, in this work the phase is treated as the stoichiometric UY_6O_{12} compound, with the heat capacity, C_p , approximated with the Neumann-Kopp rule and the heat of formation determined from the system optimization.

$$C_p^{UY_6O_{12}} = C_p^{UO_3} + 3C_p^{Y_2O_3} \tag{6}$$

A second rhombohedral phase, $U_nY_{8-n}O_{15}$ (RII), where n varies between 2 and 3.9 was determined be metastable [6, 13] and therefore is not included in the current optimization

3.5 Fluorite phase

As is well known, the fluorite structure $\text{UO}_{2\pm x}$ phase has a wide homogeneity range, and RE elements and Y readily dissolve in the phase with the metal atoms sharing a single cubic site. The phase can therefore be represented as $\text{U}_{1-y}\text{Y}_y\text{O}_{2\pm x}$.

The structure is modeled with three sub-lattices after Guéneau et al. [4]. The first sub-lattice represents the cation sites; the second represents the oxygen anions and vacancies tetrahedrally coordinated with U cations, and the third represents octahedrally coordinated sites for oxygen interstitials.

In the CEF representation the phase is treated as a mixture of the end-members given in Table 1.

Yttrium does not exist as a stable dioxide, therefore a lattice stability, $\Delta G_{\text{YO}_2}^{\text{YO}_{1.5} \rightarrow \text{YO}_2}$, for the fictive fluorite structure yttrium cation end-members was estimated as $\Delta E_{\text{YO}_2}^{\text{YO}_{1.5} \rightarrow \text{YO}_2}$ computed from density functional theory (DFT) at 0K using the generalized gradient approximation (GGA) and projector-augmented wave (PAW) potentials to describe the exchange-correlation and ion-electron interactions respectively. An energy cutoff of 500 eV was used for the plane wave basis while Gaussian broadening with a width of 0.05 eV smeared the density of states. The total energy E of a given phase was then calculated using the Vienna Ab initio package (VASP) [14, 15] and the following relation:

$$\Delta E_{\text{YO}_2}^{\text{YO}_{1.5} \rightarrow \text{YO}_2} = E_{\text{YO}_2} - \left(E_{\text{YO}_{1.5}} + \frac{1}{4} E_{\text{O}_2} \right) \quad (7)$$

where $\frac{1}{4}$ of the energy of O_2 gas was added to the sesquioxide $\text{YO}_{1.5}$ compound to adjust for stoichiometry. Using this approach, the lattice stability for fluorite YO_2 was computed to be +34.175 kJ/mol.

To obtain Gibbs energy values for the other fictive yttrium constituents in Table 1, the Gibbs energy for appropriate moles of O_2 gas was added or subtracted from that for $\text{YO}_{1.5}$ to adjust the stoichiometry and are determined as follows:

$${}^\circ G_{\text{Y}^{3+}:\text{O}:\text{O}} = \frac{1}{2} {}^\circ G_{\text{Y}_2\text{O}_3} + \frac{3}{4} {}^\circ G_{\text{O}_2} + \Delta E_{\text{YO}_{1.5}}^{\text{YO}_{1.5} \rightarrow \text{YO}_2} \quad (8)$$

$$^{\circ}G_{Y^{3+}:O:Va} = \frac{1}{2}^{\circ}G_{Y_2O_3} + \frac{1}{4}^{\circ}G_{O_2} + \Delta E_{YO_{1.5}}^{YO_{1.5} \rightarrow YO_2} \quad (9)$$

$$^{\circ}G_{Y^{3+}:Va:Va} = \frac{1}{2}^{\circ}G_{Y_2O_3} - \frac{3}{4}^{\circ}G_{O_2} + \Delta E_{YO_{1.5}}^{YO_{1.5} \rightarrow YO_2} \quad (10)$$

Given the very low likelihood of its stability, the value for $^{\circ}G_{Y^{3+}:Va:O}$ was arbitrarily set to +100,000 J/mol after Guéneau et al. [4]

4. Results

4.1 Optimization

The oxygen potential data from Hagemark and Broli [9] along with phase equilibria data from Bartram et al. [6] were used to optimize the adjustable parameters of the CEF model for $Y_{1-x}O_{2+x}$ and the standard state enthalpy and entropy values of the rhombohedral phase Gibbs function. The Optisage module of the FactSage thermochemical computational software [16] was used for the optimization. The thermodynamic functions and models from the U-O system [4], along with those from Y-O [5] were combined and augmented by adding the representations of the ternary phases. For the optimization, the enthalpy and entropy of the fluorite and rhombohedral phases were adjusted, as well as selected interaction parameters of the fluorite and liquid phases. For the fluorite phase, changes to the Gibbs energy functions for the yttrium containing end-member required in the optimization were large in comparison $\Delta E_{YO_{1.5}}^{YO_{1.5} \rightarrow YO_2}$; therefore the lattice stability computed from DFT served as a starting point for the optimization but otherwise made a small contribution to the overall assessment results. The compiled thermodynamic functions from this work, and those from [4, 5] that comprise the U-Y-O assessment, are listed in Table 2. .

4.1 The U-Y binary

All condensed metallic phases were assumed to be immiscible for this assessment based on the extremely limited inter-solubilities of Y and U of Haeffling and Daane [17]. A tentative diagram of the U-Y binary is shown in Fig.1.

4.2 Y_2O_3 - UO_2 pseudo-binary

There are no reported measurements of the solidus or liquidus along the Y_2O_3 - UO_2 isoplethal section. Therefore, the results of this optimization were solely used and resulted in the pseudo-binary diagram given in Fig. 2 which can be used to compare the solubility of Y_2O_3 in UO_2 with other trivalent RE sesquioxides, e.g. Gd_2O_3 and La_2O_3 .

4.3 Y_2O_3 - UO_2 - UO_3 pseudo-ternary system

The thermodynamic functions and models determined in the current work were used to compute the 1500°C phase diagram of Fig. 3. As described in section 2, the phase equilibria data of Bartram et al. [6] were used in the optimization, and while their measurements are shown as symbols in the figure, not all of them were determined at the nominal temperature of the phase diagram. Sample compositions were analyzed using XRD after treatment at 1700°C in H₂ or 10CO₂:1CO at 1500°C, and at 1000°C in air; the observed phase assemblages under the first two conditions are believed to be well represented by the UO₂-UO₃-Y₂O₃ pseudoternary proposed by Bartram et al. [6]. The models developed in this work reproduce the fluorite and RI phase regions except for the one composition corresponding to 60 mole % Y₂O₃ and 40 mole % UO₃ treated at 1000°C in air. Here, the models predict the U_{1-y}Y_yO_{2±x} + RI + O₂ three phase equilibrium while Bartram et al. report only a single fluorite phase. Diehl and Keller [18] observed extremely slow reactions for forming similar rhombohedral compounds at these temperatures in the U-La-O system. The fluorite and RI phase structures are very similar, with the RI phase viewed as a fluorite derivative [19]; indeed, the authors point out the similarity in the lattice parameter between the RI and U_{1-y}Y_yO_{2±x} at this composition. Thus the sluggish formation of RI, or the inability to distinguish the RI XRD pattern may have caused it not to be included in reported phase equilibria. Since the balance of the phase equilibria measurements are well reproduced by the models and U_{1-y}Y_yO_{2±x} is predicted to be the dominant phase at this temperature and composition, it is possible that the RI diffraction pattern was missed or absent during analysis.

4.4 Equilibrium vapor pressures over U_{y-1}Y_yO_{2±x}

The computed oxygen pressures over U_{y-1}Y_yO_{2±x} agree well with the values reported by Hagemark and Broli [9] and the measured UO₂ vapor pressures from Nakajima et al. [10] as can be seen in Figs. 4, 5, and 6. However, the oxygen pressures determined by Nakajima et al. [10] differ substantially from those of Hagemark and Broli [9]. In addition, good fits to the experimentally determined U and UO vapor pressures from Nakajima et al. [10] using the CEF for U_{y-1}Y_yO_{2±x} that were also consistent with the reported phase equilibria of Bartram et al. [6] and oxygen potentials of Hagemark and Broli [9] were not possible. Furthermore, the well-accepted CEF model for fluorite-structure UO_{2±x} [4] yields computed values for the UO vapor pressures over UO_{2.003} that are several orders of magnitude lower than the two data points reported by Nakajima et al. [10] (Figs. 7 and 8). Nakajima et al. [10] do report significant fragmentation of UO₂ in the KEMS measurements which may explain their high values for U and UO vapor species.

4.5 Computed U-Y-O phase diagrams

Figures 9a-c are computed U-Y-O isothermal ternary sections at 1273K, 1523K, and 1773K, which agree well with the phase relations seen in analogous uranium-RE-oxygen systems where RE = Gd, Pr, and La [8, 18, 20, 21]. These include the extensive fluorite solid solution region and the emergence of at least one rhombohedral phase at the higher yttrium or RE

concentrations. The computed solubility of Y in the urania fluorite solution from this work is smaller than that of Gd, Pr, and La, consistent with the trend of increasing solubility with increasing ionic radius among this group.

5. Conclusion

An assessment of the U-Y-O system has been performed by combining the binary the U-O and Y-O assessments from Guéneau et al. [4] and Djurovic et al. [5], respectively, extending the CEF representation for $\text{UO}_{2\pm x}$ to include Y^{3+} , and determining a Gibbs function for the rhombohedral YU_6O_{12} RI phase. The models presented in this work fairly well reproduce the phase equilibria proposed by Bartram et al. [6]. The CEF computed oxygen pressures for $\text{U}_{y-1}\text{Y}_y\text{O}_{2\pm x}$ also agree well with the measurements of Hagemark and Broli [9]. While both thermochemical and phase equilibria data were used to optimize the adjustable parameters for a self-consistent thermodynamic representation of the U-Y-O system, the data is limited to oxygen potential measurements at low Y composition. No ternary melting data is reported in the literature which prevented confirmation of the computed solidus/liquidus. This work calls for phase equilibria studies with a particular emphasis on characterizing the extent of yttrium solubility in the fluorite phase along with an investigation of ternary solidus/liquidus boundaries. Oxygen potential measurements at higher yttrium compositions and over a more extensive compositional range are warranted along with a more comprehensive investigation of UO pressures over $\text{UO}_{2\pm x}$ in order to understand the discrepancies with reported measurements in Nakajima et al. [10].

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References

- [1] R. Devanathan, L. Van Brutzel, A. Chartier, C. Guéneau, A. E. Mattsson, V. Tikare, T. Bartel, T. Besmann, M. Stan, P. Van Uffelen, *Energy & Environmental Science*, 3 (10) (2010) 1406-26.
- [2] M. Stan, *Nucl. Eng. and Technol.*, 41 (2009) 39-52.
- [3] R. Williamson, J. Hales, S. Novascone, M. Tonks, D. Gaston, C. Permann, D. Andrs, R. Martineau, *J. Nucl. Mater.*, 423 (1) (2012) 149-63.
- [4] 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.
- [5] D. Djurovic, M. Zinkevich, F. Aldinger, *CALPHAD*, 31 (4) (2007) 560-6.
- [6] S. Bartram, E. Juenke, E. Aitken, *J. Am. Ceram. Soc.*, 47 (4) (1964) 171-5.
- [7] E. Aitken, R. Joseph, *The Journal of Physical Chemistry*, 70 (4) (1966) 1090-7.
- [8] J. W. McMurray, D. Shin, B. W. Slone, T. M. Besmann, *J. Nucl. Mater.*, 452 (1-3) (2014) 397-406.
- [9] K. Hagemark, M. Broli, *J. Am. Ceram. Soc.*, 50 (11) (1967) 563-7.
- [10] K. Nakajima, T. Ohmichi, Y. Arai, *J. Nucl. Mater.*, 304 (2) (2002) 176-81.
- [11] *Scientific Group Thermodata Europe (SGTE), Thermodynamic Properties of Inorganic Materials*, Heidelberg Berlin, Springer Verlag, 1999.
- [12] C. Guéneau, D. Baichi, C. Labroche, B. Chatillon, B. Sundman, *J. Nucl. Mater.*, 304 (2002) 161.
- [13] E. A. Aitken, S. F. Bartram, E. F. Juenke, *Inorg. Chem.*, 3 (7) (1964) 949-54.
- [14] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.*, 6 (1) (1996) 15-50.
- [15] G. Kresse, J. Furthmüller, *Phys. Rev. B* 11 - PRB, 54 (16) (1996) 11169-86.
- [16] 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) 39.
- [17] J. Haefling, A. Daane, *Trans. Met. Soc. AIME*, 215 (1959)
- [18] H. G. Diehl, C. Keller, *J. Solid State Chem.*, 3 (4) (1971) 621-36.
- [19] M. Tang, K. S. Holliday, C. Jiang, J. A. Valdez, B. P. Uberuaga, P. O. Dickerson, R. M. Dickerson, Y. Wang, K. R. Czerwinski, K. E. Sickafus, *J. Solid State Chem.*, 183 (4) (2010) 844-8.
- [20] J. McMurray, D. Shin, T. Besmann, *J. Nucl. Mater.*, 456 (2015) 142-50.

[21] I. B. De Alleluia, M. Hoshi, W. G. Jocher, C. Keller, *Journal of Inorganic and Nuclear Chemistry*, 43 (8) (1981) 1831-4.

List of figure

Fig. 1: Computed phase diagram for the U-Y binary system.

Fig. 2: Computed phase diagram for the pseudo-binary system $\text{UO}_2\text{-Y}_2\text{O}_3$ where F and RI refer to the fluorite and rhombohedral phases, respectively.

Fig. 3: Computed phase diagram for $\text{Y}_2\text{O}_3\text{-UO}_2\text{-UO}_3$ pseudo-ternary at 1500°C with data from Bartram et al. [5] shown as symbols where F and RI refer to the fluorite and rhombohedral phases, respectively. The dashed line represents the model predictions for the $\text{F} + \text{U}_3\text{O}_8 + \text{GAS}$ three phase boundary at 1000°C corresponding to the temperatures used in [6].

Fig. 4: Oxygen pressure data for 2.5% Y in $\text{U}_{1-y}\text{Y}_y\text{O}_{2+x}$ from Hagemark and Broli [9] (symbols) and computed values (lines).

Fig. 5: Oxygen pressure data for 4.8% Y in $\text{U}_{1-y}\text{Y}_y\text{O}_{2+x}$ from Hagemark and Broli [9] (symbols) and computed values (lines)

Fig. 6: Partial pressures of $\text{UO}_2(\text{g})$ over $\text{U}_{1-y}\text{Y}_y\text{O}_{2+x}$ computed using the CEF from this work (lines) and compared to measurements (symbols) taken by Nakajima et al. [10].

Fig. 7: Equilibrium O_2 pressures over $\text{U}_{1-y}\text{Y}_y\text{O}_{2+x}$ computed (lines) using the CEF model compared to those calculated by Nakajima et al. [10]. (symbols) using $\text{UO}(\text{g})$, $\text{UO}_2(\text{g})$ Knudsen measurements

Fig. 8: Computed (lines) UO gas pressures over the urania-yttria fluorite solid solution versus temperature and those from [10] (symbols).

Fig. 9: Computed isothermal sections of the ternary U-Y-O system at (a) 1273K, (b) 1523K, and (c) 1773K.

Table 1: List of end-members for fluorite-structure model of $U_{1-y}Y_yO_{2+x}$

$U^{3+}:O^{2-}:O^{2-}$	$U^{4+}:O^{2-}:O^{2-}$	$U^{5+}:O^{2-}:O^{2-}$	$U^{6+}:O^{2-}:O^{2-}$	$Y^{3+}:O^{2-}:O^{2-}$
$U^{3+}:O^{2-}:Va$	$U^{4+}:O^{2-}:Va$	$U^{5+}:O^{2-}:Va$	$U^{6+}:O^{2-}:Va$	$Y^{3+}:O^{2-}:Va$
$U^{3+}:Va:O^{2-}$	$U^{4+}:Va:O^{2-}$	$U^{5+}:Va:O^{2-}$	$U^{6+}:Va:O^{2-}$	$Y^{3+}:Va:O^{2-}$
$U^{3+}:Va:Va$	$U^{4+}:Va:Va$	$U^{5+}:Va:Va$	$U^{6+}:Va:Va$	$Y^{3+}:Va:Va$

Table 2

Table 2: Thermodynamic values for phases in the U-Y-O system.

Thermodynamic Parameters (J/mole)	Ref.
Gas Phase	
$^{\circ}G_O$	[11]
$^{\circ}G_{O_2}$	[11]
$^{\circ}G_{O_3}$	[11]
$^{\circ}G_Y$	[11]
$^{\circ}G_{Y_2}$	[11]
$^{\circ}G_{YO}$	[11]
$^{\circ}G_{Y_2O}$	[11]
$^{\circ}G_{Y_2O_2}$	[11]
$^{\circ}G_{YO_2}$	[11]
$^{\circ}G_U$	[11]
$^{\circ}G_{UO}$	[20]
$^{\circ}G_{UO_2}$	[20]
$^{\circ}G_{UO_3}$	[20]
Pure elements and stoichiometric compounds	T Range (K)
$^{\circ}G_U^{\alpha}$	[11]
$^{\circ}G_U^{\beta}$	[11]
$^{\circ}G_U^{\gamma}$	[11]
$^{\circ}G_{UO_3}$	[4]
$^{\circ}G_{U_3O_8}^{\alpha}$	[4]
$^{\circ}G_{U_3O_8}^{\beta}$	[4]
$^{\circ}G_{U_3O_8}^{\gamma}$	[4]
$^{\circ}G_{U_3O_8}^{\delta}$	[4]
$^{\circ}G_{U_4O_9}^{\alpha}$	[4]
$^{\circ}G_{U_4O_9}^{\beta}$	[4]
$^{\circ}G_{U_4O_9}^{\gamma}$	[4]
$^{\circ}G_{UY_6O_{12}} = -8166779.6 + 3219.3843T - 471.37980T \ln(T) -$ $4.7526 \cdot 10^{-3}T^2 - 3.18099 \cdot 10^{-6}T^{-1} +$ $4138736T^{-2}$	$T < 1833$ This work
$\alpha\text{-Y(Y)}_1(\text{Va}, \text{O})_1$	
$^{\circ}G_{Y:Va}^{\alpha-Y}$	[5]
$^{\circ}G_{Y:O}^{\alpha-Y}$	[5]
$\beta\text{-Y(Y)}_1(\text{Va}, \text{O})_1$	
$^{\circ}G_{Y:Va}^{\beta-Y}$	[5]
$^{\circ}G_{Y:O}^{\beta-Y}$	[5]
${}^0L_{Y:Va,O}^{\beta-Y}$	[5]
${}^1L_{Y:Va,O}^{\beta-Y}$	[5]
$\alpha\text{-Y}_2\text{O}_3(\text{Y}^{2+}\text{Y}^{3+})_2(\text{O}^{2-}, \text{Va})_3$	

${}^{\circ}G_{Y^{2+};Va}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{2+};O^{2-}}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{3+};Va}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{2+};O^{2-}}^{\alpha-Y_2O_3}$	[5]
<hr/>	
$\beta\text{-Y}_2\text{O}_3(\text{Y}^{2+}\text{Y}^{3+})_2(\text{O}^{2-})_2(\text{Va}, \text{O}^{2-})_1$	
${}^{\circ}G_{Y^{2+};O^{2-};Va}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{2+};O^{2-};O^{2-}}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{3+};O^{2-};Va}^{\alpha-Y_2O_3}$	[5]
${}^{\circ}G_{Y^{3+};O^{2-};O^{2-}}^{\alpha-Y_2O_3}$	[5]
<hr/>	
Liquid	
${}^{\circ}G_{Y^{3+};Va}^{liq}$	[5]
${}^{\circ}G_{Y^{3+};O^{2-}}^{liq}$	[5]
${}^{\circ}G_{U^{3+};Va}^{liq}$	[4]
${}^{\circ}G_{U^{3+};O^{2-}}^{liq}$	[4]
$L_{U^{4+};O^{2-};Va}^0$	[4]
$L_{U^{4+};O^{2-};Va}^1$	[4]
$L_{U^{4+};O^{2-};Va}^2$	[4]
$L_{U^{4+};O^{2-};O}^0$	This work
$L_{Y^{3+};U^{4+};O^{2-}}^0 = 769964.63 - 360.8234T$	This work
$L_{Y^{3+};U^{4+};O^{2-}}^1 = 719997.34 - 276.69697T$	This work
$L_{Y^{3+};U^{4+};O^{2-}}^2 = 10006.25 - 28.9668T$	This work
$L_{Y^{3+};U^{4+};Va}^0 = 1000000$	This work
$L_{Y^{3+};O^{2-};Va}^0 = 633817 - 370.04T$	[5]
$L_{Y^{3+};O^{2-};Va}^1 = -221673 + 131.465T$	[5]
<hr/>	
Fluorite	
${}^{\circ}G_{Y_2O_3}$	[16]
${}^{\circ}G_{U^{3+};O^{2-};O^{2-}}$	[4]
${}^{\circ}G_{U^{3+};O^{2-};Va}$	[4]
${}^{\circ}G_{U^{3+};Va;O^{2-}}$	[4]
${}^{\circ}G_{U^{3+};Va;Va}$	[4]
${}^{\circ}G_{U^{4+};O^{2-};O^{2-}}$	[4]
${}^{\circ}G_{U^{4+};O^{2-};Va}$	[4]
${}^{\circ}G_{U^{4+};Va;O^{2-}}$	[4]
${}^{\circ}G_{U^{4+};Va;Va}$	[4]
${}^{\circ}G_{U^{5+};O^{2-};O^{2-}}$	[4]
${}^{\circ}G_{U^{5+};O^{2-};Va}$	[4]
${}^{\circ}G_{U^{5+};Va;O^{2-}}$	[4]
${}^{\circ}G_{U^{5+};Va;Va}$	[4]
${}^{\circ}G_{U^{6+};O^{2-};O^{2-}}$	[8]
${}^{\circ}G_{U^{6+};O^{2-};Va}$	[8]

${}^{\circ}G_{U^{6+};Va:O^{2-}}$	[8]
${}^{\circ}G_{U^{6+};Va:Va}$	[8]
${}^{\circ}G_{Y^{3+};O^{2-};O^{2-}} = \frac{1}{2}{}^{\circ}G_{Y_2O_3} + \frac{3}{4}{}^{\circ}G_{O_2} + 132005.1 - 7.47855T$	This work
${}^{\circ}G_{Y^{3+};O^{2-};Va} = \frac{1}{2}{}^{\circ}G_{Y_2O_3} + \frac{1}{4}{}^{\circ}G_{O_2} + 41628.1 - 26.8759T$	This work
${}^{\circ}G_{Y^{3+};Va:O^{2-}} = 10000$	This work
${}^{\circ}G_{Y^{3+};Va:Va} = \frac{1}{2}{}^{\circ}G_{Y_2O_3} - \frac{3}{4}{}^{\circ}G_{O_2} + 607223.2 - 54.0359T$	This work
$L_{U^{3+},U^{4+};O^{2-};Va}^0$	[4]
$L_{U^{3+},U^{4+};O^{2-};Va}^1$	[4]
$L_{U^{4+},U^{5+};O^{2-};O^{2-}}^0$	[4]
$L_{U^{4+},Y^{3+};O^{2-};Va}^0 = -65000$	This work
$L_{U^{4+},Y^{3+};Va:Va}^0 = -472289.19$	This work
$L_{U^{5+},Y^{3+};O^{2-};O^{2-}}^0 = -427375.75$	This work
$L_{U^{5+},Y^{3+};O^{2-};Va}^0 = -70000 - 10T$	This work
$L_{U^{5+},Y^{3+};O^{2-};Va}^1 = -54989.001$	This work
$L_{U^{5+},Y^{3+};Va:Va}^0 = -786023.31 - 217T$	This work
$L_{U^{6+},Y^{3+};O^{2-};Va}^0 = -75000$	This work

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