The Modified Quasi-chemical Model: Part IV. Two-Sublattice Quadruplet Approximation

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The modified quasi-chemical model is further extended, in the quadruplet approximation, to treat, simultaneously, first-nearest-neighbor (FNN) and second-nearest-neighbor (SNN) short-range ordering (SRO) in solutions with two sublattices. When one sublattice is occupied by only one species, or is empty, the model reduces to the modified quasi-chemical model for one sublattice in the pair approximation. The coordination numbers and the ratio of the number of sites on the two sublattices are permitted to vary with composition, thereby making the model ideally suited to the treatment of liquid solutions such as molten salts. The model also applies to solid solutions if the number of sites and coordination numbers are held constant and may be combined with the compound-energy formalism to treat SRO in a wide variety of types of solutions. A significant computational simplification is achieved by formally treating the quadruplets as the "components" of the solution.

I. INTRODUCTION

IN the first two articles in the present series,[1,2] the modified quasi-chemical model for short-range ordering (SRO) in the pair approximation was developed for solutions in which the species mix on only one lattice or sublattice. The application of the model was illustrated in two accompanying articles by the evaluation and optimization of all available thermodynamic and phase-equilibrium data for the common-anion systems Li,Na,K,Rb,Cs,Mg,Ca//Cl[3] and Li,Na,K,Mg,Ca//F.[4] The next article in the series[5] developed the model, in the pair approximation, for SRO involving first-nearest-neighbor (FNN) pairs in solutions with two sublattices. The present article extends the treatment, in the quadruplet approximation, to take account, simultaneously, of FNN SRO between sublattices and of second-nearest-neighbor (SNN) SRO within a sublattice.

In solid solutions, the existence of two sublattices is a manifestation of long-range ordering. For example, in a solid ionic solution, one can distinguish anionic and cationic sublattices. In a liquid solution, on the other hand, there is no long-range ordering and, strictly speaking, it is incorrect to speak of sublattices. In molten NaCl, for example, the Na^+ and Cl^- ions should be treated as residing on one sublattice, but with a very high degree of SRO, such that the nearest-neighbors of Na^+ ions are almost exclusively Cl^- ions, and *vice versa*. Solutions of molten salts could, thus, in principle, be treated with a single-sublattice model. However in such solutions, in which the degree of SRO is very high, it is conceptually and mathematically simpler to treat the liquid solution as if it consisted of two distinct sublattices. This does not preclude the possibility of a small number of cation-cation or anion-anion nearest neighbors, since these can be treated within the two-sublattice model as substitutional defects (cations on anion sites and anions on cation sites).

In a solid solution, the ratio of the number of sites on the two sublattices is necessarily constant. However, in a liquid, this ratio can vary with composition. For example, in molten $NaCl-CaCl_2$ solutions, the ratio of cation to anion sites varies from 1/1 to 1/2 as the composition varies from pure NaCl to pure $CaCl_2$.

It is an important feature of the present model that the ratio of the number of sites on the two sublattices is permitted to vary with composition. Further flexibility is also provided by permitting coordination numbers to vary with composition. The model is, thus, ideally suited to describing molten ionic solutions.

In an accompanying article,[6] the use of the model is illustrated by application to the thermodynamic evaluation/optimization of the Li,Na,K,Mg,Ca/F,Cl system.

II. THE MODEL

A. *Definitions and Coordination Numbers*

The solution consists of two sublattices, I and II. Let *A,B,C,* . . . and *X,Y,Z,* . . . be the species that reside on sublattices I and II, respectively. In a salt solution, for example, *A,B,C,* . . . are the cations and *X,Y,Z,* . . . are the anions, and, in the present article, we shall refer to them as "cations" and "anions." However, the model is also applicable to other solutions. For example, in a solid spinel solution, sublattices I and II would be associated with the tetrahedral and octahedral cationic sublattices. Although there is a third anionic sublattice, as long as this is occupied by only one species (O^{2-}), the present model can be applied. In other examples, lattice vacancies could also be considered as "species," or the same chemical species could occupy both sublattices. For instance, in an ordered Cu-Au alloy, Cu and Au reside mainly on the I and II sublattices, respectively. However, due to substitutional disordering, some Cu is found on the II sublattice and some Au on the I sublattice. That is, in this example, *A* and *X* would both be Cu, and *B* and *Y* would both be Au.

When sublattice II is occupied only by the *X* species, then the model, as developed in the previous publications,[1–4] considered the formation of SNN (*A*-[*X*]-*B*) pairs from SNN (*A*-[*X*]-*A*) and (*B*-[*X*]-*B*) pairs, according to

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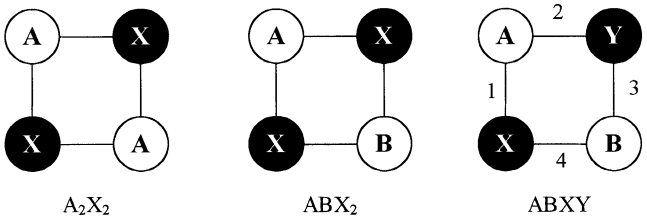

Fig. 1—Some quadruplets.

$$(A\text{-}[X]\text{-}A) + (B\text{-}[X]\text{-}B) = 2(A\text{-}[X]\text{-}B)\ \Delta g_{AB/X} \qquad [1]$$

The entropy expression was obtained[1,2] by distributing the pairs over "pair positions." The term $\Delta g_{AB/X}$ is an empirical parameter of the model, which may be composition dependent. If $\Delta g_{AB/X} = 0$, then ideal random mixing results. If $\Delta g_{AB/X} < 0$, then reaction [1] is displaced to the right and SRO results, with (*A*-[*X*]-*B*) pairs becoming predominant. Similarly, when sublattice I is occupied only by the *A* species, the model considered the formation of (*X*-[*A*]-*Y*) SNN pairs, according to

$$(X\text{-}[A]\text{-}X) + (Y\text{-}[A]\text{-}Y) = 2(X\text{-}[A]\text{-}Y)\ \Delta g_{A/XY} \qquad [2]$$

In the next article in the present series,[5] the following exchange reaction among FNN pairs was considered:

$$(A\text{-}X) + (B\text{-}Y) = (A\text{-}Y) + (B\text{-}X)\ \Delta g^{\text{exchange}}_{AB/XY} \qquad [3]$$

and the FNN pairs were distributed over pair positions. If $\Delta g^{\text{exchange}}_{AB/XY} < 0$, then there is SRO of FNN pairs, with (*A*-*X*) and (*B*-*Y*) pairs predominating. As a result, the probability of an (*A*-[*X*]-*B*) pair is less than that in a random mixture, and so the contribution of the (*A*-[*X*]-*B*) SNN energy ($\Delta g_{AB/X}$) to the total Gibbs energy of the solution is reduced. It was shown[5] that this effect becomes very important when $|\Delta g^{\text{exchange}}|$ is greater than about 50 kJ/mol.

Since the previous article[5] considered the quasi-chemical model only in the pair approximation, it was not possible to treat both FNN and SNN SRO simultaneously. For systems such as K,Mg//Cl,F, a large degree of SNN SRO is observed in the binary KCl-$MgCl_2$ and KF-MgF_2 subsystems, and this cannot be neglected in a quantitative model. In the present article, we consider the distribution, not of pairs, but of "quadruplets:" A_2X_2, ABX_2, A_2XY, *ABXY, etc.* As illustrated in Figure 1, each quadruplet consists of two SNN cations and two SNN anions, the cations and anions being mutual FNNs. Both FNN and SNN SRO can, thereby, be treated simultaneously.

In a solid, all the various possible configurations of the quadruplets on the sublattices could be considered, as is done in the cluster variation method (CVM),[7] and this is necessary for the full quantitative modeling of order-disorder phenomena. However, this additional complexity is neither necessary nor possible in the case of liquid solutions and can also be neglected in the modeling of solid solutions with a limited amount of SRO.

Let n_i ($i = A,B, \ldots X,Y \ldots$) be the number of moles of species *i*; $n_{A/X}$ the number of moles of FNN (*A*-*X*) pairs; and n_{A_2/X_2}, n_{AB/X_2}, $n_{AB/XY}$, *etc.*, the numbers of moles of A_2X_2, ABX_2, *ABXY, etc.*, quadruplets. (Note that n_{AB/X_2} and n_{BA/X_2} represent the same quantity and can be used interchangeably.) Let Z_A be the SNN coordination number of *A* (*i.e.*, the number of SNN pairs emanating from an *A* species). Since each quadruplet contains just one SNN pair, Z_A is also the number of quadruplets emanating from an A species. The term Z_X is defined similarly. Then,

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \cdots \qquad [4]$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \cdots \qquad [5]$$

Overall mole (or site) fractions (X_i), FNN pair fractions (X_{ij}), and quadruplet fractions ($X_{ij/kl}$) are defined as

$$X_A = n_A/(n_A + n_B + \cdots) \qquad X_X = n_X/(n_X + n_Y + \cdots) \qquad [6]$$

$$X_{A/X} = n_{A/X}/(n_{A/X} + n_{B/X} + n_{A/Y} \cdots) \qquad [7]$$

$$X_{AB/XY} = n_{AB/XY}/\sum n_{ij/kl} \qquad [8]$$

where ($\Sigma\ n_{ij/kl}$) is the total number of moles of quadruplets. From Eqs. [4] and [5],

$$2(\sum n_{ij/kl}) = (Z_A n_A + Z_B n_B + \cdots) = (Z_X n_X + Z_Y n_Y + \cdots) \qquad [9]$$

The "coordination-equivalent site fraction" (Y_i) is defined as

$$Y_A = Z_A n_A/(Z_A n_A + Z_B n_B + \cdots) \qquad Y_X = Z_X n_X/(Z_X n_X + Z_Y n_Y + \cdots) \qquad [10]$$

These are called coordination-equivalent fractions to distinguish them from the more usual "charge-equivalent" fractions, in which the n_i values are multiplied by the ionic charges rather than by the coordination numbers. It may be noted that the Y_i values, as defined in Eq. [10], are identical to those defined in the previous publications.[1,2] Substitution into Eqs. [4] and [5] gives

$$Y_A = X_{A_2/X_2} + X_{A_2/Y_2} + X_{A_2/XY} + \tfrac{1}{2}X_{AB/X_2} + \tfrac{1}{2}X_{AB/XY} + \cdots \qquad [11]$$

$$Y_X = X_{A_2/X_2} + X_{B_2/X_2} + X_{AB/X_2} + \tfrac{1}{2}X_{A_2/XY} + \tfrac{1}{2}X_{AB/XY} + \cdots \qquad [12]$$

In a solid solution, it is clearly required that $Z_A = Z_B = Z_C = \ldots$ and that $Z_X = Z_Y = Z_Z = \ldots$ However, in a liquid, this is not necessary and, furthermore, the coordination numbers can vary with composition. As shown previously,[1–5] the use of variable coordination numbers is an important feature of the present model, which provides the necessary flexibility to fix the compositions of maximum SRO in each subsystem.

Let $Z^A_{AB/XY}$ be the SNN coordination number of an *A* species when (hypothetically) all *A* species exist in *ABXY* quadruplets. We then let

$$\frac{1}{Z_A} = \frac{\dfrac{2n_{A_2/X_2}}{Z^A_{A_2/X_2}} + \dfrac{2n_{A_2/Y_2}}{Z^A_{A_2/Y_2}} + \dfrac{2n_{A_2/XY}}{Z^A_{A_2/XY}} + \dfrac{n_{AB/X_2}}{Z^A_{AB/X_2}} + \dfrac{n_{AB/XY}}{Z^A_{AB/XY}} + \cdots}{2n_{A_2}/x_2 + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/XY} + \cdots} \qquad [13]$$

$$\frac{1}{Z_X} = \frac{\dfrac{2n_{A_2/X_2}}{Z^X_{A_2/X_2}} + \dfrac{2n_{B_2/X_2}}{Z^X_{B_2/X_2}} + \dfrac{2n_{AB/X_2}}{Z^X_{AB/X_2}} + \dfrac{n_{A_2/XY}}{Z^X_{A_2/XY}} + \dfrac{n_{AB/XY}}{Z^X_{AB/XY}} + \cdots}{2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{AB/XY} + \cdots} \quad [14]$$

This composition dependence is chosen because substitution of Eqs. [13] and [14] into Eqs. [4] and [5] yields the following simple relations:

$$n_A = \frac{2n_{A_2/X_2}}{Z^A_{A_2/X_2}} + \frac{2n_{A_2/Y_2}}{Z^A_{A_2/Y_2}} + \frac{2n_{A_2XY}}{Z^A_{A_2/XY}} + \frac{n_{AB/X_2}}{Z^A_{AB/X_2}} + \frac{n_{AB/XY}}{Z^A_{AB/XY}} + \cdot\cdot \quad [15]$$

$$n_X = \frac{2n_{A_2/X_2}}{Z^X_{A_2/X_2}} + \frac{2n_{B_2/X_2}}{Z^X_{B_2/X_2}} + \frac{2n_{AB/X_2}}{Z^X_{AB/X_2}} + \frac{n_{A_2/XY}}{Z^X_{A_2/XY}} + \frac{n_{AB/XY}}{Z^X_{AB/XY}} + \cdot\cdot \quad [16]$$

Note that in the *A, B, C, . . .//X* subsystem, where sublattice II is occupied only by the *X* species, the Z^i_{ij/X_2} values are identical to the SNN coordination numbers $Z^i_{ij/X}$, defined in the previous articles.[1–4]

As in the previous article,[5] we may also define the FNN coordination number z_A as the number of FNN pairs emanating from an *A* species and similarly for z_X. Let $\zeta/2$ be the ratio of SNN to FNN pairs:

$$Z_i/z_i = \zeta/2 \quad [17]$$

In the general case, the ratios Z_A/z_A, Z_B/z_B, Z_C/z_C, *etc.*, could all be different and could even depend upon composition. However, this would make the model unnecessarily complex, particularly for the case of liquids. Hence, it is assumed that the ratio Z_i/z_i is the same for all species *i*.

It follows that the coordination-equivalent fractions defined in Eq. [10] are also given by

$$Y_A = z_A n_A/(z_A n_A + z_B n_B + \cdots) \quad [18]$$

and similarly for Y_X; the total numbers of pairs and quadruplets are related by

$$\sum n_{i/j} = (4/\zeta) \sum n_{ij/kl} \quad [19]$$

Each quadruplet contains one SNN pair and two FNN pairs emanating from a given ion. Hence, ζ is equal to the number of quadruplets emanating from, or containing, a FNN pair. Therefore,

$$\zeta\, n_{A/X} = 4n_{A_2/X_2} + 2n_{AB/X_2} + 2n_{A_2/XY} + n_{AB/XY} + \cdots \quad [20]$$

and so, from Eq. [19],

$$X_{A/X} = X_{A_2/X_2} + \tfrac{1}{2}X_{AB/X_2} + \tfrac{1}{2}X_{A_2/XY} + \tfrac{1}{4}X_{AB/XY} + \cdots \quad [21]$$

B. *Formal Treatment of Quadruplets as "Complexes" or "Molecules"*

The quadruplet *ABXY* may be treated formally as the complex or molecule $A_{1/Z^A_{AB/XY}}B_{1/Z^B_{AB/XY}}X_{1/Z^X_{AB/XY}}Y_{1/Z^Y_{AB/XY}}$. Similarly, an A_2X_2 quadruplet is formally treated as $A_{2/Z^A_{A_2/X_2}}X_{2/Z^X_{A_2/X_2}}$, *etc.* For example, in molten KCl-$MgCl_2$ solutions, if we were to choose $Z^{K}_{KMg/Cl_2} = 3$, $Z^{Mg}_{KMg/Cl_2} = 6$, and $Z^{Cl}_{KMg/Cl_2} = 3$, then the quadruplet $KMgCl_2$ is formally treated as a $K_{1/3}Mg_{1/6}Cl_{2/3}$ complex.

It must be stressed that this is only a formalism. The entropy expression in the quasi-chemical model (Section II–D) is not obtained by distributing the quadruplets as if they were molecules (as is, in fact, done in various "associate models"). It is not essential that this formalism be used. However, it aids in the conceptualization and in many derivations. For example, if n_{A_2/X_2}, $n_{A_2/XY}$, *etc.*, in Eq. [15] are replaced by $n_{A_2/Z^A_{A_2/X_2}X_2/Z^X_{A_2/X_2}}$, $n_{A_2/Z^A_{A_2/XY}X_1/Z^X_{A_2/XY}Y_1/Z^Y_{A_2/XY}}$, *etc.*, then the number of moles of A is the same on both sides of the equation, which, thereby, becomes a "normal" mass-balance equation.

Furthermore, it can be seen that all quadruplets such as $K_{1/3}Mg_{1/6}Cl_{2/3}$ in a molten salt solution must be electrically neutral. This stoichiometry represents the composition of a hypothetical solution formed exclusively of these quadruplets and containing one mole of quadruplets. That is, one mole of $KMgCl_2$ quadruplets contains 1/3 mol K^+, 1/6 mol Mg^{2+}, and 2/3 mol Cl^-.

In general, for a molten salt solution, if q_A, q_B, . . . and q_X, q_Y, . . . are the absolute cationic and anionic charges, then the charge-neutrality condition for *ABXY* (*i.e.* $A_{1/Z^A_{AB/XY}}B_{1/Z^B_{AB/XY}}X_{1/Z^X_{AB/XY}}Y_{1/Z^Y_{AB/XY}}$) quadruplets is as follows:

$$\frac{q_A}{Z^A_{AB/XY}} + \frac{q_B}{Z^B_{AB/XY}} = \frac{q_X}{Z^X_{AB/XY}} + \frac{q_Y}{Z^Y_{AB/XY}} \quad [22]$$

This equation also holds when $A = B$ and/or when $X = Y$. The previous example of $K^+_{1/3}Mg^{2+}_{1/6}Cl^-_{2/3}$ clearly satisfies Eq. [22]. In the most general form of the model, it is not essential for Eq. [22] to apply. However, in practice, for liquid solutions, which can be described as consisting of two "sublattices," this equation will almost always be satisfied.

Figure 2 shows a traditional composition square of a reciprocal ternary, *A,B//X,Y* system. One charge equivalent of each pure component is shown at each corner. For example, in the Na,Ca//F,SO_4 system, where the absolute ionic charges are $q_A = 1$, $q_B = 2$, $q_X = 1$, and $q_Y = 2$, the components would be NaF, $Ca_{1/2}F$, $Na(SO_4)_{1/2}$, and $Ca_{1/2}(SO_4)_{1/2}$. The axes are the usual charge-equivalent fractions Y'_A and Y'_X (not to be confused with Y_A and Y_X in Eq. [10]). The formal compositions of quadruplets such as $A_{2/Z^A_{A_2/X_2}}X_{2/Z^X_{A_2/X_2}}$ are at the corners. (Note that, from Eq. [22], the ratio $Z^A_{A_2/X_2}/Z^X_{A_2/X_2}$, is the same as the ratio (q_A/q_X).) The formal compositions of quadruplets such as $A_{1/Z^A_{AB/X_2}}B_{1/Z^B_{AB/X_2}}X_{2/Z^X_{AB/X_2}}$ are found on the sides of the square, as shown in Figure 2.

Choice of $Z^m_{ij/kl}$

For a solid solution, it is required that all cationic coordination numbers ($Z^i_{ij/kl}$) be equal and that all anionic coordination numbers ($Z^k_{ij/kl}$) be equal. For liquid solutions, on the other hand, Z^A_{AB/X_2} and Z^B_{AB/X_2} are chosen to correspond to the composition of maximum SNN SRO in the *A,B//X* binary subsystem, as discussed previously.[1–4] For example, for KCl-$MgCl_2$ solutions, SRO is at a maximum near the composition K_2MgCl_4. Hence, we set $Z^{Mg}_{KMg/Cl_2}/Z^{K}_{KMg/Cl_2} = 2.0$.

Since the quasi-chemical expression for the entropy (Section II–D) is, of necessity, only approximate, it is not necessary that the values of $Z^m_{ij/kl}$ used in the model correspond exactly to the actual coordination numbers. In fact, it is found that better representations are frequently obtained with

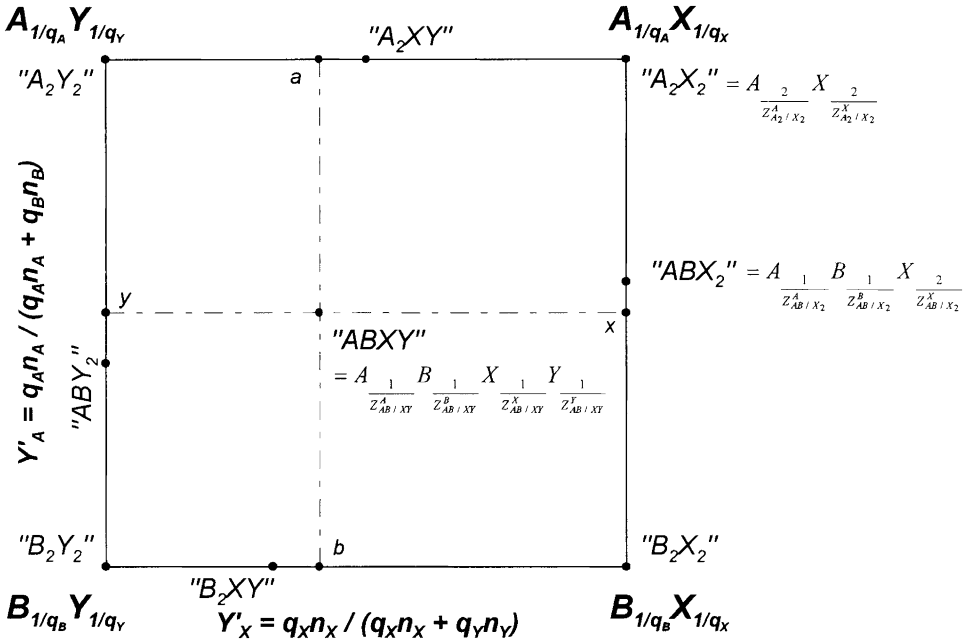

Fig. 2—Composition square of the AB//XY reciprocal ternary system showing formal "compositions" of the various quadruplets.

intentionally nonphysical values of $Z^m_{ij/kl}$, since one can thereby partially compensate for the error caused by the entropy approximation. However, it is important that the ratios of $Z^m_{ij/kl}$ correspond to the compositions of maximum SRO, as discussed previously.

The coordination numbers $Z^i_{AB/XY}$, for the "reciprocal" *ABXY* quadruplets ($A \neq B$, $X \neq Y$) can be chosen to reflect a tendency to SRO at some particular composition in the reciprocal *A,B//X,Y* solutions. However, in many cases, there will be no such tendency, and one can set the value of $Z^i_{AB/XY}$ as an "average" of the values in the A_2XY, B_2XY, ABX_2, and ABY_2 quadruplets. It is suggested that this be done by defining the "composition" of the *ABXY* quadruplets as lying at the average of the values of Y'_X of the quadruplets A_2XY and B_2XY and at the average of the values of Y'_A of the quadruplets ABX_2 and ABY_2, as illustrated in Figure 2. This construction corresponds to the following "default" values:

$$\frac{1}{Z^A_{AB/XY}} = \left(\frac{Z^X_{AB/X_2}}{q_XZ^A_{AB/X_2}} + \frac{Z^Y_{AB/Y_2}}{q_YZ^A_{AB/Y_2}}\right)F$$
$$\frac{1}{Z^X_{AB/XY}} = \left(\frac{Z^A_{A_2/XY}}{q_AZ^X_{A_2/XY}} + \frac{Z^B_{B_2/XY}}{q_BZ^X_{B_2/XY}}\right)F \quad [23]$$

and similarly for $Z^B_{AB/XY}$ and $Z^Y_{AB/XY}$, where

$$F = \frac{1}{8}\left(\frac{q_X}{Z^X_{AB/X_2}} + \frac{q_Y}{Z^Y_{AB/Y_2}} + \frac{q_A}{Z^A_{A_2/XY}} + \frac{q_B}{Z^B_{B_2/XY}}\right) \quad [24]$$

C. *Gibbs Energy Equation*

We now define

$$g^\circ_{A_2/X_2} = \left(\frac{2q_A}{Z^A_{A_2/X_2}}\right)g^\circ_{A_{1/q_A}X_{1/q_X}} = \left(\frac{2q_X}{Z^X_{A_2/X_2}}\right)g^\circ_{A_{1/q_A}X_{1/q_X}} \quad [25]$$

where $g^\circ_{A_{1/qA}X_{1/qX}}$ is the standard Gibbs energy of the pure component per charge equivalent. For Al_2O_3, for example,

$$g^\circ_{Al_2/O_2} = \left(\frac{6}{Z^{Al}_{Al_2/O_2}}\right)g^\circ_{Al_{1/3}O_{1/2}} = \left(\frac{4}{Z^{O}_{Al_2/O_2}}\right)g^\circ_{Al_{1/3}O_{1/2}} \quad [26]$$

That is, $g^\circ_{Al_2/O_2}$ is the standard Gibbs energy of Al_2O_3 per mole of Al_2O_2 quadruplets.

Previously,[5] $g^\circ_{A/X}$ was defined as the standard Gibbs energy per mole of FNN pairs. Therefore,

$$g^\circ_{A_2/X_2} = (4/\zeta)g^\circ_{A/X} \quad [27]$$

The Gibbs energy of the solution is given by the model as

$$G = (n_{A_2/X_2}g^\circ_{A_2/X_2} + n_{B_2/X_2}g^\circ_{B_2/X_2} + n_{A_2/Y_2}g^\circ_{A_2/Y_2} + \cdots)$$
$$+ (n_{AB/X_2}g_{AB/X_2} + n_{AB/Y_2}g_{AB/Y_2} + n_{A_2/XY}g_{A_2/XY} + \cdots) \quad [28]$$
$$+ (n_{AB/XY}g_{AB/XY} + \cdots) - T\,\Delta S^{\text{config}}$$

where g_{AB/X_2}, $g_{AB/XY}$, *etc.*, are the Gibbs energies of one mole of the quadruplets.

Let us consider the following reaction for the formation of quadruplets:

$$(A_2X_2)_{\text{quad}} + (B_2X_2)_{\text{quad}} = 2(ABX_2)_{\text{quad}} \quad \Delta g_{AB/X_2} \quad [29]$$

for which the Gibbs energy change is $\Delta g_{AB/X_2}$. If we do not use the shorthand notation, the Eq. [29] is written:

$$\left(\frac{Z^A_{A_2/X_2}}{Z^A_{AB/X_2}}\right)A_{2/Z^A_{A_2/X_2}}\,X_{2/Z^X_{A_2/X_2}} + \left(\frac{Z^B_{B_2/X_2}}{Z^B_{AB/X_2}}\right)B_{2/Z^B_{B_2/X_2}}\,X_{2/Z^X_{B_2/X_2}}$$
$$= 2A_{1/Z^A_{AB/X_2}}\,B_{1/Z^B_{AB/X_2}}\,X_{2/Z^X_{AB/X_2}} \quad [30]$$

When $\Delta g_{AB/X_2} = 0$, the binary *A,B//X* system is ideal. In this case,

$$2g_{AB/X_2} = \left(\frac{Z^A_{A_2/X_2}}{Z^A_{AB/X_2}}\right)g^\circ_{A_2/X_2} + \left(\frac{Z^B_{B_2/X_2}}{Z^B_{AB/X_2}}\right)g^\circ_{B_2/X_2} \quad [31]$$

Now $\Delta g_{AB/X_2}$ is an empirical parameter of the model. It may be expressed as

$$\Delta g_{AB/X_2} = \Delta g^\circ_{AB/X_2} + (\Delta g_{AB/X_2} - \Delta g^\circ_{AB/X_2}) \qquad [32]$$

where $\Delta g^\circ_{A_2/X_2}$ is a constant, independent of composition, and $(\Delta g_{AB/X_2} - \Delta g^\circ_{AB/X_2})$ is expanded as an empirical polynomial in the quadruplet fractions $X_{ij/kl}$.

As discussed in Section II–E, $\Delta g_{AB/X_2}$ in the *A,B,C,* . . .// *X* subsystem is identical to $\Delta g_{AB/X}$ of reaction [1] in this subsystem, and $\Delta g^\circ_{AB/X_2}$ and the coefficients of the polynomial expansion of $(\Delta g_{AB/X_2} - \Delta g^\circ_{AB/X_2})$ are all numerically equal to the coefficients obtained from optimization of data in this subsystem, as described previously.[2,3,4]

We now define the "standard molar Gibbs energy of the ABX_2 quadruplets" as

$$2g^\circ_{AB/X_2} = \left(\frac{Z^A_{A_2/X_2}}{Z^A_{AB/X_2}}\right) g^\circ_{A_2/X_2} + \left(\frac{Z^B_{B_2/X_2}}{Z^B_{AB/X_2}}\right) g^\circ_{B_2/X_2} + \Delta g^\circ_{AB/X_2} \qquad [33]$$

Similarly, for the quadruplet formation reaction,

$$(A_2X_2)_{\text{quad}} + (A_2Y_2)_{\text{quad}} = 2(A_2XY)_{\text{quad}} \quad \Delta g_{A_2/XY} \qquad [34]$$

we define

$$2g^\circ_{A_2/XY} = \left(\frac{Z^X_{A_2/X_2}}{Z^X_{A_2/XY}}\right) g^\circ_{A_2/X_2} + \left(\frac{Z^Y_{A_2/Y_2}}{Z^Y_{A_2/XY}}\right) g^\circ_{A_2/Y_2} + \Delta g^\circ_{A_2/XY} \qquad [35]$$

To now define $g^\circ_{AB/XY}$ for the reciprocal *ABXY* quadruplet, consider that in an ideal solution, $g_{AB/XY}$ (when normalized per charge equivalent) would vary linearly with composition in Figure 2 between points *x* and *y* and between points *a* and *b*. To this linear variation is added the sum of $\Delta g^\circ_{AB/X_2}$, $\Delta g^\circ_{AB/Y_2}$, $\Delta g^\circ_{A_2/XY}$, and $\Delta g^\circ_{B_2/XY}$ (which were included in Eqs. [33] and [35]) corrected to the same molar basis, and finally we add the composition-independent term $\Delta g^\circ_{AB/XY}$ of the Gibbs energy change $\Delta g^\circ_{AB/XY}$ of the quadruplet formation reaction:

$$\begin{aligned} &\tfrac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY) \\ &\Delta g_{AB/XY} = \Delta g^\circ_{AB/XY} + (\Delta g_{AB/XY} - \Delta g^\circ_{AB/XY}) \end{aligned} \qquad [36]$$

where $\Delta g_{AB/XY}$ is an empirical parameter of the model, obtained from optimization of data for the reciprocal *A,B*// *X,Y* system, as discussed in Section II–E. In the ideal case, $\Delta g_{AB/XY} = 0$. The resultant definition of $g^\circ_{AB/XY}$ is

$$\begin{aligned} g^\circ_{AB/XY} = &\left(\frac{q_X}{Z^X_{AB/XY}} + \frac{q_Y}{Z^Y_{AB/XY}}\right)^{-1} \left(\frac{q_X Z^A_{A_2/X_2}}{2Z^A_{AB/XY}Z^X_{AB/XY}} \cdot g^\circ_{A_2/X_2}\right. \\ &+ \frac{q_X Z^B_{B_2/X_2}}{2Z^B_{AB/XY}Z^X_{AB/XY}} \cdot g^\circ_{B_2/X_2} + \frac{q_Y Z^A_{A_2/Y_2}}{2Z^A_{AB/XY}Z^Y_{AB/XY}} \cdot g^\circ_{A_2/Y_2} \\ &\left. + \frac{q_Y Z^B_{B_2/Y_2}}{2Z^B_{AB/XY}Z^Y_{AB/XY}} \cdot g^\circ_{B_2/Y_2}\right) \\ &+ \frac{1}{4}\left(\frac{Z^X_{AB/X_2}}{Z^X_{AB/XY}} \Delta g^\circ_{AB/X_2} + \frac{Z^Y_{AB/Y_2}}{Z^Y_{AB/XY}} \Delta g^\circ_{AB/Y_2} + \frac{Z^A_{A_2/XY}}{Z^A_{AB/XY}}\right. \\ &\left. \Delta g^\circ_{A_2/XY} + \frac{Z^B_{B_2/XY}}{Z^B_{AB/XY}} \Delta g^\circ_{B_2/XY}\right) + \Delta g^\circ_{AB/XY} \end{aligned} \qquad [37]$$

Note that Eq. [22] applies, and that the definition in Eq. [37] holds, even if one does not choose to define $Z^i_{AB/XY}$ as in Eqs. [23] and [24].

Substitution of Eqs. [33], [35], and [37] into Eq. [28] gives

$$\begin{aligned} G = &(n_{A_2/X_2}g^\circ_{A_2/X_2} + \cdots + n_{AB/X_2}g^\circ_{AB/X_2} + n_{A_2/XY}g^\circ_{A_2/XY} \\ &+ \cdots + n_{AB/XY}g^\circ_{AB/XY} + \cdots) \\ &+ \frac{1}{2}\left(n_{AB/X_2} + \frac{Z^X_{AB/X_2}}{2}\left(\frac{n_{AB/XY}}{Z^X_{AB/XY}} + \frac{n_{AB/XZ}}{Z^X_{AB/XZ}} + \cdots\right)\right) \\ &(\Delta g_{AB/X_2} - \Delta g^\circ_{AB/X_2}) + \frac{1}{2}\left(n_{A_2/XY} + \frac{Z^A_{A_2/XY}}{2}\left(\frac{n_{AB/XY}}{Z^A_{AB/XY}}\right.\right. \\ &\left.\left. + \frac{n_{AC/XY}}{Z^A_{AC/XY}} + \cdots\right)\right)(\Delta g_{A_2/XY} - \Delta g^\circ_{A_2/XY}) + \frac{1}{2}\cdots \\ &+ \frac{1}{2}(n_{AB/XY}(\Delta g_{AB/XY} - \Delta g^\circ_{AB/XY}) + n_{AB/YZ} \\ &(\Delta g_{AB/YZ} - \Delta g^\circ_{AB/YZ}) + \cdots) - T\,\Delta S^{\text{config}} \end{aligned} \qquad [38]$$

D. *The Configurational Entropy*

In Eq. [38], ΔS^{config} is given by distributing all the quadruplets randomly over "quadruplet positions." Unfortunately, an exact mathematical expression for this is unknown, and so approximations must be made. Letting ΔS^{config} equal $-\text{R}\,\Sigma\,(n_{ij/kl}\ln X_{ij/kl})$ would clearly overcount the number of possible configurations. The following expression is proposed:

$$\begin{aligned} (-\Delta S^{\text{config}}/\text{R}) = &(n_A \ln X_A + n_B \ln X_B + \cdots \\ &+ n_X \ln X_X + n_Y \ln X_Y + \cdots) \\ &+ \left(n_{A/X} \ln \frac{X_{A/X}}{Y_A Y_X} + n_{B/X} \ln \frac{X_{B/X}}{Y_B Y_X}\right. \\ &\left. + n_{A/Y} \ln \frac{X_{A/Y}}{Y_A Y_Y} + \cdots\right) \\ &+ \left(n_{A_2/X_2} \ln \frac{X_{A_2/X_2}}{X^4_{A/X}/Y^2_A Y^2_X} + \cdots\right. \\ &+ n_{AB/X_2} \ln \frac{X_{AB/X_2}}{2X^2_{A/X}X^2_{B/X}/Y_A Y_B Y^2_X} \\ &+ n_{A_2/XY} \ln \frac{X_{A_2/XY}}{2X^2_{A/X}X^2_{A/Y}/Y^2_A Y_X Y_Y} + \cdots \\ &\left. + n_{AB/XY} \ln \frac{X_{AB/XY}}{4X_{A/X}X_{B/X}X_{A/Y}X_{B/Y}/Y_A Y_B Y_X Y_Y} + \cdots\right) \end{aligned} \qquad [39]$$

Consider the case when all $\Delta g_{ij/kl}$ values for reactions [32], [34], and [36] are zero and also when all $\Delta g^{\text{exchange}}_{ij/kl}$ values (as in reaction [3]) are zero. In this case, the distributions of *A,B,C,* . . . and *X,Y,Z,* . . . on each sublattice are completely random. There is neither FNN nor SNN SRO. Hence, the probability of finding an *A-X* FNN pair is equal to $(Y_A X_X)$, that is,

$$X_{i/j} = Y_i Y_j \qquad [40]$$

Furthermore, the probability of finding an *ABXY* quadruplet is given, with reference to Figure 1, by the probability that pair 1 is an *A-X* pair, times the conditional probabilities that pairs 2, 3, and 4 are *A-Y*, *Y-B*, and *B-X* pairs, respectively, times 4.0, which is the number of possible permutations of this order of bonds. Hence,

$$X_{AB/XY} = 4X_{A/X}\,(X_{A/Y}/Y_A)\,(X_{B/Y}/Y_Y)\,(X_{B/X}/Y_BY_X) \qquad [41]$$

Similarly, one can derive

$$X_{AB/X_2} = 2X^2_{A/X}X^2_{B/X}/(Y_AY_BY^2_X) \text{ and } X_{A_2/X_2} = X^4_{A/X}/Y^2_AY^2_X \qquad [42]$$

Substitution of Eqs. [40] through [42] into Eq. [39] gives the correct ideal (Temkin) entropy: $-\mathrm{R}(n_A \ln X_A + n_B \ln X_B + \cdots + n_X \ln X_X + n_Y \ln X_Y + \cdots)$. Also, for this ideal case, substitution of Eqs. [20], [27], [33], [35], and [37] into Eq. [38] gives the correct expression for an ideal solution:

$$\begin{aligned} G = {} & (n_{A/X}g^\circ_{A/X} + n_{A/Y}g^\circ_{A/Y} + \cdots) \\ & + \mathrm{R}T\,(n_A \ln X_A + n_B \ln X_B + n_X \ln X_X + \cdots) \end{aligned} \qquad [43]$$

Consider next the case, where the $\Delta g^{\text{exchange}}_{ij/kl}$ values of reaction [3] are not all zero, so that there is FNN SRO. In this case, Eq. [40] does not hold. Equations [41] and [42] hold exactly in subsystems such as *A,B,C,* . . .*//X* or *A//X,Y,Z,* . . . , where one sublattice is occupied exclusively by one species, but do not hold exactly in general, because they were derived under the assumption of a random distribution of FNN pairs. Nevertheless, calculations show that Eqs. [41] and [42] still hold approximately, and their use results in errors of only a few percent for absolute values of $\Delta g^{\text{exchange}}_{ij/kl}$ as large as 100 kJ/mol. The approximation, of course, becomes exact as $\Delta g^{\text{exchange}}$ approaches zero. Substitution of Eqs. [41] and [42] into Eq. [39] gives the expression

$$\begin{aligned} (-\Delta S^{\text{config}}/\mathrm{R}) = {} & (n_A \ln X_A + n_B \ln X_B + \cdots) \\ & + (n_X \ln X_X + n_Y \ln X_Y + \cdots) \\ & + \left(n_{A/X} \ln \frac{X_{A/X}}{Y_AY_X} + n_{B/Y} \ln \frac{X_{B/Y}}{Y_BY_Y} + \cdots\right) \end{aligned} \qquad [44]$$

which is identical to that given previously[5] for the two-sublattice quasi-chemical model with FNN, but no SNN, SRO.

E. *Second-Nearest-Neighbor Interaction Terms*

The term $\Delta g_{AB/X_2}$ is an empirical parameter of the model, obtained by optimization of data in the *A,B,C,*. . .*//X* subsystem, which is related to the Gibbs energy of formation of SNN pairs according to reactions [29] or [1]. As in Eq. [30] of the previous publication,[2] in the *A,B,C,*. . .*//X* subsystem, $\Delta g_{AB/X_2}$ is expanded as

$$\begin{aligned} \Delta g_{AB/X_2} = {} & \Delta g^\circ_{AB/X_2} + \sum_{(i+j)\geq 1} \chi^i_{AB/X_2}\chi^j_{BA/X_2}g^{ij}_{AB/X_2} \\ & + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi^i_{AB/X_2}\chi^j_{BA/X_2}\left(\sum_l g^{ijk}_{AB(l)/X_2}Y_l(1 - \xi_{AB/X_2} \right. \\ & \left. - \xi_{BA/X_2})^{k-1} + \sum_m g^{ijk}_{AB(m)/X_2}\left(\frac{Y_m}{\xi_{BA/X_2}}\right)\left(1 - \frac{Y_B}{\xi_{BA/X_2}}\right)^{k-1} \right. \\ & \left. + \sum_n g^{ijk}_{AB(n)/X_2}\left(\frac{Y_n}{\xi_{AB/X_2}}\right)\left(1 - \frac{Y_A}{\xi_{AB/X_2}}\right)^{k-1}\right) \end{aligned} \qquad [45]$$

where the summations over *l*, *m*, and *n* are as described previously.[2] Equation [45] may be compared to Eq. [32]. The empirical coefficients $\Delta g^\circ_{AB/X_2}$ and g^{ij}_{AB/X_2} are found by optimization of data in the *A,B//X* binary system, the other terms in Eq. [45] all being equal to zero in this binary system. For example, if all g^{ij}_{AB/X_2} values are zero and if $\Delta g^\circ_{AB/X_2}$ is small, then the model approaches regular-solution behavior, with $\Delta g^\circ_{AB/X_2}$ as the regular-solution parameter. The coefficients $g^{ijk}_{AB(C)/X_2}$ are ternary parameters, which should not be large and which give the influence of the presence of a third cation, C, upon the energy of formation of SNN (*A*-[*X*]-*B*) pairs. These are found by optimization of available data in the *A,B,C//X* ternary subsystem. In the absence of such data, these coefficients can be set to zero. The variables, Y_i, χ_{AB/X_2}, χ_{BA/X_2}, ξ_{AB/X_2}, and ξ_{BA/X_2} were defined previously.[2] They are functions of the quadruplet fractions X_{ij/X_2}, which are equal to the SNN bond fractions in the *A,B,C,*…*//X* subsystem.

The coefficients $\Delta g^\circ_{AB/X_2}$, g^{ij}_{AB/X_2}, and $g^{ijk}_{AB(C)/X_2}$ are identical to the coefficients Δg°_{AB}, g^{ij}_{AB}, and $g^{ijk}_{AB(C)}$ of the previous articles,[2,3,4] in which the quasi-chemical model was developed and applied for the case where sublattice II is occupied solely by the *X* species.

Equation [45] holds for the *A,B,C,*…*//X* subsystem. The composition variables χ_{AB/X_2} and χ_{BA/X_2} were defined in Eq. [27] of the previous article[2] in terms of ratios of the quadruplets fractions X_{ij/X_2}. For example, if the symmetric (Kohler) model is used in all ternary subsystems (Reference 2), then $\chi_{AB/X_2} = (X_{A_2/X_2}/(X_{A_2/X_2} + X_{AB/X_2} + X_{B_2/X_2}))$. In the multicomponent *A,B,C,*. . .*//X,Y,Z,*. . . system, we assume that $\Delta g_{AB/X_2}$ is constant along composition paths where these ratios are constant. Hence, the factors χ_{AB/X_2} and χ_{BA/X_2} in Eq. [45] remain unchanged in the multicomponent system.

In the *A,B,C,*. . .*//X* subsystem, from Eq. [11], the equivalent fraction Y_i is equal to $(X_{i_2/X_2} + \frac{1}{2}(X_{iA/X_2} + X_{iB/X_2} + \cdots))$, which, from Eq. [21], is equal to $X_{i/X}$ in this subsystem. In the multicomponent system, we assume that the ternary terms in Eq. [45] are constant along lines of constant $X_{i/X}/Y_X$ values (where $Y_X = 1$ in the *A,B,C,*. . .*//X* subsystem). Therefore, the Y_i factors in Eq. [45] are replaced by $X_{i/X}/Y_X$. The factors ξ_{AB/X_2} and ξ_{BA/X_2} were defined previously[2] as sums of Y_A, Y_B, Y_C … Hence, in Eq. [45], these are replaced by the corresponding sums of $X_{A/X}/Y_X, X_{B/X}/Y_X, X_{C/X}/Y_X$, *etc.*

Finally, then, $\Delta g_{AB/X_2}$ is given in the multicomponent system by

$$\begin{aligned} \Delta g_{AB/X_2} = {} & \Delta g^\circ_{AB/X_2} + \sum_{(i+j)\geq 1} \chi^i_{AB/X_2}\chi^j_{BA/X_2}g^{ij}_{AB/X_2} \\ & + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi^i_{AB/X_2}\chi^j_{BA/X_2}\left(\sum_l g^{ijk}_{AB(l)/X_2}\frac{X_{l/X}}{Y_X}(1 - \xi_{AB/X_2} \right. \\ & \left. - \xi_{BA/X_2})^{k-1} + \sum_m g^{ijk}_{AB(m)/X_2}\left(\frac{X_{m/X}}{Y_X\xi_{BA/X_2}}\right) \right. \\ & \left. \left(1 - \frac{X_{B/X}}{Y_X\xi_{BA/X_2}}\right)^{k-1} + \sum_n g^{ijk}_{AB(n)/X_2}\left(\frac{X_{n/X}}{Y_X\xi_{AB/X_2}}\right)\right) \end{aligned} \qquad [46]$$

$$\left(1 - \frac{X_{A/X}}{Y_X \xi_{AB/X_2}}\right)^{k-1} + \sum_{Y \neq X} g^{ijk}_{AB/X_2(Y)} Y_Y (1 - Y_X)^{k-1}\Bigg)$$

where χ_{AB/X_2} and χ_{BA/X_2} are ratios of χ_{ij/X_2}, as defined previously,[2] and where ξ_{AB/X_2} and ξ_{BA/X_2}, defined previously[2] as sums of $Y_A, Y_B, Y_C, \ldots$, are now the corresponding sums of $X_{A/X}/Y_X$, $X_{B/X}/Y_X$, *etc.*

The final term in Eq. [46] is zero in the *A,B,C,. . .//X* subsystem. The empirical coefficients $g^{ijk}_{AB/X_2(Y)}$ are reciprocal ternary coefficients that give the effect of the presence of a *Y* anion upon the energy of formation of ABX_2 quadruplets. These coefficients, which should not be large, are found by optimization of available data for the *A,B//X,Y* reciprocal ternary subsystem. In the absence of such data, these coefficients may be set to zero.

A similar expansion of $\Delta g_{A_2/XY}$ for the formation of A_2XY quadruplets may be written:

$$\begin{aligned}\Delta g_{A_2/XY} = {} & \Delta g^{\circ}_{A_2/XY} + \sum_{(i+j)\geq 1} \chi^{i}_{A_2/XY} \chi^{j}_{A_2/YX} g^{ij}_{A_2/XY} \\ & + \sum_{\substack{i\geq 0 \\ j\geq 0 \\ k\geq 1}} \chi^{i}_{A_2/XY} \chi^{j}_{A_2/YX} \left(\sum_{l} g^{ijk}_{A_2/XY(l)} \frac{Y_{A/l}}{Y_A} (1 - \xi_{A_2/XY} \right. \\ & \left. - \xi_{A_2/YX})^{k-1} + \sum_{m} g^{ijk}_{A_2/XY(m)} \left(\frac{X_{A/m}}{Y_A \xi_{A_2/YX}} \right) \right. \\ & \left(1 - \frac{X_{A/Y}}{Y_Y \xi_{A_2/YX}} \right)^{k-1} + \sum_{n} g^{ijk}_{A_2/XY(n)} \left(\frac{X_{A/n}}{Y_A \xi_{A_2/XY}} \right) \\ & \left. \left(1 - \frac{X_{A/X}}{Y_A \xi_{A_2/XY}} \right)^{k-1} + \sum_{B \neq A} g^{ijk}_{A_2(B)/XY} Y_B (1 - Y_A)^{k-1} \right)\end{aligned} \quad [47]$$

In Eq. [45], $\Delta g_{AB/X_2}$ in the *A,B,C,. . .//X* subsystem is expanded as a polynomial in the quadruplet fractions X_{ij/X_2}, which are equal to the SNN pair fractions in this subsystem. In earlier versions of the quasichemical model, $\Delta g_{AB/X_2}$ was expanded in terms of the equivalent fractions $Y_A, Y_B, Y_C \ldots$. The general expression is[2]

$$\begin{aligned}\Delta g_{AB/X_2} = {} & \Delta g^{\circ}_{AB/X_2} + \sum_{(i+j)\geq 1} \left(\frac{\xi_{AB/X_2}}{\xi_{AB/X_2} + \xi_{BA/X_2}} \right)^{i} \\ & \left(\frac{\xi_{BA/X_2}}{\xi_{AB/X_2} + \xi_{BA/X_2}} \right)^{j} q^{ij}_{AB/X_2} + \sum_{\substack{i\geq 0 \\ j\geq 0 \\ k\geq 1}} \left(\frac{\xi_{AB/X_2}}{\xi_{AB/X_2} + \xi_{BA/X_2}} \right)^{i} \\ & \left(\frac{\xi_{BA/X_2}}{\xi_{AB/X_2} + \xi_{BA/X_2}} \right)^{j} \left(\sum_{l} q^{ijk}_{AB(l)/X_2} Y_l (1 - \xi_{AB/X_2} - \xi_{BA/X_2})^{k-1} \right. \\ & + \sum_{m} q^{ijk}_{AB(m)/X_2} \left(\frac{X_m}{\xi_{BA/X_2}} \right) \left(1 - \frac{X_B}{\xi_{BA/X_2}} \right)^{k-1} \\ & \left. + \sum_{n} q^{ijk}_{AB(n)/X_2} \left(\frac{X_n}{\xi_{AB/X_2}} \right) \left(1 - \frac{X_A}{\xi_{AB/X_2}} \right)^{k-1} \right)\end{aligned} \quad [48]$$

This equation is clearly very similar to Eq. [45]. If the *A,B,C,. . .//X* subsystem was optimized using this expansion, then Eq. [48] can be substituted into Eq. [38] after first replacing all Y_i terms by $X_{i/X}/Y_X$, replacing all ξ_{AB/X_2} and ξ_{BA/X_2} terms by the corresponding sums of $X_{i/X}/Y_X$, and after adding reciprocal ternary terms if required, just as was done in Eq. [46].

In order to provide more flexibility in optimizing data in reciprocal systems, the parameter $\Delta g_{AB/XY}$ for reaction [36] can also be expanded as follows and substituted into Eq. [38]:

$$\begin{aligned}\Delta g_{AB/XY} = {} & \Delta g^{\circ}_{AB/XY} + \sum_{i\geq 1} (g^{i}_{AB/XY(AX)} X^{i}_{A_2/X_2} \\ & + g^{i}_{AB/XY(BX)} X^{i}_{B_2/X_2} \\ & + g^{i}_{AB/XY(AY)} X^{i}_{A_2/Y_2} + g^{i}_{AB/XY(BY)} X^{i}_{B_2/Y_2})\end{aligned} \quad [49]$$

where $\Delta g^{\circ}_{AB/XY}$, $g^{i}_{AB/XY(AX)}$, *etc.*, are additional empirical parameters obtainable by optimization of available data for the reciprocal ternary *A,B,//X,Y* system. In the absence of such data, these terms should be set to zero.

F. *The Quasi-chemical Model in the "Complex" Formalism*

As discussed in Section II–B, if the quadruplets *ABXY* are formally treated as complexes or molecules ($A_{1/Z^A_{AB/XY}} B_{1/Z^B_{AB/XY}} X_{1/Z^X_{AB/XY}} Y_{1/Z^Y_{AB/XY}}$), then the mass balances of Eq. [15] become "normal" mass balances. Furthermore, all the $\Delta g_{ij/kl}$ parameters in Eq. [38] have been shown in Section II–E to be expressible solely in terms of the quadruplet fractions $X_{ij/kl}$. (The pair fractions $X_{i/j}$ and equivalent fractions of Eqs. [46] and [47] can be expanded in terms of $X_{ij/kl}$ through the use of Eqs. [11], [12], and [21].) Hence, apart from the $(-T\Delta S^{\text{config}})$ term, Eq. [38] is of the same form as an expression for the Gibbs energy of a mixture of molecules ($A_{1/Z^A_{AB/XY}} B_{1/Z^B_{AB/XY}} X_{1/Z^X_{AB/XY}} Y_{1/Z^Y_{AB/XY}}$) on a single lattice, with the nonconfigurational "excess" terms expressed as polynomials in the mole fractions $X_{AB/XY}$ of these molecules. Hence, the same existing algorithms and computer subroutines that are commonly used for simple polynomial-solution models can be used directly for the quasi-chemical model merely by including the additional configurational entropy terms.

Furthermore, the fact that Eq. [38] can be written solely in terms of the fractions $X_{ij/kl}$ of the quadruplet "components" permits the chemical potentials to be calculated easily in closed explicit form. By the same argument as that leading to Eq. [36] of Reference 1, the chemical potential of the actual component $A_{1/q_A} X_{1/q_X}$ is given in terms of the "chemical potential (μ_{A_2/X_2}) of the quadruplet A_2X_2" by

$$\mu_{A_{1/q_A}X_{1/q_X}} = \mu_{A_2/X_2} (Z^A_{A_2/X_2}/2q_A) = \mu_{A_2/X_2} (Z^X_{A_2/X_2}/2q_X) \quad [50]$$

where

$$\mu_{A_2/X_2} = (\partial \mathrm{G}/\partial n_{A_2/X_2})_{n_{ij/kl}} \quad [51]$$

Substitution of Eq. [38] into Eq. [51] then gives

$$\begin{aligned}\mu_{A_2/X_2} = {} & g^{\circ}_{A_2/X_2} + \mathrm{R}T \left(\frac{2 \ln X_A}{Z^A_{A_2/X_2}} + \frac{2 \ln X_X}{Z^X_{A_2/X_2}} \right. \\ & \left. + \ln \frac{X_{A_2/X_2}}{(X^4_{A/X}/(Y^2_A Y^2_X))} + \frac{4}{\zeta} \ln \frac{X_{A/X}}{Y_A Y_X} \right) + g^{E}_{A_2/X_2}\end{aligned} \quad [52]$$

where $g^{E}_{A_2/X_2}$ is calculated from the nonconfigurational "g^E" polynomial terms of Eq. [38] in the usual way:

$$g^{E}_{A_2/X_2} = g^{E} + (\partial g^{E}/\partial X_{A_2/X_2}) - \sum_{ij/kl \neq A_2/X_2} X_{ij/kl} (\partial g^{E}/\partial X_{ij/kl}) \quad [53]$$

III. DISCUSSION

Many binary and ternary common-ion systems *A,B,C,. . .//X* have already been evaluated and optimized, by using

a random-mixing (Bragg–Williams) expression for ΔS^{config} and by expanding the excess Gibbs energy as a simple polynomial in the mole fractions. For example, in a binary *A*,*B*//*X* system, this is equivalent to writing:

$$G = (n_{A/X} g^{\circ}_{A/X} + n_{B/X} g^{\circ}_{B/X}) + RT\,(n_A \ln X_A + n_B \ln X_B) + n_{AB/X_2}\,\Delta g_{AB/X_2} \quad [54]$$

with n_{AB/X_2} now equal to $(\Sigma\, n_{ij/kl}) X_{A/X} X_{B/X}$ and with $\Delta g_{AB/X_2}$ expanded as

$$\Delta g_{AB/X_2} = \Delta g^{\circ}_{AB/X_2} + \sum_{(i+j)\geq 1} q^{ij}_{AB/X_2} Y^i_A Y^j_B \quad [55]$$

For example, if all q^{ij}_{AB/X_2} coefficients are zero, then this is a simple regular solution. Ideally, of course, all these systems should be reoptimized with the quasi-chemical model. However, this entails a great deal of work. For systems in which $\Delta g_{AB/X_2}$ is relatively small, the neglect of SRO involving SNN (*A*-[*X*]-*B*) pairs will give rise only to small errors. Hence, it would be very useful to be able to combine the large existing databases of evaluated simple polynomial coefficients for such subsystems with the quasi-chemical coefficients obtained by optimization of other subsystems where SRO is more important, in order to produce one large database for the multicomponent solution. It has been shown previously[1–4] how this combination of coefficients can easily be achieved for *A*,*B*,*C*, . . .//*X* systems. In the present case, if a binary *A*,*B*//*X* system has been optimized using a simple Bragg–Williams entropy and a polynomial expansion as in Eq. [55], then the coefficients of Eq. [55] can be substituted directly into Eq. [48]. (This is also true for simple polynomial ternary coefficients, as described previously.[2]) It is required that $Z^A_{AB/X_2} = Z^A_{A_2/X_2}$ and that $Z^B_{AB/X_2} = Z^B_{B_2/X_2}$. The term $\frac{1}{2}\,(n_{AB/X_2} + (Z^X_{AB/X_2}/2)(n_{AB/XY}/Z^X_{AB/XY} + \cdots))$ $(\Delta g_{AB/X_2} - \Delta g^{\circ}_{AB/X_2})$ in Eq. [38] is replaced by $(\Sigma\, n_{ij/kl})$ $(X_{A/X} X_{B/X}/Y_X)\,\Delta g_{AB/X_2}$, and the term $\Delta g^{\circ}_{AB/X_2}$ must be removed from Eqs. [33] and [37]. It is also recommended that if any binary subsystem of the *A*,*B*,//*X*,*Y* system has been optimized with a simple polynomial expansion, then all coefficients in the expansion for $\Delta g_{AB/XY}$ in Eq. [49] should be set to zero.

IV. CONCLUSIONS

A quasi-chemical model for treating SRO in the quadruplet approximation has been proposed for solutions with two sublattices. Both SRO of FNN pairs and SRO of SNN pairs are taken into account. If one sublattice is occupied by only one species, or is empty, then the present model reduces exactly to the quasi-chemical model for SRO on one sublattice in the pair approximation, as developed previously.[1–4] Also, by means of a minor alteration to the entropy expression, the Gibbs energy expression can be made identical to that of a randomly mixed (Bragg–Williams) solution with a simple polynomial expansion for the excess Gibbs energy. This is of much practical importance, because the large existing databases of evaluated simple polynomial coefficients of certain subsystems can, thereby, be combined in one database with the quasi-chemical coefficients of other subsystems, in order to produce one large database for a multicomponent solution.

The model is well suited to liquid solutions where the ratio of the number of sites on the two sublattices can vary with composition. Further flexibility is provided by permitting coordination numbers to vary with composition. Nevertheless, the model also applies to solid solutions if the number of lattice sites and coordination numbers are held constant. The model can, thus, be combined with the compound-energy formalism[8,9] to treat a wide range of types of solutions (slags, mattes, ceramics, salts, and alloys), point defects, order-disorder phenomena, nonstoichiometric phases, *etc*. For a discussion of applications of the compound-energy formalism, refer to References 10 and 11. If SRO is not included (by assuming Bragg–Williams random-mixing entropy, as just mentioned), the model reduces exactly to the compound-energy formalism for two (or one) sublattices.

That is, several different models are limiting cases of the present model. These models can, thus, all be treated with the same algorithms; the coefficients can all be stored in the same multicomponent databases; and different models for different subsystems can be combined, in many cases.

By formally treating the quadruplets as the components of the solution, a significant computational simplification is realized. The model can then be treated with currently available and relatively simple software.

The model has been applied to the molten salt phase in an evaluation/optimization of the Li,Na,K,Mg,Ca//F,Cl system using the F*A*C*T[12] thermodynamic computing system. This work is presented in an accompanying article.[6]

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