

Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models

P. Bajpai^a, M. Poschmann^a, M.H.A. Piro^{a,*}

^aUniversity of Ontario Institute of Technology, Oshawa, ON, Canada

Abstract

Numerous thermodynamic models have been developed to capture the behaviour of aqueous solutions, regular solid solutions, ionic ceramics, multi-sublattice metallic alloys, short and long range ordering, and much more. Classes of common thermodynamic models include regular solution, compound energy formalism, and modified quasi-chemical models. The mathematical formulation of the molar Gibbs energy of a phase represented by any of the aforementioned models takes on a unique form, which requires special consideration for use in a Gibbs energy minimizer. This paper provides derivations of the partial molar excess Gibbs energy of mixing of multiple common classes of thermodynamic models for use in a Gibbs energy minimizer.

Keywords: CALPHAD, Gibbs energy minimization, Regular Solution Model, Compound Energy Formalism, Modified Quasi-Chemical Model

Acronyms

FNN First Nearest Neighbour.

MQM Modified Quasichemical Model.

SNN Second Nearest Neighbour.

SRO Short-Range Ordering.

1. Introduction

Think about including a glossary. There will be a lot of variables, which will be difficult to keep sorted out.

*Corresponding author

Email address: markus.piro@uoit.ca ()

Specifically, one requires partial molar Gibbs energy terms to be used as input to a Hessian matrix to minimize G subject to appropriate constraints.

Consider submitting this a journal other than CALPHAD (e.g., Journal of Alloys and Compounds, Metallurgical and Materials Transactions, ...).

Give derivations of species, component, etc.

The partial molar excess Gibbs energy of mixing of species i in phase λ is by definition

$$g_{i(\lambda)}^{ex} = \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (1)$$

where n_i represents the number of moles of species i and the integral excess Gibbs energy of mixing is G_{λ}^{ex} , which is given by

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (2)$$

2. Regular Solution Model with Kohler-Toop Interpolation

2.1. Background on QKTO

Briefly describe the QKTO.

2.2. Derivation of Equations for QKTO

2.2.1. Derivation of Partial Excess Gibbs Energy of Mixing in a Sub-System

Suppose the molar excess Gibbs energy of mixing of a non-ideal solution phase sub-system is generally given by

$$g_{\lambda}^{ex} = \sum_{z=1}^Z \phi_z (x_1^{d_1} x_2^{d_2} x_3^{d_3}) \quad (3)$$

Representing the first equation in terms of n_i for all components gives

$$G_{\lambda}^{ex} = \sum_{z=1}^Z \phi_z \frac{(n_1^{d_1} n_2^{d_2} n_3^{d_3})}{n_{\lambda}^{d_1+d_2+d_3-1}} \quad (4)$$

Differentiation of equation (X) with respect to n_1 gives the partial molar excess Gibbs energy of mixing,

$$g_{1(\lambda)}^{ex} = \sum_{z=1}^Z \phi_z \left(\frac{(d_1 n_1^{d_1-1} n_2^{d_2} n_3^{d_3})}{n_{\lambda}^{d_1+d_2+d_3-1}} - (d_1 + d_2 + d_3 - 1) \frac{n_1^{d_1} n_2^{d_2} n_3^{d_3}}{n_{\lambda}^{d_1+d_2+d_3-2}} \right) \quad (5)$$

Simplifying gives the partial molar excess Gibbs energy of mixing of component 1 in a particular sub-system (note that this may not be the same as the phase):

$$g_{1(\lambda)}^{ex} = \sum_{z=1}^Z \phi_z \left((d_1 x_1^{d_1-1} + (1 - d_1 - d_2 - d_3) x_1^{d_1}) x_2^{d_2} x_3^{d_3} \right) \quad (6)$$

2.2.2. Derivation of the Partial Excess Gibbs Energy of Mixing of a Component in a Ternary Phase with a Binary Sub-System Using Kohlers Interpolation

This section considers the scenario where the sub-system contains fewer constituents than that represented by the phase. This example considers a phase with three constituents and a mixing parameter representing two of them. First, the mole fractions of all constituents are related by the following equality,

$$x_1 + x_2 + x_3 = 1 \quad (7)$$

and the total number of moles of this phase is,

$$n_1 + n_2 + n_3 = n_\lambda \quad (8)$$

The molar excess Gibbs energy of an arbitrary phase is estimated using Kohlers interpolation scheme:

$$g_\lambda^{ex} = (x_1 + x_2)^2 g_{1,2}^{ex} \quad (9)$$

where is the molar excess Gibbs energy in the 1-2 binary sub-system and is related to the integral excess Gibbs energy of the 1-2 binary sub-system:

$$g_{1,2}^{ex} = \frac{G_{1,2}^{ex}}{n_1 + n_2} \quad (10)$$

and the partial excess Gibbs energy of component 1 in the 1-2 binary sub-system is

$$g_{1(1,2)}^{ex} = \left(\frac{\partial G_{1,2}^{ex}}{\partial n_1} \right)_{n_{j \neq 1}} \quad (11)$$

and is calculated with equation (X) using the equivalent mole fractions. Multiplying equation (x) by and substitution of equation (X) gives the integral excess Gibbs energy of the phase is

$$G_\lambda^{ex} = \frac{(n_1 + n_2) G_{1,2}^{ex}}{n_\lambda} \quad (12)$$

The partial excess Gibbs energy of component 1 in phase alpha is:

$$g_1^{ex} = \frac{(n_1 + n_2) g_{1,2}^{ex}}{n_\lambda} + \frac{(n_1 + n_2) g_{1(1,2)}^{ex}}{n_\lambda} - \frac{(n_1 + n_2)^2 g_{1,2}^{ex}}{n_\lambda^2} \quad (13)$$

which simplifies to:

$$g_1^{ex} = (x_1 + x_2) \left(g_{1(1,2)}^{ex} + (1 - (x_1 + x_2)) g_{1,2}^{ex} \right) \quad (14)$$

WHAT ABOUT COMPONENT 2???

Similarly, for component 3:

$$g_3^{ex} = -(x_1 + x_2)^2 g_{1(1,2)}^{ex} \quad (15)$$

2.2.3. Derivation of the Partial Excess Gibbs Energy of Mixing of a Component in a Multicomponent (more than three) Phase with a Ternary Sub-System Using Kohlers Interpolation

The molar excess Gibbs energy of an arbitrary phase is

$$g_\lambda^{ex} = (x_1 + x_2 + x_3)^3 g_{1,2,3}^{ex} \quad (16)$$

which is expanded to:

$$g_\lambda^{ex} = \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^3 \frac{G_{1,2,3}^{ex}}{n_1 + n_2 + n_3} \quad (17)$$

The integral excess Gibbs energy of an arbitrary phase is

$$G_\lambda^{ex} = \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^2 G_{1,2,3}^{ex} \quad (18)$$

The partial molar excess Gibbs energy of mixing of component 1 is

$$g_{1(\lambda)}^{ex} = 2 \left(\frac{n_1 + n_2 + n_3}{n_\lambda^2} \right) G_{1,2,3}^{ex} + \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^2 g_{1(1,2,3)}^{ex} - 2 \left(\frac{(n_1 + n_2 + n_3)^2}{n_\lambda^3} \right) G_{1,2,3}^{ex} \quad (19)$$

which simplifies to:

$$g_{1(\lambda)}^{ex} = (x_1 + x_2 + x_3)^2 \left(g_{1(1,2,3)}^{ex} + 2g_{1,2,3}^{ex}(1 - (x_1 + x_2 + x_3)) \right) \quad (20)$$

And where the partial molar excess Gibbs energy of mixing of component j ($\neq 1, 2, 3$) is:

$$g_{j(\lambda)}^{ex} = -(x_1 + x_2 + x_3)^3 (2g_{1,2,3}^{ex}) \quad (21)$$

3. Regular Solution Model with Muggiano Interpolation

3.1. Background on RKMP

Insert background here.

3.2. Derivation of Equations for RKMP

THINK ABOUT WHICH VARIABLES SHOULD BE USED. SHOULD v OR ν BE USED FOR EXPONENTS? SHOULD WE USE 1 AND 2 TO REPRESENT SPECIES, OR A AND B?

3.2.1. Binary mixing terms

An important distinction between the Muggiano interpolation scheme and the Kohler and Toop schemes is that if Redlich-Kister polynomials are used to represent mixing parameters, then the molar excess Gibbs energy of mixing involving binary interaction parameters is simply [1] [2].

$$g_{\lambda}^{ex} = \sum_{z=1}^Z x_j x_k \sum_{\nu=0}^{\nu} L_{j,k} (x_j - x_k)^{\nu} \quad (22)$$

and the equations are simplified in comparison to Kohler/Toop schemes. Kohler/Toop interpolation schemes require special consideration when relating binary interaction parameters for the molar Gibbs energy of a phase. For the above equation, x_j and x_k are the mole fractions of species j and k that correspond to parameter index z , the total number of mixing parameters is denoted by Z and is the temperature dependent mixing parameter for the ν -th order parameter. The partial molar excess Gibbs energy of mixing of constituent i in phase λ is by definition

$$g_{i(\lambda)}^{ex} = \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (23)$$

where $n_{i(\lambda)}$ represents the number of moles of species i . The integral excess Gibbs energy of mixing for solution phase λ is,

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (24)$$

where n_{λ} represents the total number of moles of phase λ . Representing equation X in terms of molar quantities instead of mole fractions gives,

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (25)$$

Substituting equation X into equation X gives,

EQUATION (include?)

Substituting equation X into equation X gives the partial molar excess Gibbs energy of mixing of constituent 1 from parameter z in solution phase ,

EQUATION (include?)

Representing relative molar quantities by mole fractions and simplifying gives,

$$g_{1(\lambda,z)}^{ex} = {}^v L_{1,2}(x_1 - x_2)^{v-1} ((x_2 - x_1 x_2)(x_1 - x_2) + v x_1 x_2 (1 - (x_1 - x_2))) \quad (26)$$

Similarly, the partial molar excess Gibbs energy of mixing for the second constituent in mixing parameter z is,

$$g_{2(\lambda,z)}^{ex} = {}^v L_{1,2}(x_1 - x_2)^{v-1} ((x_1 - x_1 x_2)(x_1 - x_2) - v x_1 x_2 (1 + (x_1 - x_2))) \quad (27)$$

And finally any other species is,

$$g_{i \neq 1,2(\lambda,z)}^{ex} = -{}^v L_{1,2}(x_1 - x_2)^v (x_1 x_2)(1 + v) \quad (28)$$

Therefore, the partial molar excess Gibbs energy of mixing of any constituent is the sum of the partial molar excess Gibbs energy of that constituent for all mixing parameters in solution phase λ ,

$$g_{i(\lambda)}^{ex} = \sum_{z=1}^Z g_{i(\lambda,z)}^{ex} \quad (29)$$

3.2.2. Ternary Terms

Ternary terms are represented in an RKMP model with the following equation, which only contains zero-th order parameters (as opposed to higher order parameters permitted for binary interaction terms) [1]
CONFIRM that there are only zeroth order terms for ternary interaction parameters

$$g_{(\lambda)}^{ex} = x_1 x_2 x_3 \left(\frac{1 - x_1 - x_2 - x_3}{3} + x_j \right) {}^0 L_{1,2,3} \quad (30)$$

where $j = 1, 2$, or 3 . FactSage-Solution does not allow the user to manually change the exponents of the mole fractions of constituents in a RKMP phase. According to Chartrand and Pelton [1], this constraint is imposed on the user due to the little theoretical justification of using higher order exponents.

The integral Gibbs energy of mixing for a ternary parameter is,

EQUATION (include?)

Inserting from equation X into equation X and differentiating with respect to X gives

EQUATION (include?)

Let the Kronecker-Delta term be defined for convenience,

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

Thus, simplifying the above equation using mole fractions and the Kronecker-Delta term gives,

$$g_{1(\lambda,z)}^{ex} = \left[(x_2x_3 - 3x_1x_2x_3) \left(\frac{1 - x_1 - x_2 - x_3}{3} \right) + x_j \right] + x_1x_2x_3\delta_{i,j} \Big]^0 L_{1,2,3} \quad (31)$$

Similarly, the partial molar excess Gibbs energy of mixing of constituent 2 in a ternary phase is,

$$g_{2(\lambda,z)}^{ex} = \left[(x_1x_3 - 3x_1x_2x_3) \left(\frac{1 - x_1 - x_2 - x_3}{3} \right) + x_j \right] + x_1x_2x_3\delta_{i,j} \Big]^0 L_{1,2,3} \quad (32)$$

and for constituent 3 *WHY IS x_j MULTIPLIED BY THREE BELOW AND NOT ABOVE?*

$$g_{3(\lambda,z)}^{ex} = \left[(x_1x_2 - 3x_1x_2x_3) \left(\frac{1 - x_1 - x_2 - x_3}{3} \right) + 3x_j \right] + x_1x_2x_3\delta_{i,j} \Big]^0 L_{1,2,3} \quad (33)$$

and for any other constituent,

$$g_{i \neq 1,2,3(\lambda,z)}^{ex} = (x_1x_2x_3)(x_1 + x_2 + x_3 - 3x_j - \frac{2}{3})^0 L_{1,2,3} \quad (34)$$

Note that for any constituent not belonging to the ternary mixing parameter, necessarily equals zero because $j = 1, 2$ or 3 by definition.

3.2.3. Quaternary Terms

Quaternary terms are represented in an RKMP model with the following equation, which only contains zero-th order parameters (as opposed to higher order parameters permitted for binary interaction terms) [2],

$$g_{\lambda}^{ex} = x_1x_2x_3x_4^0 L_{1,2,3,4} \quad (35)$$

FactSage-Solution allows the user to enter exponents; however, they are not included in the model and are just confusing to the user. The integral Gibbs energy of mixing for a quaternary parameter is,

EQUATION (include?)

Inserting from equation (20) into equation (2) and differentiating with respect to gives

EQUATION (include?)

Thus, simplifying the above equation using mole fractions

$$g_{i(\lambda)}^{ex} = x_1x_2x_3x_4 \left(\frac{1}{x_i} - 3 \right)^0 L_{1,2,3,4} \quad (36)$$

where $i = 1, 2$, or 3 . Finally, the partial molar excess Gibbs energy of mixing for any other constituent,

$$g_{i \neq (1,2,3,4)(\lambda)}^{ex} = -3x_1x_2x_3x_4^0 L_{1,2,3,4} \quad (37)$$

3.2.4. Comments

Consider a special case where $x_1 = x_2$ and the equations above may yield infinite or non-real values. The solver must make provisions for such scenarios depending on the compiler that is used. Consider the following scenarios:

i. Consider $x_1 = x_2$ and $v_{Li,j}$ where $v = 0$. Note that $0/0=1$ and $0/0 = 1$; although some may argue that these two special cases are undefined. ii. Consider $x_1 = x_2$ and $v_{Li,j}$ where $v \neq 1$. Note that $0/1=0$ and $0/0 = 1$; although some may argue that these two special cases are undefined.

Note that Fortran returns $0/0 = 1$, $0/0 = \text{NaN}$ and $1/0 = \text{inf}$. A simple solution to this problem is to evaluate the following term independently,

(24)

and set

(25)

Therefore, q_a may be infinite if $x_1 = x_2$ and $v = 0$, but q_b

4. Compound Energy Formalism

4.1. Background on CEF

A common source of confusion with those uninitiated with the Compound Energy Formalism (CEF) is the distinction between the terms, “species”, “constituent” and “component”. Following the nomenclature of Hillert [3], the term “species” refers to a molecule, pure element, vacancy or ion, and the term “constituent” refers to a particular species on a particular sublattice. The term “component” is used in the context of the CEF to refer to a unique combination of constituents on each sublattice, or “compound end member”. The total number of components of a CEF phase is the product of the number of constituents on each sublattice.

For example, the solid solution $\text{UO}_{2\pm x}$ phase [4] may be represented by the CEF model with three sublattices, where U^{3+} , U^{4+} and U^{5+} are species on the first sublattice, O^{2-} and Va are species on the second sublattice and O^{2-} and Va are species on the third sublattice. Also, $\text{O}_{(2)}^{2-}$ and $\text{O}_{(3)}^{2-}$ represent the same species but are different constituents because they reside on different sublattices (as identified by the subscripts). Since there are three constituents on the first sublattice, two on the second and two on the third sublattice, the total number of components for this phase is twelve. These constituents can be combined to form the following components $\text{U}^{4+}:\text{O}^{2-}:\text{Va}$ (i.e., UO_2), $\text{U}^{4+}:\text{O}^{2-}:\text{O}^{2-}$ (i.e., UO_3^{2-}), in addition to several others. Continuing with the representation of components from Hillert, the constituents on each sublattice is separated by a colon, “:”. Finally, standard molar Gibbs energy expressions are defined for each component and excess Gibbs energy of mixing parameters are defined between components.

The molar Gibbs energy, g_λ , of solution phase λ based on the CEF model is generally given as,

$$g_\lambda = \sum_{i=1}^{N_\lambda} g_{i(\lambda)}^\circ \prod_{s=1}^{N_s} y_{i(s)} + RT \left(\sum_{s=1}^{N_s} a_s \sum_{c=1}^{N_c} y_{c(s)} \ln(y_{c(s)}) \right) + g_\lambda^{ex} \quad (38)$$

where $g_{i(\lambda)}^\circ$ is the standard molar Gibbs energy of the pure component i , $y_{i(s)}$ represents the site fraction on sublattice s corresponding to component i , N_λ and N_s denote the number of components and number of sublattices in solution phase λ , respectively. The ideal gas constant is represented by R , the absolute temperature by T , the stoichiometry coefficient for sublattice s is represented by a_s , the number of constituents on sublattice s is N_c and the site fraction of constituent c on sublattice s is $y_{c(s)}$. It is to be understood that $y_{i(s)}$ refers to the site fraction of constituent c associated with component i on sublattice s and is thus related to $y_{c(s)}$. Finally, the molar excess Gibbs energy of mixing of solution phase λ is g_λ^{ex} .

Several constraints are applied to a phase modelled by the CEF. First, the sum of site fractions for each sublattice must equal unity,

$$\sum_{c=1}^{N_c} y_{c(s)} = 1 \quad (39)$$

and the sum of mole fractions of all components in a solution phase (recall that the components differ from the constituents) must also equal unity,

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1 \quad (40)$$

As a natural consequence of the formulation of components from the constituents, the constraints represented by equation (40) are necessarily satisfied when equation (39) is satisfied, and vice versa. The mole fraction of a component is related to the site fraction of all associated constituents on each sublattice (i.e., a component will be represented by one constituent on every sublattice) through the following relationship,

$$x_{i(\lambda)} = \prod_{s=1}^{N_s} y_{i(s)} \quad (41)$$

As an example, the mole fraction for component $U^{4+}:O^{2-}:Va$ is computed as $x_{U^{4+}:O^{2-}:Va} = y_{U^{4+}(1)} y_{O^{2-}(2)} y_{Va(3)}$. Also, the site fraction of a constituent on a particular sublattice is related to the mole fractions of the components through the following summation relation:

$$y_{c(s)} = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \delta_{i,c(s)} \quad (42)$$

where $\delta_{i,c(s)}$ is a Kronecker delta term that is equal to unity when constituent c on sublattice s is the same as the corresponding constituent for component i and is otherwise equal to zero. At equilibrium, equations (41)

and (42) must be equivalent. However, from a numerical point of view, equation (42) is insensitive to the mole fractions of dilute components because it is a summation function. On the other hand, equation (41) is sensitive to dilute site fractions because it is a multiplicative function. This must be taken into consideration in the programming to minimize numerical errors.

An analytical derivation of $\mu_{i(\lambda)}$ that is useful for computer calculation for an ideal solution phase will be given in §?? and for a non-ideal solution phase in §??.

4.2. Derivation of Equations for CEF

The chemical potential of component i in solution phase λ represented by a CEF model is generally given as [5],

$$\mu_{i(\lambda)} = g_\lambda + \sum_{s=1}^{N_s} \left(\frac{\partial g_\lambda}{\partial y_{i(s)}} - \sum_{j=1}^{N_\lambda} y_{j(s)} \frac{\partial g_\lambda}{\partial y_{j(s)}} \right) \quad (43)$$

First, one must evaluate the partial derivative of equation (38) with respect to $y_{i(s)}$,

$$\frac{\partial g_\lambda}{\partial y_{i(s)}} = \sum_{j=1}^{N_\lambda} g_{j(\lambda)}^\circ \left(\frac{\delta_{i,j}}{y_{i(s)}} \right) \prod_{s=1}^{N_s} y_{j(s)} + RT \sum_{s=1}^{N_s} a_s \ln(y_{i(s)} + 1) \quad (44)$$

where $\delta_{i,j}$ is a Kronecker delta term that is equal to unity when the constituents correspond to i and j are the same and is otherwise equal to zero. Substituting equation (44) into equation (43) yields the chemical potential for component i in an *ideal* solution phase represented by the CEF model [5]

$$\mu_{i(\lambda)} = \sum_{j=1}^{N_\lambda} x_{j(\lambda)} g_{j(\lambda)}^\circ \left(1 - N_s + \sum_{s=1}^{N_s} \frac{\delta_{i,j}}{y_{j(s)}} \right) + RT \sum_{s=1}^{N_s} a_s \ln(y_{i(s)}) \quad (45)$$

The chemical potential of a component in a phase based on the CEF model therefore includes contributions from the standard molar Gibbs energies of all components in that phase. The ideal mixing contribution to $\mu_{i(\lambda)}$ only considers the constituents associated with component i .

The molar Gibbs energy for a non-ideal solution phase based on the CEF model is represented by equation (38) with a non-zero value for g_λ^{ex} . The molar excess Gibbs energy of mixing is generally represented as

$$g_\lambda^{ex} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_p} y_{m(s)} \right) \sum_{z=0}^{N_z} {}^z L_{j,k} (y_j - y_k)^z \quad (46)$$

where N_p denotes the number of excess mixing parameters (note: $N_p \geq N_s$), y_m is the site fraction of constituent m corresponding to mixing parameter p , N_z is the number of terms corresponding to parameter

p , and ${}^zL_{j,k}$ is the z th order mixing parameter. For example, the molar excess Gibbs energy of mixing for the $\text{UO}_{2\pm x}$ fluorite phase is

$$g_{\text{fluorite}}^{ex} = y_{\text{U}^{3+}}y_{\text{U}^{4+}}y_{\text{O}^{2-}}y_{\text{Va}} \left({}^0L_{(\text{U}^{3+},\text{U}^{4+})(\text{O}^{2-})_2}(\text{Va}) + (y_{\text{U}^{3+}} - y_{\text{U}^{4+}})^1 L_{(\text{U}^{3+},\text{U}^{4+})(\text{O}^{2-})_2}(\text{Va}) \right) + y_{\text{U}^{4+}}y_{\text{U}^{5+}}y_{\text{O}^{2-}}y_{\text{O}^{2-}}^0 L_{(\text{U}^{4+},\text{U}^{5+})(\text{O}^{2-})_2}(\text{Va}) \quad (47)$$

The partial molar excess Gibbs energy of mixing of a component in a CEF phase is derived by Sundman *et al.* [5] for the case of composition independent interaction parameters. Here, the partial molar excess Gibbs energy of mixing allows for composition dependent terms to be considered,

$$g_{i(\lambda)}^{ex} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_p} y_{m(s)} \right) \sum_{z=0}^{\infty} {}^zL_{j,k} (y_j - y_k)^z \left(-(N_s + z) + \sum_{s=1}^{N_s} \frac{\delta_{i,p}}{y_{i(s)}} - \frac{z}{(y_j - y_k)} \right) \quad (48)$$

where $\delta_{i,e}^s$ is a Kronecker delta term which is equal to unity when the constituent associated with component i on sublattice s is the same as the corresponding constituent of mixing parameter p . Unlike the contribution from the reference molar Gibbs energy, the only terms in equation (48) that are component dependent are $\delta_{i,p}$ and y_i . Thus, only component i must be considered in computing the partial molar excess Gibbs energy of mixing of component i . Also, note that the indexing scheme used here differs from that of Sundman *et al.* [5]. Sundman *et al.* use the variables z (where $z > 0$) and b to represent the order of mixing where $z = b + 1$. To minimize confusion, only z is used here (where $z \geq 0$).

As an example, consider computing $g_{i(\lambda)}^{ex}$ for component $\text{U}^{3+}:\text{O}^{2-}:\text{Va}$ in the $\text{UO}_{2\pm x}$ phase. One of the mixing parameters in this phase considers the mixing between components $\text{U}^{4+}:\text{O}^{2-}:\text{O}^{2-}$ and $\text{U}^{5+}:\text{O}^{2-}:\text{O}^{2-}$, which is commonly written in short hand notation as $(\text{U}^{4+},\text{U}^{5+})(\text{O}^{2-})(\text{O}^{2-})$. The contribution from this particular mixing parameter to the partial molar excess Gibbs energy of mixing of component $\text{U}^{3+}:\text{O}^{2-}:\text{Va}$ requires evaluation of the Kronecker delta terms for each sublattice. Since the constituent on the first sublattice of this component (i.e., U^{3+}) is not represented by this mixing parameter, the Kronecker delta term for the first sublattice is zero. However, since the constituent on the second sublattice of this component (i.e., O^{2-}) is represented by this mixing parameter, the Kronecker delta for the second sublattice is equal to unity.

The number of components in a CEF phase is equal to the product of the number of sites

5. Modified Quasichemical Model

5.1. Background on MQM

The **Modified Quasichemical Model (MQM)** in the quadruplet approximation is the most generalized thermodynamic model for treating **Short-Range Ordering (SRO)**. The **MQM** is fundamentally different than

other thermodynamic models in that the focus is not on the mixing of chemical species or constituents on a lattice, but rather the mixing of species as quadruplets to capture **SRO** of both **FNN** and **SNN** in liquid or solid solutions. The details of evolution of **MQM** from pair approximation for species mixing on only one sublattice to the current quadruplet approximation are provided by Pelton *et al.* [6, 7, 8, 9]

For a solution with two sublattices, which is occupied only by a single species on the second sublattice, the SNN pair exchange can be written as:

$$(A - [X] - A) + (B - [X] - B) = 2(A - [X] - B); \Delta g_{AB/X} \quad (49)$$

where $\Delta g_{AB/X}$ is the non-configurational Gibbs energy for the formation of 2 mol of $(A - [X] - B)$ pairs. Similarly, when there is a single species on the first sublattice, the formation of **SNN** pairs is captured via:

$$(X - [A] - X) + (Y - [A] - Y) = 2(X - [A] - Y); \Delta g_{A/XY} \quad (50)$$

where $\Delta g_{A/XY}$ is the non-configurational Gibbs energy for the formation of 2 mol of $(X - [A] - Y)$ pairs.

Among the **FNN** pairs, the following exchange reaction is considered:

$$(A - X) + (B - Y) = (A - Y) + (B - X); \Delta g_{A/XY}^{exchange} \quad (51)$$

where $\Delta g_{A/XY}^{exchange}$ is the non-configurational Gibbs energy.

Let n_i ($i = A, B, \dots, X, Y \dots$) represent the number of moles of species i , $n_{i/j}$ be the number of moles of **FNN** ($(i - j)$) pairs, and $n_{ij/kl}$ be the number of moles of the quadruplets. The relationship between the foregoing terms is [9]

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \dots \quad (52)$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \dots \quad (53)$$

where Z_A and Z_B are the coordination numbers for A and B, respectively. A generic statement for a multi-component system is (fix this equation to be a general equation !!!)

$$Z_i n_i = 2n_{ii} + \sum_{j \neq i} n_{ij} \quad (54)$$

The mole fractions then follow:

$$x_i = \frac{n_i}{\sum n_j} \quad (55)$$

$$x_k = \frac{n_k}{\sum n_l} \quad (56)$$

where the indices i and j refer to the species on first sublattice while the indices k and l refer to the species on second sublattice.

The FNN pair fractions and quadruplet fractions are defined as:

$$x_{i/k} = \frac{n_{i/k}}{\sum_j \sum_l n_{j/l}} \quad (57)$$

$$x_{ij/kl} = \frac{n_{ij/kl}}{\sum n_{ij/kl}} \quad (58)$$

Another useful term is the coordination equivalent fraction, which is

$$y_i = \frac{Z_i n_i}{\sum Z_j n_j} \quad (59)$$

$$y_k = \frac{Z_k n_k}{\sum Z_l n_l} \quad (60)$$

Since the coordination numbers of the constituents are not equal like in solid solutions and can vary with composition, a composition dependence can be defined. Assuming that all species of a constituent m exist in quadruplets with non-repeating constituents, the SNN coordination number of a species of m , $z_{ij/kl}^m$, are defined such that they result in the following relations

$$n_A = \frac{2n_{A_2/X_2}}{z_{A_2/X_2}^A} + \frac{2n_{A_2/Y_2}}{z_{A_2/Y_2}^A} + \frac{2n_{A_2/XY}}{z_{A_2/XY}^A} \quad (61)$$

The non-configurational Gibbs energy term is given by:

$$\Delta g_{AB} = \Delta g_{AB}^\circ + \sum_{p \geq 1} \sum_{q \geq 1} x_{AA}^p x_{BB}^q g_{AB}^{pq} \quad (62)$$

The integral Gibbs energy of solution is given by

$$G_\lambda = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{config} + \frac{n_{AB} \Delta g_{AB}}{2} \quad (63)$$

where g_i° is the reference molar Gibbs energy of pure i (computed from a database), T is the absolute temperature, and ΔS^{config} is the configurational entropy, given by

$$\Delta S^{config} = -R (n_A \ln(x_A) + n_B \ln(x_B) + n_{AA} \ln(x_{AA}/y_A^2) + n_{BB} \ln(x_{BB}/y_B^2) + n_{AB} \ln(x_{AB}/(2y_A y_B))) \quad (64)$$

In this derivation, one defines the quantities of the phase components as the independent variables, namely n_A and n_B . One would then have to compute the quantities of the pair fractions, which are necessarily greater in number. One could compute these quantities; however, it would require an additional iterative cycle to solve a separate system of non-linear equations. Instead, a more productive approach that Pelton *et al* recommend is to reformulate the problem such that the pair fractions are the independent variables [6]. The interested reader is referred to Pelton *et al* [6] for a derivation.

The integral Gibbs energy of a solution phase represented by MQM can be written in an alternate form that differs from equation (63):

$$\begin{aligned}
G_\lambda = & (n_{AA}g_{AA}^\circ + n_{BB}g_{BB}^\circ + n_{AB}g_{AB}^\circ) \\
& + RT \left(n_{AA}\ln(x_{AA}) + n_{BB}\ln(x_{BB}) + n_{AB}\ln(x_{AB}) \right. \\
& + n_A\ln(x_A) + n_B\ln(x_B) - n_{AA}\ln(y_A^2) - n_{BB}\ln(y_B^2) - n_{AB}\ln(2y_Ay_B) \left. \right) \\
& + G_\lambda^{ex}
\end{aligned} \tag{65}$$

where G_λ^{ex} is the integral excess Gibbs energy of mixing, given by:

$$G_\lambda^{ex} = \left(\frac{n_{AA} + n_{BB} + n_{AB}}{2} \right) \left(x_{AA}x_{AB} \sum_{p \geq 1} g_{AB}^p x_{AA}^{p-1} + x_{BB}x_{AB} \sum_{q \geq 1} g_{AB}^q x_{BB}^{q-1} \right) \tag{66}$$

Note that equation (65) is a function of the reference molar Gibbs energies of the pair fractions, not the phase components. One can compute the former as a function of the phase components through the following relationships [6]:

$$g_{AA}^\circ = \frac{2g_A^\circ}{Z_{AA}^A} \quad g_{BB}^\circ = \frac{2g_B^\circ}{Z_{BB}^B} \quad g_{AB}^\circ = \frac{\Delta g_{AB}^\circ}{2} + \frac{g_A^\circ}{Z_{AB}^A} + \frac{g_B^\circ}{Z_{BA}^B} \tag{67}$$

Finally, one will need to compute coordination numbers that may vary with respect to composition, such that:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \tag{68}$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \tag{69}$$

where Z_A and Z_B are the coordination numbers of A and B, Z_{AA}^A is the value of Z_A when all neighbors of an A are A's, and Z_{AB}^A is when all nearest neighbors of an A are B's.

To summarize, one can represent the integral Gibbs energy of a solution phase represented by the MQM model using equation (65) by treating the independent variables as the molar quantities of the pair fractions using equations (67), (68), and (69). A thermodynamic database would provide values for Z_{ij}^k and equations for the reference molar Gibbs energy of the phase components and excess molar Gibbs energy of mixing terms.

5.2. Derivation of Equations for MQM

MAKE CLEAR THAT ONE SHOULD USE THE APPROACH RECOMMENDED BY PELTON ET AL WHEREBY PAIRS ARE TREATED AS FRACTIONAL “ASSOCIATES”. THIS ALLOWS ONE TO EASILY MODIFY EXISTING GEM CODES...

The preceding section gave a summary of the MQM model and a derivation of integral Gibbs energy equations. This section provides a derivation of equations necessary to compute thermochemical equilibria.

Derivation of the chemical potential of AA gives:

$$\begin{aligned}\mu_{AA} &= \left(\frac{\partial G_\lambda}{\partial n_{AA}} \right)_{T,P,n_j \neq AA} \\ &= g_{AA}^\circ + RT \left(\frac{2\ln(x_A)}{Z_{AA}^A} + \ln \left(\frac{x_{AA}}{y_A^2} \right) \right) + g_{AA}^{ex}\end{aligned}\quad (70)$$

where g_{AA}^{ex} is the partial molar excess Gibbs energy of mixing of AA. Similarly, the chemical potential of BB is:

$$\begin{aligned}\mu_{BB} &= \left(\frac{\partial G_\lambda}{\partial n_{BB}} \right)_{T,P,n_j \neq BB} \\ &= g_{BB}^\circ + RT \left(\frac{2\ln(x_B)}{Z_{BB}^B} + \ln \left(\frac{x_{BB}}{y_B^2} \right) \right) + g_{BB}^{ex}\end{aligned}\quad (71)$$

and the chemical potential of AB is:

$$\begin{aligned}\mu_{AB} &= \left(\frac{\partial G_\lambda}{\partial n_{AB}} \right)_{T,P,n_j \neq AB} \\ &= \frac{g_A^\circ}{Z_{AB}^A} + \frac{g_B^\circ}{Z_{BA}^B} + RT \left(\ln \left(\frac{x_{AB}}{2y_A y_B} \right) + \frac{\ln(x_A)}{Z_{AB}^A} + \frac{\ln(x_B)}{Z_{BA}^B} \right) + g_{AB}^{ex}\end{aligned}\quad (72)$$

Note that equation (62) is written in a familiar form to what is given by Pelton [6, 7]. This equation can be reformulated in a more amenable form for programming such that:

$$\Delta g_{AB} = \sum_{p \geq 0} \sum_{q \geq 0} x_{AA}^p x_{BB}^q g_{AB}^{pq} \quad (73)$$

where one may interpret Δg_{AB}° as g_{AB}^{ij} with $i = 0$ and $j = 0$. One should be conscientious of the removal of Δg_{AB}° from equation (67), which is noticeable in equation (72) and is naturally included in equation (77) below. With this term, one can therefore compute the excess Gibbs energy of mixing in a simpler form.

$$G_\lambda^{ex} = \frac{n_{AB}}{2} \Delta g_{AB} \quad (74)$$

Solving for the partial molar excess Gibbs energy of mixing of AA gives:

$$\begin{aligned} g_{AA}^{ex} &= \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_{AA}} \right)_{T,P,n_j \neq AA} \\ &= \left(\frac{x_{AB} x_{AA}^{p-1} x_{BB}^q (p(x_{BB} + x_{AB}) - q x_{AA})}{2} \right) g_{AB}^{pq} \end{aligned} \quad (75)$$

Similarly, the partial molar excess Gibbs energy of mixing of BB is:

$$\begin{aligned} g_{BB}^{ex} &= \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_{BB}} \right)_{T,P,n_j \neq BB} \\ &= \left(\frac{x_{AB} x_{AA}^{p+1} x_{BB}^q (q(x_{AA} + x_{AB}) - p x_{BB})}{2 x_{AA} x_{BB}} \right) g_{AB}^{pq} \end{aligned} \quad (76)$$

Finally, the partial molar excess Gibbs energy of mixing of AB is:

$$\begin{aligned} g_{AB}^{ex} &= \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_{AB}} \right)_{T,P,n_j \neq AB} \\ &= \left(\frac{x_{AA}^{p+1} x_{BB}^q (x_{AB}(1-p-q) + x_{AA} + x_{BB})}{2 x_{AA}} \right) g_{AB}^{pq} \end{aligned} \quad (77)$$

I've found that a concern with the MQM phase is that many times the Hessian has a nearly inconsistent row and is difficult to solve the system of linear equations. Why is that exactly? I need to really wrap my head around this but in a way the system is represented by two species, but not really...why is this happening? I took some example calculations of the LiF-BeF₂ system and solved the system of linear equations in Excel in simultaneously from Thermochemica at three different iterations near one another. The molar quantities of the pairs did not change very much at all and therefore the Hessian did not change much either. Solving the system of equations in both Thermochemic and Excel yielded wildly different values for the Lagrangian multipliers for all three iterations. One would expect that they would be somewhat close – at the very least the same order of magnitude and sign – but that was not the case. I should think about how to tackle this problem. To temporarily solve this problem, I increased the maximum # of iterations to 5000 (from 3000). This seemed to solve the problem at least in the interim.

5.2.1. Special Cases for MQM

Talk about how by definition of the model one creates an under-determined Hessian matrix. Take the LiF-BeF₂ pseudo-binary system as an example. In this case, A = LiF and B = BeF₂. Therefore, one deals with AA = LiF-LiF, BB = BeF₂-BeF₂, and AB = LiF-BeF₂. In this case, the system components are taken as the chemical elements (i.e., Li, F, Be) and the independent variables are associated with the species AA,

BB, and AB. However, one cannot uniquely define a Gibbs plane by these three points because they are coincident in composition space. See figure below. *This about creating a 3D plot with the ternary as a base to demonstrate that it's not a 3D surface but rather a curve.*

It looks like Thermochemica can solve this problem just fine...small imprecisions in the stoichiometries and co-ordination numbers appear to help prevent the Hessian from having a true inconsistent row. I believe that the analogy of defining a plane by three colinear points needs to be used whereby the plane is wobbling about this line. Despite the plane wobbling about this line, the functional norm can still make great progress because the functional norm doesn't care about how much ΔG changes – it cares about how much the Gibbs Criteria is respected. For that reason, I relaxed the constraint that $d\Delta G$ is set to 100 (instead of between 1 and 5). As a result, now only does it converge, but it also converges in a small number of iterations (e.g., 10-50).

6. Conclusion

7. Acknowledgements

The authors thank P. Chartrand (Ecole Polytechnique) for stimulating discussions. 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.

References

- [1] P. Chartrand and A. Pelton, "On the choice of geometric thermodynamic models," *Journal of Phase Equilibria*, vol. 21, no. 2, pp. 141–147, 2000.
- [2] G. Eriksson and K. Hack, "Chemsage – a computer program for the calculation of complex chemical equilibria," *Metallurgical and Materials Transactions B*, vol. 21B, pp. 1013–1023, 1990.
- [3] M. Hillert, "The compound energy formalism," *Journal of Alloys and Compounds*, vol. 320, no. 2, pp. 161 – 176, 2001.
- [4] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F. D. Bruycker, D. Manara, and R. J. Konings, "Thermodynamic modelling of advanced oxide and carbide nuclear fuels: Description of the U-Pu-O-C systems," *Journal of Nuclear Materials*, vol. 419, no. 1-3, pp. 145–167, 2011.

- [5] B. Sundman and J. Ågren, “A regular solution model for phases with several components and sublattices, suitable for computer applications,” *Journal of Physics and Chemistry of Solids*, vol. 42, pp. 297–301, 1981.
- [6] A. Pelton, S. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, “The modified quasichemical model I – binary solutions,” *Metallurgical and Materials Transactions B*, vol. 31B, pp. 651–659, 2000.
- [7] A. Pelton and P. Chartrand, “The modified quasichemical model II – multicomponent solutions,” *Metallurgical and Materials Transactions A*, vol. 32A, pp. 1355–1360, 2001.
- [8] P. Chartrand and A. Pelton, “The modified quasichemical model III – two sublattices,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1397–1407, 2001.
- [9] A. Pelton, P. Chartrand, and G. Eriksson, “The modified quasichemical model IV – two-sublattice quadruplet approximation,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1409–1416, 2001.