



The exponential excess Gibbs energy model revisited

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ABSTRACT

The exponential model for the temperature (T) dependence of the excess Gibbs energy of liquid solutions within the framework of the Redlich-Kister polynomials is proven to be an efficient tool to avoid high-T artefacts, such as an artificial inverted miscibility gap, caused by the linear model. However, it has been claimed that the exponential model can lead to a low-T artefact, i.e. to the artificial low-T re-stabilization of the liquid solution. As shown here, this claim is un-supported for all the 15 binary systems studied so far by the exponential model in the literature. Still, the artefact might appear for other systems, or for lower temperatures, as the 15 systems were modelled at and above 298 K. To make sure the low-T artefact does not appear, this paper introduces a new, low-T polynomial, which is matched with the exponential model at temperature T*, defined as the lowest liquidus temperature of the given system. The low-T model is described by a four parameter polynomial, obtained analytically from the two fitted parameters of the exponential model, ensuring that the four excess functions (the excess Gibbs energy, the heat of mixing, the excess entropy and the excess heat capacity) are continuous functions of T in the whole T-interval at any composition. When the complexity of the liquid alloy requires more than two semi-empirical parameters, the combined linear-exponential model should be used instead of the exponential model, with the same matching low-T polynomial. The inherently inconsistent nature of the recent LET function (see S.M. Liang, P. Wang, R. Schmid-Fetzer, Calphad 54 (216) 82–96) is discussed, as it was introduced to replace the exponential model. It is proven by the new simplified assessment of the Mg-Si system that the exponential model can be applied to this system without any artifact, contrary to the claim of Schmid-Fetzer et al., Calphad 31 (2007) 131–142.

1. Introduction

The molar integral Gibbs energy of solution phases (G^Φ , J/mol) is usually modelled using three terms: the standard term, the ideal solution term and the excess term ($\Delta G^{E\Phi}$, J/mol) [1,2]:

$$G^\Phi = \sum_i x_i^\Phi \cdot G_i^{\circ\Phi} + R \cdot T \cdot \sum_i x_i^\Phi \cdot \ln x_i^\Phi + \Delta G^{E\Phi} \quad (1)$$

where x_i^Φ is the mole fraction of component i in phase Φ , $G_i^{\circ\Phi}$ (J/mol) is the molar Gibbs energy of a pure component i in the same phase Φ , $R=8.3145$ J/molK is the universal gas constant, T (K) is the absolute temperature. The excess term is usually written by a Redlich-Kister polynomial [1–3]. For a binary system A-B:

$$\Delta G_{A-B}^{E\Phi} = x_B^\Phi \cdot (1 - x_B^\Phi) \cdot \sum_{j=0} L_j^\Phi \cdot (1 - 2 \cdot x_B^\Phi)^j \quad (2)$$

where L_j^Φ (J/mol) are the interaction energies of j -th order for the binary A-B solution in phase Φ . These values are in principle pressure- and temperature (T) dependent. The pressure dependence is usually

neglected at low pressures, i.e. below 100 bar. The T -dependence of the interaction energies is a subject of this paper. First, the state of the art is discussed. Then the exponential model is revisited and revised.

2. The state of the art

2.1. The linear model

The T -dependence of the interaction energies is classically described by a linear equation [1,2]:

$$L_j^\Phi = a_j^\Phi + b_j^\Phi \cdot T \quad (3)$$

where a_j^Φ (J/mol) is the enthalpy-like semi-empirical coefficient for the j -th order interaction energy of the A-B solution in phase Φ , b_j^Φ (J/molK) is the entropy-like (with opposite sign) semi-empirical coefficient for the j -th order interaction energy of the A-B solution in phase Φ . Later in this paper Eq. (3) will be called “the linear model”.

Chen et al. [4] published a very important Calphad paper in 2001.

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They found that a large number of previous Calphad assessments lead to an artificial inverted miscibility gap of binary liquid solutions at high temperatures (hereinafter called a “high-T artefact”). Obviously, the original authors of those assessments were not aware of this high-T artefact, as they did not check how their assessed parameters worked at high temperatures. Since then different methods have been worked out to resolve this problem.

Soon after the paper of Chen et al. [4] the appearance of the high-T artefact was theoretically explained [5] (see also [6]): it was shown that they appear, if the linear model is applied, and if $a_0^\Phi < 0$ and if $b_0^\Phi > 2 \cdot R$. As in nature the combination of $a_0^\Phi < 0$ and $b_0^\Phi > 2 \cdot R$ occurs quite frequently at low and medium temperatures, it seems that the appearance of calculated high-T artefact is inevitable. On the other hand, we know that inverted miscibility gaps are in most cases calculated artefacts. The only logical way out of this contradiction is to replace the linear model by a more sophisticated one, which allows a T-dependence of both the enthalpy and entropy parts of the interaction energy, without increasing the number of semi-empirical parameters.¹

2.2. The exponential model

One of the models to describe the T-dependence of excess functions of liquid alloys is the exponential T-dependence of the interaction energies [5] (called hereinafter “the exponential model”):

$$L_j^\Phi = h_j^\Phi \cdot \exp\left(-\frac{T}{\tau_j^\Phi}\right) \quad (4)$$

where h_j^Φ (J/mol) is the enthalpy part of interaction energy, while τ_j^Φ (K) is a special temperature, at which the interaction energy would cross zero if it was described by the linear model (thus $\tau_j^\Phi > 0$). The exponential model contains two semi-empirical parameters: h_j^Φ and τ_j^Φ , similarly to the linear model.

The exponential model is the first model designed to obey the high-temperature boundary condition claiming that all excess properties tend towards zero as temperature approaches infinity [7,8]. This claim is supported by experimental facts [9–17]. Full Calphad assessment (with full documentation in open literature) has been run for 15 binary systems in 14 papers [18–31], concluding that the exponential model performs well (although in [18] a better performance of the associate model is also concluded). The exponential model has been successfully applied also for solid metallic solutions [32], for a ternary liquid solution [26] and for ceramic systems [33–37]. In all these papers [18–37] the exponential model is found to perform well, with no artifacts. On the other hand, paper (and based on it also papers [39–43]) claimed that the exponential model “may result in an artificial re-stabilization of the liquid phase at low T-s” (hereinafter this claim is called “the low-T artefact”). Although the appearance of such an artefact is possible in principle, it has not happened so far, when an exponential model was applied in full Calphad assessments (see Appendix A and Table 1). It should be noted that when was published only one full CALPHAD assessment was published by the exponential model around the same time [18].

In the only paper showing a low-T artefact due to the exponential model [38], the full Calphad assessment was not run. Instead, the assessment was made using only the three invariant points of the Mg-Si phase diagram. The low-T artefact in paper [38] is due to parameter L_1 , with the following sub-parameter values: $h_1^{liq} = 15.4$ MJ/mol and $\tau_1^{liq} = 120.6$ K [38]. Those, familiar with Calphad-arts have never seen any interaction enthalpy at zero Kelvin in magnitude reaching even 1 MJ/mol-atom (see Table 1 and all papers of this journal). [38] It is noted further that the value of $h_1^{liq} = 15.4$ MJ/mol is larger (in absolute

values) by more than 700 times compared to the corresponding parameters of the LET model [43] or the linear model [40] from the same corresponding author for the same system. The same parameter from the full assessment of Yuan et al. [22] is also lower by about 150 times. The negative influence of this unreasonable parameter $h_1^{liq} = 15.4$ MJ/mol at medium temperatures was compensated by the unreasonably low value of $\tau_1^{liq} = 120.6$ K [38] (compare to the average value of 3000 K [5]). [38] Unfortunately some basic data are missing from paper [38], so its calculated results cannot be reproduced. That is why a new simplified assessment of the same Mg-Si system is re-visited in the present paper (for details see Appendix B). Model parameters are given in Table 2. Only three independent parameters ($h_0^{liq} = -59,330$ J/mol, $h_1^{liq} = 2169.9$ J/mol and $\tau = \tau_0^{liq} = \tau_1^{liq} = 2968.3$ K) of the excess Gibbs energy of the liquid phase are assessed in this paper, being sufficient to match the three invariant points of the Mg-Si system, with other parameters of Table 2 taken from the literature. Using only 3 parameters to describe the liquid alloy, other details of the phase diagram and the thermodynamic properties of the liquid alloy are reasonably reproduced, although these data were not taken into account during the assessment (see Figs. B1-B3).

Although Schmid-Fetzer et al [38] used four independent parameters (h_0^{liq} , h_1^{liq} , τ_0^{liq} and τ_1^{liq}) to describe the liquid Mg-Si alloy using only three invariant points of this system, it was found here that one of these parameters is a free parameter, as the three other parameters are sufficient to match the three invariant points in the phase diagram. In the present paper parameter τ_1^{liq} was selected as a free parameter. Its value could be selected arbitrarily between 1 and 5000 K, and the values of the three independent parameters (h_0^{liq} , h_1^{liq} and τ_0^{liq}) could be assessed as function of τ_1^{liq} (see Fig. 1) such, that the three invariant points of the phase diagram could be reasonably reproduced. One can see from Fig. 1 that the value of h_0^{liq} and τ_0^{liq} are quite insensitive of τ_1^{liq} , but parameter h_1^{liq} is a very strong function of τ_1^{liq} , especially at its low values.

Additionally, the presence of the low-T artefact (i.e. the re-stabilization of the liquid below the solidus) was tested here as function of τ_1^{liq} . When a low-T artefact is found, its maximum temperature is also calculated. As follows from Fig. 1d, the low-T artefact takes place at $\tau_1^{liq} < 187$ K. In this way the results of Schmid-Fetzer et al. [38] are qualitatively reproduced (full reproduction is not possible, as some initial parameters are missing from [38]). It is important to note, however, that in the interval of τ_1^{liq} between 187 and 5000 K the low-T artefact does not take place, and the high-T artefact does not appear at any value of τ_1^{liq} . It is a clear contradiction with the results of Schmid-Fetzer et al. [38], who wrote in their paper: “...for all the model parameter settings that came close to a proper description of at least the invariant phase equilibria (in the Mg-Si system), another artifact at low temperature is observed ... the re-stabilization of the liquid phase way below the solidus” [38]. As shown in Fig. 1, the opposite conclusion has been achieved in the present paper. It was actually very easy to select a data-set, reproducing the invariant phase equilibria in the Mg-Si system and to avoid any artefact (see Table 2 and Figs. B1-B3).

The same conclusion is achieved by Yuan et al. [22], who performed full Calphad assessment of the same Mg-Si system using the exponential model, and found no low-T or high-T artefact (see also Fig. A5). [22] Thus, we can conclude that the claim of [38] on the low-T artefact caused by the exponential model is false. Later this false claim was repeatedly cited in [40–43]. Unfortunately the majority of successful assessments performed by the exponential model without any artefact [18–31] were not cited in the same papers [40–43]. In this way papers [38–43] incorrectly discredited the exponential model.

The detrimental influence of this discouragement is demonstrated here on the example of the paper of Schick et al. [40], who made a full Calphad assessment of the Mg-Si system, applying the linear model. They summarized the results at the end of their paper in the most sincere way, as: “The major remaining issue concerns the enthalpy of

¹ Another option would be applying the constraint $b_0^\Phi < 2 \cdot R$ to assessed parameters (if $a_0^\Phi < 0$). This constraint indeed helps avoiding a high-T artefact, but in some systems it fails to reproduce the middle-T experimental data, so it is not recommended in the present paper.

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