



Derivations of Partial Molar Excess Gibbs Energy of Mixing Expressions for Common Thermodynamic Models

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Submitted: 16 February 2021 / in revised form: 15 April 2021 / Accepted: 27 April 2021 / Published online: 16 May 2021
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Abstract Modern computational thermodynamics methods rely on the use of numerical models that represent chemical systems. Typically, these models are formulated in terms of the Gibbs energy, which must be minimised to find the conditions of thermodynamic equilibrium. Numerous thermodynamic models have been developed to capture the behaviour of regular solid and liquid solutions, ionic ceramics, multi-sublattice metallic alloys, short and long range ordering, and much more. Some classes of commonly used thermodynamic models include substitutional solutions and compound energy formalism. The mathematical formulation of the Gibbs energy of a solution phase represented by any of the aforementioned models takes on a unique form, which requires special consideration for obtaining the partial derivatives in the Hessian matrix of a Gibbs energy minimiser. This paper provides derivations of the partial molar excess Gibbs energy of mixing of some common classes of thermodynamic models for use in a Gibbs energy minimiser.

Keywords CALPHAD · compound energy formalism · Gibbs energy minimisation · regular solution model

1 Introduction

Thermodynamic calculations play a fundamental role in solving a variety of complicated technical problems. In particular, the CALPHAD method^[1] enables the computer calculation of phase diagrams and for calculating the properties of multicomponent, multiphase systems. Thermodynamic quantities such as Gibbs energies, heat capacities, enthalpies, chemical potentials and driving forces can be calculated using CALPHAD techniques.

Computations of thermodynamic equilibrium often exploit the Gibbs Energy Minimisation (GEM) method, which predicts a unique combination of phases and species that yield a minimum in the integral Gibbs energy of a closed isothermal, isobaric system. The objective is often achieved using the method of Lagrange multipliers that simultaneously minimises the integral Gibbs energy and the residuals of mass balance equations. In matrix form, this results in a system of linearised equations as shown by White et al.^[2] For finding the undetermined Lagrange multipliers, the expressions for the Gibbs energy of different phases and the chemical potentials of the species in those phases are required to establish the constraint vector associated with the system of equations and also for computing the molar quantities of these species when using an iterative solver. The requirement for explicit expressions of the non-ideal contribution to chemical potential, i.e. partial molar excess Gibbs energy of mixing, in GEM software is the motivation behind this paper. While the derivations of these equations and the fundamental method

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11669-021-00886-w>.

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adopted were initially motivated by the development of Thermochemica,^[3] the equations can be implemented in other software that are based on the GEM methodology,^[2] including the development of thermochemistry solver for the mesoscale corrosion modelling code Yellowjacket.^[4]

In the context of this paper, a *system* is defined as a closed isothermal-isobaric volume with a fixed composition. The system composition is represented by the *system components*, which may be equivalent to the chemical elements, a combination thereof, or an electron corresponding to ionic charge. A *species* is defined as any atom, molecule, ion or vacancy and a *constituent* refers to a certain species on a certain sublattice. In the context of a multi-sublattice phase, a fixed combination of constituents is referred to as a *compound end member*. The selection of the independent variable, for which reference Gibbs energies are defined and solved in the Hessian matrix, varies depending on the type of solution model. For example, a ‘species’ is used in an ideal gas or substitutional solution while a ‘compound end member’ is used in the Compound Energy Formalism (CEF). The derivation of chemical potentials will therefore be made with respect to the foregoing independent variables.

In a multicomponent, multiphase system, the integral Gibbs energy is given by the following expression:

$$G = \sum_{\lambda=1}^{\Lambda} n_{\lambda} g_{\lambda} + \sum_{\omega=1}^{\Omega} n_{\omega} g_{\omega}, \quad (\text{Eq 1})$$

where g_{λ} and g_{ω} represent the molar Gibbs energies (i.e., the Gibbs energy per mole of the phase) of solution phase λ and stoichiometric phase ω , respectively. Quantities n_{λ} and n_{ω} represent the mole number of solution phase λ and stoichiometric phase ω . Λ and Ω denote the number of stable solution and stoichiometric phases, respectively.

Calculation of thermodynamic equilibrium requires a multicomponent database, which provides a consistent description of the thermodynamic functions for all the possible phases in the system. These databases are derived from experimental measurements, sometimes combined with first-principles calculations, to include Gibbs energy expressions as functions of temperature, pressure, and composition. It must be mentioned that since the composition of stoichiometric phases is invariant, their thermodynamic parameters are by definition independent of composition. The solution phase functions, however, do depend on the composition, and a number of models and parameters have been proposed to model different phases. These models include ideal solution models, models for a single sublattice and models for multiple sublattices. Despite the large number of models available to represent the Gibbs energy of a particular phase, the general representative expression is as follows:

$$G_{\lambda} = G_{\lambda}^{\circ} + G_{\lambda}^{\text{id}} + G_{\lambda}^{\text{ex}} + G_{\lambda}^{\text{phys}}, \quad (\text{Eq 2})$$

where the Gibbs energy of phase λ , G_{λ} , is a sum of the reference Gibbs energy, G_{λ}° , the ideal mixing term of Gibbs energy, $G_{\lambda}^{\text{id}} = -TS_{\lambda}^{\text{id}}$, which assumes random mixing of constituents with S_{λ}^{id} denoting the entropy of mixing, and a term to account for excess mixing energy, G_{λ}^{ex} . The term $G_{\lambda}^{\text{phys}}$ captures the various physical phenomena that contribute to the Gibbs energy of the phase. The most important amongst these is the magnetic contribution to the Gibbs energy that results from the unpaired electron spins in atoms of magnetic substances. This paper focuses on the excess Gibbs energy of mixing and its contribution to the chemical potentials of the species in the system. Magnetic and other physical contributions to excess mixing energies will not be discussed here.

The chemical potential of species i of phase λ is the partial derivative of the integral Gibbs energy of the system with respect to the number of moles of that species at constant temperature, T , and pressure, P . Mathematically, this is represented as:

$$\mu_{i(\lambda)} = \left(\frac{\partial G_{\lambda}}{\partial n_{i(\lambda)}} \right)_{T,P,n_{j \neq i}}, \quad (\text{Eq 3})$$

where n_i represents the number of moles of species i . One can obtain an expanded expression for chemical potential by substituting Eq 1 and 2 into Eq 3 above, which gives the following:

$$\mu_{i(\lambda)} = \underbrace{\left(\frac{\partial G_{\lambda}^{\circ}}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_{i(\lambda)}^{\circ}} + \underbrace{\left(\frac{\partial G_{\lambda}^{\text{id}}}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_{i(\lambda)}^{\text{id}}} + \underbrace{\left(\frac{\partial G_{\lambda}^{\text{ex}}}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_{i(\lambda)}^{\text{ex}}}, \quad (\text{Eq 4})$$

where the contributions to the integral Gibbs energy are obtained as the product of number of moles of a phase and the respective molar Gibbs energy contribution (i.e., $G_{\lambda}^{\circ} = n_{\lambda} g_{\lambda}^{\circ}$, $G_{\lambda}^{\text{id}} = n_{\lambda} g_{\lambda}^{\text{id}}$ and $G_{\lambda}^{\text{ex}} = n_{\lambda} g_{\lambda}^{\text{ex}}$), with g_{λ}° , g_{λ}^{id} and g_{λ}^{ex} denoting the molar reference Gibbs energy, the molar ideal Gibbs energy of mixing and the molar excess Gibbs energy of mixing, respectively. The partial derivative terms are referred to as the partial reference molar Gibbs energy, partial molar ideal Gibbs energy of mixing and partial molar excess Gibbs energy of mixing and are denoted by $\mu_{i(\lambda)}^{\circ}$, $\mu_{i(\lambda)}^{\text{id}}$, and $\mu_{i(\lambda)}^{\text{ex}}$ respectively.

The expressions for molar Gibbs energy terms depend on the solution model used to describe the phase. This paper presents the derivation of the partial excess molar Gibbs energy terms for some commonly employed solution models and the partial molar reference Gibbs energy and partial molar ideal Gibbs energy terms are briefly presented

for completeness. While there are multiple papers in the open literature that describe these models, none give a full derivation of the partial molar excess Gibbs energy of mixing. Section 2 provides background to substitutional solution theory and presents the various parameters used in those models. Sections 3 and 4 provide the derivation of the partial molar excess Gibbs energy of mixing terms for the two most common substitutional models, i.e. the simple polynomial model with Kohler–Toop interpolation and the Redlich–Kister polynomial model with Muggiano interpolation. Section 5 describes the multi-sublattice CEF and the derivation of chemical potential for the compound end members of the model is presented. Furthermore, the methodology adopted for deriving the expressions is applicable to other thermodynamic models as well. The remainder of the paper will focus on calculations within a single solution phase, and therefore going forward the phase identifier λ will be omitted to simplify the notation.

2 Substitutional Solution Theory

Several solids and liquids conform to substitutional solution behaviour, which is based on the assumption that the constituents mix randomly on a single lattice.^[5] The reference Gibbs energy of solution phase λ represents the Gibbs energy of an unreacted mixture of the different species and is given as follows:

$$G_{\lambda}^{\circ} = n_{\lambda} \sum_i x_{i(\lambda)} g_{i(\lambda)}^{\circ} \quad (\text{Eq 5})$$

where $x_{i(\lambda)}$ denotes the mole fraction of species i of phase λ and is related to the molar amount of species i , $n_{i(\lambda)}$ per mole of phase λ , n_{λ} (i.e., $x_{i(\lambda)} = n_{i(\lambda)} / n_{\lambda}$). Since the reference molar Gibbs energy of the independent species, denoted by $g_{i(\lambda)}^{\circ}$, depends only on the temperature and pressure of the system, the molar reference Gibbs energy of the phase is given as:

$$\mu_{i(\lambda)}^{\circ} = g_{i(\lambda)}^{\circ} \quad (\text{Eq 6})$$

The term $g_{i(\lambda)}^{\circ}$ is obtained from a thermodynamic database.

The second term of Eq 4 relates to the ideal Gibbs energy of mixing, which is written as:

$$G_{\lambda}^{\text{id}} = n_{\lambda} RT \sum_i x_{i(\lambda)} \ln x_{i(\lambda)} \quad (\text{Eq 7})$$

where R is the ideal gas constant. This results in the following expressions for the partial molar ideal Gibbs energy of mixing:

$$\mu_{i(\lambda)}^{\text{id}} = RT \ln x_{i(\lambda)}. \quad (\text{Eq 8})$$

Substitutional solution models represent the excess Gibbs energy of mixing through a polynomial function, which helps in extrapolating the properties of higher order systems from lower order systems. In general, for a multi-component system, the excess molar Gibbs energy of mixing results from binary, ternary and quaternary interactions, which can be described separately as follows:

$$g^{\text{ex}} = g_{\text{bin}}^{\text{ex}} + g_{\text{ter}}^{\text{ex}} + g_{\text{qua}}^{\text{ex}}, \quad (\text{Eq 9})$$

where the right subscripts bin, ter and qua denote the species interacting in the binary, ternary and quaternary subsystems, respectively.

For a multi-species substitutional solution phase, the binary interactions result in the following contribution to excess molar Gibbs energy of mixing:

$$g_{\text{bin}}^{\text{ex}} = \sum_i \sum_{j>i} x_i x_j L_{ij}. \quad (\text{Eq 10})$$

The solution parameter L_{ij} represents the interaction between the two species and is, in general, a function of both temperature and composition.

Redlich and Kister^[6] proposed a symmetrical form of the interaction parameter, which is now widely used because of the ease of extrapolating it to ternary and higher-order systems. This is commonly referred to as the Redlich–Kister polynomial and is represented as follows:

$$L_{ij} = \sum_{v \geq 0} {}^v L_{ij} (x_i - x_j)^v, \quad (\text{Eq 11})$$

where the parameters ${}^v L_{ij}$ are independent of composition but can be temperature dependent, and the number of terms used can be chosen to make an appropriate fit to the available experimental data. The superscript v denotes the order of the interaction parameter terms.

While the Redlich–Kister polynomials are most commonly used to represent a solution parameter, a number of other forms have been proposed, such as simple polynomial form, Lagrange series, etc. Among these, the simple polynomial form is the most commonly used and results in the following:

$$L_{ij} = \sum_{u,v \geq 0} {}^{uv} Q_{ij} x_i^u x_j^v, \quad (\text{Eq 12})$$

where parameters ${}^{uv} Q_{ij}$ are independent of composition but can be temperature dependent. The two formulations are identical in the case of binary systems and the interaction parameters can be easily converted from one form to another. However, in the case of higher order systems, the interpolations would depend on the series used and the interpolation method.

Considering ternary mixing, interaction requires an additional summation resulting in the following:

$$g_{\text{ter}}^{\text{ex}} = \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k L_{ijk}. \quad (\text{Eq 13})$$

Like the binary subsystems, the interaction parameters for the ternary subsystems can be determined experimentally or based on a number of analytical methods. According to Hillert,^[7] in case of composition dependence, there is no unique way of predicting the binary contribution to ternary and higher order systems and as a result a number of different expressions have been proposed with preference given to the expression suggested by Redlich and Kister.^[6] To interpolate ternaries from their binaries, a number of interpolation schemes have been proposed by Kohler,^[8] Toop,^[9] Colinet,^[10] and Muggiano.^[11] A combination of these models, most commonly Kohler–Toop and Muggiano–Toop, can be used to estimate the energies of higher order systems from their binary subsystems. Among the four interpolation methods, Kohler, Colinet and Muggiano methods are symmetric and treat all the binary subsystems in the same way, but the ternary excess terms are related to the binary excess terms through the composition paths depicted in Fig. 1. It must be emphasised that the components in the illustrated figures refer to the species and not the system components. For example, in Fig. 1(a), the phase has three species i , j and k , which are denoted at the vertices of the triangle.

The composition of the ternary phase is denoted by point p and the points a , b and c represent the binary compositions obtained using the interpolation model in question. In the following discussion, the functional form $g_{ij}(\alpha; \beta)$ will be used to refer to the molar Gibbs energy contribution from a binary system, with α and β representing the projected concentrations of the two species of the binary subsystem. For example, the excess Gibbs energy of mixing in the $i-j$ binary subsystem should be calculated at point a and is given as $g_{ij}^{\text{ex}}(\alpha; \beta)$, where α and β are the equivalent concentrations of species i and j in the binary subsystem, respectively, and $\alpha + \beta = 1$.

- **Kohler:** The Kohler interpolation scheme shown in Fig. 1(a) is symmetric. On the line ap , the ratio $x_j/(x_i + x_j)$ remains constant and the binary contribution of the $i-j$ subsystem to the ternary can be computed by evaluating the binary excess Gibbs energy of mixing of the $i-j$ subsystem at point a .^[13] For a multi-species phase, the ternary excess Gibbs energy is then given as the following:

$$g^{\text{ex}} = \sum_i \sum_{j>i} (x_i + x_j)^2 \cdot g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right), \quad (\text{Eq 14})$$

where the expression $g_{ij}^{\text{ex}}(\alpha; \beta)$ denotes that excess Gibbs energy of mixing of binary subsystem $i-j$ evaluated at molar equivalent composition α and β and the factor $(x_i + x_j)^2$ is a result of using the interpolation formula instead of the composition of the system.

- **Muggiano:** The Muggiano interpolation scheme is based on the fact that along the line ap shown in Fig. 1(b), the ratios $(1 + x_i - x_j)/2$ and $(1 - x_i + x_j)/2$ both remain constant.^[13] The excess Gibbs energy of mixing takes the following form:

$$g^{\text{ex}} = \sum_i \sum_{j>i} \frac{4x_i x_j}{(1 + x_i - x_j)(1 + x_j - x_i)} \cdot g_{ij}^{\text{ex}}\left(\frac{1 + x_i - x_j}{2}; \frac{1 + x_j - x_i}{2}\right). \quad (\text{Eq 15})$$

- **Kohler–Toop:** The Kohler–Toop interpolation scheme shown in Fig. 1(c) is an asymmetrical model, which is often used when one species of the subsystem belongs to a group different from the others.^[13] Since the mole fraction x_i is constant along the line ac , and the line bp follows from Kohler interpolation, the excess molar Gibbs energy can be written as follows^[14]

$$g^{\text{ex}} = \frac{x_j}{1 - x_i} \cdot g_{ij}^{\text{ex}}(x_i; 1 - x_i) + \frac{x_k}{1 - x_i} \cdot g_{ik}^{\text{ex}}(x_i; 1 - x_i) + (1 - x_i)^2 \cdot g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j + x_k}; \frac{x_k}{x_j + x_k}\right). \quad (\text{Eq 16})$$

The Kohler–Toop model depends on the choice of symmetric and asymmetric species and in the Eq 16, species i of Fig. 1(c) has been selected as the Kohler component.

An advantage of using Redlich–Kister polynomials is the fact that when using the Muggiano interpolation method, the binary terms can be used directly in the ternary extrapolations. This is an outcome of the fact that along the line ap shown in Fig. 1(b), the quantity $x_i - x_j$ remains constant.^[13, 15] This results in what is commonly referred to as the Redlich–Kister–Muggiano polynomial model. Also, it must be mentioned that the composition independent parameter ${}^0L_{ij}$ scales the same way irrespective of the model used.

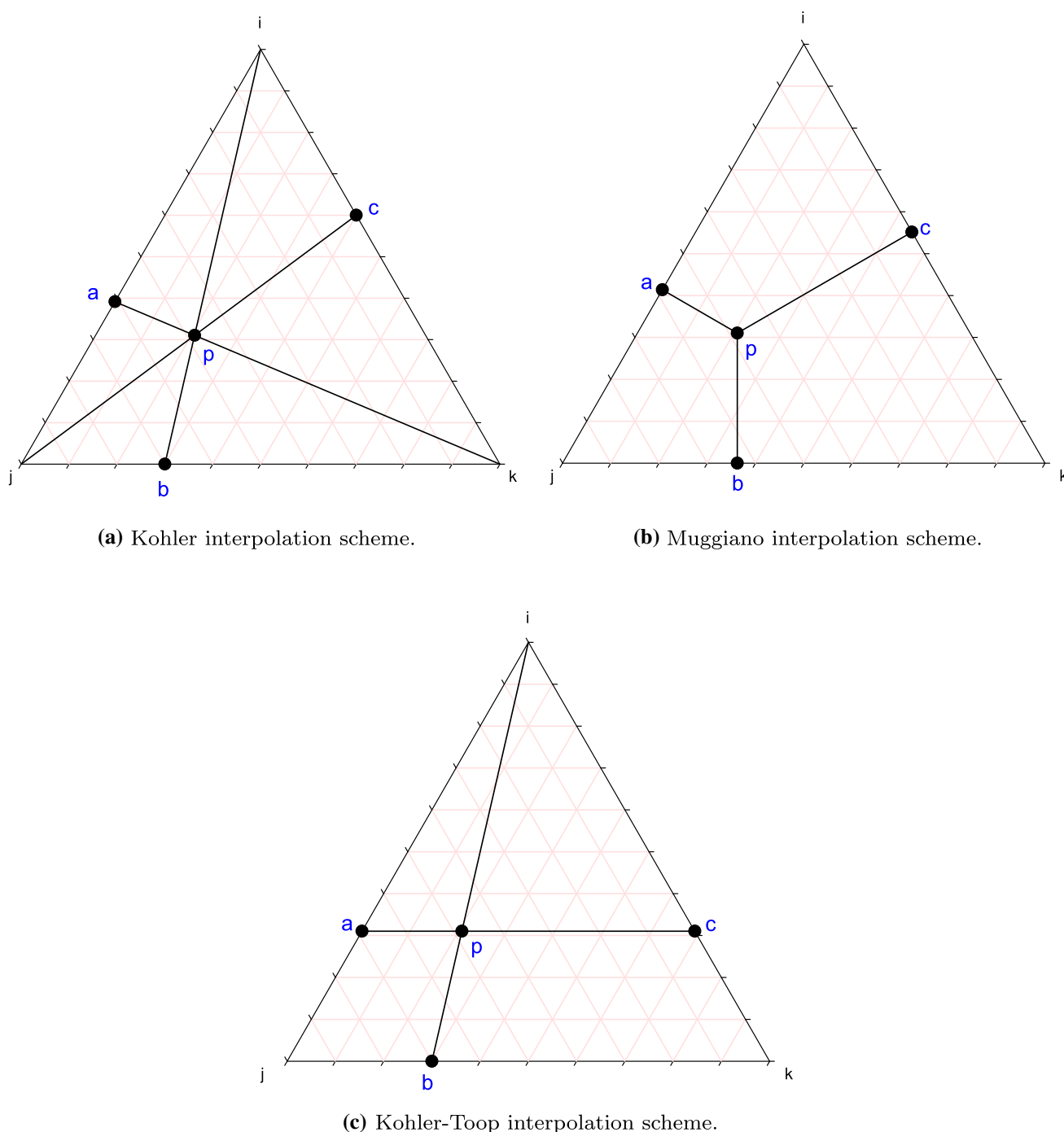


Fig. 1 Commonly used interpolation models^[12]

3 Simple Polynomial Solution Model with Kohler–Toop Interpolation

Substitutional solution models using the simple polynomial form of the interaction parameters often utilise the Kohler–Toop interpolation scheme. The choice of the interpolation scheme for a system of interest is based on the judgement of the model developer, with physical and thermodynamic

factors such as the similarity of species playing key roles in the choice between the symmetric Muggiano or the asymmetric Kohler–Toop models. Chartrand and Pelton have provided a detailed description of the reasoning behind the preferability of the Kohler–Toop model in a number of cases.^[13] While Redlich–Kister polynomials can also be used in place of simple polynomials, the latter has been the standard notation adopted when using the Kohler–

Toop interpolation model. A derivation for the partial molar excess Gibbs energy for this case follows.

3.1 Derivation of Partial Excess Gibbs Energy of Mixing for a Solution Model with Kohler–Toop Interpolation

3.1.1 Derivation of Terms for a Subsystem Modelled by a Simple Polynomial Formulation

In the substitutional solution model using simple polynomials, the molar excess Gibbs energy of mixing is generally given in terms of binary and ternary mixing parameters:

$${}^{\text{SP}}g_{ijk}^{\text{ex}}(x_i; x_j; x_k) = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} x_i^u x_j^v x_k^w, \quad (\text{Eq 17})$$

where the left-superscript SP indicates the Simple Polynomial formulation and the exponents u , v and w are integers.

Denoting the number of moles of the phase by n , where n is equal to the sum of the number of moles of each species of the solution phase (i.e. $n = \sum_i n_i$) the integral excess Gibbs energy of mixing is:

$${}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_{\text{interp}}) = n_{\text{interp}} \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{n_i}{n_{\text{interp}}}; \frac{n_j}{n_{\text{interp}}}; \frac{n_k}{n_{\text{interp}}}\right). \quad (\text{Eq 18})$$

Equation 18 makes explicit how one may interpolate into subsystems, which will become very useful in the following subsections. The first argument ($\{n_i; n_j; n_k\}$) is the list of molar quantities of species used in the excess mixing term, while the second argument (n_{interp}) is the total number of moles to consider when interpolating into the desired subsystem. For the moment, one may consider the entire system by setting $n_{\text{interp}} = n$ as the second argument.

$$\begin{aligned} {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n) &= n \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{n_i}{n}; \frac{n_j}{n}; \frac{n_k}{n}\right) \\ &= n \cdot \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} x_i^u x_j^v x_k^w \\ &= n \cdot \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \frac{n_i^u n_j^v n_k^w}{n^{u+v+w}} \\ &= \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} (n_i^u n_j^v n_k^w) (n^{1-u-v-w}). \end{aligned} \quad (\text{Eq 19})$$

The partial molar excess Gibbs energy of mixing of species i resulting from parameters involving species i, j , and k , $\mu_{i(jk)}^{\text{ex}}$, is obtained by taking the partial derivative of Eq 19

with respect to the number of moles of the species, n_i , as per Eq 3:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}} &= \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{u n_i^{u-1} n_j^v n_k^w}{n^{u+v+w-1}} \right. \\ &\quad \left. - (u + v + w - 1) \frac{n_i^u n_j^v n_k^w}{n^{u+v+w}} \right]. \end{aligned} \quad (\text{Eq 20})$$

Substituting molar quantities, i.e. $x_i = \frac{n_i}{n}$, into Eq 20 gives:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}} &= \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{u (n x_i)^{u-1} (n x_j)^v (n x_k)^w}{n^{u+v+w-1}} \right. \\ &\quad \left. - (u + v + w - 1) \frac{(n x_i)^u (n x_j)^v (n x_k)^w}{n^{u+v+w}} \right] \\ &= \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{u x_i^{u-1} x_j^v x_k^w n^{u+v+w-1}}{n^{u+v+w-1}} \right. \\ &\quad \left. - (u + v + w - 1) \frac{x_i^u x_j^v x_k^w n^{u+v+w}}{n^{u+v+w}} \right]. \end{aligned} \quad (\text{Eq 21})$$

Simplifying, the following partial molar excess Gibbs energy of mixing of species i in the subsystem is obtained:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}}(x_i; x_j; x_k) &= \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} [u x_i^{u-1} + (1 - u - v - w) x_i^u] x_j^v x_k^w. \end{aligned} \quad (\text{Eq 22})$$

It is worth mentioning that the expressions for a three species phase can be directly used for a binary phase by setting the exponent w equal to zero. Thus, for a binary phase, the following expression for the integral excess Gibbs energy of mixing is obtained:

$$\begin{aligned} {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_{\text{interp}}) &= n_{\text{interp}} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{n_i}{n_{\text{interp}}}; \frac{n_j}{n_{\text{interp}}}\right). \end{aligned} \quad (\text{Eq 23})$$

The molar excess Gibbs energy of mixing is:

$${}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; x_j) = \sum_{u,v > 0} {}^{uv}Q_{ij} x_i^u x_j^v, \quad (\text{Eq 24})$$

and the partial molar excess Gibbs energy is:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(j)}^{\text{ex}}(x_i; x_j) &= \sum_{u,v > 0} {}^{uv}Q_{ij} [u x_i^{u-1} + (1 - u - v) x_i^u] x_j^v. \end{aligned} \quad (\text{Eq 25})$$

3.1.2 Derivation of Ternary Phase from Binary Subsystems of a Substitutional Solution Model Using Kohler Interpolation

When modelling the ternary phase by geometrically interpolating binary subsystems using Kohler interpolation (indicated in the following with left-superscript KO), the following expression is obtained by substituting Eq 24 into Eq 14 (and including ternary mixing terms as well):

$$\begin{aligned} {}^{\text{KO}}g_{ijk}^{\text{ex}} &= (x_i + x_j)^2 \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) \\ &+ (x_i + x_k)^2 \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}\left(\frac{x_i}{x_i + x_k}; \frac{x_k}{x_i + x_k}\right) \\ &+ (x_j + x_k)^2 \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j + x_k}; \frac{x_k}{x_j + x_k}\right) \\ &+ \sum_{u,v,w > 0} {}^{uvw}Q_{ijk}x_i^u x_j^v x_k^w, \end{aligned} \quad (\text{Eq 26})$$

where the binary subsystems are evaluated as described in section 2, and the summation in the last term is only over ternary parameters. In a ternary subsystem, this summation can be evaluated straightforwardly, and in subsystems with more species the procedure is described in section 3.1.4. For the moment, the focus will be on the evaluation of the binary terms within a ternary subsystem.

Owing to the symmetric nature of the preceding equation, the equations for partial molar excess Gibbs energies can be derived for a single binary subsystem and the contribution from each subsystem can be summed together. Considering the contribution of the $i - j$ binary subsystem:

$${}^{\text{KO}}g_{ij}^{\text{ex}} = (x_i + x_j)^2 \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right), \quad (\text{Eq 27})$$

the integral excess Gibbs energy of mixing contribution of the subsystem can be written as follows:

$$\begin{aligned} {}^{\text{KO}}G_{ij}^{\text{ex}} &= n \cdot {}^{\text{KO}}g_{ij}^{\text{ex}} \\ &= \frac{(n_i + n_j)^2}{n} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) \end{aligned} \quad (\text{Eq 28})$$

The interpolated integral excess Gibbs energy of the binary subsystem is weighted such that:

$$\begin{aligned} {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_i + n_j) &= (n_i + n_j) \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right), \end{aligned} \quad (\text{Eq 29})$$

and the equation then becomes:

$${}^{\text{KO}}G_{ij}^{\text{ex}} = \frac{(n_i + n_j)}{n} \cdot {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_i + n_j). \quad (\text{Eq 30})$$

Taking the partial derivative of Eq 30 with respect to n_i :

$$\begin{aligned} {}^{\text{KO}}\mu_{i(ij)}^{\text{ex}} &= \frac{(n_i + n_j)}{n} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) \\ &+ \frac{(n_i + n_j)}{n} \cdot {}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) \\ &- \frac{(n_i + n_j)^2}{n^2} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right). \end{aligned} \quad (\text{Eq 31})$$

The previous equation simplifies to the following expression, which is applicable to both species of the binary subsystem¹:

$$\begin{aligned} {}^{\text{KO}}\mu_{i(ij)}^{\text{ex}} &= \left[{}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) + (1 - x_i - x_j) \right. \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right) \left. \right] (x_i + x_j), \end{aligned} \quad (\text{Eq 32})$$

where the term ${}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}$ is the chemical potential of species i in binary subsystem $i - j$ and can be calculated using Eq 25. For any remaining species (i.e., the species not part of the binary subsystem):

$$\begin{aligned} {}^{\text{KO}}\mu_{k(ij)}^{\text{ex}} &= -(x_i + x_j)^2 \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j}\right). \end{aligned} \quad (\text{Eq 33})$$

In Eq 31, 32 and 33, the definitions of ${}^{\text{SP}}g_{ij}^{\text{ex}}$ and ${}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}$ given in Eq 24 and 25 can be used directly. Therefore, in a ternary phase evaluated using Kohler interpolation, the total of the binary contributions to the chemical potential of species i will be:

$$\begin{aligned} {}^{\text{KO}}\mu_{i(ijk)}^{\text{ex}} &= {}^{\text{KO}}\mu_{i(ij)}^{\text{ex}} \\ &+ {}^{\text{KO}}\mu_{i(ik)}^{\text{ex}} + {}^{\text{KO}}\mu_{i(jk)}^{\text{ex}}. \end{aligned} \quad (\text{Eq 34})$$

3.1.3 Derivation of Ternary Phase from Binary Subsystems of a Substitutional Solution Model Using Kohler-Toop Interpolation

When modelling the ternary phase of a three species subsystem by geometrically interpolating binary subsystems

¹ Unless specified otherwise, all the expressions for chemical potentials account for the chain rule and the expressions from the referenced equations can be directly substituted.

using Kohler–Toop interpolation (indicated in the following by the left-superscript KT), the expression shown in Eq 16 is obtained:

$$\begin{aligned} {}^{\text{KT}}g_{ijk}^{\text{ex}} &= \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ (1-x_i)^2 \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right), \end{aligned} \quad (\text{Eq 35})$$

where the binary subsystems are evaluated as mentioned in section 2. Since the model is asymmetric, the expression for the partial molar excess Gibbs energy will depend on the choice of the Kohler component, which has been selected to be species i in the previous equation.

Expressing the previous equation in terms of molar quantities and multiplying by the molar amount of the phase, n , the following ternary contribution to the integral Gibbs energy is obtained:

$$\begin{aligned} {}^{\text{KT}}G_{ijk}^{\text{ex}} &= n \left[\frac{n_j}{n-n_i} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \right. \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &\left. + \left(\frac{n-n_i}{n}\right)^2 \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \right]. \end{aligned} \quad (\text{Eq 36})$$

The integral excess Gibbs energy of mixing contribution of the ij pair and non-Kohler subsystems can be written as follows:

$${}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n-n_i\}, n) = n \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i), \quad (\text{Eq 37})$$

making use of this plus the earlier definition in Eq 29

$$\begin{aligned} {}^{\text{KT}}G_{ijk}^{\text{ex}} &= \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n-n_i\}, n) \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}G_{ik}^{\text{ex}}(\{n_i; n-n_i\}, n) \\ &+ \frac{(n-n_i)^2}{n \cdot (n_j+n_k)} \cdot {}^{\text{SP}}G_{jk}^{\text{ex}}(\{n_i; n_j\}, n_i+n_j). \end{aligned} \quad (\text{Eq 38})$$

The partial molar excess Gibbs energy of species j can be calculated by taking the partial derivative of Eq 36 with respect to n_j :

$$\begin{aligned} {}^{\text{KT}}\mu_{j(ijk)}^{\text{ex}} &= n \left(\frac{1}{n-n_i} - \frac{n_j}{(n-n_i)^2} \right) \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}\mu_{j(ij)}^{\text{ex}}(x_i; 1-x_i) \\ &- n \frac{n_k}{(n-n_i)^2} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}\mu_{j(ik)}^{\text{ex}}(x_i; 1-x_i) \\ &+ \left(\frac{2}{n-n_i} - \frac{1}{n} - \frac{1}{n_j+n_k} \right) \left(\frac{(n-n_i)^2}{n} \right) \\ &\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\ &+ \frac{(n-n_i)^2}{n \cdot (n_j+n_k)} \\ &\cdot {}^{\text{SP}}\mu_{j(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \end{aligned} \quad (\text{Eq 39})$$

$$\begin{aligned} &= \left(\frac{1}{1-x_i} - \frac{x_j}{(1-x_i)^2} \right) \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{j(ij)}^{\text{ex}}(x_i; 1-x_i) \\ &- \frac{x_k}{(1-x_i)^2} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{j(ik)}^{\text{ex}}(x_i; 1-x_i) \\ &+ \left(2(1-x_i) - (1-x_i)^2 - \frac{(1-x_i)^2}{x_j+x_k} \right) \\ &\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\ &+ \frac{(1-x_i)^2}{x_j+x_k} \\ &\cdot {}^{\text{SP}}\mu_{j(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right). \end{aligned}$$

Similarly, the partial molar excess Gibbs energy of mixing of species k can be calculated by taking the partial derivative of Eq 36 with respect to n_k :

$$\begin{aligned}
& {}^{\text{KT}}\mu_{k(ijk)}^{\text{ex}} \\
&= -\frac{x_j}{(1-x_i)^2} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\
&+ \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{k(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&+ \left(\frac{1}{1-x_i} - \frac{x_k}{(1-x_i)^2} \right) \\
&\cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\
&+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{k(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&+ \left(2(1-x_i) - (1-x_i)^2 - \frac{(1-x_i)^2}{x_j+x_k} \right) \\
&\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\
&+ \frac{(1-x_i)^2}{x_j+x_k} \\
&\cdot {}^{\text{SP}}\mu_{k(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right).
\end{aligned} \tag{Eq 40}$$

Finally, the partial molar excess Gibbs energy of species i can be calculated by taking the partial derivative of Eq 36 with respect to n_i :

$$\begin{aligned}
& {}^{\text{KT}}\mu_{i(ijk)}^{\text{ex}} \\
&= \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}\mu_{i(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&- \frac{(n-n_i)^2}{n^2} \\
&\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\
&= \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{i(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&- (1-x_i)^2 \\
&\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right).
\end{aligned} \tag{Eq 41}$$

In the previous equations, the definitions of ${}^{\text{SP}}g_{ij}^{\text{ex}}$ and ${}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}$ given in Eq 24 and 25 can be used directly.

3.1.4 Derivation of Terms of a Ternary Subsystem Using Kohler Interpolation

A multi-species phase can be extrapolated from the ternary phase following the same principle used for extrapolating the ternary from a binary. The molar excess Gibbs energy of mixing of such a phase can be represented as:

$$\begin{aligned}
g^{\text{ex}} &= \sum_{i,j,k \geq 0} (x_i + x_j + x_k)^3 \\
&\cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{x_i}{x_i+x_j+x_k}; \frac{x_j}{x_i+x_j+x_k}; \frac{x_k}{x_i+x_j+x_k}\right),
\end{aligned} \tag{Eq 42}$$

and expanding this expression in terms of molar quantities instead of mole fractions:

$$\begin{aligned}
g^{\text{ex}} &= \sum_{i,j,k \geq 0} \left(\frac{n_i + n_j + n_k}{n} \right)^3 \\
&\cdot \frac{{}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k)}{n_i + n_j + n_k}.
\end{aligned} \tag{Eq 43}$$

Evidently, the integral excess Gibbs energy of mixing of the phase is defined as:

$$\begin{aligned}
G^{\text{ex}} &= \sum_{i,j,k \geq 0} \left(\frac{n_i + n_j + n_k}{n} \right)^2 \\
&\cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k).
\end{aligned} \tag{Eq 44}$$

As before, the focus can be on a single ternary subsystem for finding the relevant partial molar quantities. The partial molar excess Gibbs energy of mixing of species i due to the ijk ternary subsystem is the following:

$$\begin{aligned}
& \mu_{i(ijk)}^{\text{ex}} \\
&= 2 \left(\frac{n_i + n_j + n_k}{n^2} \right) \\
&\cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k) \\
&+ \left(\frac{n_i + n_j + n_k}{n} \right)^2 \\
&\cdot {}^{\text{SP}}\mu_{i(ijk)}^{\text{ex}}\left(\frac{x_i}{x_i+x_j+x_k}; \frac{x_j}{x_i+x_j+x_k}; \frac{x_k}{x_i+x_j+x_k}\right) \\
&- 2 \frac{(n_i + n_j + n_k)^2}{n^3} \\
&\cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k).
\end{aligned} \tag{Eq 45}$$

In a simplified form, the previous equation can be written as follows:

$$\begin{aligned} \mu_{i(jk)}^{\text{ex}} &= (x_i + x_j + x_k)^2 \left[{}^{\text{SP}}\mu_{i(jk)}^{\text{ex}} \left(\frac{x_i}{x_i + x_j + x_k}; \right. \right. \\ &\quad \left. \left. \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \right. \\ &\quad \left. + 2(1 - x_i - x_j - x_k) \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}} \right. \\ &\quad \left. \left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \right] \end{aligned} \quad (\text{Eq 46})$$

The partial molar excess Gibbs energy of mixing of species m ($m \neq i, j, k$) is:

$$\begin{aligned} \mu_{m(ijk)}^{\text{ex}} &= -2(x_i + x_j + x_k)^3 \\ &\quad \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}} \left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \end{aligned} \quad (\text{Eq 47})$$

In the preceding equations, the definitions of ${}^{\text{SP}}g_{ijk}^{\text{ex}}$ and ${}^{\text{SP}}\mu_{i(jk)}^{\text{ex}}$ given in Eq 17 and 22 can be used directly.

4 Redlich–Kister Polynomial Model with Muggiano Interpolation

The substitutional solution model employing a Redlich–Kister polynomial formulation has several advantages over the simple polynomial formulation. These advantages have already been mentioned in the previous section. Starting with the Redlich–Kister formalism, the Muggiano interpolation is the simplest higher-order interpolation scheme and the resultant formalism, often called Redlich–Kister–Muggiano polynomial formalism, is widely used in thermodynamic modelling of symmetric phases. The derivations of the relevant terms for computing the chemical potential of a phase modelled using a Redlich–Kister polynomial with Muggiano interpolation are presented in the following discussion.

4.1 Derivation of Partial Excess Gibbs Energy of Mixing

4.1.1 Derivation of Terms of a Multi-species Phase with only Binary Excess Mixing Terms

If Redlich–Kister polynomials are used to represent interaction parameters, then the binary contribution to the molar excess Gibbs energy of mixing of a multi-species phase is simply:

$$g_{\text{bin}}^{\text{ex}} = \sum_i \sum_{j>i} x_i x_j \sum_v {}^v L_{ij} (x_i - x_j)^v. \quad (\text{Eq 48})$$

The equations are simplified in comparison to the Kohler–Toop scheme, which requires special consideration when relating binary interaction parameters for the molar Gibbs energy of a phase.

The integral excess Gibbs energy of the phase, considering only binary contributions, is defined as follows:

$$\begin{aligned} G_{\text{bin}}^{\text{ex}} &= n \sum_i \sum_{j>i} x_i x_j \sum_v {}^v L_{ij} (x_i - x_j)^v \\ &= \sum_i \sum_{j>i} \frac{n_i n_j}{n} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v. \end{aligned} \quad (\text{Eq 49})$$

For deriving the partial molar excess Gibbs energy of mixing of species k in a multi-species phase, the binary contribution to the integral Gibbs energy of mixing can be subdivided into three cases based on the presence or absence of species k in the binary subsystems. This results in the following form of Eq 49:

$$\begin{aligned} G_{\text{bin}}^{\text{ex}} &= \underbrace{\sum_{j>k} \frac{n_k n_j}{n} \sum_v {}^v L_{kj} \left(\frac{n_k - n_j}{n} \right)^v}_{i=k} \\ &\quad + \underbrace{\sum_{i<k} \frac{n_i n_k}{n} \sum_v {}^v L_{ik} \left(\frac{n_i - n_k}{n} \right)^v}_{j=k} \\ &\quad + \underbrace{\sum_i \sum_{j>i} \frac{n_i n_j}{n} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v}_{i,j \neq k}. \end{aligned} \quad (\text{Eq 50})$$

Taking the partial derivative of Eq 50 with respect to n_k , the partial molar excess Gibbs energy of mixing can be given as follows:

$$\begin{aligned} \mu_{k(\text{bin})}^{\text{ex}} &= \sum_{j>k} \left[\left(\frac{n_j}{n} - \frac{n_k n_j}{n^2} \right) \sum_v {}^v L_{kj} \left(\frac{n_k - n_j}{n} \right)^v + \frac{n_k n_j}{n} \sum_v {}^v L_{kj} v \left(\frac{n_k - n_j}{n^2} \right)^{v-1} \left(\frac{1}{n} - \frac{n_k - n_j}{n^2} \right) \right] \\ &\quad + \sum_{i<k} \left[\left(\frac{n_i}{n} - \frac{n_i n_k}{n^2} \right) \sum_v {}^v L_{ik} \left(\frac{n_i - n_k}{n} \right)^v + \frac{n_i n_k}{n} \sum_v {}^v L_{ik} v \left(\frac{n_i - n_k}{n^2} \right)^{v-1} \left(-\frac{1}{n} - \frac{n_i - n_k}{n^2} \right) \right] \\ &\quad + \sum_i \sum_{j>i} \left[-\frac{n_i n_j}{n^2} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v - \frac{n_i n_j}{n} \sum_v {}^v L_{ij} v \left(\frac{n_i - n_j}{n^2} \right)^{v-1} \left(\frac{n_i - n_j}{n^2} \right) \right], \end{aligned} \quad (\text{Eq 51})$$

which simplifies to the following expression for the partial molar excess Gibbs energy of mixing of species k when considering only binary contributions:

$$\begin{aligned}
\mu_{k(\text{bin})}^{\text{ex}} &= \sum_{j>k} \left[\underbrace{(x_j - x_k x_j) \sum_v {}^v L_{kj} (x_k - x_j)^v + x_k x_j (1 - (x_k - x_j)) \sum_v {}^v L_{kj} v (x_k - x_j)^{v-1}}_{i=k} \right] \\
&+ \sum_{i<k} \left[\underbrace{(x_i - x_i x_k) \sum_v {}^v L_{ik} (x_i - x_k)^v - x_i x_k (1 + (x_i - x_k)) \sum_v {}^v L_{ik} v (x_i - x_k)^{v-1}}_{j=k} \right] \\
&- \underbrace{\sum_i \sum_{j>i} \left[x_i x_j \sum_v {}^v L_{ij} (1 + v) (x_i - x_j)^v \right]}_{i,j \neq k}.
\end{aligned}$$

(Eq 52)

4.1.2 Derivation of Terms of a Multi-species Phase with only Ternary Excess Mixing Terms

Using Muggiano interpolation, the ternary contribution to the molar Gibbs energy of a multi-species solution phase can be represented by the following expression^[13]:

$$\begin{aligned}
g_{\text{ter}}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - x_i - x_j - x_k}{3} + x_l \right),
\end{aligned}$$

(Eq 53)

where the interaction parameter ${}^0 L_{l(ijk)}$ is only temperature dependent (i.e., only a zeroth-order interaction term, independent of composition) and the right superscript $l = i, j$ and k denotes the species for which the parameter has been established.

The integral excess Gibbs energy of mixing is given as the following:

$$\begin{aligned}
G_{\text{ter}}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} \frac{n_i n_j n_k}{n^3} \sum_l {}^0 L_{l(ijk)} \\
&\left(\frac{n - n_i - n_j - n_k}{3} + n_l \right).
\end{aligned}$$

(Eq 54)

For a general species w of the multi-species phase, the partial molar excess Gibbs energy can be derived by taking the partial derivative of Eq 54 with respect to the molar quantity of w , n_w

$$\begin{aligned}
\mu_{w(\text{ter})}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} \left[\left\{ \frac{1}{n^3} (\delta_{iw} n_j n_k + \delta_{jw} n_i n_k + \delta_{kw} n_i n_j) \right. \right. \\
&- \left. \frac{3 n_i n_j n_k}{n^4} \right\} \sum_l {}^0 L_{ijk}^l \left(\frac{n - n_i - n_j - n_k}{3} + n_l \right) \\
&+ \left. \frac{n_i n_j n_k}{n^3} \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - \delta_{iw} - \delta_{jw} - \delta_{kw}}{3} + \delta_{lw} \right) \right],
\end{aligned}$$

(Eq 55)

where the Kronecker delta function δ_{ij} is defined as:

$$\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j. \end{cases}$$

Equation 55 simplifies into the following form valid for any species:

$$\begin{aligned}
\mu_{w(\text{ter})}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \\
&\left[\left(\sum_u \frac{\delta_{uw}}{x_u} - 3 \right) \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - x_i - x_j - x_k}{3} + x_l \right) \right. \\
&+ \left. \sum_l {}^0 L_{ijk}^l \left(\frac{1 - \delta_{iw} - \delta_{jw} - \delta_{kw}}{3} + \delta_{lw} \right) \right],
\end{aligned}$$

(Eq 56)

where the species index $u = i, j$ and k .

4.1.3 Derivation of Terms of a Multi-species Phase with only Quaternary Excess Mixing Terms

In a multi-species phase modelled by the Redlich–Kister polynomials with Muggiano interpolation, the quaternary contribution to the molar Gibbs energy can be represented with the following equation:

$$g_{\text{qua}}^{\text{ex}} = \sum_i \sum_{j>i} \sum_{k>j} \sum_{l>k} x_i x_j x_k x_l L_{ijkl},$$

(Eq 57)

where the interaction parameter L_{ijkl} is only temperature dependent (i.e. only a zeroth-order interpolation term, independent of composition).^[13]

The integral excess Gibbs energy of the phase can then be written as follows:

$$G_{\text{qua}}^{\text{ex}} = \sum_i \sum_{j>i} \sum_{k>j} \sum_{l>k} \left(\frac{n_i n_j n_k n_l}{n^3} \right) L_{ijkl}.$$

(Eq 58)

For a general species v of the multi-species phase, the quaternary contribution to the partial molar excess Gibbs energy of mixing can be derived by taking the partial derivative of the previous equation with respect to the molar quantity of v , n_v :

$$\begin{aligned} \mu_{w(qua)}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_k \sum_{l>k} \left[\frac{1}{n^3} (\delta_{iw} n_j n_k n_l + \delta_{jw} n_i n_k n_l \right. \\ &\quad \left. + \delta_{kw} n_i n_j n_l + \delta_{lw} n_i n_j n_k) - \frac{3n_i n_j n_k n_l}{n^4} \right] L_{ijkl}. \end{aligned} \quad (\text{Eq 59})$$

The previous expression can be simplified using the definition of mole fractions:

$$\begin{aligned} \mu_{w(qua)}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_k \sum_{l>k} x_i x_j x_k x_l \left(\sum_u \frac{\delta_{uw}}{x_u} - 3 \right) L_{ijkl}, \end{aligned} \quad (\text{Eq 60})$$

where the species index $u = i, j, k$ and l .

5 Compound Energy Formalism

The CEF was developed to account for the existence of multiple sublattices and the mixing of constituents within a sublattice. The CEF is applicable to an arbitrary number of sublattices with any number of constituents on each sublattice. It has been widely applied to the modelling of a variety of phases, such as interstitial solutions, intermetallic phases, etc.

Following the nomenclature of Hillert,^[16] while there can be multiple sets of species with the same chemical formula, they can be distinguished as compound end members with different constituents on the sublattices. To reiterate earlier definitions, in the context of the CEF, a *compound end member* refers to a unique combination of constituents formed by picking one constituent from each sublattice. The total number of end members of a phase modelled by the CEF is the product of the number of constituents on each sublattice. The CEF is based on the principle that each compound end member has its own Gibbs energy of formation.

5.1 Gibbs Energy of Compound Energy Formalism Phases

In CEF, the molar Gibbs energy expressions are defined for each compound end member and excess Gibbs energy of mixing parameters are defined for interactions between the constituents. The molar Gibbs energy, g , of a solution phase modelled using the CEF model is generally given as^[16]:

$$\begin{aligned} g &= \sum_{k=1}^N g_k^\circ \prod_{s=1}^{N_s} y_{k(s)} \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right) + g^{\text{ex}}, \end{aligned} \quad (\text{Eq 61})$$

where g_k° is the reference molar Gibbs energy of the compound end member k , $y_{j(s)}$ represents the site fraction on sublattice s corresponding to constituent j , N and N_s denote the number of compound end members and number of sublattices in the solution phase, respectively. The site fractions of constituents of an end member can be related to the mole fraction of the end member as $x_k = \prod_{s=1}^{N_s} y_{j(s)}$. The stoichiometry coefficient for sublattice s is represented by v_s , the number of constituents on sublattice s is C_s . Finally, the molar excess Gibbs energy of mixing of the solution phase is g^{ex} and is generally defined as follows:

$$\begin{aligned} g^{\text{ex}} &= \sum_{p=1}^{N_p} y_{j_p(s_p)} y_{k_p(s_p)} \left(\prod_{\substack{s=1 \\ s \neq s_p}}^{N_s} y_{l_p(s)} \right) \\ &\quad \sum_{v=0}^{V_p} {}^v L_{j_p(s_p)k_p(s_p)} (y_{j_p(s_p)} - y_{k_p(s_p)})^v, \end{aligned} \quad (\text{Eq 62})$$

where N_p denotes the number of excess mixing terms, s_p is the sublattice on which mixing is taking place, $j_p(s_p)$ and $k_p(s_p)$ are the constituents being mixed on that sublattice, $l_p(s)$ are the constituents corresponding to the mixed end members on all sublattices other than s_p , and ${}^v L_{jk}$ denotes the interaction parameter of order v . V_p denotes the number of interaction parameters corresponding to the excess mixing term p .

Equation 61 can be represented in the following form which is more conducive to the subsequent mathematics and explicitly states the meaning of the first term in the previous equation:

$$\begin{aligned} g &= \sum_{k=1}^N g_k^\circ \prod_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{k(s)j(s)} y_{j(s)} \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right) + g^{\text{ex}}, \end{aligned} \quad (\text{Eq 63})$$

where $\delta_{k(s)j(s)}$ is a Kronecker delta term that is equal to unity when the constituent j on sublattice s matches that of end member k on sublattice s and is otherwise equal to zero.

5.2 Derivation of Chemical Potential

In models with multiple sublattices including the CEF, the chemical potentials are defined for the compound end members—not the species or constituents—because the reference Gibbs energies are defined for the compound end members.^[16] Applying Eq 3 in this context, the chemical potential of compound end member i in the solution phase represented by the CEF model is generally given as^[17]:

$$\mu_i = g + \underbrace{\sum_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{i(s)j(s)} \frac{\partial g}{\partial y_{j(s)}}}_{\text{constituents in end member}} \quad (\text{Eq 64})$$

$$\underbrace{\sum_{s=1}^{N_s} \sum_{j=1}^{C_s} y_{j(s)} \frac{\partial g}{\partial y_{j(s)}}}_{\text{all constituents}}.$$

5.2.1 Derivation of Partial Molar Reference Gibbs Energy and Partial Molar Ideal Gibbs Energy of Mixing Contributions to Chemical Potential

Defining the derivative of the site fraction of constituent k on a sublattice a with respect to the site fraction of constituent j on a sublattice s as:

$$\frac{\partial y_{k(a)}}{\partial y_{j(s)}} = \delta_{as} \delta_{j(s)k(s)}, \quad (\text{Eq 65})$$

one can compute the partial derivative of Eq 63 with respect to $y_{j(s)}$ for all constituents j of compound end member i . Neglecting the partial excess Gibbs energy contribution, the following is obtained for a particular constituent:

$$\frac{\partial (g - g^{\text{ex}})}{\partial y_{j(s)}} = \sum_{k=1}^N g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \prod_{a=1}^{N_s} y_{k(a)} + RT v_s (1 + \ln (y_{j(s)})). \quad (\text{Eq 66})$$

Substituting Eq 66 into Eq 64 yields the reference and ideal mixing contributions to the chemical potential of compound end member i ^[17]:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= (g - g^{\text{ex}}) + \sum_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{i(s)j(s)} \left(\sum_{k=1}^N g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \right. \\ &\quad \left. \prod_{a=1}^{N_s} y_{k(a)} + RT v_s (1 + \ln (y_{j(s)})) \right) \\ &\quad - \sum_{s=1}^{N_s} \sum_{j=1}^{C_s} y_{j(s)} \left(\sum_{k=1}^N g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \prod_{a=1}^{N_s} y_{k(a)} \right. \\ &\quad \left. + RT v_s (1 + \ln (y_{j(s)})) \right), \end{aligned} \quad (\text{Eq 67})$$

which simplifies to the following:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= (g - g^{\text{ex}}) + \sum_{s=1}^{N_s} \sum_{k=1}^N g_k^{\circ} x_k \left(\frac{\delta_{i(s)k(s)}}{y_{k(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s (1 + \ln (y_{i(s)})) \\ &\quad - N_s \sum_{k=1}^N g_k^{\circ} x_k - RT \sum_{s=1}^{N_s} v_s \left(1 + \sum_{j=1}^{C_s} y_{j(s)} \ln (y_{j(s)}) \right). \end{aligned} \quad (\text{Eq 68})$$

Replacing the expression for $g - g^{\text{ex}}$ from Eq 61 into the preceding equation, the following is obtained:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= \sum_{k=1}^N g_k^{\circ} x_k \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln (y_{j(s)}) \right) + \sum_{s=1}^{N_s} \sum_{k=1}^N g_k^{\circ} x_k \left(\frac{\delta_{i(s)k(s)}}{y_{k(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s (1 + \ln (y_{i(s)})) \\ &\quad - N_s \sum_{k=1}^N g_k^{\circ} x_k - RT \sum_{s=1}^{N_s} v_s \left(1 + \sum_{j=1}^{C_s} y_{j(s)} \ln (y_{j(s)}) \right), \end{aligned} \quad (\text{Eq 69})$$

which simplifies to the following expression for reference and ideal mixing contributions to chemical potential of compound end member i :

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= \sum_{k=1}^N g_k^{\circ} x_k \left(1 - N_s + \sum_{s=1}^{N_s} \frac{\delta_{i(s)k(s)}}{y_{i(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s \ln (y_{i(s)}). \end{aligned} \quad (\text{Eq 70})$$

The chemical potential of a compound end member therefore includes contributions from the reference molar Gibbs energies of all compound end members in that phase and the ideal mixing contribution to μ_i only considers the constituents associated with the compound end member i .

5.2.2 Derivation of Partial Molar Excess Gibbs Energy of Mixing Contribution to Chemical Potential

Considering only the composition-independent interaction parameters, Sundman and Ågren gave an expression for the partial molar excess Gibbs energy of mixing of an end member in a CEF phase.^[17] However, a full derivation of partial molar excess Gibbs energy of mixing requires considering composition-dependent terms as well. Accounting for these interaction terms results in the following general expression:

$$\begin{aligned} \mu_i^{\text{ex}} = & \sum_{p=1}^{N_p} y_{j_p(s_p)} y_{k_p(s_p)} \left(\prod_{\substack{s=1 \\ s \neq s_p}}^{N_s} y_{l_p(s)} \right) \sum_{v=0}^{V_p} {}^v L_{j_p(s_p)k_p(s_p)}(y_{j_p(s_p)} \\ & - y_{k_p(s_p)})^v \cdot \left(-(N_s + v) + \frac{\delta_{i(s_p)j_p(s_p)}}{y_{j_p(s_p)}} + \frac{\delta_{i(s_p)k_p(s_p)}}{y_{k_p(s_p)}} \right. \\ & \left. + \sum_{s=1}^{N_s} \frac{\delta_{i(s)l_p(s)}}{y_{l_p(s)}} + \frac{v(\delta_{i(s_p)j_p(s_p)} - \delta_{i(s_p)k_p(s_p)})}{(y_{j_p(s_p)} - y_{k_p(s_p)})} \right) \\ & s \neq s_p \end{aligned} \quad (\text{Eq 71})$$

where terms such as $\delta_{i(s_p)j_p(s_p)}$ are Kronecker deltas equal to unity when the constituent associated with compound end member i on the mixing sublattice s_p is the same as the corresponding constituent of mixing parameter p , $j_p(s_p)$. Equation 71 depends only on the constituents j_p and k_p , and compound end member i . Therefore, this computation does not require looping over other end members and their constituents. Also, note that the indexing scheme used here differs from that of Sundman and Ågren.^[17] Sundman et al. use the variables $z > 0$ and b to represent the order of mixing where $z = b + 1$. To minimise confusion, $v \geq 0$ is used here.

6 Conclusion

Chemical potentials play a key role in the calculation of thermodynamic equilibrium of an isothermal, isobaric system. Explicit expressions for chemical potentials of the

independent variables are required by Gibbs energy minimisers for the formulation of the constraint vector associated with the Hessian matrix of the undetermined Lagrange multipliers and to update the system. A large number of classes of thermodynamic models have been proposed to describe the excess Gibbs energy of mixing for a wide variety of solution phases. While several papers are available in the literature that have described the development of those classes of models, derivations of the chemical potentials ready for implementation in a Gibbs energy minimiser have been absent from the literature. This paper provides full derivations of the chemical potentials of the species in several commonly-used classes of thermodynamic models, such as the substitutional solution model with Kohler–Toop and Muggiano interpolation schemes, and compound energy formalism. These derivations will enable researchers in developing new thermodynamic equilibrium solvers and in integrating the models described in this paper into their pre-existing software.

7 Supplementary Materials

To aid the readers in exploring and verifying the equations presented, Mathematica notebooks are available as supplementary material. Readers without a Mathematica license can use the free Wolfram Player (<https://www.wolfram.com/player/>) to view and interact with the notebooks. A sample PDF output from the notebooks is also attached.

Acknowledgments This research was funded, in part, by the U.S. Department of Energy Nuclear Energy Advanced Modeling and Simulation program. This research was undertaken, in part, thanks to funding from the Canada Research Chairs program and the Discovery Grant Program of the Natural Sciences and Engineering Research Council of Canada.

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