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DELIVERABLE

D4.4 Final report on thermodynamic models of U-Pu-Am-Np-O systems

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Glossary

ADS	Accelerator Driven System
DSC	Differential Scanning Calorimetry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
EPMA	Electron Probe Microanalyser
FPC	Fuel Performance Code
KEMS	Knudsen Effusion Mass Spectrometry
LAF	Laser Flash
LFR	Lead-cooled Fast Reactor
MA	Minor Actinide
PPMS	Physical Property Measurement System
SFR	Sodium-cooled Fast Reactor
XRD	X-Ray Diffraction

1 Introduction

Transmutation of Minor Actinides (MA) is planned in several Generation IV systems, including the specific Accelerator Driven Systems (ADS) combining an accelerator and a Lead-cooled Fast Reactor (LFR) (MYRRHA prototype), and fast reactor concepts such as Sodium-cooled Fast Reactors (SFR) (ASTRID-type) or LFRs (ALFRED). In Europe, oxide fuels containing MAs have emerged as the reference to meet the Generation IV assigned performances and reliability goals, based on historical experience and know-how accumulated with the current fleet of Light Water Reactors.

Transmutation of MAs can be done by homogeneous recycling, with MAs diluted at a low content (< 5%) in the standard driver fuel (U,Pu)O₂, or by heterogeneous recycling with higher MAs content (10%-15%) in UO₂ based fuels located into the radial blankets (outer part of the core). Americium, in particular the ²⁴¹Am isotope, is the main contributor to the heat load of long-lived high-level radioactive waste. For this reason, studies on americium in the framework of partitioning and transmutation require dedicated research efforts.

The Domain 2 of PATRICIA is dedicated to the safety assessment of transmutation type fuels, in particular Am-bearing fuels, under normal operating conditions, but also under off-normal and accidental conditions. It is commonly assumed that the thermal and thermo-chemical properties of the fuel yield the dominant contribution to the uncertainties in thermal evaluation within Fuel Performance Codes (FPCs). Key thermal-physical and thermal-chemical properties are thus investigated here, with the aim to enhance the reliability of fuel behaviour calculations and contribute to the design of safer fuel elements with lower uncertainties.

More specifically, experimental measurements and atomic scale calculations were performed on selected mixed oxides in the U-Pu-Am-Np-O system, as reported in Deliverable D4.3. The data obtained served as input to develop thermodynamic models of the U-Am-O, U-Np-O, Pu-Am-O, Pu-Np-O ternary systems, and higher order U-Pu-Am-Np-O system, as presented herein in Deliverable D4.4. The development of a comprehensive model for the highly complex U-Pu-Am-Np-O system is key for the understanding and prediction of the behaviour of fast reactor/ADS fuels including minor actinides (Am,Np) and a high Pu content.

New atomic scale calculations results on AmO_{2-x} and (Pu,Am)O_{2-x} are first presented, followed by a brief description of the CALPHAD methodology used to build the thermodynamic models. Second, an

overview of the developed thermodynamic models is presented, detailing the calculated phase diagrams and thermodynamic properties in the U-Pu-Am-Np-O system, together with a comparison to the experimental results (Deliverable D4.3) and simulations.

2 Atomic scale modelling results

2.1 Methodology

The cubic phases of Am-bearing oxides were studied using a combination of empirical interatomic potentials for the Am-O and Pu-Am-O systems and electronic structural calculations for AmO₂.

First, The Cooper-Rushton-Grimes (CRG) formalism [2014Cooper] was applied. The formal definition for the potential energy of an atom i is as follows:

$$E_i = \frac{1}{2} \sum_{j \neq i} \varphi_{\alpha\beta}(r_{ij}) - G_{\alpha} \sqrt{\sum_{j \neq i} \sigma_{\beta}(r_{ij})}$$

where the term $\varphi_{\alpha\beta}(r_{ij})$ is the sum of the long-range Coulomb and of the short-range Morse and Buckingham potentials. The contribution from the short-range potentials is calculated with a 11 Å cutoff. The second term is the N -body contribution representing the embedding energy of the atom i in the electronic density owing to its neighbours. The original potential had previously been augmented with new terms regarding the Am³⁺ and U⁵⁺ oxidation states [2023Labonne2023,2023Rochedy]. The parameters regarding the Am⁴⁺ species were reoptimized in a second stage to lower the melting temperature yielded at the atomic scale for stoichiometric AmO₂ [2025Labonne], bringing it from (3350±7.9) K to (2792±5.7) K.

The evolution of structural and energetic properties with temperature is obtained using the *Heat Until it Melts* (HUM) approach consisting in a simulation of the supercells at constant pressure with a progressive increase of the temperature. The elastic constants of the materials are also calculated as a function of temperature by applying finite deformations to the equilibrated supercells and computing the stress versus strain relationship. Derivative properties and elastic moduli are then calculated. The melting temperature yielded by the HUM method is significantly overestimated due to the small supercell size and to the short duration simulated. We thus use the *Moving Interface* (MI) method, in which a solid and a liquid phase with the same composition are put in contact before imposing the temperature and pressure, for the estimation of the melting temperature. The relative proportions of the two phases at the end of the simulation allow one to determine if the applied temperature was significantly below, significantly above or very near the melting temperature of the compound. Performing several simulations at various final temperatures allows one to evaluate the melting temperature.

Empirical interatomic potential calculations were complemented by electronic structure calculations in temperature using Density Functional Theory. Ab initio molecular dynamics calculations were performed on 96-atom supercells from 300 K to 3300 K every 300 K using the opt-PBE functional [2010Klimes] including van der Waals interactions and a 2x2x2 k -points grid. A Hubbard-like term was added to americium atoms in the Liechtenstein approach to account for the strong electronic correlations in americium dioxide, with $U = 6.00$ eV and $J = 0.75$ eV. The enthalpy obtained was corrected for the non-zero pressure contributions in postprocessing [2019Talla-noutack].

2.2 Results on AmO₂

2.2.1 Empirical potential results

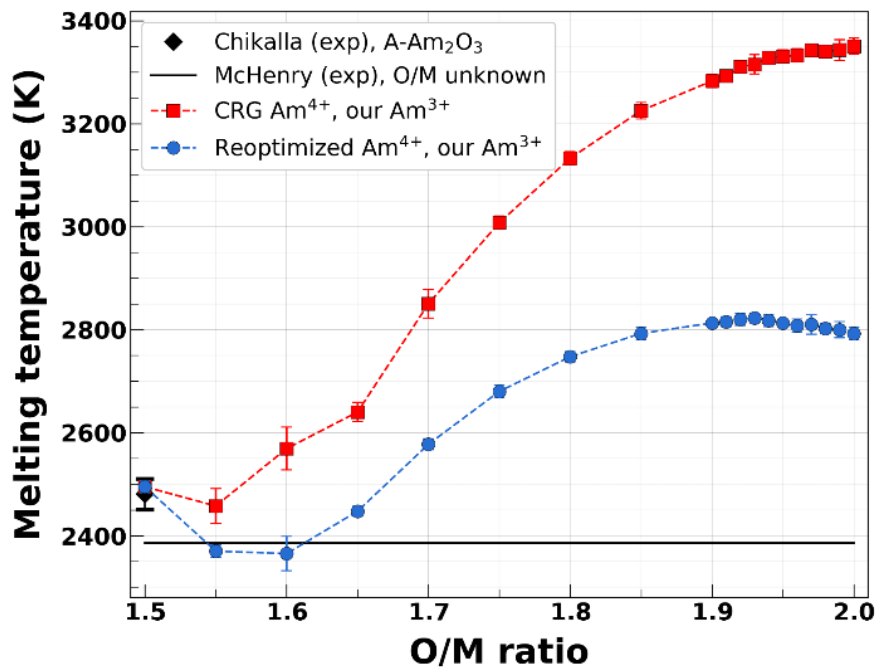


Figure 1: Evolution with oxygen to metal ratio of the melting temperature estimated for AmO_{2-x} oxides with $0 \leq x \leq 0.5$ with the original 2014 CRG parameters for Am⁴⁺ (red squares) and our re-optimised parameters (blue circles), compared with the value measured for A-Am₂O₃ by Chikalla [1973Chikalla] (black square) and that given for AmO₂ by McHenry [1965Mchenry] (black line).

Figure 1 shows the melting temperature of the AmO_{2-x} oxides estimated by the MI method using the original 2014 CRG terms for Am⁴⁺ and our re-optimised parameters, together with the experimental value for A-Am₂O₃ measured by Chikalla [1973Chikalla]. The horizontal line corresponds to the experimental temperature given for AmO₂ by McHenry [1965Mchenry], for which the O/M ratio was not controlled during the experiment or measured afterwards. Significant differences are observed between the melting temperatures estimated with the two sets of interatomic potential parameters over the entire O/M range studied. As expected, the calculated melting temperatures are lower using the re-optimised terms, which was the aim of the re-optimisation. The largest diminutions in melting temperature are obtained for O/M ratios close to 2, with the melting temperature of the dioxide falling from (3350 ± 7.9) K with the original 2014 terms to (2792 ± 5.7) K with our parameters.

Only the melting temperature of the AmO_{1.55} composition is lower than that of the C-Am₂O₃ sesquioxide with the original 2014 CRG terms, whereas this is the case for AmO_{1.55}, AmO_{1.60} and AmO_{1.65} using the re-optimised terms. This allows to recover the experimental value given by McHenry [1965Mchenry] at 2386 K for AmO₂ for O/M ratios between 1.55 and 1.60 with our re-optimisation. The original 2014 CRG terms do not allow the temperature of 2386 K to be obtained. The value obtained for C-Am₂O₃, common to both datasets due to the absence of Am⁴⁺ ion for this composition, is in excellent agreement with the experimental value for A-Am₂O₃ [1973Chikalla]. Although the simulated cubic solid phase is metastable, the potential predicts the phase transition at the correct temperature.

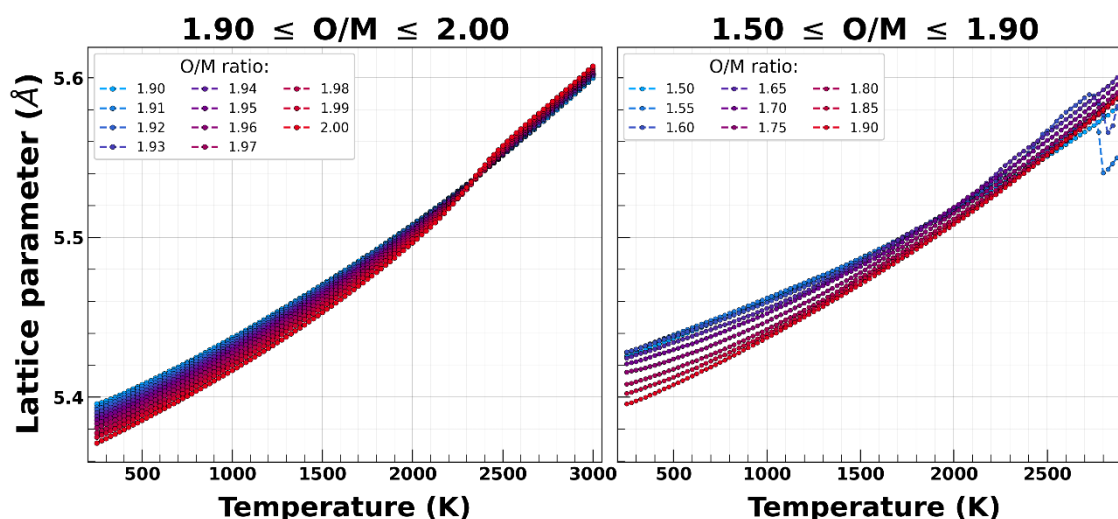


Figure 2: Evolution with temperature of the lattice parameter for AmO_{2-x} oxides with $0 \leq x \leq 0.1$ (left) and $0.1 \leq x \leq 0.5$ (right)

Figure 2 shows the evolution with temperature of the lattice parameter of AmO_{2-x} oxides with small deviations from stoichiometry, i.e. $0 \leq x \leq 0.1$, and large deviations from stoichiometry, i.e. $0.1 \leq x \leq 0.5$. For small deviations from stoichiometry, the lattice parameter evolution is linear up to 2000 K with the slope (i.e., thermal expansion) increasing with the O/M up to 2000 K. The inflection in the evolution of the lattice parameter with temperature, associated with a Bredig transition [1968Bredig], seems to be present only for O/M ratios very close to 2. At temperatures above 2500 K, the lattice parameters are relatively close, they evolve linearly with temperature and the O/M no longer seems to have an impact on the thermal expansion of these compounds.

For large deviations from stoichiometry, the evolution of the lattice parameter with temperature is convex, particularly for medium O/M ratios, and the thermal expansion seems to increase with the O/M ratio up to 1700 K. Beyond that, the evolution of the lattice parameter with temperature is more complex: for $\text{AmO}_{1.55}$, $\text{AmO}_{1.60}$ and $\text{AmO}_{1.65}$, it increases more strongly than for all the other compounds before decreasing abruptly for $\text{AmO}_{1.55}$ and $\text{AmO}_{1.60}$. This decrease corresponds to a phase transition towards a space group that is difficult to identify due to thermal agitation at high temperature. However, the OVITO software partially identifies this as a centred cubic structure, which may correspond to the $\text{AmO}_{1.61+x}$ phase observed experimentally [1968Chikalla,2017Epifano] for these O/M ratios but at lower temperatures, between 700 K and 1300 K.

Figure 3 shows the evolution with temperature of the enthalpy increment of AmO_{2-x} oxides, again separating results obtained for oxides with small and large deviations from stoichiometry. For low deviations from stoichiometry, the enthalpy increment varies relatively little with the O/M up to 2000 K. Beyond that, the inflection associated with the Bredig transition increases the differences between the enthalpy increment values for different O/M ratios for a given temperature, confirming that this transition decreases in intensity as the O/M ratio decreases. Similarly to the evolution with temperature of the lattice parameter, the O/M ratio no longer seems to have an impact on the slope beyond this transition. For large deviations from stoichiometry, the enthalpy increment decreases significantly with decreasing O/M ratio, which is consistent with the measurements of this property by Nishi [2011Nishi] for AmO_2 and for the hexagonal phase of the sesquioxide $\text{A-Am}_2\text{O}_3$. Our values are also in excellent agreement with the experimental data, as shown by the enlargement on the right-hand side of Figure 3 for the sesquioxide. We can also observe a jump in the enthalpy increment at 2800 K for $\text{AmO}_{1.55}$ and 2300 K for $\text{AmO}_{1.60}$, corresponding to the phase transition mentioned in the previous section.

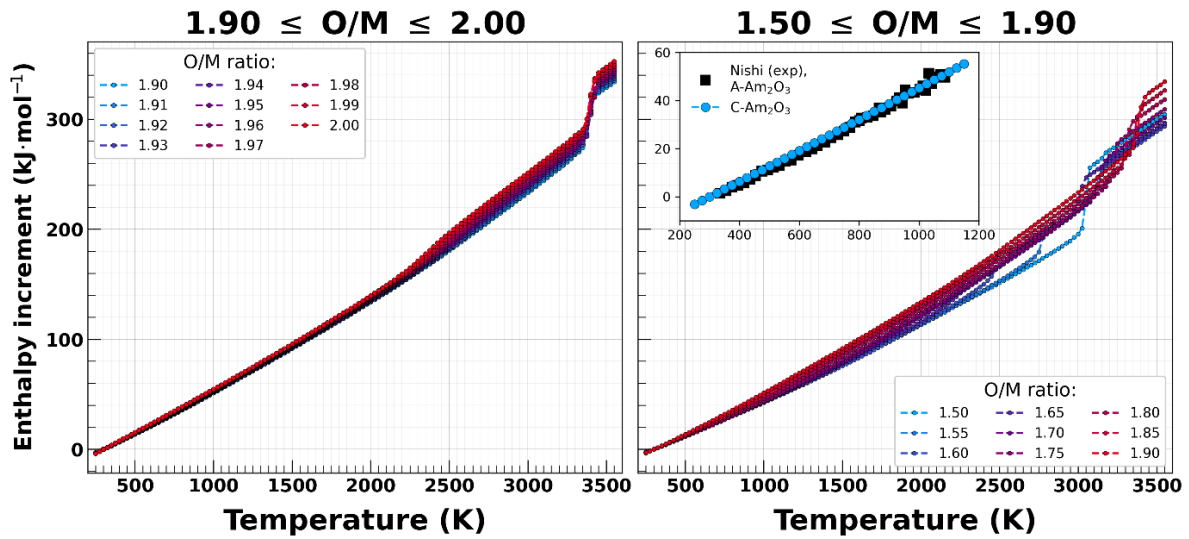


Figure 3: Evolution with temperature of the enthalpy increment for AmO_{2-x} with $0 \leq x \leq 0.1$ (left) and $0.1 \leq x \leq 0.5$ (right)

Figure 4 shows the evolution with temperature of the specific heat capacity of AmO_{2-x} oxides for small and large deviations from stoichiometry. For small deviations from stoichiometry, the C_p values are virtually unchanged up to 2000 K, i.e., up to the start of the peak associated with the Bredig transition, which gradually flattens out as the O/M ratio decreases to form a plateau for O/M values around 1.93. The temperature of the peak maximum increases progressively when the O/M ratio decreases. The effect of the O/M ratio on C_p at low temperature is qualitatively different between low and high deviations from stoichiometry: while no significant difference is observed for $0 \leq x \leq 0.1$, C_p decreases when the O/M ratio decreases for $0.1 \leq x \leq 0.5$ with differences of up to $10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The large fluctuations, however, make it impossible to establish a clear relationship between O/M and C_p . These fluctuations are due to the way the enthalpy increments are calculated by averaging them over several atomic configurations and velocity initialisations and are amplified by the derivation process. The peaks observed in the derived properties for the strong deviations from stoichiometry for are not related to a Bredig transition and are of two different natures. The peaks at 2500 K and 2200 K in the temperature evolution C_p for $\text{AmO}_{1.60}$ and $\text{AmO}_{1.55}$, respectively, correspond to a partial amorphisation of the crystals. This amorphisation is followed by recrystallisation in the bcc phase for $\text{AmO}_{1.55}$ as the temperature rises. The $\text{AmO}_{1.60}$ compound remains amorphous up to its melting temperature.

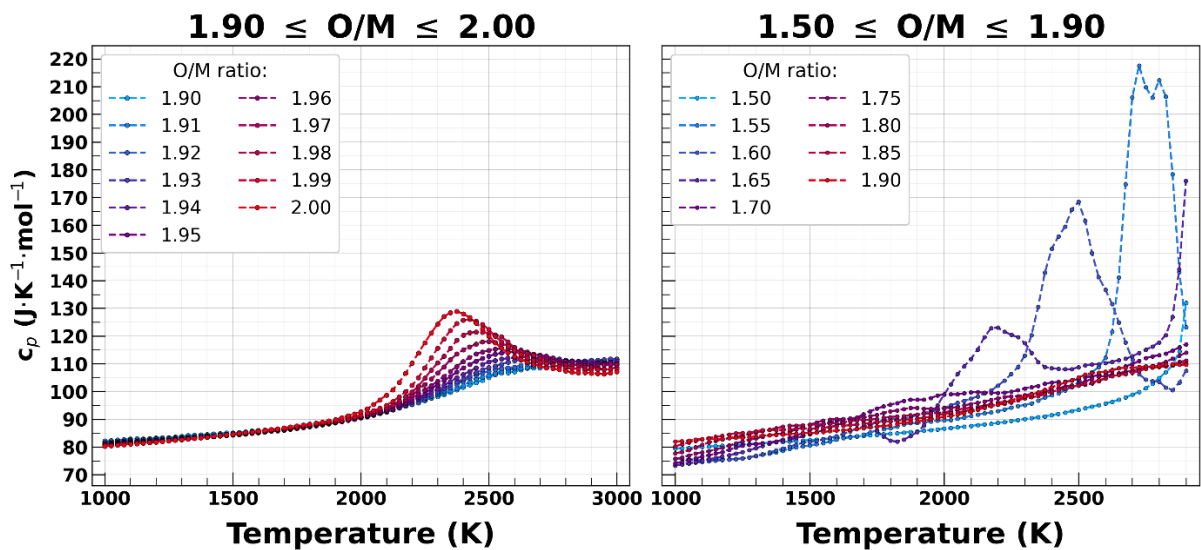


Figure 4: Evolution with temperature of the specific heat capacity for AmO_{2-x} with $0 \leq x \leq 0.1$ (left) and $0.1 \leq x \leq 0.5$ (right)

The large amount of data yielded by the empirical interatomic potential is important to complement the existing TAF-ID database used for the CALPHAD modelling of nuclear fuels, in particular in domains of temperature and composition for which data is scarce or inexistant. Emphasis is given on the fact that the properties yielded for metastable compounds can be incorporated in databases and are inaccessible to experiments. In particular, stoichiometric AmO_2 is not stable for temperatures higher than ≈ 1100 K but the progressive reduction cannot be observed due to the potential formalism used. Thus, high temperature *ab initio* molecular dynamics (AIMD) were therefore performed on this compound.

2.2.2 Electronic structure results

The specific heat capacity calculated using AIMD simulations in this work is reported in Figure 5 and compared with the calculations of Talla-Noutack [2019Talla-noutack] and the CALPHAD modelling. Three enthalpy increment derivation methods are used to obtain the specific heat capacity from our AIMD simulations: finite difference without taking neighbouring values into account, finite difference taking a neighbouring value into account, and convolution with a Gaussian kernel taking $\sigma = 0.68$ as parameter.

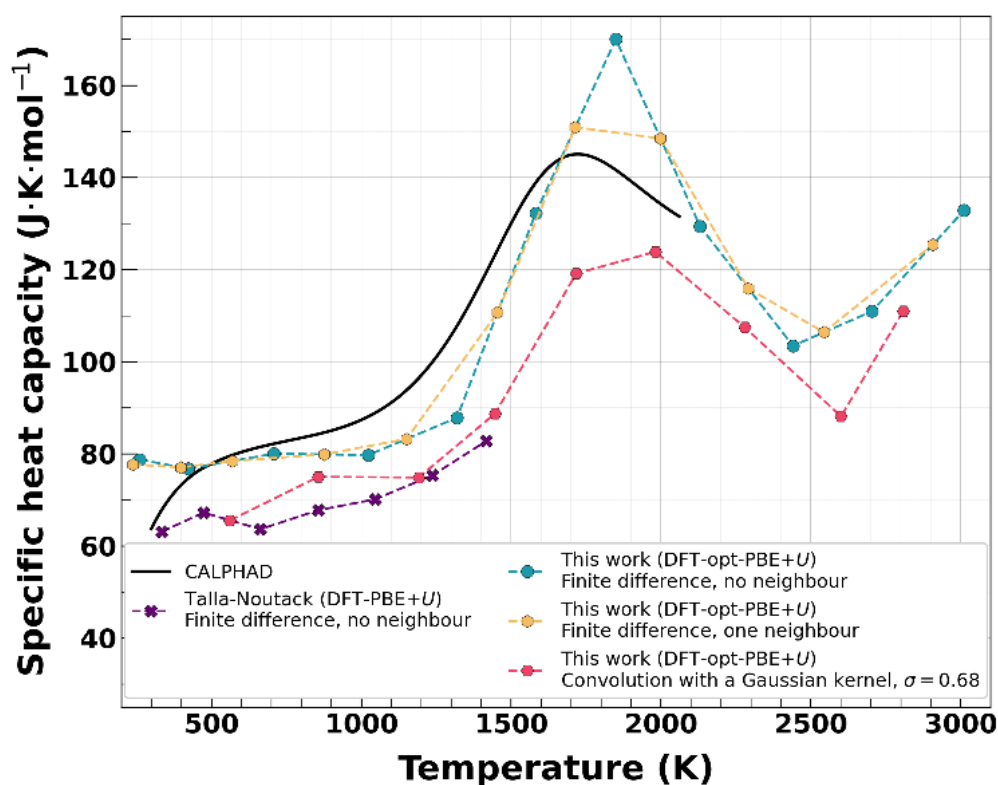


Figure 5: Specific heat capacity yielded by CALPHAD modelling (black line), derived from *ab initio* molecular dynamics without including van der Waals interactions [2019Talla-noutack] (purple crosses) and derived from *ab initio* molecular dynamics including van der Waals interactions using three derivation methods (green circles, yellow hexagons, red hexagons)

These three techniques are qualitatively in agreement on the evolution of the specific heat capacity with temperature. Quantitative differences, however, are observed, particularly for convolution with a Gaussian kernel, for which the values are lower than those obtained by the two finite-difference techniques. Due to the small number of values calculated by Talla-Noutack, only the first technique is applied to its enthalpy increment values to obtain the associated specific heat capacity. The calculations incorporating van der Waals interactions yield C_p values that are closer to the CALPHAD results, confirming the improvement in the description of the energy properties observed in UO_2 and $(\text{U,Pu})\text{O}_2$ [2017Vathonne] when non-local interactions are taken into account. The shift of the peak

towards higher temperatures in the case of the AIMD calculations compared with the CALPHAD modelling is probably due to the small size of the supercell simulated (96 atoms). According to the CALPHAD modelling, the peak corresponds to an excess enthalpy caused by the progressive reduction of americium dioxide as the temperature rises. This seems to suggest that our AIMD calculations reproduce the reduction of AmO_2 to $\{\text{AmO}_{2-x} + \text{O}_2\}$ by isolating oxygen atoms from the rest of the crystal.

To explore this possibility, the partial radial distribution functions $g(r)$ obtained in our calculation at 2285 K were calculated and are presented in Figure 6. They show the existence of an oxygen-oxygen peak around $r = 1.45 \text{ \AA}$, corresponding to segregated oxygen dimers.

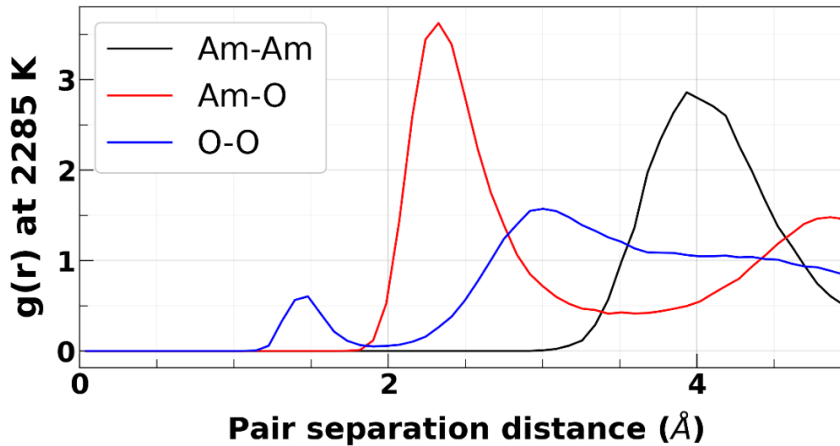


Figure 6: Partial radial distribution functions yielded by AIMD calculations at 2285 K

The integration of this first peak for all temperatures simulated allows us to access the coordination number n of the oxygen atoms and thus to quantify these dimers and to compute a pseudo-O/M ratio. The coordination number n is calculated as:

$$n = 4\pi\rho_{\text{oxygen}} \int_0^{r_{\text{cut}}} g_{\text{O-O}}(r)r^2 dr$$

The corresponding O/M ratio is shown in Figure 7 for various r_{cut} values and compared to the results of the CALPHAD modelling. We observe that the reduction starts at a higher temperature in our AIMD simulations, between 1500 K and 1700 K, compared with the CALPHAD modelling in which it starts at around 1050 K. This is in agreement with the shift observed for the peak in the specific heat capacity studied in the previous section. Moreover, the reduction is more pronounced in our simulations, reaching lower O/M ratios than those obtained by CALPHAD modelling from 1987 K onwards. There are several possible explanations for this discrepancy. First, since dimers can only be formed by integer multiples of oxygen atom dimers, the low number of atoms simulated means that each dimer represents 3.125% of the oxygen atoms in the crystal, giving a reduction in the O/M ratio of 0.0625. This effect, however, should be mitigated by the time average over the total simulated time, as dimers form and are reintegrated into the crystal throughout the calculation. Most probably, through the use of periodic boundary conditions, the oxygen dimers are actually integrated into the crystal and contribute to its electronic structure. They are therefore not completely dissociated from the crystal, potentially allowing a larger quantity of dimers to be formed. Finally, it should be added that CALPHAD calculations are based on a limited number of data and that the model is extrapolated for temperatures above 1445 K.

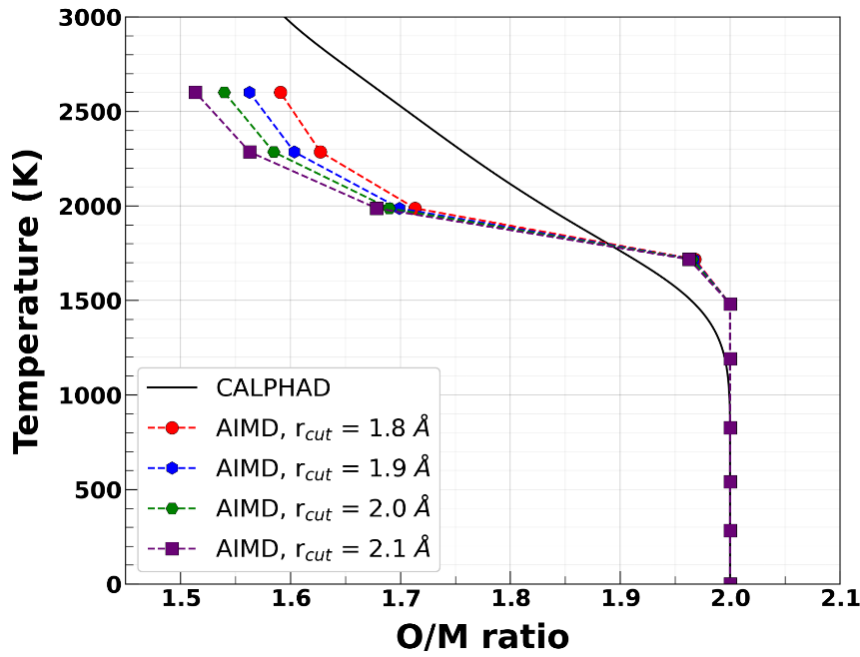


Figure 7: Evolution with temperature of the O/M ratio computed using various r_{cut} and compared to CALPHAD calculations

2.3 Results on (Pu,Am)O_{2-x}

2.3.1 Structural properties

Figure 8 shows the room-temperature lattice parameter as a function of the Am content for several O/M ratios, as well as the lattice parameter as a function of temperature for stoichiometric (Pu,Am)O₂ compounds.

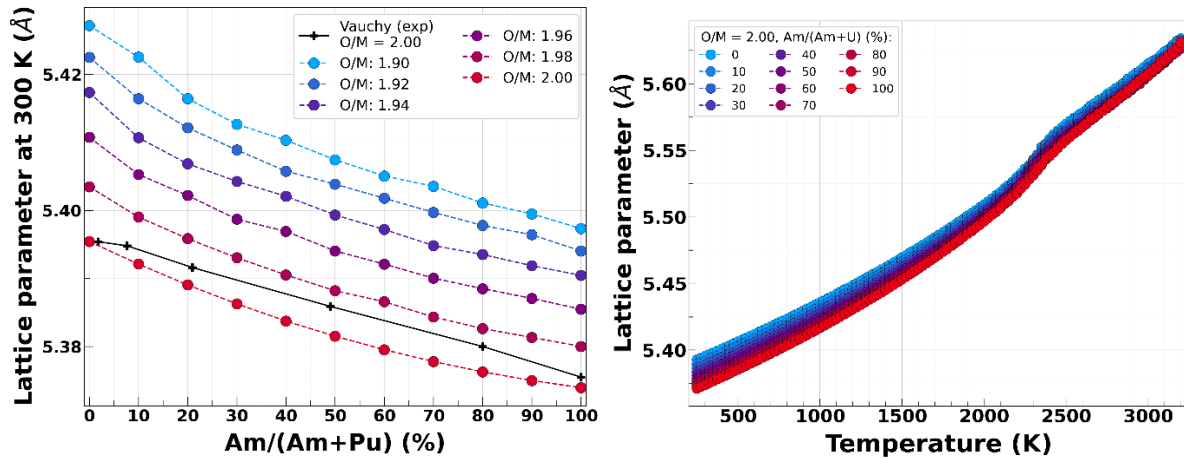


Figure 8: Room temperature lattice parameter as a function of Am content (left) and lattice parameter as a function of temperature (right)

Compared to the values measured by Vauchy [2017Vauchy], the potential quantitatively reproduces the room temperature lattice parameter of stoichiometric oxides with nonetheless a very small but systematic underestimation reaching -0.08% for Pu_{0.5}Am_{0.5}O₂. As observed in the U-Am-O system [2023Rochedy], the room temperature lattice parameter increases with an increasing deviation from stoichiometry for all Am contents. As with the (U,Am)O₂ oxides, the evolution of the lattice parameter with temperature is almost linear up to 2000 K. The small differences at room temperature between the lattice parameters of (Pu,Am)O₂ oxides (maximum 0.02 Å between PuO₂ and AmO₂, i.e. 0.3 %) tends to decrease with temperature, indicating that thermal expansion increases with an increasing

americium content. For all compositions, there is an inflection associated to the Bredig transition. The temperature of the inflexion does not seem to depend on the americium content, unlike in the U-Am-O system.

2.3.2 Energetic properties

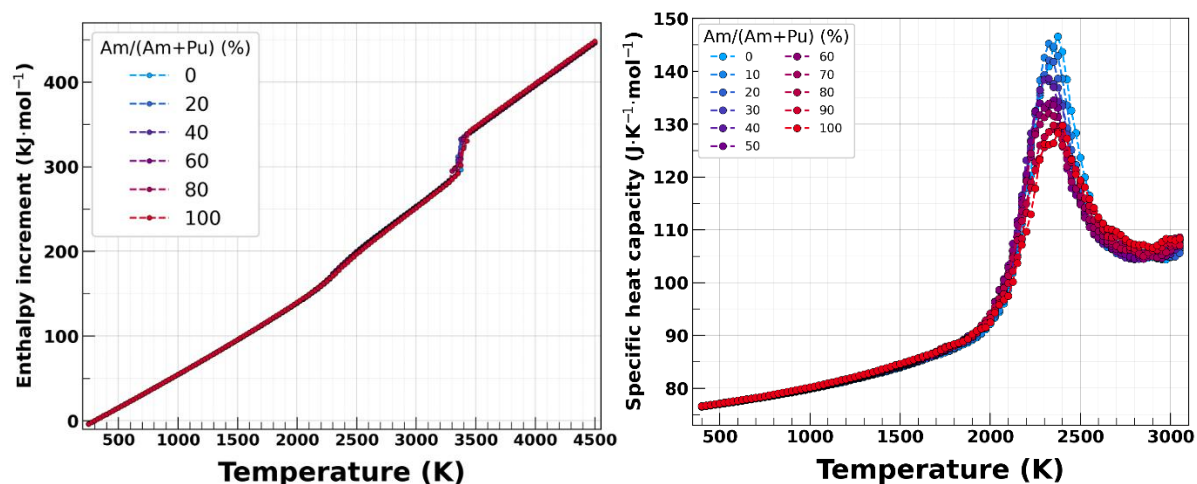


Figure 9: Computed enthalpy increment (left) and specific heat capacity (right) as a function of temperature for various americium contents

Figure 9 shows the enthalpy increments yielded by the calculations for stoichiometric $(\text{Pu},\text{Am})\text{O}_2$ compounds and the specific heat capacities derived using the finite difference method. We can observe that the americium content has little impact on energetic properties up to 2000 K. At higher temperature, a peak associated to the Bredig transition occurs for all compositions. The temperature of the maximum of this peak does not seem to depend on the composition, whereas the amplitude of the peak decreases steadily when the Am content increases. This behaviour is different from that observed in $(\text{U},\text{Am})\text{O}_2$ compounds in which the existence of a peak is clear for low and high Am contents but no peak can be observed for medium Am contents [2023Rochedy,2023Labonne]. These differences can be explained by the differences in the oxidation states present in the two systems. The Bredig transition has been predicted in UO_2 , PuO_2 and MOX using the CRG potential [2014Cooper,2015Cooper], in UO_2 using machine-learning interatomic potentials [2024Dubois] and in UO_2 and PuO_2 using *ab initio* molecular dynamics [2025Bathellier].

2.3.3 Melting temperature estimates

The melting temperatures estimated for the $(\text{Pu},\text{Am})\text{O}_{2-x}$ oxides by the moving interface method are shown in Figure 10 and compared with the experimental data available for PuO_2 [2011Debruycker, 2014Böhler] and $\text{Pu}_{0.49}\text{Am}_{0.51}\text{O}_{2-x}$ with O/M ratio values estimated at 1.824, 1.813 and 1.806 [2022Fouquet]. Due to the small difference between the melting temperatures of PuO_2 and AmO_2 obtained with the interatomic potential used, the melting temperature calculated for stoichiometric oxides is relatively independent of the americium content, although it is slightly lower for mixed oxides containing between 30% and 90% Am/(Am+Pu). The discrepancy between the simulations for $\text{Pu}_{0.5}\text{Am}_{0.5}\text{O}_{2-x}$ oxides and the measurements carried out on $\text{Pu}_{0.49}\text{Am}_{0.51}\text{O}_{2-x}$ oxides is difficult to interpret, as the experimental samples are much more hypostoichiometric than the simulated compounds.

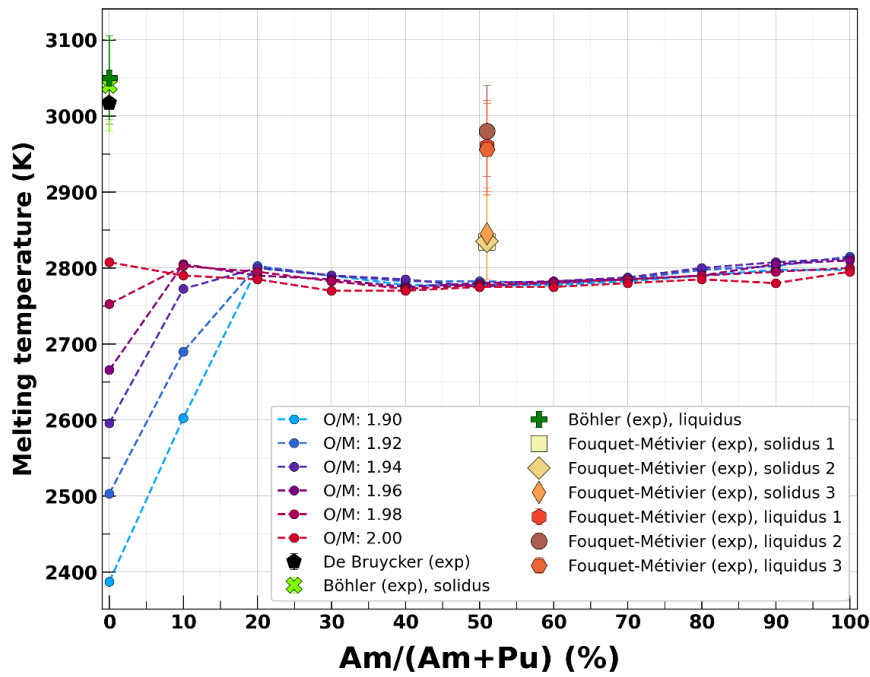


Figure 10: Estimate of the melting temperature as a function of Am content for various O/M ratios

For americium contents greater or equal to 20%, the effect of the O/M ratio is much less significant than in the U-Am-O system [2023Rochedy]. It is only about 10 K here compared with up to 100 K in the (U,Am)O_{2-x} oxides studied. For americium contents of 10% or less, however, the melting temperature falls sharply with the deviation from O/M = 2. This corresponds to compositions containing Pu³⁺ ions, for which the parameters were only optimised for the thermal expansion of U_{0.70}Pu_{0.30}O_{1.99}, U_{0.70}Pu_{0.30}O_{1.98} and U_{0.70}Pu_{0.30}O_{1.97} oxides [2020Takoukam-takoundjou], indicating that these terms are probably not suitable for determining the melting temperature of Pu_{1-y}Am_yO_{2-x} compounds.

3 CALPHAD method

In this work, the thermodynamic modelling is performed with the Thermo-Calc software (<https://thermocalc.com>). All the Gibbs energy functions are referred to the enthalpy of the pure elements in their stable state at 298.15 K under 1 atm (designated as H_i^{SER}).

3.1 Pure elements and stoichiometric compounds

The Gibbs energy functions for the pure elements are taken from the SGTE pure database [1991Dinsdale]. For the pure elements and all the stoichiometric compounds, the Gibbs energy function is expressed as follows:

$$G_m^\phi - \sum_i b_i^\phi H_i^{SER} = a_0 + a_1 T + a_2 T \ln(T) + a_3 T^2 + a_4 T^{-1} + a_5 T^3$$

Where, b_i^ϕ is the stoichiometric factor of element i in the compound ϕ .

3.2 Non stoichiometric solid phases

The Compound Energy Formalism [2007Lukas] allows the description of all types of non-stoichiometric phases. The relationship between the structure and the thermodynamic properties of a non-stoichiometric phase is made possible by using the concept of sublattices. A sublattice corresponds to a crystalline site in the structure. All the phases having the same crystalline structure are described by the same sublattice model.

The Gibbs energy is the combination of three different terms:

$$G_m^\emptyset = {}^{srf}G_m + {}^{cnf}S_m + {}^EG_m$$

Where, ${}^{srf}G_m$, the reference surface, is expressed by:

$${}^{srf}G_m = \sum_{I_0} P_{I_0(Y)} {}^0G_{I_0}$$

I_0 is an end-member (a constituent array specifying one constituent in each sublattice). $P_{I_0(Y)}$ is the product of the constituent fractions specified by I_0 . ${}^0G_{I_0}$ is the Gibbs energy parameter for the end-member I_0 .

The configurational term, ${}^{cnf}S_m$, is the configurational entropy term related to the mixing of the species in the different sublattices:

$${}^{cnf}S_m = -R \sum_{s=1}^n a_s \sum_{i=1}^{n_s} y_i^{(s)} \ln(y_i^{(s)})$$

a_s is the number of sites in each sublattice and $y_i^{(s)}$ is the constituent fraction of i on sublattice s .

EG_m is the excess term which contains sums over possible interaction parameters L between the species in the sublattices:

$${}^EG_m = \sum_{I_1} P_{I_1(Y)} L_{I_1} + \sum_{I_2} P_{I_2(Y)} L_{I_2} + \dots$$

P_{I_1} and P_{I_2} are component arrays of the first and second order containing one and two extra constituents in one sublattice, respectively.

3.3 C1 phase

The mixed oxide with the fluorite structure is described by the following three sublattice model [2021Gueneau]:



The first sublattice corresponds to the site for cations, whereas the second and third ones are the normal and interstitial sites for oxygen, respectively. Vacancies “Va” are introduced to vary the occupancy rate for oxygen on these sites.

The phase must remain neutral. The change in the oxygen stoichiometry is accommodated by the change in the cation oxidation states related to the reduction/oxidation of the metals.

3.4 C-M₂O₃

This intermediate oxide phase with an O/M ratio close to 1.6, known as C-type bixbyite, exists in Pu-O and Am-O systems. This phase, with a bcc structure related to the fluorite structure, is stable at high temperature only, and exhibits a composition range. It is designated as C-M₂O₃ in our database.

As no experimental data exist on the uranium solubility in the bixbyite in Am-O and Pu-O systems, it could not be described in our model. Measurements would be very useful to improve the modelling of this phase.

The sublattice model to describe this phase is: $(Am^{+3}, Am^{+4}, Pu^{+3}, Pu^{+4})_2(O^{-2}, Va)_3(O^{-2}, Va)$

3.5 Liquid phase

The two sublattice ionic model is used to describe the liquid phase [2007Lukas]:

$$(C^{v_c})_P(A^{v_A}, N^0, Va^{Q-})_Q$$

The first sublattice contains cations C (with a charge v_c) whereas in the second sublattice, anions A (with a charge v_A), neutral species and charged vacancies Va^{Q-} with a charge equal to (Q^-) are introduced.

In this model, the neutral charge balance is maintained thanks to the introduction of charged vacancies. P and Q , the site numbers of the two sublattices, are then defined as:

$$P = \sum_j v_j y_{A_j} + Q y_{va}, \quad Q = \sum_i v_i y_{C_i}$$

with y_i the fraction of the species i .

The Gibbs energy is expressed by:

$$G^{liq} = G_{ref}^{liq} + G_{id}^{liq} + G_{ex}^{liq}$$

with:

$$G_{ref}^{liq} = \sum_i \sum_j y_{C_i} y_{A_j} {}^\circ G_{(C_i)(A_j)}^{liq} + Q \cdot y_{va} \sum_i y_{C_i} {}^\circ G_{(C_i)}^{liq} + Q \sum_i y_{N_i} {}^\circ G_{(N_i)}^{liq}$$

G_{ref}^{liq} is a linear combination of Gibbs energy of the different end-members.

$$G_{id}^{liq} = RT \left[P \sum_i y_{C_i} \ln(y_{C_i}) + Q \left(\sum_i y_{A_i} \ln(y_{A_i}) + y_{va} \ln(y_{va}) + \sum_i y_{N_i} \ln(y_{N_i}) \right) \right]$$

G_{id}^{liq} corresponds to the configurational entropy in both sublattices. The excess term, not described here, contains interaction parameters [2007Lukas].

3.6 Gas phase

The gas phase is described by an ideal mixture of the gaseous species on a single sublattice. The Gibbs energy is expressed as follows:

$$G^{gas} = \sum_i y_i \left[{}^\circ G_i^{gas} - \sum_j b_{ij} H_j^{SER} + RT \ln y_i \right] + RT \ln \left(\frac{p}{p_0} \right)$$

Where, ${}^\circ G_i^{gas}$ is the Gibbs energy of the gaseous species i , b_{ij} is the number of atoms j in the species i . The standard pressure p_0 is set to 10^5 Pa. The partial pressure of species i p_i is related to the constituent fraction by: $p_i = y_i p$ where p is the total pressure.

4 Thermodynamic models

The source of the models is given in Table 1 for the binary sub-systems. In case the models are published, the reference is reported. Only the model on Am-O system has been modified in this work. Among the ternary sub-systems, none of the metallic ones in the U-Pu-Am-Np system has been assessed. They are all calculated by extrapolation from the binary sub-systems. For the systems containing oxygen which are the most important ones to model, information is given in Table 2.

Systems	U			
Pu	[2021TAF-ID]	Pu		
Am	[2020Kurata]	[2011Gotcu]	Am	
Np	[2020Kurata]	[2021TAF-ID]	[2020Kurata]	Np
O	[2011Gueneau]	[2011Gueneau]	[2017Epifano,This work]	[2016Smith]

Table 1: Source of the models for the binary sub-systems

Systems	Reference	Comments
U-Pu-O	[2011Gueneau,2023Fouquet]	The model on U-Pu-O was published by Guéneau et al in 2011. In [2023Fouquet], the model for only the liquid phase has been modified by Fouquet-Métivier.
U-Am-O	[2017Epifano_B, 2020Epifano, This work]	The model on U-Am-O was published by Epifano in 2017 [2017Epifano_B]. The model for the liquid has been modified by the authors in 2020 [2020Epifano]. It has been reassessed by Guéneau et al in frame of this work.
U-Np-O	This work	The model on U-Np-O has been assessed by Smith et al. in frame of this work.
Pu-Am-O	[2022Fouquet]	The model on Pu-Am-O has been assessed by Fouquet-Métivier [Fouquet].
Pu-Np-O	This work	The model on Pu-Np-O has been assessed by Rochedy et al. in frame of this work.
Am-Np-O	NM	This model has not been assessed in PATRICIA. It will be in future studies by Cette, Smith and Guéneau.

Table 2: Source of the models for the ternary sub-systems. "NM": Not modelled, extrapolated from binaries.

4.1 Am-O

The parameters for the solid phases are published in [2017Epifano] and have not been modified. Only the model for the liquid phase has been reassessed to take into account the solidus temperature data calculated using empirical potentials (section 2.2.1).

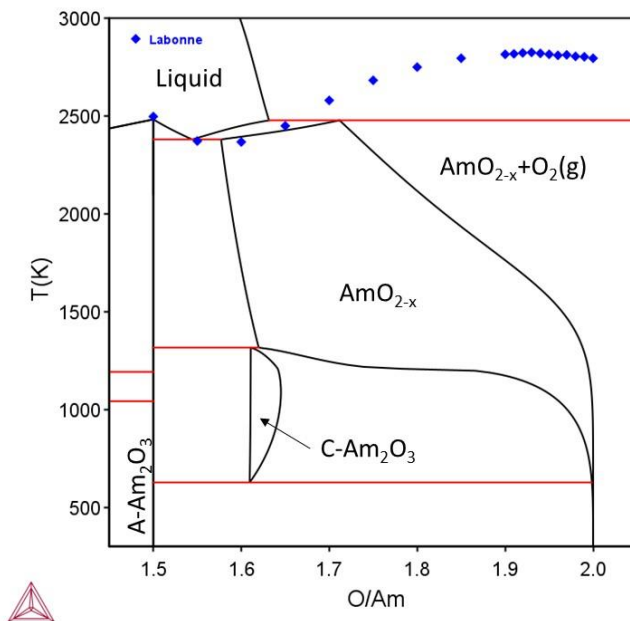


Figure 11: Calculated Am-O phase diagram. The blue symbols are the melting temperature data calculated using molecular dynamics (see section 2.2.1).

The calculated phase diagram is presented in Figure 11. The calculated phase diagram shows that americium dioxide is reduced above 1100 K until it starts to melt at about 2500 K at a predicted O/M ratio of 1.72.

This modified model has been used to reassess the U-Am-O and Pu-Am-O systems.

4.2 U-Am-O

In the model published by Epifano [2017Epifano_B], two metastable miscibility gaps existed in the hyperstoichiometric region ($O/M > 2$). This model was mainly based on the oxygen potential data measured for $(U_{0.5}Am_{0.5})O_{2\pm x}$ by Bartscher and Sari [1983Bartscher]. Measurements of oxygen potential for $(U_{0.85}Am_{0.15})O_{2-x}$ were very recently published by Watanabe et al. [2024Watanabe]. The aim of the present work was to reassess the ternary system in order to suppress the metastable miscibility gaps for $O/M > 2$ and to take into account the two oxygen potential datasets.

Additional interaction parameters have been added to suppress the miscibility gaps. The phase diagrams calculated at 300 K and 1000 K are presented in Figure 12. The two miscibility gaps have been successfully suppressed.

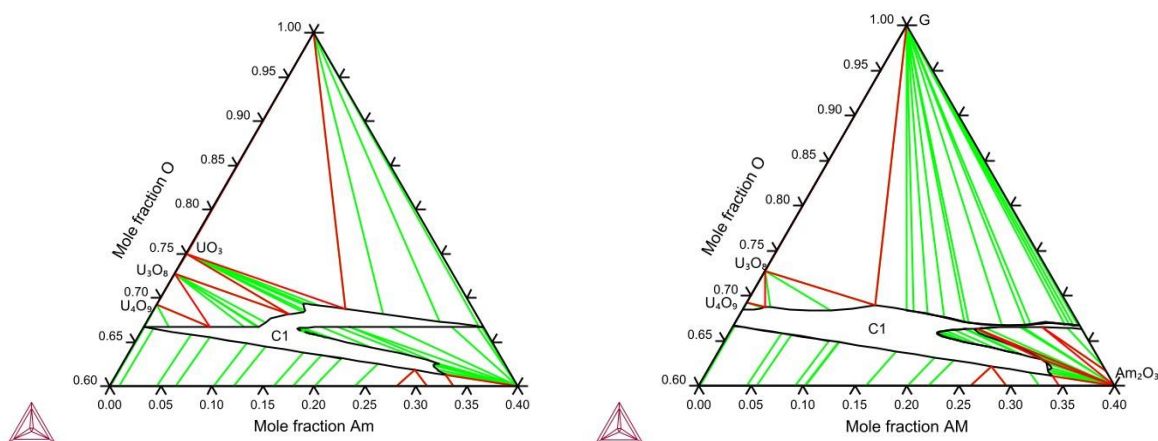


Figure 12: Calculated U-Am-O phase diagram at 300 K (left) and 1000 K (right)

The calculated isopleth section UO_2 - AmO_2 is presented in Figure 13. The solidus temperature data are in very good agreement with the measurements under argon by Prieur et al. [2016Prieur] and Epifano et al. [2020Epifano] up to 50 % Am, using laser heating.

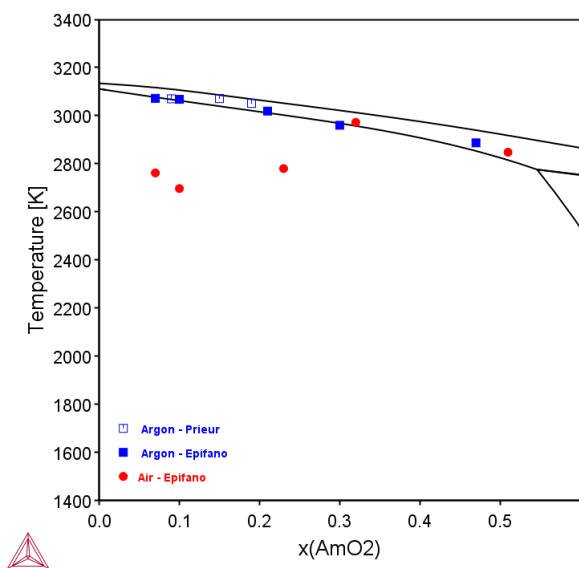


Figure 13: Calculated isopleth section UO_2 - AmO_2

The calculated oxygen potential data are compared to the experimental data in Figure 14.

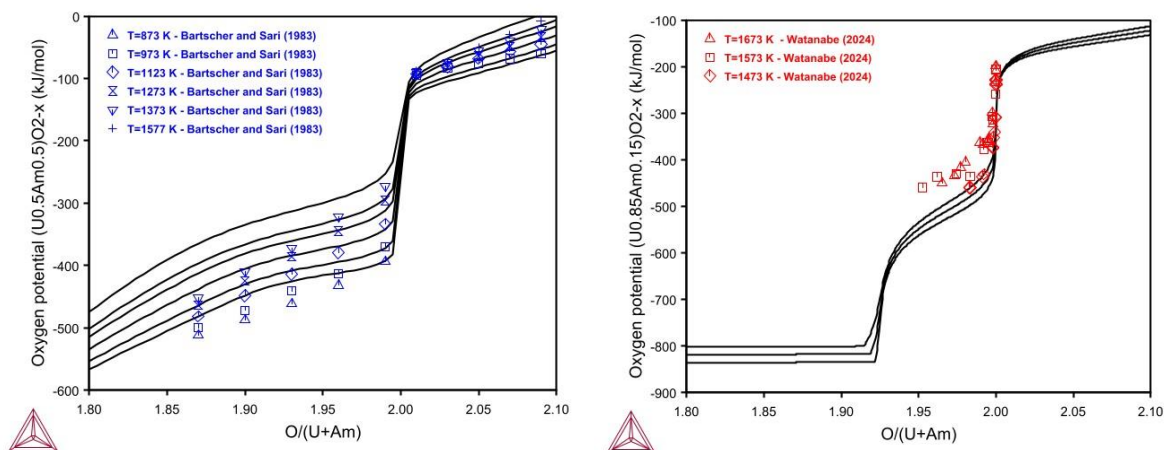


Figure 14: Calculated oxygen potential data above $(U_{0.5}Am_{0.5})O_{2-x}$ (left) and $(U_{0.85}Am_{0.15})O_{2-x}$ (right)

The model tends to overestimate the oxygen potential for 50 % Am whereas the calculated values are lower than the experimental data for 15 % Am. It was not possible to reach a good agreement with both experimental datasets. A reasonable agreement with the scarce experimental data has been obtained. However, there is a lack of oxygen potential and phase diagram data in the region with high Am content ($>50\%$ Am) and $O/M < 2$.

4.3 Pu-Am-O

A first model has been published by Gotcu et al in 2011 [2011Gotcu].

Following the re-evaluation of the Am-O system by Epifano in 2017 [2017Epifano], the ternary system has been reassessed [2019Guéneau]. Oxygen potential data have been measured by Matsumoto et al. [2015Matsumoto] on $(Pu_{0.928}Am_{0.072})O_{2-x}$, Osaka et al. [2006Osaka] on $(Pu_{0.91}Am_{0.09})O_{2-x}$, and Otobe et al. [2009Otobe] on $(Pu_{0.5}Am_{0.5})O_{2-x}$. More recently, new measurements of oxygen potential on $(Pu_{0.8}Am_{0.2})O_{2-x}$ and melting temperature of $(Pu_{0.5}Am_{0.5})O_2$ have been conducted by Fouquet-Métivier in 2022 [2022Fouquet] who have improved the model using these new data.

The phase relationships in Pu-O and Am-O systems are complex due to the existence of several intermediate oxides. There are almost no experimental phase diagram data on the ternary, thus the calculated phase diagram is considered as tentative. The calculated phase diagrams at 500 K, 1000 K, 1500 K and 2000 K are presented in Figure 15. A continuous solid solution between hexagonal A- Am_2O_3 and A- Pu_2O_3 is assumed to exist, which is reasonable as the Pu-O and Am-O phase diagrams are very close.

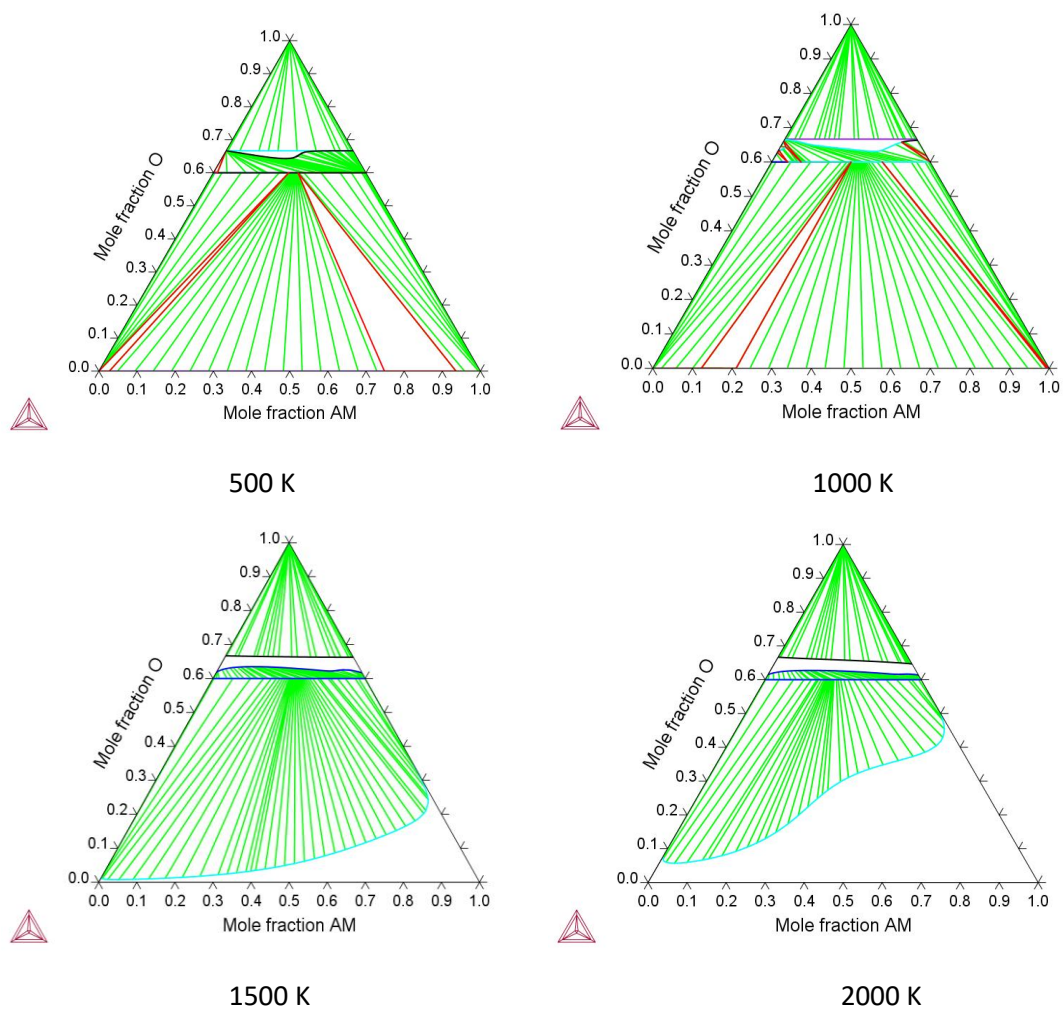


Figure 15: Calculated Pu-Am-O phase diagram at 500 K, 1000 K, 1500 K and 2000 K

The solidus/liquidus temperatures measured by Fouquet-Metivier on $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ are reasonably well reproduced by our model although the final O/M ratio of the sample is not known.

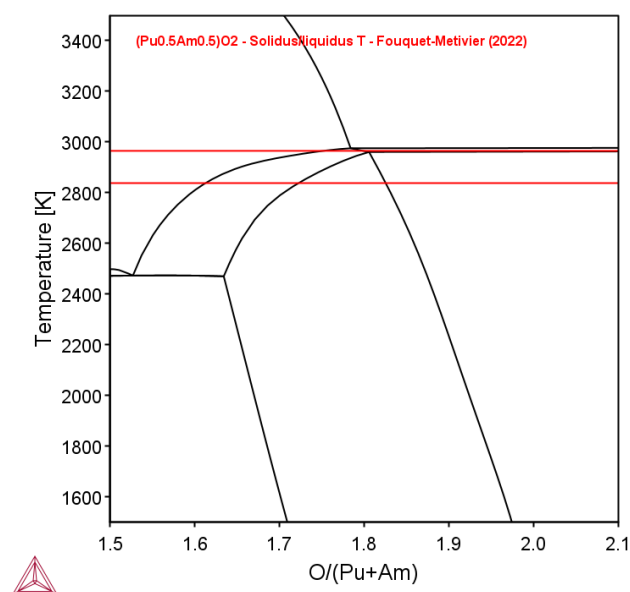


Figure 16: Calculated isopleth section for Pu/Am=1

The calculated oxygen potential data are in reasonable good agreement with the measurements by Matsumoto *et al.* on $(\text{Pu}_{0.928}\text{Am}_{0.072})\text{O}_{2-x}$, Osaka *et al.* on $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$, and Otake *et al.* on $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$, whereas it tends to underestimate the oxygen potential on $(\text{Pu}_{0.8}\text{Am}_{0.2})\text{O}_{2-x}$ compared to the experimental data of Fouquet-Metivier.

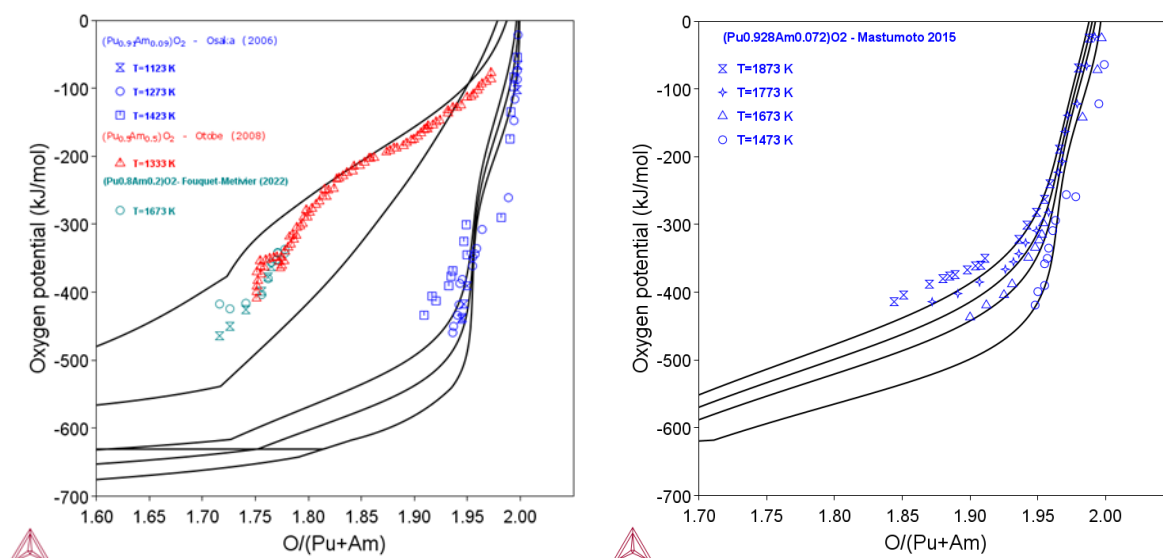


Figure 17: Calculated oxygen potential data above $(\text{Pu}_{0.91}\text{Am}_{0.09})\text{O}_{2-x}$, $(\text{Pu}_{0.8}\text{Am}_{0.2})\text{O}_{2-x}$ and $(\text{Pu}_{0.5}\text{Am}_{0.5})\text{O}_{2-x}$ (left) and $(\text{Pu}_{0.928}\text{Am}_{0.072})\text{O}_{2-x}$ (right).

New measurements are needed to improve the description of this system.

4.4 U-Np-O

A limited number of phase diagram data are available on the U-Np-O system. Isothermal calculations at 500 K and 1273 K are shown in Figure 18 and Figure 19, respectively. The $(\text{U,Np})\text{O}_{2\pm x}$ fluorite phase is stable across a rather large composition range, both in the hypo- and hyper-stoichiometric ranges. The extent of the stability domain for this phase is in good agreement with the literature data at 500 K. The reported domain at 1273 K by Yamashita *et al.* is more extended towards the hyperstoichiometric compositions than in the calculations (Figure 19).

Attempts were made to extend the domain of stability with the current description of the $(\text{U,Np})\text{O}_{2\pm x}$ phase, but remained unsuccessful. It would be extremely useful to confirm the results of Yamashita *et al.* [1994Yamashita] with complementary measurements. Moreover, a certain solubility of Np into the U_3O_8 phase was introduced in the model, in accordance with the results of Finch *et al.* [2003Finch].

Pseudo-binary sections between UO_{2-x} and NpO_{2-x} were moreover optimized to fit the reported experimental data by Chollet *et al.* [2015Chollet]. The agreement is generally good (Figure 20), especially considering that the stoichiometry of the melted samples could not be determined. We expect those to be reduced. We have thus plotted the section between UO_2 and NpO_2 , and congruently melting $\text{UO}_{1.98}$ and $\text{Np}_{1.90}$. With the present model, the melting temperature of the two end members and the solidus temperatures of the mixed oxide are in good agreement with the experimental measurements.

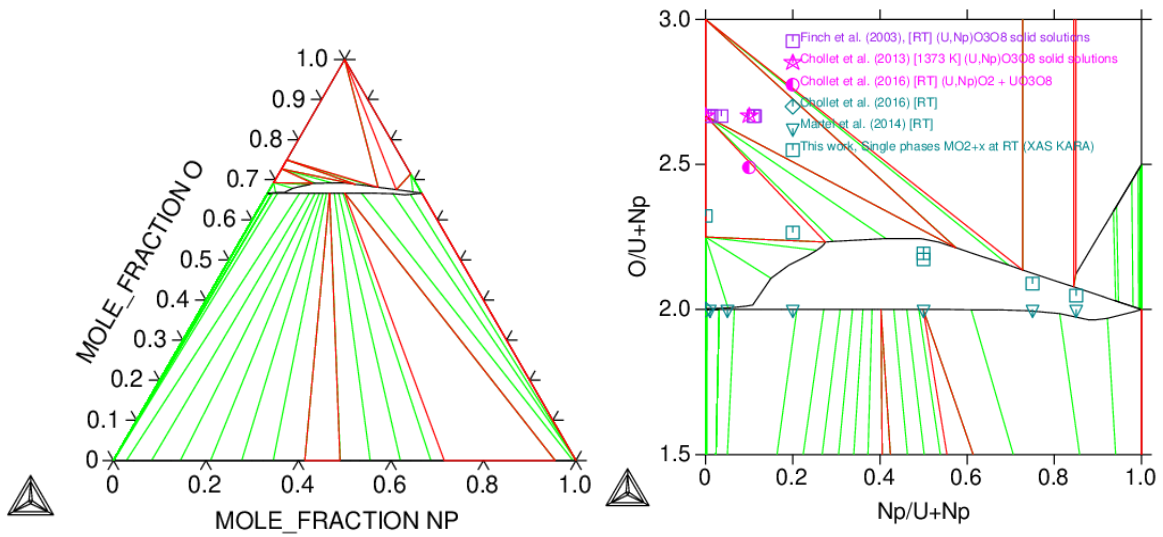


Figure 18: U-Np-O isotherm at 500 K

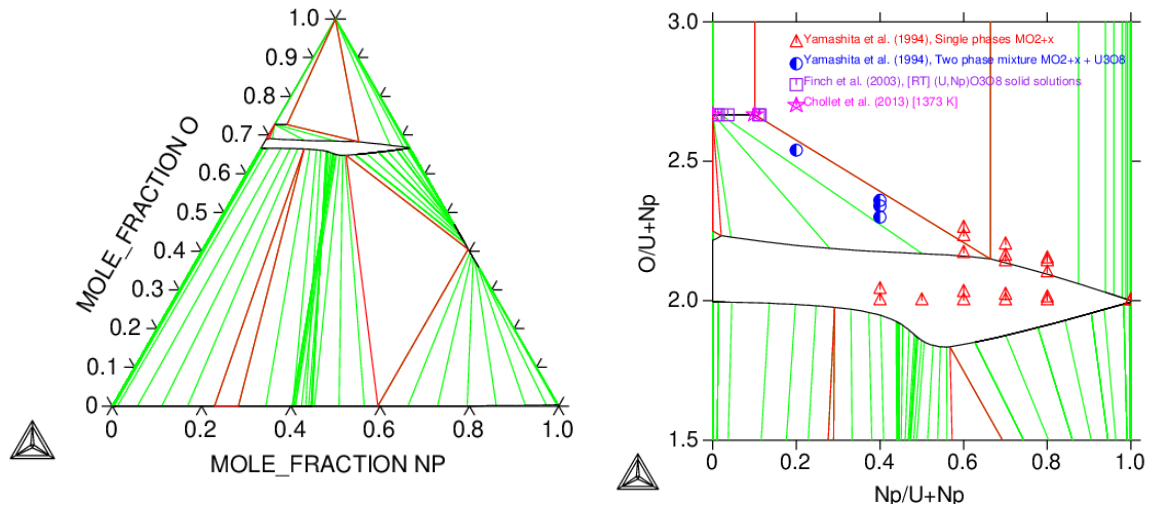


Figure 19: U-Np-O isotherm at 1273 K

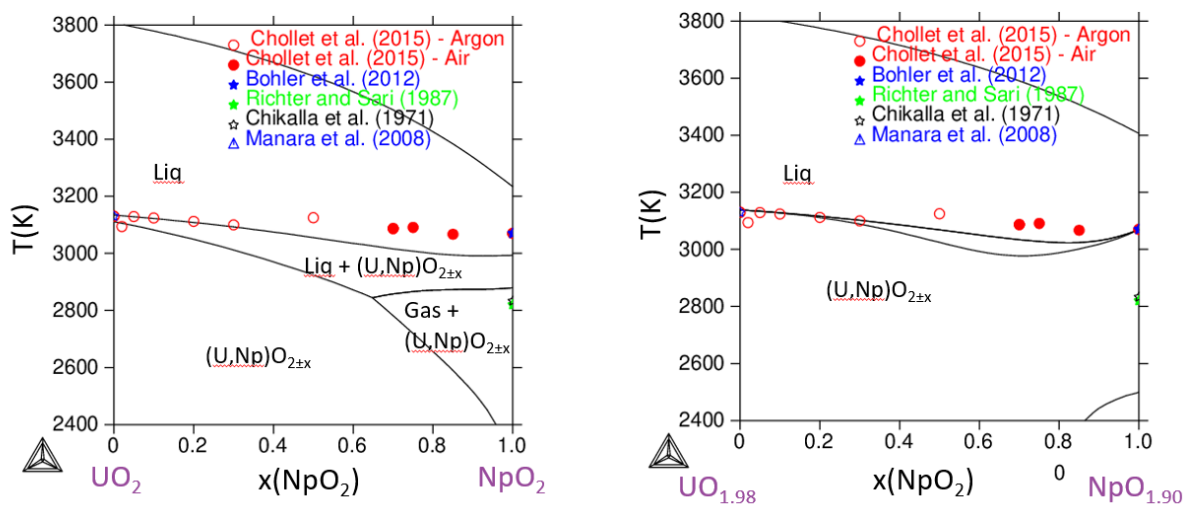


Figure 20: Calculated pseudo-binary sections UO₂-NpO₂ (left) and UO_{1.98}-Np_{1.90} (right), and comparison with the experimental data.

Enthalpy increment calculations were moreover performed and compared with the results of the experimental studies performed at JRC (unpublished data, prior to PATRICIA), and obtained within PATRICIA (see deliverable D4.3). The agreement is generally very good. As an illustration, the comparison with the experimental data for $\text{U}_{0.80}\text{Np}_{0.20}\text{O}_2$ is shown in Figure 21. The calculation performed at several U/Np ratios shows a very limited dependence of the enthalpy increment on composition.

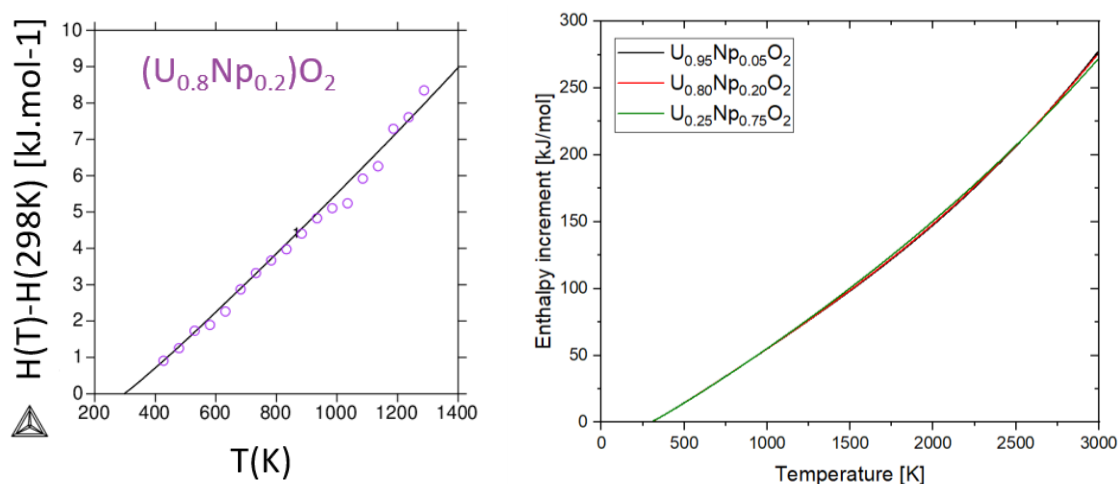


Figure 21: Calculated enthalpy increment for $(\text{U},\text{Np})\text{O}_2$ oxides. (Left) Comparison with the experimental data for $\text{U}_{0.80}\text{Np}_{0.20}\text{O}_2$. (Right) Calculation for the $\text{U}_{0.95}\text{Np}_{0.05}\text{O}_2$, $\text{U}_{0.80}\text{Np}_{0.20}\text{O}_2$ and $\text{U}_{0.25}\text{Np}_{0.75}\text{O}_2$ compositions.

Oxygen potential data have not been reported in the U-Np-O system, which makes the modelling challenging. We have compared the calculation at 1373 K for $(\text{U}_{0.50}\text{Np}_{0.50})\text{O}_{2\pm x}$, with the same data calculated in the U-Th-O, U-Pu-O, and U-Am-O systems. Considering the trends along the actinide series, we would expect the oxygen potential for $(\text{U}_{0.50}\text{Np}_{0.50})\text{O}_{2\pm x}$ to be in-between that calculated for $(\text{U}_{0.50}\text{Th}_{0.50})\text{O}_{2\pm x}$ and $(\text{U}_{0.50}\text{Pu}_{0.50})\text{O}_{2\pm x}$. This is indeed the case, both in the hypo- and hyper-stoichiometric domains with the current model.

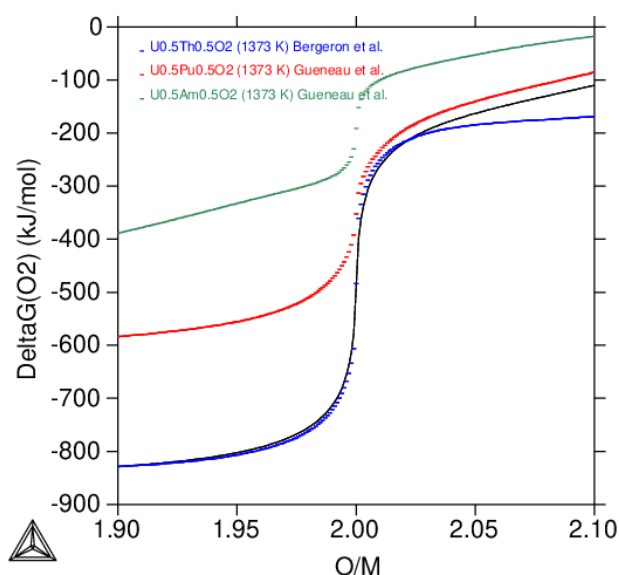


Figure 22: Calculated oxygen potential of $\text{U}_{0.5}\text{Np}_{0.5}\text{O}_{2\pm x}$ at 1373 K. The calculations are represented by a black line and they are compared to calculated oxygen potential for $\text{U}_{0.5}\text{Th}_{0.5}\text{O}_{2\pm x}$, $\text{U}_{0.5}\text{Pu}_{0.5}\text{O}_{2\pm x}$ and $\text{U}_{0.5}\text{Am}_{0.5}\text{O}_{2\pm x}$.

4.5 Pu-Np-O

The thermodynamic model of ternary system Pu-Np-O was developed based on the experimental data presented in deliverable D4.3. The model presented below has been optimized on the basis of melting temperature measurements and oxygen potential data for U-Pu-Np-O and U-Pu-Np-Am-O available in the literature.

The calculated pseudo-binary diagram between $\text{NpO}_{1.9}$ and $\text{PuO}_{1.95}$ is presented in Figure 23. The compositions of the two end-members in this diagram are those of their congruent melting. The experimental melting temperatures of NpO_{2-x} , PuO_{2-x} , $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_{2-x}$ and $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_{2-x}$ are shown for comparison. With the present model, the melting temperature of the two end-members and the solidus temperatures of the mixed oxide are in good agreement with the experimental measurements.

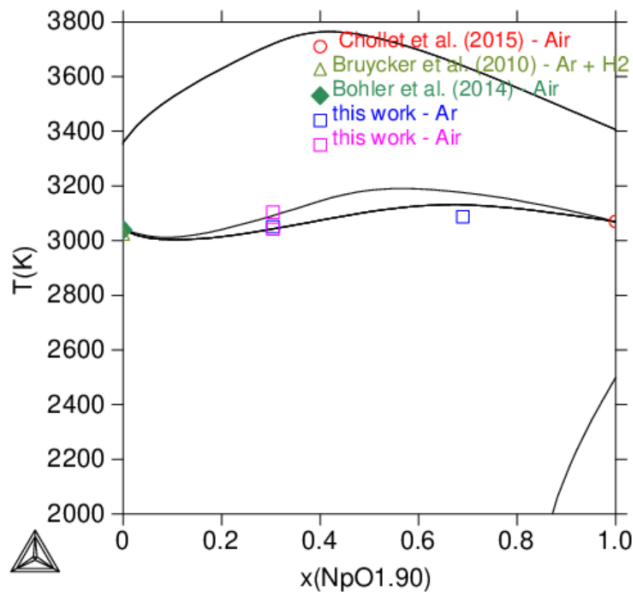


Figure 23: Calculated pseudo-binary $\text{PuO}_{1.95}\text{-NpO}_{1.90}$. The experimental melting temperature of $(\text{Pu,Np})\text{O}_{2-x}$ measured at JRC Karlsruhe and presented in deliverable D4.3 are represented by squares. The melting temperature of NpO_2 from [2015Chollet] is symbolised by circles and those of PuO_2 from [2011DeBruycker, 2011DeBruyckerB, 2014Bohler] are illustrated by diamonds.

An isothermal calculation at 1273 K is shown in Figure 24. The $(\text{Pu,Np})\text{O}_{2\pm x}$ fluorite phase is stable across a rather large composition range in the hypostoichiometric range. At present, there are no data available in the literature for comparison.

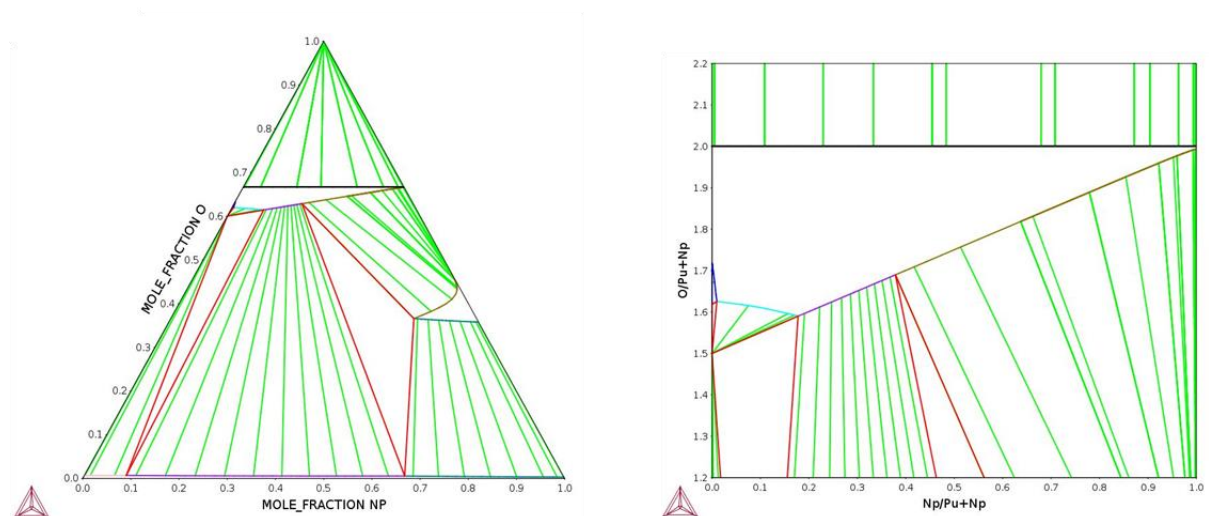


Figure 24: Isotherm calculated at 1273 K

Figure 25 shows the results of the enthalpy increments calculation for $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ and $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$. For the two mixed oxide compositions, the calculated enthalpy increments are very close. No experimental data are available for comparison.

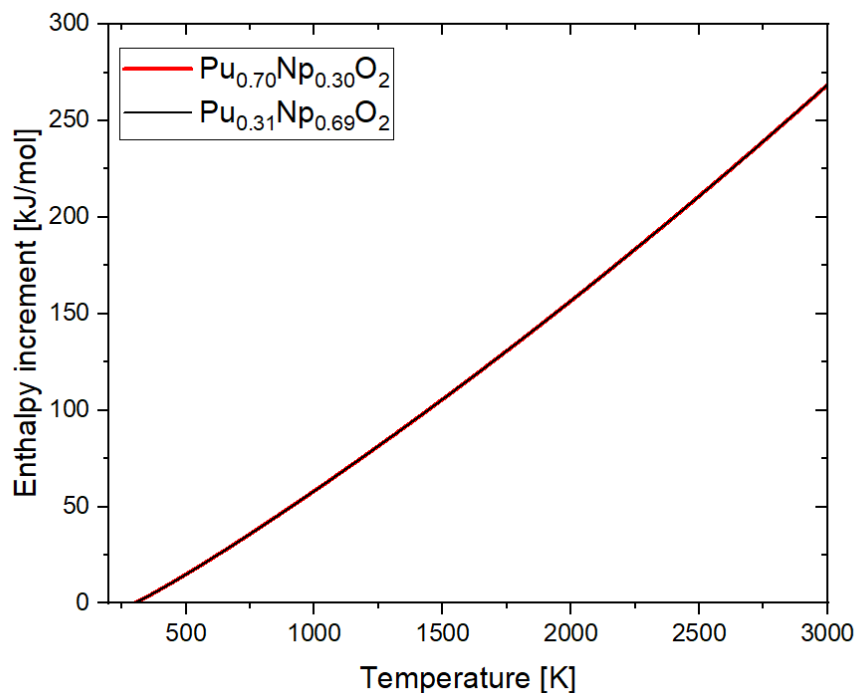


Figure 25: Enthalpy increment calculated with the present model for $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ and $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$

Figure 26 shows calculations of the partial vapour pressures of Np and Pu gaseous species (Np , NpO , NpO_2 , Pu , PuO and PuO_2) for $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ and $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$. Experimental vapour pressure measurements were done on those two compositions $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ and $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$, but the interpretation is still on-going. They are thus not presented in this document.

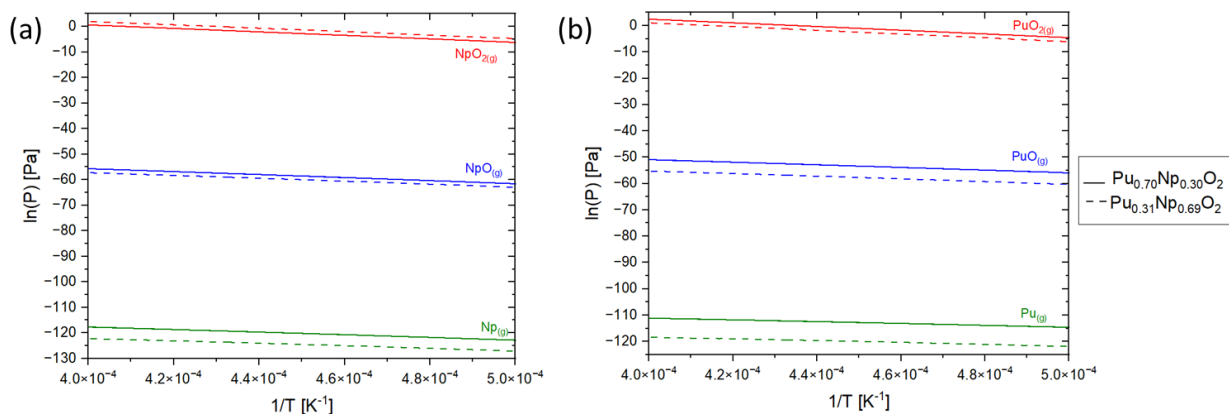


Figure 26: Vapour pressures calculated of the Np (a) and Pu (b) gaseous species for $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ and $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$

4.6 Extrapolation to the higher order system U-Pu-Am-Np-O

4.6.1 U-Pu-Am-O

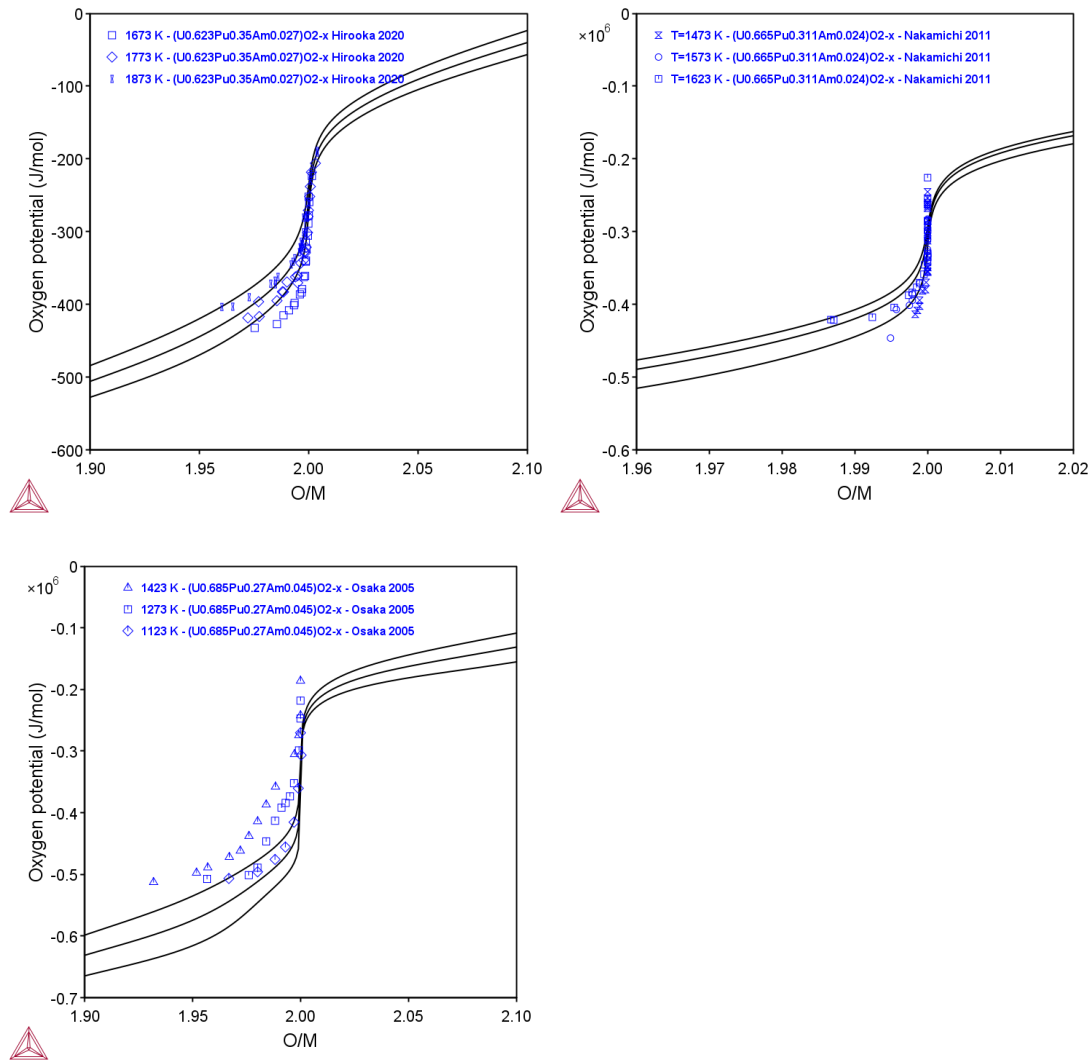


Figure 27: Calculated oxygen potential on $(U_{0.623}Pu_{0.35}Am_{0.027})O_{2-x}$, $(U_{0.665}Pu_{0.311}Am_{0.024})O_{2-x}$ and $(U_{0.685}Pu_{0.27}Am_{0.045})O_{2-x}$. Comparison with the experimental data from Hirooka et al [2020Hirooka], Nakamichi et al [2011Nakamichi] and Osaka et al [2005Osaka].

Measurements of oxygen potential have been performed by Hirooka et al. [2020Hirooka] on $(U_{0.623}Pu_{0.35}Am_{0.027})O_{2-x}$, by Nakamichi et al. [2011Nakamichi] on $(U_{0.665}Pu_{0.311}Am_{0.024})O_{2-x}$, and by Osaka et al. [2005Osaka] on $(U_{0.685}Pu_{0.27}Am_{0.045})O_{2-x}$. The model tends to slightly overestimate the oxygen potential compared to these experimental data of Hirooka et al. [2020Hirooka] and Nakamichi et al. [2011Nakamichi]. However, the agreement remains reasonable. The model underestimates the oxygen potential data compared to the experimental data of Osaka et al. [2005Osaka].

4.6.2 U-Pu-Am-Np-O

Finally, a comparison can be made with the oxygen potential data measured by Nakamichi et al. [2011Nakamichi] on $Am_{0.01}Pu_{0.29}U_{0.58}Np_{0.12}O_{2\pm x}$, and with the data by Hirooka et al. [2020Hirooka] on $Am_{0.015}Pu_{0.285}U_{0.553}Np_{0.147}O_{2\pm x}$. The agreement with the latter data is rather good, giving some confidence with the predictions of the multi-component database.

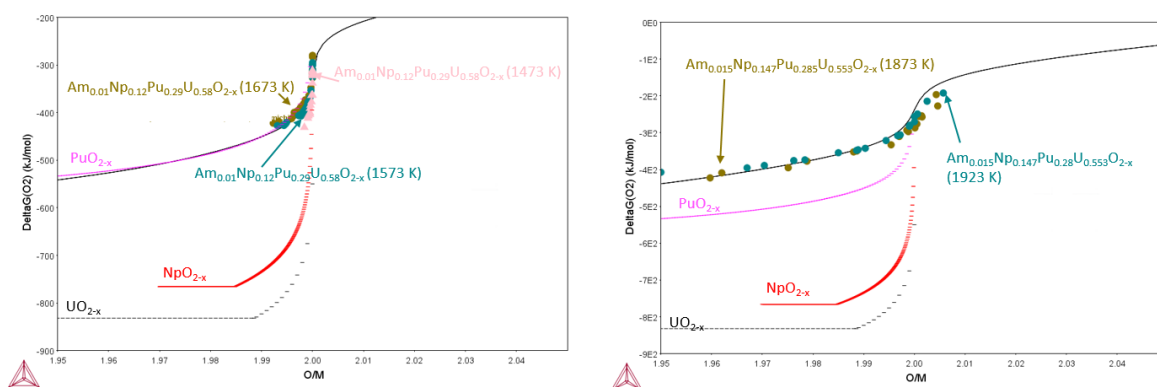


Figure 28: Calculated oxygen potential on $\text{Am}_{0.01}\text{Pu}_{0.29}\text{U}_{0.58}\text{Np}_{0.12}\text{O}_{2-x}$ at 1473 K and $\text{Am}_{0.015}\text{Pu}_{0.285}\text{U}_{0.553}\text{Np}_{0.147}\text{O}_{2-x}$ at 1873 K. Comparison with the experimental data from Nakamichi et al [2011Nakamichi] and Hirooka et al [2020Hirooka].

5 Conclusions

Atomic scale calculations on AmO_{2-x} and $(\text{Pu},\text{Am})\text{O}_{2-x}$ are reported herein that complement the results reported in Deliverable 4.3 on $(\text{U},\text{Am})\text{O}_2$. A thermodynamic database of the U-Am-Np-Pu-O system has moreover been developed for the first time, which required to assess all sub-constituting ternary systems. The models for U-Pu-O, and Pu-Am-O were taken from previous studies, the U-Am-O model was improved, while the assessments of U-Np-O, Pu-Np-O were performed for the first time as part of the PATRICIA project. Given the lack of experimental data on the quinary system, the reliability of the U-Am-Np-Pu-O model needs to be confirmed by comparison with experimental information and calculations. Nevertheless, this work constitutes a key milestone in the development of models of the thermochemical behaviour of advanced nuclear fuels for transmutation purposes.

6 References

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