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# Ternary Interaction Parameters in Calphad Solution Models

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**Abstract** For random, diluted, multicomponent solutions, the excess chemical potentials can be expanded in power series of the composition, with coefficients that are pressure- and temperature-dependent. For a binary system, this approach is equivalent to using polynomial truncated expansions, such as the Redlich-Kister series for describing integral thermodynamic quantities. For ternary systems, an equivalent expansion of the excess chemical potentials clearly justifies the inclusion of ternary interaction parameters, which arise naturally in the form of correction terms in higher-order power expansions. To demonstrate this, we carry out truncated polynomial expansions of the excess chemical potential up to the sixth power of the composition variables.

**Keywords** Thermodynamics · Redlich-Kister polynomials · Solution models · Calphad method · Ternary parameters

## 1 Introduction

The Wagner formalism [1] for the thermodynamics of dilute solutions was proposed in the first half of the twentieth cen-

tury. Still popular in metallurgy, it is in particular widely applied in calculations describing steelmaking processes. This popularity contrasts with the history of the formalism, which is inapplicable to concentrated solutions and was shown to be thermodynamically inconsistent by [2]. A correction to the Wagner formalism was proposed [3, 4], to motivate a recent study that has challenged its uniqueness and deflated confidence in results drawn from the corrected formulation [5].

An alternative is available. Physical quantities of thermodynamical interest in this context can either be integral, such as the Gibbs energy, or derived, such as the excess chemical potential. While the Wagner formalism gives attention to the latter with no regard for thermodynamic consistency, Calphad-type models [6] start from the former, cover the entire compositional range, are always thermodynamically consistent, and have been successfully applied to various systems and situations [6]. These advantages may seem to outshine other theoretical constructions. Nonetheless, interest in the Wagner formalism persists, in spite of its inconsistency with equilibrium conditions, because it is simple and accurate within its range of applicability.

The present paper can be regarded as an extension of Wagner's treatment of dilute solutions [1]. It is not our aim to obtain another correction to the Wagner formalism, a development that would be pointless since the formalism may be corrected in infinitely many ways [5]. Instead, we want to offer an interpretation for the ternary-interaction parameters in ternary systems. To this end, we will begin at the starting point of Wagner's treatment [1] and proceed to show that the ternary-interaction parameters in Calphad models and the binary parameters in the Redlich-Kister or other polynomial expansions have the same origin. It is quite possible that Mats Hillert had the same idea in mind when he published his proposals for ternary solution models [7],

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and that Pelton and Bale [8], who realized that a polynomial description of integral functions (e.g., the excess Gibbs energy) is equivalent to a truncated polynomial expansion of partial excess quantities (e.g., the excess chemical potentials or, equivalently, activity coefficients), were also moved by that idea. Nonetheless, refs. [7] and [8] only stated this equivalence without explicitly expressing the connection between Wagner's treatment and the Calphad solution models, except for the first-order approximation and a few general guidelines for higher-order extrapolations [9]. The present authors, by contrast, argue that the equivalence should be proved in detail, at least for binary and ternary systems.

The procedure we adopt to prove the equivalence is not unique. We could, for instance, postulate an expression for an integral function, as Pelton has done [8], to offer a proof that, albeit more difficult to extend to higher polynomial degrees, would be more compact and simpler. But Wagner's theory is not expressed in terms of integral quantities. The whole idea behind working with the Wagner interaction parameters (and their extension to concentrated solutions) is that, unlike integral functions, partial quantities, such as the activity coefficients, can be directly related to measurable quantities (activities, electrochemical measurements, vapor pressure measurements, and so on).

We have no intention to develop new methodology. Our work is centered on the fundamentals of certain Calphad solution models. We also limit our discussion to substitutional solution models, for the sake of simplicity. We focus our analysis on ternary parameters and discuss none of the several "geometric" extrapolation methods in the literature, referring the reader to Malakhov [10] for a recent review of those very convenient extrapolations, which are sometimes used instead of ternary interaction parameters to derive parameters for a ternary system based on binary data only.

Our work is organized as follows. Section 2 presents a general, brief overview of selected aspects of Calphad disordered solution models. We then derive series expansions for the excess chemical potentials in powers of the composition to show their equivalence, first, in Section 4, to Redlich-Kister series for binary systems, and then, in Section 5, to a mix of Redlich-Kister polynomials and ternary interaction parameters for ternary systems. Finally, Section 6 brings us to our final discussion and conclusions.

## 2 Calphad Solution Models

Let us say we need to describe a solution phase $\phi$ in a multicomponent system. In one of the most widespread methodologies, one would write its molar Gibbs energy as the following sum of four contributions, each of which is

(or may be) a function of the temperature $T$, the pressure $p$, and the molar fractions of the components $x_i$, $x_j$, ... [6]:

$$G_m(p, T, x_i, x_j, \ldots) = {}^{ser}G_m + {}^{id}G_m + {}^{phys}G_m + {}^{ex}G_m$$

(1)

Here, ${}^{ser}G_m$ is the molar Gibbs energy of a standard energy reference state, e.g., the mechanical mixture of the pure components at the same temperature, pressure, and structure as the phase $\phi$ under consideration; ${}^{id}G_m$ is the molar Gibbs energy of an ideal solution, equivalent to a Bragg-Williams treatment [11] and the only term on the right-hand side explicitly accounting for the configurational part of the Gibbs energy; and ${}^{phys}G_m$ is the contribution due to such physical phenomena as ferromagnetism. The last term on the right-hand side, the excess molar Gibbs energy for the phase $\phi$, measures the inadequacy of the previous terms to describe physical reality.

Until physically sounder methods and models become available, one is forced to use excess quantities, which should parameterize all uncertainties inherent to the model in (1). Artificial as it may at first seem, this definition proves useful because approximate mathematical expressions for the excess term, such as polynomial fits, can be derived to describe the temperature-pressure-composition dependence of the molar Gibbs energy. Examples are the truncated expansions that generate Redlich-Kister [12], Legendre [8], Margules [13], and other polynomials for binary systems. Here, we will show that, applied to ternary systems, the same truncated expansions yield ternary-interaction parameters.

## 3 Excess Chemical Potentials as Power Series

The excess term in (1) can be written in terms of the so-called excess chemical potentials $\mu_i^{ex}$ in the form

$${}^{ex}G_m = \sum_i x_i \mu_i^{ex}$$

(2)

The excess chemical potentials $\mu_i^{ex}$ are related to each other by the Gibbs-Duhem differential equation, which can be written in as follows:

$$\sum_i x_i \, d\mu_i^{ex} = 0.$$

(3)

For a completely random solution, it is possible to express the excess chemical potentials $\mu_i^{ex}$ in terms of composition, pressure, and temperature. To the best of our knowledge, Margules [14] was the first to develop such an expansion to describe the thermodynamics of a system, an idea that, half a century later, would be further explored by Wagner [1]. The methodology was also employed by Wohl [15], who developed expressions up to

the fifth power of composition. Two years later, Redlich and Kister [12] independently introduced their power series for integral quantities, such as the excess Gibbs energy, following an idea put forward by Guggenheim [16]. Cheng and Ganguly [17] later demonstrated the equivalence between the series expansions by Wohl [15] and by Redlich and Kister [12]. Ansara [18] compared different models. Even though Redlich and Kister [12] cite the work of Margules [14], no explicit demonstration that the two approaches are equivalent was presented, since they took the equivalence for granted, as did the authors of more recent work [7, 8, 19, 20], who preferred to work directly with integral excess quantities rather than with activity coefficients, an approach still employed today.

We start out our discussion with binary disordered solutions.

## 4 Binary Solution Phases

In the case of a random, diluted solution of two species, labelled $A$ and $B$, it is possible to expand the excess chemical potentials in terms of the molar fractions, so that after Wagner [1], we may write the following expression

$$\mu_i^{ex} = \Omega_{i,1}(1-x_i) + \frac{\Omega_{i,2}}{2}(1-x_i)^2 + \frac{\Omega_{i,3}}{3}(1-x_i)^3 + \dots \quad (4)$$

where $i = A,\ B$, and the unknown parameters $\Omega_{i,\eta}$ ($\eta = 1, 2, 3, \dots$) are supposed to be functions of pressure and temperature, so that $\mu_A^{ex}$ ($\mu_B^{ex}$) depends only upon $p$, $T$, and $1 - x_A = x_B$ ($1 - x_B = x_A$).

The unknown coefficients $\Omega_{i,\eta}$ in (4) reflect the a priori unknown relationship between the composition and the other two variables, $p$ and $T$. Of course, the series must be truncated at some power of $(1-x_i)$. The $\Omega_{i,\eta}$ should be regarded as fitting parameters, in the very sense of a Calphad optimization. It should be also clear that the truncated expansion of $\mu_i^{ex}$ is strictly valid for $x_i \to 1$, i.e., for infinite dilution of the second component. One cannot treat concentrated solutions without considering interactions between groups of atoms. Replacing $^{id}G_m$ in (1) by more precise entropic terms, such as those given by the Cluster variation method [21] or the cluster-site approximation [22], is an alternative that could be used instead of (or simultaneously with) increasing the order of the series expansions in (4). In the following, however, we will keep the ideal term in (1).

Since the power expansions in (4) must obey the Gibbs-Duhem relation (3), the $\Omega_{i,\eta}$ cannot be independent. If we adopt the $\Omega_{A,\eta}$ as our fitted quantities, the parameters $\Omega_{B,\eta}$

for the second element ($B$) should be written in terms of $\Omega_{A,\eta}$. In the Appendix, we prove that $\Omega_{A,1} = \Omega_{B,1} = 0$ and

$$\Omega_{B,\eta} = \sum_{\lambda=\eta}^{\eta_{max}} \binom{\lambda - 2}{\eta - 2}(-1)^\eta \Omega_{A,\lambda} \qquad (\eta \geq 2) \quad (5)$$

where $\eta_{max}$ is the maximum degree of the truncated polynomials of $(1-x_i)$ in (4), and we have assumed that the the expansions of $\mu_A^{ex}$ and of $\mu_B^{ex}$ have the same $\eta_{max}$.

One may now use (2) and the power expansions to rewrite the excess molar Gibbs energy in the following form:

$$^{ex}G_m = x_A x_B \sum_{\eta=2}^{\eta_{max}} \frac{\Omega_{A,\eta} x_B{}^{\eta-1} + \Omega_{B,\eta} x_A{}^{\eta-1}}{\eta}. \quad (6)$$

To obtain the Redlich-Kister polynomials, we introduce the following transformations, first proposed by Hillert [7]:

$$x_A \leftarrow \frac{1}{2} + \frac{x_A - x_B}{2}, \qquad x_B \leftarrow \frac{1}{2} - \frac{x_A - x_B}{2}. \quad (7)$$

Equation 7 are valid as long as $x_A + x_B = 1$. Under this condition, which is only valid for the binary systems here considered, the two relations are identities, and we can replace the arrows by equal symbols. When the right-hand sides are substituted for $x_A$ and $x_B$ in (2), we obtain the expression

$$^{ex}G_m = x_A x_B \sum_{\nu=0}^{\eta_{max}-2} (x_A - x_B)^\nu$$
$$\left\{ \sum_{\eta=g(\nu)}^{\eta_{max}} \frac{1}{\eta \cdot 2^{\eta-1}} \binom{\eta-1}{\nu} \left[ \Omega_{A,\eta}(-1)^\nu + \Omega_{B,\eta} \right] \right\}, \quad (8)$$

with the function $g(\nu)$ defined by the equality

$$g(\nu) = 1 + \frac{\nu + 1 + |\nu - 1|}{2}. \quad (9)$$

The term within the curly braces on the right-hand side of (8), a linear combination of the coefficients $\Omega_{A,\eta}$, is unique for each running index $\nu$. We call it $L_\nu$ and rewrite (8) as follows:

$$^{ex}G_m = x_A x_B \sum_{\nu=0}^{\nu_{max}} L_\nu (x_A - x_B)^\nu \quad (10)$$

with $\nu_{max} = \eta_{max} - 2$.

The polynomials defined by the sum on the right-hand side of (10) are identical to the so-called Redlich-Kister polynomials [12].

Of course, from the Redlich-Kister parameters $L_\nu$, it is also possible to derive the $\Omega_{i,\eta}$ parameters, if one prefers to consider them as the dependent variables. It is likewise possible to derive other series, such as Legendre or Chebyshev polynomials, which are truncated series of orthogonal polynomials, and hence offer the advantage that the addition of a new higher-order term has only small or no effect

upon the lower-order terms [7, 8]. For additional discussion of the conversion between different polynomial series, a point of secondary importance for our purposes, the reader is referred to the works of Hillert [7], Tomiska [23–25], and Pelton and Bale [8].

## 5 Ternary Solution Phases

Ternary systems $A-B-C$ pose a more interesting problem. In analogy with the binary case, one can write the excess chemical potentials of $A$, $B$ and $C$ as series expansions of the composition. Under the same assumptions (dilute, random solution), we can write, say, $\mu_A^{ex}$ in terms of the concentrations of the two other components, $x_B$ and $x_C$, as follows:

$$\mu_A^{ex} = \frac{1}{2}\left(\Omega_{BB}^A x_B{}^2 + 2\Omega_{BC}^A x_B x_C + \Omega_{CC}^A x_C{}^2\right)$$
$$+ \frac{1}{3}\left(\Omega_{BBB}^A x_B{}^3 + 3\Omega_{BBC}^A x_B{}^2 x_C +\right.$$
$$\left. 3\Omega_{BCC}^A x_B x_C{}^2 + \Omega_{CCC}^A x_C{}^3\right) + \dots, \quad (11)$$

a generalization of (4) to ternary systems.

The $\Omega$ coefficients on the right-hand side of (11) are interpreted as in Section 4, that is, they are simply mathematical interaction parameters extracted from fits to experimental data. The series should be truncated at some maximum power of the compositions. Similar equations hold for the excess chemical potentials of the other two species.

On the right-hand side of (11), we have already dropped the linear terms $\Omega_i^j x_i$ $(i, j = A, B, C)$, since their contribution vanishes as a consequence of the Gibbs-Duhem equation. Explicitly, from (3), we derive two equations involving the coefficients in (11), namely,

$$x_A \left(\frac{\partial \mu_A^{ex}}{\partial x_B}\right)_{x_C} + x_B \left(\frac{\partial \mu_B^{ex}}{\partial x_B}\right)_{x_C} + x_C \left(\frac{\partial \mu_C^{ex}}{\partial x_B}\right)_{x_C} = 0, \quad (12a)$$

and

$$x_A \left(\frac{\partial \mu_A^{ex}}{\partial x_C}\right)_{x_B} + x_B \left(\frac{\partial \mu_B^{ex}}{\partial x_C}\right)_{x_B} + x_C \left(\frac{\partial \mu_C^{ex}}{\partial x_C}\right)_{x_B} = 0. \quad (12b)$$

It is obvious that not all three composition variables are independent. For this reason, on the right-hand side of (12a, b), we regard $x_A$ as dependent on $x_B$ and $x_C$, that is, given by the expression $x_A = 1 - x_B - x_C$. This choice is arbitrary, not unique, but the final result will not depend on it.

In addition to the relations imposed by (12a, b) and the condition $x_A + x_B + x_C = 1$, a constraint relating the $\Omega$

coefficients is introduced by the following thermodynamic identity:

$$\frac{\partial\left(\mu_B^{ex} - \mu_A^{ex}\right)}{\partial x_C} = \frac{\partial\left(\mu_C^{ex} - \mu_A^{ex}\right)}{\partial x_B}, \quad (13)$$

which is valid as long as $x_B$ and $x_C$ are the independent variables and leads to Darken's criterion for thermodynamic consistency in ternary systems [2].

Equation (11) and its analogues for $\mu_B^{ex}$ and $\mu_C^{ex}$ introduce three sets of parameters, which consist of the $\Omega^A$, $\Omega^B$ and $\Omega^C$ variables. Given (12a, b) and (13), however, we see that only one of those sets, or a linear combination of the three sets, is independent. Therefore, as in the binary case, to insure thermodynamical compatibility of the proposed model, we have to reduce the number of parameters.

### 5.1 Regular Solution Model

Let us first consider the simpler case, in which the coefficients of third or higher order are ignored, that is, let us start by assuming that $\Omega_{ijk\dots}^l = 0$, so that only the $\Omega_{ij}^k$ $(i, j, k, l, \dots = A, B, C)$ are nonzero. Equations (12a, b) and (13) then yield the result

$$\Omega_{ii}^j = \Omega_{jk}^i + \Omega_{ik}^j \quad (i, j, k = A, B, C). \quad (14)$$

Therefore, out of the nine $\Omega_{ij}^k$ parameters, only three are independent. We choose $\Omega_{BC}^A$, $\Omega_{AC}^B$, and $\Omega_{AB}^C$. Using (2), we can then write the excess molar Gibbs energy for a ternary system $A - B - C$ in the form

$$^{ex}G_m = \left(\frac{\Omega_{BC}^A + \Omega_{AC}^B}{2}\right) x_A x_B + \left(\frac{\Omega_{BC}^A + \Omega_{AB}^C}{2}\right) x_A x_C +$$
$$+ \left(\frac{\Omega_{AC}^B + \Omega_{AB}^C}{2}\right) x_B x_C, \quad (15)$$

which can be rewritten as follows:

$$^{ex}G_m = L_0^{AB} x_A x_B + L_0^{AC} x_A x_C + L_0^{BC} x_B x_C. \quad (16)$$

The right-hand side of (15) contains no term dependent on the product $x_A x_B x_C$. This immediate consequence of neglecting third-order terms in our expansion for the excess chemical potential shows that this approximation is equivalent to Muggianu's "geometrical" extrapolation [26], an equivalence that has been established by Saulov [27] in a multicomponent context.

As stated in the introduction, the above procedure is not the only way to prove the equivalence. One could postulate (16) and derive (14) and (15). Although simpler, this route is not as easily extended to accommodate higher powers of the composition on the right-hand side of (11).

### 5.2 Subregular Solution Model

We now consider terms up to third power on the right-hand side of (11). There are now 21 $\Omega$ parameters, but the Gibbs-Duhem (12a, b) and (13) reduce the number of independent parameters to seven, included among them at least one of the third-order $\Omega$'s to allow for ternary interactions.

We chose to keep the $\Omega^A$ parameters as the independent ones, and solve for the others. The following lists of equations results:

$$\Omega_{AA}^B = \Omega_{BB}^A + \Omega_{BBB}^A \qquad (17a)$$

$$\Omega_{AC}^B = \Omega_{BB}^A - \Omega_{BC}^A + \Omega_{BBB}^A - \Omega_{BBC}^A \qquad (17b)$$

$$\Omega_{CC}^B = \Omega_{BB}^A + \Omega_{CC}^A - 2\Omega_{BC}^A + \Omega_{BBB}^A - 2\Omega_{BBC}^A + \Omega_{BCC}^A \qquad (17c)$$

$$\Omega_{AAA}^B = -\Omega_{BBB}^A \qquad (17d)$$

$$\Omega_{AAC}^B = -\Omega_{BBB}^A + \Omega_{BBC}^A \qquad (17e)$$

$$\Omega_{ACC}^B = -\Omega_{BBB}^A + 2\Omega_{BBC}^A - \Omega_{BCC}^A \qquad (17f)$$

$$\Omega_{CCC}^B = -\Omega_{BBB}^A + 3\Omega_{BBC}^A - 3\Omega_{BCC}^A + \Omega_{CCC}^A \qquad (17g)$$

$$\Omega_{AA}^C = \Omega_{CC}^A + \Omega_{CCC}^A \qquad (17h)$$

$$\Omega_{AB}^C = -\Omega_{BC}^A + \Omega_{CC}^A - \Omega_{BCC}^A + \Omega_{CCC}^A \qquad (17i)$$

$$\Omega_{BB}^C = \Omega_{BB}^A + \Omega_{CC}^A - 2\Omega_{BC}^A + \Omega_{BBB}^A - 2\Omega_{BCC}^A + \Omega_{CCC}^A \qquad (17j)$$

$$\Omega_{AAA}^C = -\Omega_{CCC}^A \qquad (17k)$$

$$\Omega_{AAB}^C = \Omega_{BCC}^A - \Omega_{CCC}^A \qquad (17l)$$

$$\Omega_{ABB}^C = -\Omega_{BBC}^A + 2\Omega_{BCC}^A - \Omega_{CCC}^A \qquad (17m)$$

$$\Omega_{BBB}^C = \Omega_{BBB}^A - 3\Omega_{BBC}^A + 3\Omega_{BCC}^A - \Omega_{CCC}^A \qquad (17n)$$

With the reduction relations in (17a–n), we can relate the excess molar Gibbs energy in (2) to the $\Omega^A$ coefficients.

Straightforward algebra yields the following expression for the excess molar Gibbs energy:

$$
\begin{aligned}
{}^{ex}G_m = {}& x_A x_B \left[ L_0^{AB} + L_1^{AB}(x_A - x_B) \right] + \\
& + x_A x_C \left[ L_0^{AC} + L_1^{AC}(x_A - x_C) \right] + \\
& + x_B x_C \left[ L_0^{BC} + L_1^{BC}(x_B - x_C) \right] + \\
& + x_A x_B x_C \, L_{ABC},
\end{aligned} \qquad (18)
$$

where the $L$-coefficients are defined as follows:

$$L_0^{AB} = \frac{2\Omega_{BB}^A + \Omega_{BBB}^A}{4} \qquad (19a)$$

$$L_1^{AB} = -\frac{\Omega_{BBB}^A}{12} \qquad (19b)$$

$$L_0^{AC} = \frac{2\Omega_{CC}^A + \Omega_{CCC}^A}{4} \qquad (19c)$$

$$L_1^{AC} = -\frac{\Omega_{CCC}^A}{12} \qquad (19d)$$

$$L_0^{BC} = \frac{2\Omega_{BB}^A + 2\Omega_{CC}^A - 4\Omega_{BC}^A + +\Omega_{BBB}^A - \Omega_{BBC}^A - \Omega_{BCC}^A + \Omega_{CCC}^A}{4} \qquad (19e)$$

$$L_1^{BC} = \frac{\Omega_{BBB}^A - 3\Omega_{BBC}^A + 3\Omega_{BCC}^A - \Omega_{CCC}^A}{12} \qquad (19f)$$

$$L_{ABC} = \frac{3\Omega_{BBC}^A + 3\Omega_{BCC}^A - 2\Omega_{BBB}^A - 2\Omega_{CCC}^A}{12} \qquad (19g)$$

It is also possible, if required, to invert (19a–g) to express the $\Omega^A$ coefficients as linear combinations of the $L$ parameters and then invert (17a–n) to also write the $\Omega^B$ and $\Omega^C$ coefficients in terms of the $L$ parameters.

Equation 18 show that if the series for the excess chemical potentials in (11) is expanded up to power three, all three binary systems will be described as subregular solutions. More importantly, a ternary term $x_A x_B x_C L_{ABC}$ emerges naturally from the equations. With that in view, we can say that the ternary interaction parameter $L_{ABC}$ is part of the subregular solution model extrapolated to ternary systems. In other words, if all three binaries are described as subregular solutions, Muggianu's "geometric" extrapolation [26] is insufficient to describe ternary systems. That extrapolation is only appropriate for special systems, ones with special properties that may a priori justify the approximation $L_{ABC} \approx 0$.

### 5.3 Higher-Order Approximations

We can add higher powers to (11) and, using the Gibbs-Duhem relations (12a, b) plus equation 13, obtain expressions for ${}^{ex}G_m$. To save space, we will not present here

the details of the calculation, which follows the analysis in Section 5.2 and involves a large number of equations. For details, please contact the authors. This procedure yields the following expression for the Gibbs energy:

$$^{ex}G_m = {}^{ex}G_m^{(bin)} + {}^{ex}G_m^{(tern)} \tag{20}$$

where $^{ex}G_m^{(bin)}$ is a sum of Redlich-Kister polynomials coming from the three binaries,

$$^{ex}G_m^{(bin)} = \sum_{i=A,B,C} \sum_{j>i} x_i x_j \sum_{v=0}^{\eta_{max}-2} L_v^{ij} (x_i - x_j)^v. \tag{21}$$

Here, $\eta_{max}$ is the maximum power in the series on the right-hand side of (11).

The cases $\eta_{max} = 2$ and $\eta_{max} = 3$ have already been described, in Sections 5.1 and 5.2, respectively. As (21) shows, each new power $v$ added to (11) adds three new $L_v^{ij}$ Redlich-Kister coefficients, one for each binary system $i - j$. As explained in Section 4, the polynomial expression (21) is by no means the only possible expansion. One could work, for instance, with Legendre polynomials.

Ternary terms are also required, as indicated by the term $^{ex}G_m^{(tern)}$ in (20). As we have seen, there is no ternary term for $\eta_{max} = 2$, so that $^{ex}G_{m\,(\eta_{max}=2)}^{(tern)} = 0$. For $\eta_{max} = 3$, the ternary excess term is the last term on the right-hand side of (18). For a maximum power of four in (11) ($\eta_{max} = 4$), the ternary parameter $L_{ABC}$ is replaced by three coefficients, so that (20) is complemented by the ternary excess term as follows:

$$^{ex}G_{m\,(\eta_{max}=4)}^{(tern)} = x_A x_B x_C (x_A L_A + x_B L_B + x_C L_C) \tag{22}$$

The right-hand side of (22) is exactly the ternary term proposed by Hillert [7], which is commonly used in ternary assessments. The result is also equivalent to the Margules-type polynomial expansion proposed by Gokcen and Baren [28]. As (21) shows, to take full advantage of the series expansion, one has to introduce appropriate $L_2$ coefficients for the binary terms. This procedure has been bypassed in certain treatments, the ternary parameters $L_A$, $L_B$, and $L_C$ in (22) having to be modified to account for the corrections due to missing $L_2^{AB}$, $L_2^{AC}$, and $L_2^{BC}$ terms. Whether this procedure is valid or unreliable will depend on the particular system being modelled.

The next power ($\eta_{max} = 5$) yields the ternary term

$$^{ex}G_{m\,(\eta_{max}=5)}^{(tern)} = {}^{ex}G_{m\,(\eta_{max}=4)}^{(tern)} + x_A x_B x_C (x_A x_B L_{AB} + \\ + x_A x_C L_{AC} + x_B x_C L_{BC}) \tag{23}$$

in addition to three $L_3$ binary interaction parameters.

We are unaware of any work having reached this degree of approximation, $\eta_{max} = 5$, even though Gokcen and Moser [29] have discussed it. In any case, for the vast majority of systems, such high-order corrections are expected to make negligible contributions. The same can be said about the approximation $\eta_{max} = 6$, which yields an $L_4$ interaction parameter for each of the tree binary systems, plus a ternary correction with four additional parameters, which can be written in the following form

$$
\begin{aligned}
^{ex}G_{m\,(\eta_{max}=6)}^{(tern)} = {}& {}^{ex}G_{m\,(\eta_{max}=5)}^{(tern)} \\
& + x_A x_B x_C \Big[ x_A x_B x_C L_{ABC}^0 \\
& \quad + x_A^2 (x_B - x_C) L_{ABC}^A \\
& \quad + x_B^2 (x_A - x_C) L_{ABC}^B \\
& \quad + x_C^2 (x_A - x_B) L_{ABC}^C \Big]
\end{aligned} \tag{24}
$$

## 6 Conclusion

As we ventured to show, the inclusion of ternary interaction parameters is mathematically justified on the same grounds as the inclusion of binary interaction parameters. We have been led to an agreement with the analyses of Helffrich and Wood [30] and Saulov [31], who have followed different approaches to reach conclusions that are similar to ours. Contrary to Janz and Schmid-Fetzer's statement [32], ternary parameters should not be avoided, notwithstanding the counterintuitive behavior reported by those authors, also commented by Saulov [31]. Nor should one conclude, on the other hand, that our treatment of the excess ternary Gibbs energy is unique or preclusive of alternative formulations such as the extrapolation scheme proposed by Chartrand and Pelton [33].

## Appendix: Proof of (5)

Equation 5 is but a generalization of the expansion proposed by [1], who presented only the first few terms. The proof of the general expression, using the Gibbs-Duhem equation, may be of some interest. To that end, we write (3) in the following form

$$x_B \frac{d\mu_B^{ex}}{dx_A} = x_A \frac{d\mu_A^{ex}}{dx_B}, \tag{A1}$$

which is valid for a binary system $A - B$. More compactly, (4) can be rewritten as follows:

$$\mu_A^{ex} = \sum_{\eta=1}^{\eta_{max}} \frac{\Omega_{A,\eta}}{\eta} x_B{}^\eta, \qquad \mu_B^{ex} = \sum_{\eta=1}^{\eta_{max}} \frac{\Omega_{B,\eta}}{\eta} x_A{}^\eta. \qquad (A2)$$

Substitution of the right-hand sides in (A2) for the excess chemical potentials in (A1) yields the equality

$$x_B \left( \Omega_{B,1} + \sum_{\eta=2}^{\eta_{max}} \Omega_{B,\eta} x_A{}^{\eta-1} \right) = x_A \left( \Omega_{A,1} + \sum_{\eta=2}^{\eta_{max}} \Omega_{A,\eta} x_B{}^{\eta-1} \right). \qquad (A3)$$

From (A3), we deduce immediately that $\Omega_{A,1} = \Omega_{B,1} = 0$, as pointed out by Darken [34]. We also have to equate the sums within the parentheses on both sides of (A3). Division of both sides by the product $x_A x_B$ then yields the expression

$$\sum_{\eta=2}^{\eta_{max}} \Omega_{B,\eta} x_A{}^{\eta-2} = \sum_{\eta=2}^{\eta_{max}} \Omega_{A,\eta} x_B{}^{\eta-2} \qquad (A4)$$

We now recall that $x_B = 1 - x_A$ and use the binomial theorem to expand the resulting powers of $1 - x_A$, which leads to the equality

$$\sum_{\eta=2}^{\eta_{max}} \Omega_{B,\eta} x_A{}^{\eta-2} = \sum_{\eta=2}^{\eta_{max}} \sum_{\lambda=0}^{\eta-2} \Omega_{A,\eta} \binom{\eta-2}{\lambda} (-1)^\lambda x_A{}^\lambda \qquad (A5)$$

Since the right-hand side of (A5) is a polynomial in $x_A$, we can easily reverse the order of the double sum, to find that

$$\sum_{\eta=2}^{\eta_{max}} \Omega_{B,\eta} x_A{}^{\eta-2} = \sum_{\lambda=0}^{\eta_{max}-2} \sum_{\eta=\lambda+2}^{\eta_{max}} \Omega_{A,\eta} \binom{\eta-2}{\lambda} (-1)^\lambda x_A{}^\lambda \qquad (A6)$$

The formal transformations $\lambda \to \eta - 2$ and $\eta \to \lambda$ adjusts the power of $x_A$ in the summand on the right-hand side of (A6) to make it identical to the power in the summand on the left-hand side:

$$\sum_{\eta=2}^{\eta_{max}} \Omega_{B,\eta} x_A{}^{\eta-2} = \sum_{\eta=2}^{\eta_{max}} \sum_{\lambda=\eta}^{\eta_{max}} \Omega_{A,\lambda} \binom{\lambda-2}{\eta-2} (-1)^\eta x_A{}^{\eta-2} \qquad (A7)$$

since $(-1)^{\eta-2} = (-1)^\eta$.

Comparison between the coefficients of $x_A^{\eta-2}$ in the summands on both sides of (A7) then yields the final result

$$\Omega_{B,\eta} = \sum_{\lambda=\eta}^{\eta_{max}} \Omega_{A,\lambda} \binom{\lambda-2}{\eta-2} (-1)^\eta. \qquad (A8)$$

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