The Modified Quasi-Chemical Model: Part II. Multicomponent Solutions

ARTHUR D. PELTON and PATRICE CHARTRAND

Further improvements to the modified quasi-chemical model in the pair approximation for short-range ordering (SRO) in liquids are extended to multicomponent solutions. The energy of pair formation may be expanded in terms of the pair fractions or in terms of the component fractions, and coordination numbers are permitted to vary with composition. The model permits complete freedom of choice to treat any ternary subsystem with a symmetric or an asymmetric model. An improved general functional form for "ternary terms" in the excess Gibbs energy expression is proposed. These terms are related to the effect of a third component upon the binary pair interaction energies. It is shown how binary subsystems that have been optimized with the quasi-chemical model can be combined in the same multicomponent Gibbs energy equation with binary subsystems that have been optimized with a random-mixing Bragg-Williams model and a polynomial expression for the excess Gibbs energy. This is of much practical importance in the development of large databases for multicomponent solutions. The model also applies to SRO in solid solutions as a special case, when the number of lattice sites and coordination numbers are constant.

I. INTRODUCTION

IN a series of articles,[1–4] we introduced the modified quasi-chemical model for short-range order in liquids in the pair approximation. In these articles, the classical quasi-chemical model of Fowler and Guggenheim[5] was modified (1) to permit the composition of maximum short-range ordering (SRO) in a binary system to be freely chosen, (2) to express the energy of pair formation as a function of composition, and (3) to extend the model to multicomponent systems. The model has since been applied to the critical evaluation and optimization of several hundred liquid-oxide, salt, and alloy solutions. In such optimizations, the empirical binary and ternary parameters are found by critical evaluation of available experimental thermodynamic and phase-equilibrium data. The model is then used to predict the properties of multicomponent systems containing these binaries and ternaries as subsystems.

In the current series of articles, further modifications and extensions to the model are described. The first article[6] dealt with binary systems. The present article treats multicomponent solutions. Subsequent articles in this series will treat extensions to liquids with two "sublattices."

II. MODEL EQUATIONS

Atoms or molecules of the components 1, 2, 3 . . ., N of a solution are distributed over the sites of a quasi lattice. In the pair approximation, we consider the pair-exchange reactions

$$(m\text{-}m) + (n\text{-}n) = 2(m\text{-}n); \quad \Delta g_{mn} \qquad [1]$$

where (m and n = 1, 2, . . ., N) and (m-m), (n-n), and (m-n) represent first-nearest-neighbor (FNN) pairs.

ARTHUR D. PELTON, Professor, and PATRICE CHARTRAND, Research Fellow, are with the CRCT, École Polytechnique, Montreal, PQ, Canada H3C 3A7.

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The nonconfigurational Gibbs energy change for the formation of two moles of (m-n) pairs is Δg_{mn}. Let n_m and Z_m be the number of moles and the coordination number of component m, respectively, and let n_{mn} be the number of moles of (m-n) pairs (where n_{mn} and n_{nm} represent the same quantity and can be used interchangeably). Then,

$$Z_m n_m = 2n_{mm} + \sum_{n \neq m} n_{mn} \qquad [2]$$

In the case of a solid solution, clearly, it is required that $Z_1 = Z_2 = \ldots = Z_N$.

Pair fractions (X_{mn}), overall mole (or site) fractions (X_m), and "coordination-equivalent" fractions (Y_m) are defined as

$$X_{mn} = n_{mn} / \sum n_{ij} \qquad [3]$$

$$X_m = n_m / \sum n_i \qquad [4]$$

$$Y_m = Z_m n_m / \sum (Z_i n_i) = Z_m X_m / \sum (Z_i X_i) \qquad [5]$$

(where X_{mn} and X_{nm} represent the same quantity and can be used interchangeably). Substitution of Eq. [2] into Eqs. [3] and [5] gives

$$Y_m = X_{mm} + \sum_{n \neq m} X_{mn}/2 \qquad [6]$$

The Gibbs energy of the solution is given by

$$G = \sum n_m g_m^\circ - T \Delta S^{\text{config}} + \sum_{n>m} \sum n_{mn} (\Delta g_{mn}/2) \qquad [7]$$

where g_m° is the molar Gibbs energy of pure component m, and ΔS^{config} is an approximate expression for the configurational entropy of mixing, given by randomly mixing the (m-n) pairs:

$$\Delta S^{\text{config}} = -R \sum n_m \ln X_m - R \left(\sum n_{mm} \ln (X_{mm}/Y_m^2) + \sum_{m>n} \sum n_{mn} \ln (X_{mn}/2Y_m Y_n) \right) \qquad [8]$$

In the m-n binary system, the energy parameter Δg_{mn} may

be expanded as an empirical polynomial in the component fractions Y_m:

$$\Delta g_{mn} = \Delta g^{\circ}_{mn} + \sum_{(i+j)\geq 1} q^{ij}_{mn} Y^i_m Y^j_n \qquad [9]$$

where Δg°_{mn} and q^{ij}_{mn} are empirical binary coefficients, which may be functions of temperature and pressure. (These were previously[1–4,6] written as $q^{ij}_{mn} = (\omega^{ij}_{mn} - \eta^{ij}_{mn}T)$.) Alternatively, Eq. [9] can be rearranged into the "Redlich–Kister" form:

$$\Delta g_{mn} = \Delta g^{\circ}_{mn} + \sum_{i\geq 1} {}^{i}L_{mn}\,(Y_m - Y_n)^i \qquad [10]$$

where the set of empirical coefficients ${}^{i}L_{mn}$ can clearly be calculated from the set q^{ij}_{mn}, and *vice versa*, since $(X_m + X_n) = 1$ in the binary system. The empirical binary coefficients Δg°_{mn} and q^{ij}_{mn} or ${}^{i}L_{mn}$ are found by optimization of experimental data in the binary subsystems.

In the preceding article,[6] it was proposed to replace the expansion of Eqs. [9] or [10] by an expansion in terms of the pair fractions X_{mm} and X_{nn}:

$$\Delta g_{mn} = \Delta g^{\circ}_{mn} + \sum_{(i+j)\geq 1} g^{ij}_{mn} X^i_{mm} X^j_{nn} \qquad [11]$$

where Eq. [11] applies in the *m-n* binary system and Δg°_{mn} and g^{ij}_{mn} are empirical coefficients, which may be temperature and pressure dependent. This representation has been found,[6] in general, to result in improved and easier optimizations. In practice, in most cases, only the coefficients g^{i0}_{mn} and g^{0j}_{mn} need be included.

In the preceding article,[6] composition-dependent coordination numbers were also introduced. This provides greater flexibility and permits the composition of maximum SRO to be chosen independently in each binary subsystem:

$$\frac{1}{Z_1} = \frac{1}{2n_{11} + \sum_{j\neq 1} n_{1j}} \left(\frac{2n_{11}}{Z^1_{11}} + \sum_{j\neq 1} \frac{n_{1j}}{Z^1_{1j}} \right) \qquad [12]$$

$$\frac{1}{Z_2} = \frac{1}{2n_{22} + \sum_{j\neq 2} n_{2j}} \left(\frac{2n_{22}}{Z^2_{22}} + \sum_{j\neq 2} \frac{n_{2j}}{Z^2_{2j}} \right) \qquad [13]$$

etc.

where Z^1_{11} and Z^1_{12} are, respectively, the value of Z_1 when all nearest neighbors of a 1 are also 1 and the (hypothetical) value of Z_1 when all nearest neighbors of a 1 are a 2. (Note that Z^1_{12} and Z^1_{21} represent the same quantity and can be used interchangeably.)

The term Z^m_{mm} is a constant for each pure component m and is the same for all solutions containing m. The composition of maximum SRO in each binary subsystem is determined by the ratio Z^m_{mn}/Z^n_{mn}. The choice of the constants Z^m_{mm} and Z^m_{mn} was discussed previously.[6] Substitution of Eqs. [12] and [13] into Eq. [2] gives

$$n_m = 2n_{mm}/Z^m_{mm} + \sum_{n\neq m} n_{mn}/Z^m_{mn} \qquad [14]$$

Clearly, in the case of a solid solution, all coordination numbers must be equal. That is, $Z^m_{mm} = Z^n_{nn} = Z^m_{mn} = Z^n_{mn}$. The standard Gibbs energies g°_{mm} and g°_{mn} are defined as

$$g^{\circ}_{mm} = 2g^{\circ}_m/Z^m_{mm} \qquad [15]$$

$$g^{\circ}_{mn} = \Delta g^{\circ}_{mn}/2 + g^{\circ}_m/Z^m_{mn} + g^{\circ}_n/Z^n_{mn} \qquad [16]$$

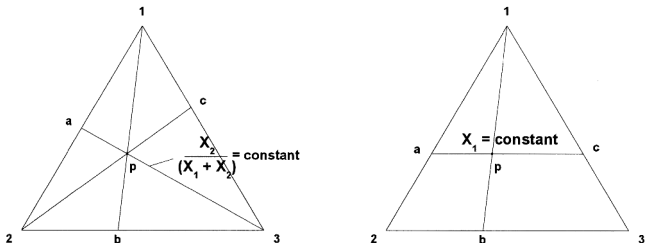

Fig. 1.—Symmetric (left) and asymmetric (right) schemes for interpolation from binary to ternary solutions.

where Δg°_{mn} is the binary parameter from Eqs. [9], [10], or [11]. Substitution into Eq. [7] then gives

$$G = (n_{11}g^{\circ}_{11} + n_{12}g^{\circ}_{12} + n_{22}g^{\circ}_{22} + n_{13}g^{\circ}_{13} + \ldots.) - T\,\Delta S^{\text{config}} + \sum_{n>m}\sum (n_{mn}/2)(\Delta g_{mn} - \Delta g^{\circ}_{mn}) \qquad [17]$$

with ΔS^{config} given by Eq. [8] and Δg_{mn} by Eqs. [9], [10], or [11]. Dividing, though, by Σn_{ij} gives

$$\begin{aligned} g \text{ (per mole of pairs)} = {} & (X_{11}g^{\circ}_{11} + X_{12}g^{\circ}_{12} + X_{22}g^{\circ}_{22} + X_{13}g^{\circ}_{13} + \ldots.) \\ & + \mathrm{R}T(X_{11} \ln X_{11} + X_{12} \ln X_{12} + X_{22} \ln X_{22} + \ldots) \\ & + \mathrm{R}T\left(\sum \frac{2X_m}{Z_m} \ln X_m - X_{11} \ln Y^2_1 - X_{22} \ln Y^2_2 \right. \\ & \left. - X_{12} \ln (2Y_1Y_2) - \ldots \right) + g^E \end{aligned} \qquad [18]$$

where

$$g^E = \left(\frac{X_{12}}{2}\right)(\Delta g_{12} - \Delta g^{\circ}_{12}) + \left(\frac{X_{13}}{2}\right)(\Delta g_{13} - \Delta g^{\circ}_{13}) + \ldots \qquad [19]$$

The coefficients of Eqs. [9], [10], or [11] are obtained by optimization of binary experimental data. Eqs. [9], [10], or [11] only apply in the binary subsystems. It is now required to write expressions for Δg_{mn} for compositions within the *N*-component system for use in Eq. [17].

III. INTERPOLATION FORMULAE

A. *When* Δg_{mn} *in a Binary System is Given by Eqs. [9] or [10]*

Suppose Δg_{12} in the 1-2 binary subsystem has been expressed as a polynomial in the fractions Y_1 and Y_2 by Eq. [9]. We now want an expression for Δg_{12} in a multicomponent solution. We shall consider first a ternary system 1-2-3.

1. *Symmetric model*

With the symmetric model illustrated in Figure 1(a), Δg_{12} in the ternary solution is given by

$$\Delta g_{12} = \left(\Delta g^{\circ}_{12} + \sum_{(i+j)\geq 1} q^{ij}_{12} \left(\frac{Y_1}{Y_1 + Y_2} \right)^i \left(\frac{Y_2}{Y_1 + Y_2} \right)^j \right) + \sum_{\substack{k\geq 1 \\ i\geq 0 \\ j\geq 0}} q^{ijk}_{12(3)} \left(\frac{Y_1}{Y_1 + Y_2} \right)^i \left(\frac{Y_2}{Y_1 + Y_2} \right)^j Y^k_3 \qquad [20]$$

where the first term on the right-hand side of Eq. [20] is constant along the line 3-*a* in Figure 1(a) and is equal to Δg_{12} in the 1-2 binary at point *a* (where $(Y_1 + Y_2) = 1$). That is, it is assumed that the binary 1-2 pair interaction energy is constant at a constant Y_1/Y_2 ratio. The second summation in Eq. [20] consists of "ternary terms" that are all zero in the 1-2 binary, and which give the effect of the presence of component 3 upon the energy Δg_{12} of the 1-2 pair interactions. The empirical ternary coefficients $q^{ijk}_{12(3)}$ are found by optimization of experimental ternary data.

Similar equations give Δg_{23} and Δg_{31}, with the binary terms equal to their values at points *b* and *c*, respectively, in Figure 1(a) and with the ternary coefficients $q^{ijk}_{23(1)}$ and $q^{ijk}_{31(2)}$, which give the effect of the presence of component 1 upon the pair energy Δg_{23} and of component 2 upon Δg_{31}, respectively. It has been proposed[7] that this functional form for the ternary terms is preferable to traditional expressions such as $Y^i_1 Y^j_2 Y^k_3$.

Alternatively, if Δg_{12} is expressed in the 1-2 binary system by a Redlich–Kister expansion, as in Eq. [10], then the first summation in Eq. [20] is replaced by $\sum_{i\geq 1} {}^iL_{12}\left(\frac{Y_1 - Y_2}{Y_1 + Y_2}\right)^i$, which is also constant along the line 3-*a* and equal to Δg_{12} at point *a*.

This model is "symmetric" in that the three components are treated in the same fashion. For certain systems, however, in which one component is chemically different from the other two (*e.g.*, SiO_2-CaO-MgO, S-Fe-Cu, Na-Au-Ag, *etc.*), it is more appropriate to use the "asymmetric" model illustrated in Figure 1(b), where component 1 is the "asymmetric component."

2. *Asymmetric model*

In this case, Δg_{12} in the ternary solution is given by

$$\Delta g_{12} = \left(\Delta g^\circ_{12} + \sum_{(i+j)\geq 1} q^{ij}_{12} Y^i_1 (1 - Y_1)^j\right) + \sum_{\substack{k\geq 1\\ i\geq 0\\ j\geq 0}} q^{ijk}_{12(3)} Y^i_1 (1 - Y_1)^j \left(\frac{Y_3}{Y_2 + Y_3}\right)^k \quad [21]$$

where the binary terms are constant along the line *ac* and equal to their values at point *a* in Figure 1(b). A similar expression is written for Δg_{31}, while Δg_{23} is given by an expression similar to Eq. [20]. If Δg_{12} is expressed in the binary system by a Redlich–Kister expansion, then the binary terms in Eq. [21] are replaced by $\sum_{i\geq 1} {}^iL_{12}(2Y_1 - 1)^i$.

It has been shown[7] that, for systems with large composition-dependent deviations from ideality, the choice of a symmetric or an asymmetric model can often give very different results. An incorrect choice can even give rise to spurious miscibility gaps.

3. *Multicomponent solutions*

In order to extend this symmetric/asymmetric dichotomy to *N*-component solutions, while still maintaining complete flexibility to treat any ternary subsystem as symmetric or asymmetric, we define[7]

$$\xi_{ij} = Y_i + \sum_k Y_k \quad [22]$$

where the summation is over all *k* components in asymmetric

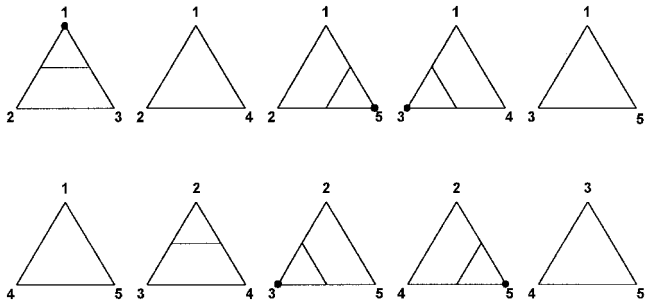

Fig. 2.—A five-component example solution illustrating which ternary subsystems are to be treated by a symmetric model and which are to be treated with an asymmetric model.

i-j-k ternary subsystems in which *j* is the asymmetric component. This is best presented by an example.[17] For the five-component system in Figure 2, the ternary subsystems 1-2-3 and 1-2-5 are asymmetric with 1 and 5, respectively, as asymmetric components, the system 1-2-4 is symmetric, and so on, as illustrated schematically in the figure. In this example, then,

$$\begin{aligned}
\xi_{12} &= Y_1 & \xi_{21} &= Y_2 + Y_3\\
\xi_{13} &= Y_1 + Y_4 & \xi_{31} &= Y_3 + Y_2\\
\xi_{14} &= Y_1 & \xi_{41} &= Y_4\\
\xi_{15} &= Y_1 + Y_2 & \xi_{51} &= Y_5\\
\xi_{23} &= Y_2 + Y_5 & \xi_{32} &= Y_3 + Y_4\\
\xi_{24} &= Y_2 & \xi_{42} &= Y_4 + Y_3\\
\xi_{25} &= Y_2 + Y_1 + Y_4 & \xi_{52} &= Y_5\\
\xi_{34} &= Y_3 & \xi_{43} &= Y_4 + Y_1\\
\xi_{35} &= Y_3 & \xi_{53} &= Y_5 + Y_2\\
\xi_{45} &= Y_4 + Y_2 & \xi_{54} &= Y_5
\end{aligned} \quad [23]$$

Then, in the multicomponent system,

$$\begin{aligned}
\Delta g_{12} = \Delta g^\circ_{12} &+ \sum_{(i+j)\geq 1} \left(\frac{\xi_{12}}{\xi_{12} + \xi_{21}}\right)^i \left(\frac{\xi_{21}}{\xi_{12} + \xi_{21}}\right)^j q^{ij}_{12}\\
&+ \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \left(\frac{\xi_{12}}{\xi_{12} + \xi_{21}}\right)^i \left(\frac{\xi_{21}}{\xi_{12} + \xi_{21}}\right)^j\\
&\left(\sum_l q^{ijk}_{12(l)} Y_l (1 - \xi_{12} - \xi_{21})^{k-1} + \sum_m q^{ijk}_{12(m)} \left(\frac{Y_m}{\xi_{21}}\right)\right.\\
&\left.\left(1 - \frac{Y_2}{\xi_{21}}\right)^{k-1} + \sum_n q^{ijk}_{12(n)} \left(\frac{Y_n}{\xi_{12}}\right)\left(1 - \frac{Y_1}{\xi_{12}}\right)^{k-1}\right)
\end{aligned} \quad [24]$$

where the summations of ternary terms are over (1) all *l* components in 1-2-*l* ternary subsystems, which are either symmetric or in which *l* is the asymmetric component; (2) all *m* components in 1-2-*m* subsystems, in which 1 is the asymmetric component; and (3) over all *n* components in 1-2-*n* subsystems, in which 2 is the asymmetric component.

Eq. [24] reduces to Eq. [20] in symmetric ternary subsystems (when $(Y_1 + Y_2 + Y_3) = 1$) and to Eq. [21] in asymmetric ternary subsystems, as can be verified by substitution of

Eqs. [23]. The form of the ternary terms in Eq. [24] has been chosen such that if two components (for example, 3 and 4) have the same effect upon Δg_{12} (that is, if $q^{ijk}_{12(3)} = q^{ijk}_{12(4)}$), then the effect of the presence of both 3 and 4 will be additive. This has been discussed previously.[7] If a Redlich–Kister expansion, as in Eq. [10], is used in the 1-2 binary system, then the binary terms (the first summation) in Eq. [24] are replaced by $\sum_{i\geq 1} {}^{i}L_{12}((\xi_{12} - \xi_{21})/(\xi_{12} + \xi_{21}))^i$.

Other examples of the application of Eq. [22] were given previously.[7] For example, suppose all components are grouped as either "acids" (group I) or "bases" (group II), where a ternary system is symmetric if all three components are in the same group, and asymmetric otherwise. It then follows from the definition of ξ_{ij} that $\xi_{12} = Y_1$ and $\xi_{12}/(\xi_{12} + \xi_{21}) = Y_1/(Y_1 + Y_2)$ if 1 and 2 are in the same group, while $\xi_{12} = \sum_{\text{group I}} Y_i \equiv \xi_{\text{I}}$ and also $\xi_{12}/(\xi_{12} + \xi_{21}) = \xi_{\text{I}}$ if 1 and 2 are in groups I and II, respectively.

B. *When* Δg_{mn} *in a Binary System is Given by Eq. [11]*

Suppose that Δg_{12} in the binary system has been expressed, as in Eq. [11], by a polynomial in terms of the pair fractions. Let us consider first a ternary system 1-2-3.

1. *Symmetric model*

In a symmetric ternary system, as in Figure 1(a), the following equation for Δg_{12} is proposed:

$$\Delta g_{12} = \Delta g^{\circ}_{12} + \sum_{(i+j)\geq 1} g^{ij}_{12} \left(\frac{X_{11}}{X_{11} + X_{12} + X_{22}}\right)^i \left(\frac{X_{22}}{X_{11} + X_{12} + X_{22}}\right)^j + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} g^{ijk}_{12(3)} \left(\frac{X_{11}}{X_{11} + X_{12} + X_{22}}\right)^i \left(\frac{X_{22}}{X_{11} + X_{12} + X_{22}}\right)^j Y_3^k \quad [25]$$

As with Eq. [11], in practice, it is usually sufficient to include only terms with $i = 0$ or with $j = 0$. The form of this expression has been chosen for the following reason. As Δg_{12}, Δg_{23}, and Δg_{31} become small, the solution approaches ideality, and $Y_{11} \to Y_1^2$, $Y_{22} \to Y_2^2$, and $Y_{12} \to 2Y_1Y_2$. In this case, $X_{11}/(X_{11} + X_{12} + X_{22}) \to (Y_1/(Y_1 + Y_2))^2$ and Eq. [25] approaches Eq. [20], which, in the limit, becomes the well-known Kohler[8] equation for symmetrical ternary systems.

From Eq. [6], it can be seen that the factor Y_3 in the ternary terms in Eq. [25] is equal to $(X_{33} + X_{31}/2 + X_{23}/2)$. In principle, the effect of these three terms upon Δg_{12} could easily be represented by three independent ternary coefficients. However, this additional complexity is probably not required.

2. *Asymmetric model*

In an asymmetric ternary system, as in Figure 1(b), the following equation is proposed:

$$\Delta g_{12} = \Delta g^{\circ}_{12} + \sum_{(i+j)\geq 1} g^{ij}_{12} X^i_{11} (X_{22} + X_{23} + X_{33})^j + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} g^{ijk}_{12(3)} X^i_{11} (X_{22} + X_{23} + X_{33})^j \left(\frac{Y_3}{Y_2 + Y_3}\right)^k \quad [26]$$

In the limit of ideality, this equation reduces to Eq. [21], which, in the limit, becomes the well-known Kohler–Toop[9] equation for asymmetrical ternary systems.

3. *Multicomponent solutions*

To extend this symmetric/asymmetric dichotomy to multicomponent solutions, we define

$$\chi_{12} = \sum_{i=1,k} \sum_{j=1,k} X_{ij} \Big/ \sum_{i=1,2,k,l} \sum_{j=1,2,k,l} X_{ij} \quad [27]$$

where k represents all values of k in 1-2-k asymmetric ternary subsystems in which 2 is the asymmetric component, and l represents all values of l in asymmetric 1-2-l subsystems in which 1 is the asymmetric component. The term χ_{ij} is analogous to the ratio $\xi_{ij}/(\xi_{ij} + \xi_{ji})$, defined by Eq. [22] and used in Eq. [24]. Taking the example of Figure 2, from Eq. [23],

$$\frac{\xi_{23}}{\xi_{23} + \xi_{32}} = \frac{(Y_2 + Y_5)}{(Y_2 + Y_5) + (Y_3 + Y_4)} \quad [28]$$

whereas

$$\chi_{23} = \frac{(X_{22} + X_{55}) + X_{25}}{(X_{22} + X_{55}) + (X_{33} + X_{44}) + X_{25} + X_{23} + X_{24} + X_{53} + X_{54} + X_{34}} \quad [29]$$

That is, starting from Eq. [28], we can write the expression for χ_{23} in Eq. [29] by replacing the sums $(Y_i + Y_j + Y_k + \ldots)$ in the numerator and denominator of Eq. [28] by the sum of $(X_{ii} + X_{jj} + X_{kk} + \ldots)$ plus all cross terms $(X_{ij} + X_{ik} + X_{ik} + \ldots)$.

In the case where all components are grouped as either acids (group I) or bases (group II), it follows from the definitions and from Eq. [6] that $\chi_{12} = X_{11}/(X_{11} + X_{12} + X_{22})$ if components 1 and 2 are in the same group and $\chi_{12} = \sum_{\text{group I}} Y_i \equiv \xi_1$ if components 1 and 2 are in groups I and II, respectively.

Then, in the multicomponent system,

$$\Delta g_{12} = \Delta g^{\circ}_{12} + \sum_{(i+j)\geq 1} \chi^i_{12}\chi^j_{21} g^{ij}_{12} + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi^i_{12}\chi^j_{21} \left(\sum_l g^{ijk}_{12(l)} Y_l (1 - \xi_{12} - \xi_{21})^{k-1} + \sum_m g^{ijk}_{12(m)} \left(\frac{Y_m}{\xi_{21}}\right) \left(1 - \frac{Y_2}{\xi_{21}}\right)^{k-1} + \sum_n g^{ijk}_{12(n)} \left(\frac{Y_n}{\xi_{12}}\right) \left(1 - \frac{Y_1}{\xi_{12}}\right)^{k-1} \right) \quad [30]$$

where the summations over l, m, and n are as was described following Eq. [24]. Equation [30] reduces to the correct symmetric or asymmetric ternary equation (Eq. [25] or [26]) in any ternary subsystem. The analogy to Eq. [24] is evident.

IV. DISCUSSION

Substitution of Eqs. [24] or [30] into Eq. [17] gives an equation for G in terms of the pair fractions X_{mn}. For any overall composition given by $(n_1, n_2, \ldots, n_N)$, the equilibrium pair fractions are then calculated by minimizing G, subject to the mass-balance constraints of Eq. [14]. This

Gibbs energy minimization is greatly facilitated by the form of Eq. [17]. When expressed per mole of pairs, as in Eq. [18], the Gibbs energy equation is identical, apart from the second configurational entropy term, to commonly used expressions for the Gibbs energy of a randomly mixed solution of "components" (11, 12, 22, . . .); the "excess" terms in Eq. [19] are polynomials in the fractions X_{mn}, since Δg_{mn} from Eqs. [24] or [30] is expressed only in terms of X_{mn} (Y_m being given in terms of X_{mn} by Eq. [6]). Therefore, the same existing algorithms and computer subroutines that are commonly used for polynomial solution models can be used directly for the quasi-chemical model by simply including the extra entropy terms.

That is, a significant simplification is achieved by formally considering the *mn* pairs as the components of the solution. A further computational simplification can also be achieved[6] by formally treating these components as the "associates" or "molecules" $m_{1/Z^m_{mn}} n_{1/Z^n_{mn}}$. For example, if $Z^m_{mm} = 6$, $Z^n_{nn} = 6$, $Z^m_{mn} = 3$, and $Z^n_{mn} = 6$, then the formal components would be $m_{2/6}$, $n_{2/6}$, and $m_{1/3}n_{1/6}$. Setting

$$n_{m_{1/Z^m_{mn}} n_{1/Z^n_{mn}}} = n_{mn} \qquad [31]$$

and substituting into Eq. [14] gives

$$n_m = 2n_{m_{2/Z^m_{mm}}}/Z^m_{mm} + \sum_{n \neq m} n_{m_{1/Z^m_{mn}} n_{1/Z^n_{mn}}}/Z^m_{mn} \qquad [32]$$

which is now a "true" chemical mass balance, in that the number of moles of *m* is the same on both sides of the equation.

The fact that Eq. [18] is written solely in terms of the fractions X_{mn} of the *mn* components permits the chemical potentials to be easily calculated in closed explicit form. As shown previously,[6] the chemical potential of *m* is given by

$$\mu_m = (\partial G/\partial n_m)_{n_i} = (Z^m_{mm}/2)\,(\partial G/\partial n_{mm})_{n_{ij}} \qquad [33]$$

Hence,

$$\mu_m = g^\circ_m + RT \ln X_A + \left(\frac{Z^m_{mm}}{2}\right)\left(RT \ln \frac{X_{mm}}{Y^2_m} + g^E_{mm}\right) \qquad [34]$$

where the partial excess term g^E_{mm} can be calculated in the usual way from the polynomial expansion for g^E in Eq. [19]:

$$g^E_{mm} = g^E + (\partial g^E/\partial X_{mm}) - \sum_{(ij \neq mm)} X_{ij}\,(\partial g^E/\partial X_{ij}) \qquad [35]$$

where Eq. [6] is used to express Y_m in terms of X_{mn}.

A. *Reduction to the Random Mixing (Bragg–Williams) Model*

Suppose that it is desired to suppress the formation of SRO and to employ the following commonly used Bragg–Williams model for a solution with random mixing and a polynomial expression for g^E:

$$G = \sum n_m g^\circ_m + RT \sum n_m \ln X_m + \sum_{n>m}\sum X_{mn}(\Delta g_{mn}) \qquad [36]$$

with Δg_{mn} given as a polynomial expansion in terms of Y_i by Eq. [24]. This can be done by simply replacing all n_{mn} factors ($m \neq n$) in Eq. [17] by $(\sum Z^i_{ii} n_i) Y_m Y_n$ which is the value in a randomly mixed (Bragg-Williams) solution. It is also necessary in this case to set all values of $Z^m_{mn} = Z^m_{mm}$. Eqs. [15] and [16] are still used to give g°_{mm} and g°_{mn}. The excess terms, then, have no effect upon the calculated pair distributions, and so the Gibbs energy minimization will result in a random mixture. That is, the second entropy term in Eq. [8] will automatically become zero, and the result will be the same as if Eq. [36] had been used for *G*.

Hence, the same model subroutine that is used for the quasi-chemical model can be used, with one minor alteration, for the random-mixing Bragg-Williams model.

B. *Combining Models in One Multicomponent-Solution Database*

The major importance of this fact is that it is now possible to "mix models" in one multicomponent solution. This is of much practical value. For example, in developing the F*A*C*T[10] database for multicomponent molten salt solutions, we have already performed optimizations on well over 100 binary and ternary common-anion alkali-halide, carbonate, sulfate, nitrate and hydroxide systems using the Bragg–Williams polynomial model, which is satisfactory for these systems, in which deviations from ideality are relatively small. We are now including alkaline-earth salts in this database. Several of the binary liquid solutions (*e.g.*, $MgCl_2$-KCl) exhibit large negative deviations from ideality and a large degree of SRO and require the quasi-chemical model. Ideally, of course, all previously optimized systems should be reoptimized with the quasi-chemical model, but the amount of work involved is considerable.

However, it is now easy to combine the models in one multicomponent-solution database. If a binary subsystem *m-n* has been optimized with the quasi-chemical model with Eqs. [9] or [10] for Δg_{mn}, then Eq. [24] for Δg_{mn} is substituted into Eq. [17]. If another binary subsystem *i-j* has been optimized with the quasi-chemical model with Eq. [11] for Δg_{ij}, then Eq. [30] for Δg_{ij} is substituted into Eq. [17]. If yet another binary subsystem *k-l* has been optimized using the random-mixing Bragg–Williams model with Eqs. [9] or [10] for Δg_{kl}, then Δg_{kl} from Eq. [24] is substituted into Eq. [17] and, furthermore, n_{kl} is replaced everywhere in Eq. [17] by $(\sum Z^i_{ii} n_i) Y_k Y_l$.

V. CONCLUSIONS

Improvements to the quasi-chemical model introduced in the first article in the present series[6] have been extended to multicomponent solutions with SRO. The energies of pair formation (Δg_{mn}) may be expanded as polynomials in the pair fractions, rather than the component fractions. Composition-dependent coordination numbers may also be used. Both these improvements provide better representations by providing greater flexibility.

The properties of a ternary solution may be estimated from optimized data for its binary subsystems by either a symmetric or an asymmetric model. In the former, all components are treated in the same fashion, while in the latter, one component, being chemically different from the other two, is singled out. It has been shown how this symmetric/asymmetric dichotomy can be extended into the *N*-component solution while still permitting complete flexibility to choose either a symmetric or an asymmetric model for any ternary subsystem.

An improved general functional form for "ternary terms"

in the excess Gibbs energy expression has been proposed. These terms are related to the effect of a third component upon the binary pair-interaction energies.

By treating the nearest-neighbor pairs as components, a Gibbs energy expression is obtained which is a function of only the pair fractions X_{mn}. This expression is identical, apart from a configurational entropy term, to the equations for a randomly mixed solution of these components with a polynomial expression for the excess Gibbs energy. This permits the quasi-chemical model to be treated with currently available and relatively simple software. Furthermore, closed explicit equations for the chemical potentials are, thereby, easily obtained.

By means of a minor alteration, the Gibbs energy expression in the quasi-chemical model can be made identical to that of a randomly mixed Bragg–Williams solution with a polynomial expansion for g^E. This is of much practical importance, because binary subsystems that have previously been optimized with a Bragg–Williams polynomial model can be combined with binary subsystems optimized with the quasi-chemical model in the same multicomponent-solution database.

Although the model has been developed primarily for liquid solutions, it can be applied to treat SRO in solid solutions. In this case, all coordination numbers must be the same.

The model of the present article takes account of mixing on only one lattice. It can, however, be applied to systems with more than one sublattice, as long as mixing occurs on only one of the sublattices. For example, it can be applied to common-ion salt systems such as LiCl-NaCl-KCl-$MgCl_2$, where all anion lattice sites are occupied by Cl, such that mixing occurs only on the cation sublattice.

Subsequent articles in the present series will describe extensions to solutions with mixing on two quasi-sublattices, such as reciprocal molten salt solutions with intrasublattice as well as intersublattice SRO. It will be shown that the large degree of flexibility in the model also permits the treatment of phenomena such as complexation, polymerization, and multiple compositions of maximum SRO.

An example of the application of the model of the present article to liquid LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ solutions is given in an accompanying publication.[11]

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