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On the abilities and limitations of the linear, exponential and combined models to describe the temperature dependence of the excess Gibbs energy of solutions

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ABSTRACT

In this paper the performance of the linear, exponential and combined models to describe the temperature dependence of the excess Gibbs energy of solutions in the framework of the Redlich–Kister model is discussed. The models are not compared to existing Calphad optimized databases, rather they are tested against the 209 binary solid and liquid metallic alloys, for which reliable experimental data exist on the heat of mixing and Gibbs energy of mixing in the handbook of Predel. It was found that the linear model often leads to high-T artifact (artificial inverted miscibility gaps) and the excess Gibbs energy approaches infinity at high temperatures, which seems unreasonable. It was also found that although both the exponential and combined models can in principle lead to low-T artifact (liquid re-stabilization), in real systems it probably does not take place, at least for the "normal" systems (a system is "normal", if the heat of mixing, excess entropy of mixing and excess Gibbs energy of mixing have the same sign at the temperature of measurement; 86% of all systems are found "normal"). The problem with the exponential model is that it is unable to describe the "exceptional" systems (14% of all systems). It is shown that the combined model is able to describe also these "exceptional" systems, as well. An algorithm is worked out to ensure that the combined model does not run into any high-T or low-T artifact, even when it is used to describe the "exceptional" systems. It is concluded that the T-dependence of the interaction energies for all solution phases described by the Redlich–Kister polynomials should be described by the combined model. In this way an improved databank on excess Gibbs energies of solution phases can be gradually built, not leading to any artifact.

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1. Introduction

Temperature dependence (T-dependence) of the excess Gibbs energy of mixing (ΔG^E) of solutions is one of the key features to obtain realistic assessed thermodynamic data by the Calphad method [1–6]. When any solution phase is modeled, experimental data usually exist only around the liquidus range of its phase diagram. Using this limited information at a medium temperature, the model to be created should be capable to describe both low-temperature and high-temperature ranges in addition to the middle temperature range in a reasonable way. The extrapolation of thermodynamic data of solutions to high temperatures should be made in accordance with [7,8], claiming that the excess Gibbs energy of mixing and all its derivatives (the heat of mixing, the excess entropy of mixing, the excess heat capacity of mixing, etc.) tend towards zero

at high temperatures at any given composition and pressure, if the standard states are selected properly, as it is usually done within the Calphad community [1–6] (i.e. the standard states are selected identical for all components and for the given solution phase).

The Gibbs energy of a solution phase Φ (G_Φ, J/mol) is usually written using the following formalism [1–6]:

$$G_\Phi = G_\Phi^o + \Delta G_\Phi \tag{1}$$

$$\Delta G_\Phi = \Delta G_\Phi^{id} + \Delta G_\Phi^E \tag{2}$$

where G_Φ^o (J/mol) is the Gibbs energy of the mechanical mixture, ΔG_Φ (J/mol) is the Gibbs energy of mixing, i.e. the Gibbs energy change accompanying the change from the mechanical mixture to the real solution, ΔG_Φ^{id} (J/mol) is the Gibbs energy change accompanying the change from the mechanical mixture to the ideal solution and ΔG_Φ^E (J/mol) is the Gibbs energy change accompanying the change from the ideal solution to the real solution. The latter is usually written by the Redlich–Kister polynomial [9]. For binary solutions:

$$\Delta G_\Phi^{id} = RT[x \ln x + (1-x)\ln(1-x)] \tag{3}$$

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$$\Delta G_\Phi^E \cong x(1-x)\sum_{j=0} L_\Phi^j (1-2x)^j \qquad (4)$$

where $R = 8.3145$ J/mol K is the universal gas constant, T (K) is the absolute temperature, x (dimensionless) is the mole fraction of the second component in the solution, L_Φ^j (J/mol) is the interaction energy between the components within the solution phase Φ of order j (usually $j = 0, 1, 2$). For condensed (solid and liquid) phases the pressure dependence of the interaction energies is negligible below 100 bar, so it is usually not considered. However, the temperature dependence of the interaction energies is not negligible, as follows from its definition:

$$\Delta G_\Phi^E \equiv \Delta H_\Phi - T\,\Delta S_\Phi^E \qquad (5)$$

where ΔH_Φ (J/mol) is the heat of mixing, ΔS_Φ^E (J/mol K) is the excess entropy of mixing. Both quantities have a similar concentration dependence as written by Eq. (4). If for simplicity both ΔH_Φ and ΔS_Φ^E are considered T-independent quantities, the temperature dependence of the interaction energies can be approximated by a linear model, as [1–6]:

$$L_\Phi^j \cong h_\Phi^j - T s_\Phi^j \qquad (6)$$

where h_Φ^j (J/mol) and s_Φ^j (J/mol K) are the enthalpy- and excess entropy-parts of the interaction energy, respectively. The linear model Eq. (6) is widely used in the literature and provides a good approximation in a limited temperature range around the liquidus for the majority of the systems. However, Eq. (6) contradicts [8], as it predicts that the interaction energies and the excess Gibbs energy of mixing will become infinitely large (instead of approaching zero) at infinitely large temperatures. As a result, Eq. (6) leads to unreasonable results, if extrapolated to high temperatures, such as the artificial inverted miscibility gaps (AIMGs) [10–15].

To avoid the appearance of AIMGs and other high-T artifacts, the exponential model was introduced by the author [11]:

$$L_\Phi^j \cong h_{\Phi,0}^j \exp\left(-\frac{T}{\tau_\Phi^j}\right) \qquad (7)$$

where $h_{\Phi,0}^j$ (J/mol) is the enthalpy part of the interaction energy extrapolated to $T = 0$ K, τ_Φ^j (K) is a special temperature. Although Eq. (7) indeed removes the possibility of AIMGs, it might, in principle, lead to low-T artifacts [5].

Summarizing the above: the linear model leads to high-T artifacts, while the exponential model might lead to low-T artifacts. As a compromise between these two extreme cases, the following combined model is offered in this paper:

$$L_\Phi^j \cong (h_{\Phi,0}^j - T s_{\Phi,0}^j)\exp\left(-\frac{T}{\tau_\Phi^j}\right) \qquad (8)$$

where $s_{\Phi,0}^j$ (J/mol K) is the entropy part of the interaction energy extrapolated to $T = 0$ K. Although Eq. (8) seems new, it is one of the simplified forms of a more general equation suggested by the author before [11]. It will be shown here that Eq. (8) is less prone to high-T artifacts compared to Eq. (6), while it is also less prone to low-T artifacts compared to Eq. (7).

It should be made clear at this point that Eqs. (1)–(3) and (5) are theoretically founded equations, while Eqs. (4) and (6)–(8) are only convenient model equations, worked out to describe the concentration and temperature dependence of the excess Gibbs energy of solutions. Therefore, Eqs. (4) and (6)–(8) can be replaced by other empirical equations in the future, if they show better performance. This paper is written to help the Calphad community to select from Eqs. (6)–(8).

The goal of this paper is to compare the performances of the linear model, the exponential model and the combined model to describe the T-dependence of the interaction energies. In the present paper a simplified theoretical analysis will be presented,

limiting ourselves only to the leading term of the interaction energy with $j = 0$. Thus, the excess Gibbs energy of the same solution Φ will be compared in the following three forms:

the linear model : $\Delta G_\Phi^E \cong x(1-x)(h - Ts)$ (9a)

the exponential model : $\Delta G_\Phi^E \cong x(1-x)h_e \exp\left(-\frac{T}{\tau_e}\right)$ (9b)

the combined model : $\Delta G_\Phi^E \cong x(1-x)(h_c - Ts_c)\exp\left(-\frac{T}{\tau_c}\right)$ (9c)

where h (J/mol) and s (J/mol K) are the T-independent enthalpy- and entropy terms of the linear model, h_e (J/mol) and τ_e (K) are the zero-Kelvin enthalpy term and the special temperature of the exponential model, while h_c (J/mol), s_c (J/mol K) and τ_c (K) are the zero-Kelvin enthalpy term, the zero-Kelvin entropy term and the special temperature of the combined model, respectively. For simplicity the indexes Φ and $j = 0$ are not shown in these parameters. At this point let us mention that if one of the above equations turns out to be well suited to describe the L_0 term, it will be similarly well suited to describe higher order terms, such as L_1, L_2, etc.

One of the artifacts mentioned above is the liquid solution de-stabilization at high temperatures. It takes place if the following thermodynamic condition is satisfied:

$$\frac{d^2 \Delta G}{dx^2} < 0 \qquad (10a)$$

As all Eq. (9a–c) are written with a single term with $j = 0$, it is sufficient to check whether condition (10a) takes place at $x = 0.5$. This check will be performed for all the three models (9a–c). For the case of the exponential and combined models, equations for the heat of mixing, excess entropy of mixing and excess heat capacity of mixing will be derived, in accordance with the following generally valid equations:

$$\Delta S_\Phi^E = -\frac{d\Delta G_\Phi^E}{dT} \qquad (10b)$$

$$\Delta H_\Phi = \Delta G_\Phi^E - T\frac{d\Delta G_\Phi^E}{dT} \qquad (10c)$$

$$\Delta C_{p,\Phi}^E = -T\frac{d^2\Delta G_\Phi^E}{dT^2} \qquad (10d)$$

2. On the classification of systems based on their measured thermodynamic data

Before analyzing the performance of different equations, it is worth to see what are they expected to describe. Although a huge Calphad assessed dataset exists in this and other journals, it will not be considered here, as the Calphad assessed parameters of solutions are dependent on, and might be contaminated by the assessed parameters of other (compound) phases in the same system.

In this paper only those data are considered, which are obtained experimentally and are included in the handbook of Predel on thermodynamics of solid and liquid alloys [16]. Within this dataset, only those systems are considered, for which at least one experimental source exists for the heat of mixing and at least one experimental source exists for Gibbs energy of mixing of a given solid or liquid solution in the full concentration range, measured at the same (or similar) temperature. In Tables 1 and 2 the temperature, the measured enthalpy of mixing, the measured excess Gibbs energy of mixing (calculated from the measured Gibbs energy of mixing by Eqs. (2) and (3)) and calculated by Eq. (5) excess entropy