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THERMODYNAMIC EVALUATION OF LIQUID-GAS SURFACE TENSION FOR $U - O - Zr$ MIXTURES USING THE BUTLER EQUATION

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ABSTRACT

In this work, the Butler equation is assessed for evaluating the liquid/gas surface tension for three compositions in the ternary $U - Zr - O$ system over a wide temperature range 2600 – 3100 K. In this approach, the liquid phase Gibbs energy is obtained from two CALPHAD-type databases, NUCLEA and TAF-ID. Two formulations of the Butler equation makes use of an ideal phase mixing hypothesis (φ being the weighting factor) with and without surface tension laws for pure components. A third formulation corresponds to the classical form of the Butler equation found in the literature where the interfacial Gibbs excess energy is assumed to be proportional to to the liquid one (the multiplicative factor k_{Γ} being related to the ratio of broken bounds). Computed surface tensions are compared to experimental values obtained by C. Denier in her Ph.D. thesis in the VITI facility at CEA Cadarache. Three different compositions corresponding to different Zirconium oxydation degree, C0, C30 and C50 are considered. It is shown through a limited parametric analysis that the choice of the CALPHAD database affects both the slope w.r.t temperature and the level of the interfacial energy while parameters φ and k_{Γ} mainly affects the level and only slightly the slope. Considering pure component surface tension data has a significant impact on both and, considering the C0 composition measurements, it is shown that parameters φ and k_{Γ} can be successfully calibrated for reproducing these data. However, the steep variation of the interfacial energy w.r.t temperature exhibited by experimental results for the C30 composition is, in any case, not correctly captured. This shows the need for further improvement of the liquid thermodynamic modelling and a path forward is proposed.

KEYWORDS

surface tension, corium, Butler equation, CALPHAD

1. INTRODUCTION

Estimating the physical properties of materials involved in nuclear safety is an important aspect for the accuracy of associated simulations. This process can be particularly difficult in cases where experimental data are scarce. Corium jet fragmentation is one such example. In the event of a severe accident in a nuclear reactor, the corium resulting from core meltdown may relocate at the bottom of the reactor pressure vessel or reactor pit in case of vessel failure. The possible presence of water can lead to a fuel-coolant interaction where a high temperature corium jet fragmentates into droplets while vaporising a large amount of water due to high heat transfer [1]. In the worst

case scenario, the steam film enclosing the droplets can be destabilised in such a way that the direct contact between water and corium would lead to further fragmentations and a steam explosion. Such an event could compromise the vessel or containment integrity [2]. Fragmentation phenomena are highly dependent on the surface tension between liquid corium and water vapour as exhibited by empirical fragmentation laws based on the Weber number. However, there is little to no data on this property for liquid corium mixtures due to the very high temperature and components involved [3].

In an effort to provide such data, experimental measurements were successfully carried out recently for $U - O - Zr$ mixtures at CEA Cadarache in the VITI facility of the PLINIUS platform. Those were performed using the maximum bubble pressure method with argon gas injection into the liquid corium [4, 5]. Because of the complexity of such measurements, only a limited set of corium compositions and temperatures have been investigated. In an attempt to construct surface tension laws over a larger range of composition and temperature, the work presented in this paper makes use of a thermodynamic modelling approach using the Butler equation [6] and two different CALPHAD-type thermodynamic databases (NUCLEA [7], TAF-ID [8]) in order to evaluate surface tension between $U - O - Zr$ liquid mixtures and Argon atmosphere. Two different models are considered: on the one hand, the Butler formulation commonly applied for liquid-gas interfaces that incorporates surface tension data of pure components and, on the other hand, a more straightforward formulation of the Butler equation already used in the literature for liquid-liquid interfaces. Those models are presented in the following section 2. In section 3, the numerical solutions for these models is summarized while numerical results are presented and discussed in comparison with recent experimental measurements in section 4. Finally, short conclusions and perspectives of this work are given in section 5.

2. INTERFACE MODELLING

The Butler model was chosen in this work as a full-thermodynamic approach compatible with the CALPHAD method to study surface tensions as described by Butler [6]. Its derivation from fundamental Gibbs equations has been recently revised by Kaptay in [9, 10] obtaining the equations without the monolayer approximation. In this Gibbsian approach, it is considered that the zero-volume interface can be fully characterized by an average composition. Despite its apparent simplicity and approximations¹, the Butler equation was successfully applied to compute surface energies of various binary systems such as liquid alloys, ionic and oxide melts [11]; also using the CALPHAD method to evaluate partial molar excess Gibbs energies [12, 13]. This model can be readily extended to n -components system by using $n - 1$ equations as it was applied for liquid ternary $CaO - SiO_2 - Al_2O_3$ [14], and quaternary $Sn - Zn - Sb - Bi$ [15]. Recently, it was successfully applied to corium systems ($U - O$ and $U - O - Zr - Fe$) for calculating the liquid-liquid interface energy in the miscibility gap region of such systems [23].

2.1. Butler equation

Let us consider a thermodynamic system of N_c components with a known temperature T (K), pressure P (Pa) and global composition written as a molar fractions vector \mathbf{x} . The Gibbs energy of this system is denoted \mathcal{G} (J). We consider cases where, at equilibrium, the system contains two stable bulk phases α , β associated respectively with their Gibbs energy \mathcal{G}_α and \mathcal{G}_β (J). The

¹Santos and Reis in [16] studied its robustness and have shown that Butler equation does not take into account the composition dependency of reference state leading to slightly overestimate ($< 5\%$) surface tension values.

chemical potential $\mu_{i,\alpha}$ (J/mol) of component i in phase α (resp. β) is defined as

$$\mu_{i,\alpha} = \frac{\partial \mathcal{G}_\alpha}{\partial n_i} \quad (1)$$

Gibbs showed that at equilibrium the chemical potential of a component i is uniform over all the stable phases [17] *i.e.*

$$\mu_{i,\alpha} = \mu_{i,\beta} = \mu_i \quad (2)$$

In the Butler model, the interface is depicted as a planar phase with associated Gibbs energy \mathcal{G}_Γ , a mean composition \mathbf{x}_Γ and a surface area A_Γ as seen in figure 1 as its thickness is neglected. The total Gibbs energy of the system is the sum over its stable phases of the different Gibbs energies $\mathcal{G} = \mathcal{G}_\alpha + \mathcal{G}_\beta + \mathcal{G}_\Gamma$.

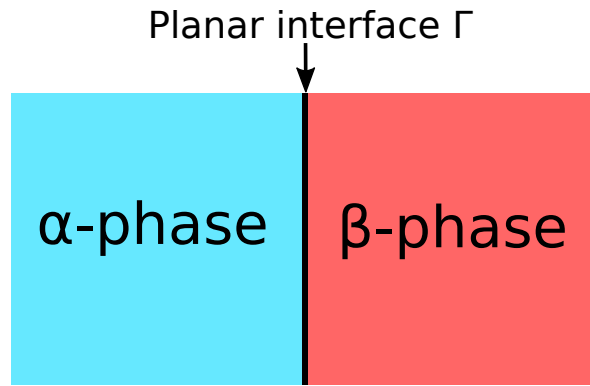


Figure 1. Schematic representation of 2 stable phases, α and β , at equilibrium with a planar interface Γ .

For the interface Γ , the chemical potential $\mu_{i,\Gamma}$ of component i is written as

$$\begin{cases} \mu_{i,\Gamma} = \mu_{i,\Gamma}^* - \omega_{i,\Gamma} \sigma_\Gamma \\ \sigma_\Gamma = \frac{\partial \mathcal{G}_\Gamma}{\partial A_\Gamma} \\ \mu_{i,\Gamma}^* = \frac{\partial \mathcal{G}_\Gamma}{\partial n_i} \end{cases} \quad (3)$$

with σ_Γ ($J.m^{-2}$) the interfacial energy, independent from the component i , and $\omega_{i,\Gamma}$ (m^2/mol) the partial molar surface of component i in interface Γ . The term $\mu_{i,\Gamma}^*$ is called the reduced chemical potential.

The equilibrium conditions (equation 1) as extended by Butler [6] lead to

$$\mu_i = \mu_{i,\Gamma} \quad (4)$$

Writing equations 3 and condition 4 for all components, the first form of the Butler equations can be deduced as, $\forall j \in [1, N_c]$

$$\sigma_\Gamma = \frac{\mu_{j,\Gamma}^* - \mu_j}{\omega_{j,\Gamma}} \quad (5)$$

The independence of the surface tension value from the components constrains the interface composition through the reduced chemical potentials and equation 5 gives a non-linear system of dimension $N_c - 1$ whose independent variables are associated with the interface composition.

The chemical potentials are usually expressed as a sum of three terms [18, 19, 20]

$$\mu_{i,\alpha} = \mu_{i,\alpha}^0 + RT \ln(x_{i,\alpha}) + \Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\alpha) \quad (6)$$

$$\mu_{i,\Gamma}^* = \mu_{i,\Gamma}^{0,*} + RT \ln(x_{i,\Gamma}) + \Delta\mathcal{G}_{i,\Gamma}^E(\mathbf{x}_\Gamma) \quad (7)$$

where

- $\mu_{i,\alpha}^0$ (resp. $\mu_{i,\Gamma}^{0,*}$) is the chemical potential of pure component i in phase α (resp. Γ) with same temperature and pressure ;
- $RT \ln(x_{i,\alpha})$ is the entropic contribution with R ($J/(mol \cdot K)$) the universal gas constant, and $x_{i,\alpha}$ (resp. $x_{i,\Gamma}$) the molar fraction of component i in phase α (resp. in interface Γ) ;
- $\Delta\mathcal{G}_{i,\alpha}^E$ (J/mol) (resp. $\Delta\mathcal{G}_{i,\Gamma}^E$) is the partial molar excess Gibbs energy function for phase α (resp. interface Γ) at composition \mathbf{x}_α (resp. \mathbf{x}_Γ). This term is the deviation from an ideal solution.

A similar expression as equation 6 exists for phase $\mu_{i,\beta}$.

Using these equations 6 and 7, the Butler equation 5 can be written in its second form [10]

$$\begin{cases} \sigma_\Gamma = \frac{\omega_{i,\Gamma}^0}{\omega_{i,\Gamma}} \sigma_{i,\Gamma}^0 + \frac{RT}{\omega_{i,\Gamma}} \ln\left(\frac{x_{i,\Gamma}}{x_{i,\alpha}}\right) + \frac{\Delta\mathcal{G}_{i,\Gamma}^E - \Delta\mathcal{G}_{i,\alpha}^E}{\omega_{i,\Gamma}} \\ \sigma_{i,\Gamma}^0 = \frac{\mu_{i,\Gamma}^0 - \mu_{i,\alpha}^0}{\omega_{i,\Gamma}^0} \end{cases} \quad (8)$$

where $\sigma_{i,\Gamma}^0$ is associated with the interface energy in the pure component i case.

2.2. Modelling the thermodynamic quantities

In precedent works on liquid/gas surface energies using the second Butler formulation, an hypothesis is made to solve the rightmost term of the equation 8 [11, 12, 13, 21, 10]. Considering the phase α to be the liquid phase and β the gaseous one, this hypothesis can be written as

$$\Delta\mathcal{G}_{i,\Gamma}^E(\mathbf{x}_\Gamma) = k_\Gamma \Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\Gamma) \quad (9)$$

where $k_\Gamma = Z_\Gamma/Z_\alpha$ is the ratio of the interface coordination number for components over the liquid coordination number for the components. $k_\Gamma \in [0, 1]$ as the components form less bonds in the surface, $Z_\Gamma < Z_\alpha$ [10].

In this work, an ideal phase mixture hypothesis was also tested to model the interface Gibbs energy such as

$$\mathcal{G}_\Gamma = \varphi \mathcal{G}_\alpha(\mathbf{x}_\Gamma) + (1 - \varphi) \mathcal{G}_\beta(\mathbf{x}_\Gamma), \quad \varphi \in [0, 1] \quad (10)$$

and using equation 3, leading to

$$\mu_{i,\Gamma}^* = \varphi \mu_{i,\alpha}(\mathbf{x}_\Gamma) + (1 - \varphi) \mu_{i,\beta}(\mathbf{x}_\Gamma) \quad (11)$$

This hypothesis makes use of information from the gaseous phase and the factor φ can easily be linked to k_Γ . Using equations 7, 10 and 10, it can be shown that

$$\varphi \Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\Gamma) + (1 - \varphi) \Delta\mathcal{G}_{i,\beta}^E(\mathbf{x}_\Gamma) = k_\Gamma \Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\Gamma) \quad (12)$$

in such a way that, the two formulations are equivalent under the following constraint:

$$\varphi = \frac{k_\Gamma \Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\Gamma) - \Delta\mathcal{G}_{i,\beta}^E(\mathbf{x}_\Gamma)}{\Delta\mathcal{G}_{i,\alpha}^E(\mathbf{x}_\Gamma) - \Delta\mathcal{G}_{i,\beta}^E(\mathbf{x}_\Gamma)} \quad (13)$$

For the partial molar surfaces $\omega_{i,\Gamma}$, Kaptay has proposed to use a hard-sphere model to relate it to

partial molar volumes in the liquid phase with the relation [10]

$$\begin{cases} \omega_{i,\Gamma} = f_{\Gamma} V_{mi,\alpha}^{(2/3)} N_{Av}^{(1/3)} \\ f_{\Gamma} = 1.209 \frac{f_{\alpha}^{(2/3)}}{f_{s,\Gamma}} \end{cases} \quad (14)$$

where f_{α} and $f_{s,\Gamma}$ are packing fractions of phase α and interface Γ respectively and N_{av} is the Avogadro number. In the remainder, $f_{\Gamma} = 0.806$ is considered [10].

3. SOLVING THE BUTLER EQUATION

To solve the Butler equations presented in section 2.1, in the present work, the thermodynamic equilibrium are computed using the CALPHAD method [19, 20]. This method models the Gibbs energy of components and their phases as parameterised functions of temperature, pressure and composition. These parameters are fitted using experimental and ab initio data from various binary and ternary systems. Once assessed, they are stored in a thermodynamic database allowing to evaluate equilibrium with a Gibbs energy minimiser. In this work, the version 6 of OpenCalphad [22] software was used.

In this framework, the second Butler formulation (equation 8) was rewritten with chemical potentials using both hypotheses 10 and 9 for the interface energy. Hence, three different equation systems have been considered:

- using the first Butler formulation (equation 5) and the mixing hypothesis of equation 10, the following equation system (denoted **Butler** in the remainder) is obtained:

$$\begin{cases} \sigma_{\Gamma} = \frac{\mu_{i,\Gamma}^* - \mu_i}{\omega_{i,\Gamma}} \\ \mu_{i,\Gamma}^* = \varphi \mu_{i,\alpha}(\mathbf{x}_{\Gamma}) + (1 - \varphi) \mu_{i,\beta}(\mathbf{x}_{\Gamma}) \end{cases} \quad (15)$$

- using the second Butler formulation (equation 8) and the mixing hypothesis of equation 10, the following equation system (denoted **ButlerExcess** in the remainder) is obtained:

$$\begin{cases} \sigma_{\Gamma} = \frac{\mu_{i,\Gamma}^* - \mu_{i,\alpha} + \mu_{i,\alpha}^0 - \mu_{i,\Gamma}^{*,0} + \omega_{i,\Gamma} \sigma_{i,\Gamma}^0}{\omega_{i,\Gamma}} \\ \mu_{i,\Gamma}^* = \varphi \mu_{i,\alpha}(\mathbf{x}_{\Gamma}) + (1 - \varphi) \mu_{i,\beta}(\mathbf{x}_{\Gamma}) \end{cases} \quad (16)$$

- using the second Butler formulation (equation 8) and the excess hypothesis of equation 9, the following equation system (denoted **ButlerPureExcess** in the remainder) is obtained:

$$\sigma_{\Gamma} = \frac{k_{\Gamma} \mu_{i,\alpha}^*(\mathbf{x}_{\Gamma}) - \mu_{i,\alpha} + (1 - k_{\Gamma})(\mu_{i,\alpha}^0 - RT \ln(x_{i,\Gamma})) + \omega_{i,\Gamma} \sigma_{i,\Gamma}^0}{\omega_{i,\Gamma}} \quad (17)$$

Solving these equation systems mean finding the interface composition such that the same interfacial energy value is found for each component in the interface as seen in the equation 5. Gajavalli and Le Tellier in [23] formulated the resolution of the Butler equations as a minimisation problem allowing the use of constrained minimisation algorithms to look for the solution. The same approach has been adopted here.

Regarding the partial molar volumes, their are evaluated from mass density laws and their possible dependency to composition is taken into account as described in [23].

4. RESULTS AND DISCUSSION

The models and resolution methodology were confronted to experimental results obtained by C. Denier in her Ph.D. thesis work [4, 5] in the VITI facility using a maximum bubble pressure technique in which argon gas is injected through a capillary tube in the liquid mixture of interest. The composition of the different liquid mixtures are given in table I (as deciphered by post-mortem analyses); they are denoted by their initial zirconium oxidation degree, C0, C30 and C50.

Table I. Compositions of the liquid phase in C. Denier measurements [5].

	U fraction	Zr fraction	O fraction	Temperature (K)	Surface tension ($J.m^{-2}$)
C0	0.20	0.24	0.56	2640 ± 50	0.706 ± 0.013
				2746 ± 50	0.693 ± 0.013
				2865 ± 50	0.677 ± 0.013
C30	0.19	0.22	0.59	2836 ± 50	0.712 ± 0.013
				2876 ± 50	0.664 ± 0.012
C50	0.21	0.17	0.62	2710 ± 50	0.670 ± 0.013

Two Calphad databases have been considered, NUCLEA [7, 25] (version 19) and TAF-ID [8] (version 11). Considering the liquid phase, the main difference between the two databases is the different CEF model used [26] to describe the excess term of equation 6, an ionic liquid model for TAF-ID and a non-ideal associate model for NUCLEA.

The numerical results are organized as follows. First, considering only the C0 composition and the first form of the Butler equation with ideal mixing hypothesis (**Butler**, see equation 15), a comparison of the two databases along with the impact of the φ -parameter is presented in section 4.1. Then, pure component interfacial energy data are introduced in section 4.2 through the two other formulations of the Butler equation (**ButlerPure** with equation 16 and **ButlerPureExcess**, with equation 17) and the results improvement is discussed.

4.1. Effects of φ and the database in Butler formulation

A comparison of database and φ parameter effects was done using equation 15. Results in terms of the interfacial energy as computed over the temperature range [2400, 3100]K are depicted in figure 2 for both databases and multiple values of φ .

For both databases, an optimal value for φ was calculated using a least square method considering the C0 composition experimental results: $\varphi_{nuclea}^* = 0.6038$ and $\varphi_{tafid}^* = 0.65$ are the optimised values for NUCLEA and TAF-ID databases respectively. Considering such an optimized value, the order of magnitude of the interfacial energy can be reproduced but its variation as a function of temperature, that is mostly dependent on the database, is not for the two different databases. More precisely, it can be seen that the choice of the liquid Gibbs energy model affects both the slope and the level of the interfacial energy curve while parameter φ mainly affects the level and only slightly the slope.

The derivative of the interfacial energy w.r.t. temperature is, in absolute value, about 50% larger with the NUCLEA database, highlighting the unquantified albeit large uncertainty associated with the liquid chemical potential model when used for extrapolation out of its phase equilibria values. This is consistent with the conclusion given by Gajavalli and Le Tellier in [23] about the impact on liquid/liquid interfacial energies of the lack of thermodynamic experimental information on liquid corium system at high temperature.

In figure 3, the element composition of the interface is depicted for the NUCLEA database and

different values of φ . It can be observed that φ mainly affects the molar ratio between U and Zr: the higher φ , the lower this molar ratio is.

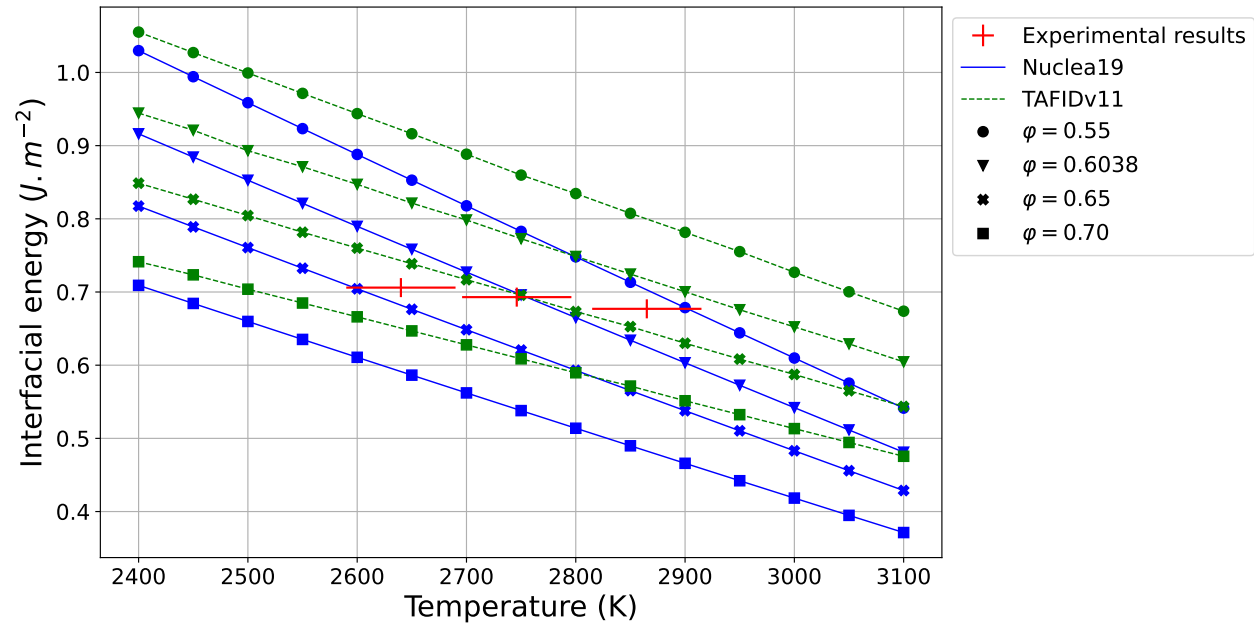


Figure 2. Interfacial energies plot using equation 15. Results obtained are shown in blue plain and green dotted curves for NUCLEA and TAF-ID respectively. Different symbols are used to show different values of φ . Experimental results are shown in red error bars.

4.2. Results improvement introducing pure component interfacial energy data

In order to improve the results, additional information coming from the knowledge associated with pure element interfacial energies are considered now with the two other Butler equation formulations (ButlerPure – equation 16 – and ButlerPureExcess – equation 17).

These data are expressed as a linear law w.r.t temperature under the following form:

$$\sigma_{\Gamma}(T) = \sigma_m + \frac{d\sigma}{dT}(T - T_m) \quad (18)$$

The associated parameters for the uranium and zirconium considered in this study as obtained from the open literature are given in table II.

Table II. Pure component interfacial energy laws for U and Zr.

Element	$\sigma_m(J.m^2)$	$\frac{d\sigma}{dT}$	$T_m(K)$	Reference
U	1.675	$0.34 \cdot 10^{-3}$	1405.45	[27]
Zr	1.462	$0.13 \cdot 10^{-3}$	2130.15	[28, 29, 30]

For pure oxygen, the interfacial energy was taken as an extrapolated 0 value from DFT results computed on liquid oxygen at low temperature range (60 – 90K) showing a decreasing in surface tension with the temperature [31]. Indeed, at the

Considering ButlerPure and ButlerPureExcess formulations, results were computed only for NUCLEA database as the ionic liquid model used in TAF-ID does not allow computations of a pure

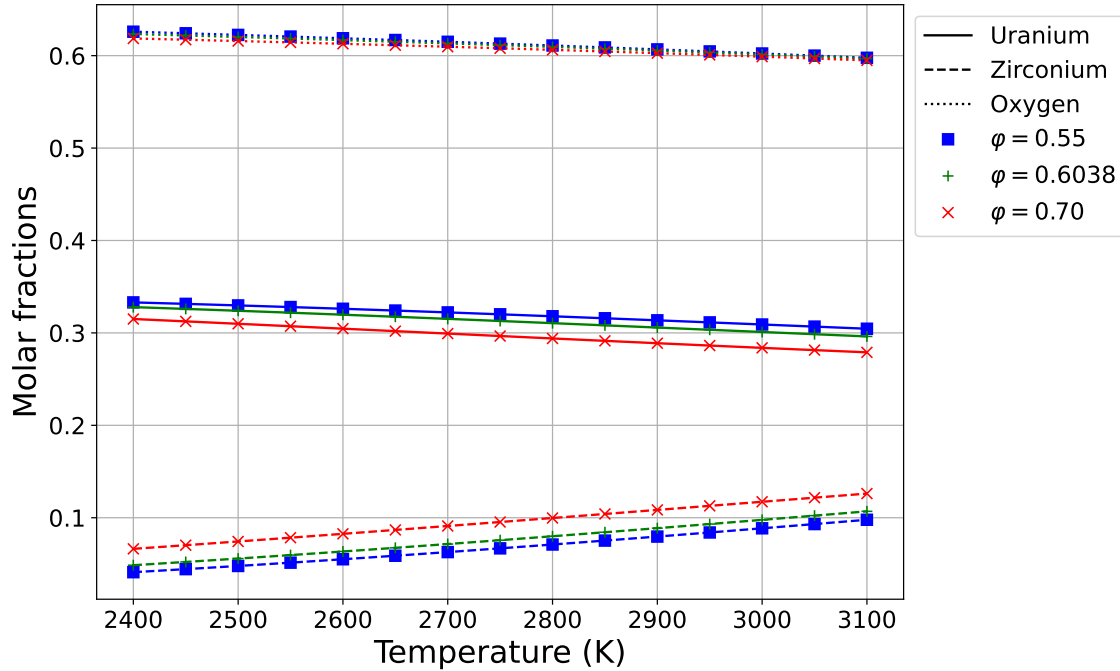


Figure 3. Interface composition computed with NUCLEA database for 3 different values of φ represented by separated symbols. Uranium, zirconium and oxygen fractions are represented by plain, dashed and dotted curves respectively.

liquid oxygen phase (no vacancies in the cation sublattice).

Using the previous optimised value $\varphi_1^* = 0.6038$ for NUCLEA, it can be seen in figure 4 that equation 16 and the use of the pure element interfacial tension data lead to an interfacial energy that is significantly lower (50% in average) than with Butler formulation with a derivative w.r.t to the temperature that is, in absolute value, significantly lower and closer to the experimental trend. Accordingly, a new optimised parameter was computed for the equation 16 with a value $\varphi_2^* = 0.9907$, successfully fitting the experimental results for the C0 composition. Considering the Butler equation formulation associated with equation 17, a similar optimization was carried out w.r.t. parameter k_Γ^* giving a value of 0.9989.

■ **Nota Bene** This value for k_Γ^* is higher than the value of 0.94 considered by Tanaka et al. for k_Γ^* for oxide melts (considering that they behave as ionic liquids) in [11] using a packing factor $f_\Gamma = 1$. Using $f_\Gamma = 1$ in our case, the optimised value of k_Γ^* is only slightly modified to 0.997. ■

Figure 5 depicts the comparison between the results obtained with equations 16 and 17 with these optimised parameters and the experimental measurements for the three different compositions, C0, C30 and C50. It can be observed that with an optimized value of k_Γ^* , the results obtained with 17 are, in any case, very close to the ones obtained with equation 16 with an optimised φ_2^* value.

With parameters calibrated on C0 composition data, it can be seen that the single C50 composition measurement is correctly reproduced while the steepest dependency of the surface tension w.r.t. temperature exhibited for the C30 composition is not correctly captured. An attempt to optimize the parameters considering the experimental data associated with this composition was found unsuccessful. This last result highlights the need for further improvement of the liquid thermodynamic modelling (through the CALPHAD databases).

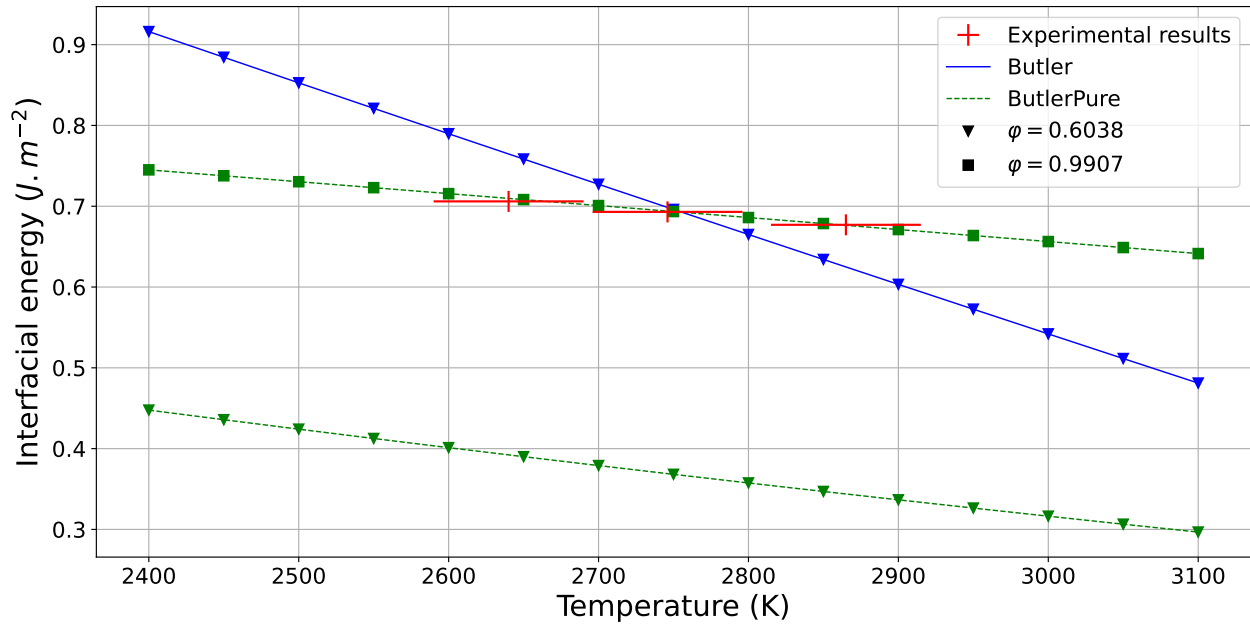


Figure 4. Interfacial energies computed with NUCLEA database with equations 15 in plain blue and 16 in dashed green. Symbols represent different ϕ -parameter values.

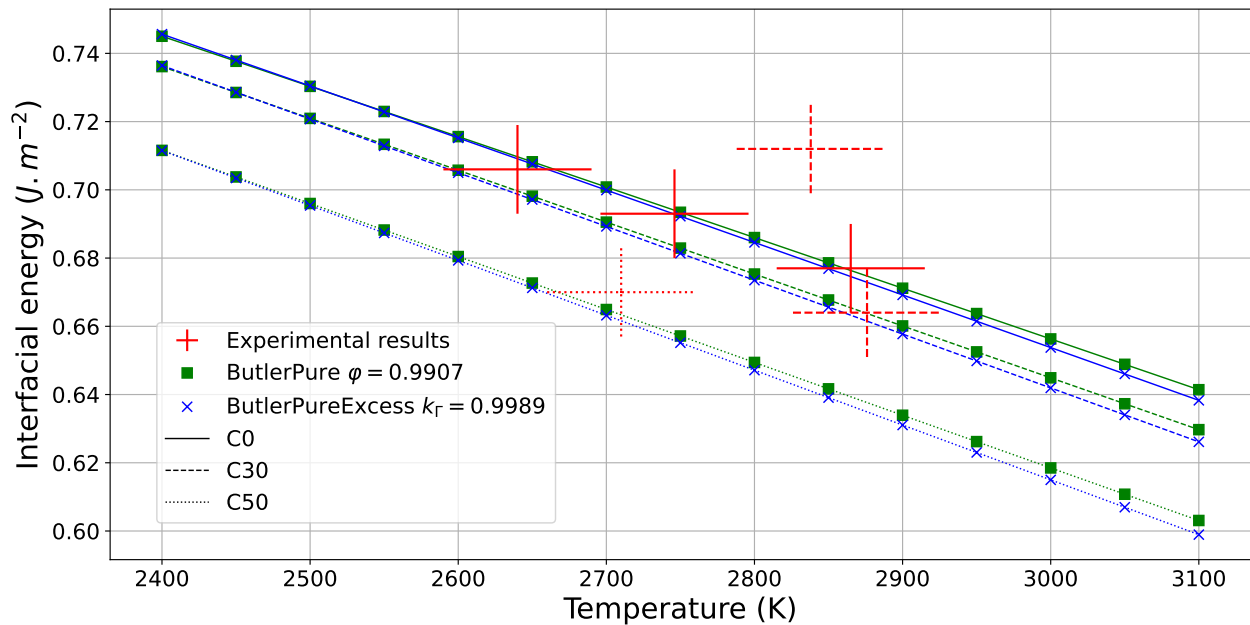


Figure 5. Interfacial energies computed with NUCLEA with equations 16 as green squares and 17 as blue cross. Plain, dashed and dotted lines represent C0, C30 and C50 compositions respectively.

5. CONCLUSIONS AND PERSPECTIVES

Different formulations of the Butler equations considering two CALPHAD databases were successfully applied to $U - Zr - O$ liquid mixtures for evaluating the associated surface tension under argon atmosphere. The impact of the database, the Butler formulation (considering or not additional information coming from pure component surface tension data) and the parameter associated with the interfacial Gibbs energy function was assessed through a comparison with experimental data. It was shown that, with a proper calibration, such a model can partly reproduce the experimental measurements and provide a valuable tool for producing surface tension laws over a wider range of composition and temperature. However, it was also found that their predictive capability is impaired by the unquantified albeit large uncertainty associated with the liquid Gibbs energy modelling in the present state of the CALPHAD databases associated with corium. Reversing the problem, considering this high sensitivity of surface tension to the underlying liquid model, surface tension data could provide valuable information on Gibbs excess energy term of the liquid phase. Accordingly, in the near future, we plan to make a proof of principle on the usage of such data in the CALPHAD assessment process.

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