The Modified Quasi-chemical Model: Part III. Two Sublattices

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The modified quasi-chemical model in the pair approximation for short-range ordering (SRO) in liquids is extended to solutions with two sublattices. Short-range ordering of nearest-neighbor pairs is treated, and the effect of second-nearest-neighbor (SNN) interactions upon this ordering is taken into account. The model also applies to solid solutions, if the number of lattice sites and coordination numbers are held constant. It may be combined with the compound-energy formalism to treat a wide variety of solution types. A significant computational simplification is achieved by formally treating the nearest-neighbor pairs as the "components" of the solution. The model is applied to an evaluation/optimization of the phase diagram of the Li,Na,K/F,Cl,SO_4 system.

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 described for solutions in which the species mix on only one lattice or sublattice. The present article extends the treatment to mixing on two sublattices. 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, be treated with the single-sublattice model described previously.[1,2] 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 numbers 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 $CaCl_2$.

A two-sublattice model for multicomponent molten salt solutions was developed in an earlier article,[3] but only for the case of random mixing of species on their respective sublattices. This was an extension and generalization of earlier work by Blander, Yosim, and Saboungi.[4,5,6] Short-range ordering of first-nearest neighbors (FNNs) was introduced into the model by Dessureault and Pelton.[7] That is, account was taken of the fact that certain FNN ("cation-anion") pairs predominate. However, only reciprocal ternary systems (with only two species on each sublattice) were considered, and only for the case of an equal and constant number of sites on the two sublattices. In the present article, this model is generalized. Simultaneous SRO of FNNs and SNNs is not treated by the present model, since this is not possible within a pair approximation. However, this will be the subject of the next article in the present series.

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 which 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.

As another example, in a spinel solid 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 example, 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.

Let $Z^A_{A/X}$ be the nearest-neighbor coordination number of an *A* species when lattice II is occupied only by *X*, and let $Z^X_{A/X}$ be the coordination number of an *X* species when lattice I is occupied only by *A*.

In a solid solution, the numbers of sublattice I and sublattice II sites per mole are necessarily constant, independent of composition. Hence,

in solid solutions,

$$Z^A_{A/X} = Z^B_{B/X} = Z^A_{A/Y} = Z^B_{B/Y} = \cdots = \text{constant} \\ = z_A = z_B = z_C = \cdots = z_I \qquad [1]$$

$$Z^X_{A/X} = Z^X_{B/X} = Z^Y_{A/Y} = Z^Y_{B/Y} = \cdots = \text{constant} \\ = z_X = z_Y = z_Z = \cdots = z_{II} \qquad [2]$$

In a liquid solution, on the other hand, the local structure

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is flexible, and the $Z^i_{i/j}$ and $Z^j_{i/j}$ values can vary with composition.

The following mass balances apply:

$$z_A n_A = n_{A/X} + n_{A/Y} + n_{A/Z} + \cdots \qquad [3]$$

$$z_X n_X = n_{A/X} + n_{B/X} + n_{C/X} + \cdots \qquad [4]$$

where z_A and z_X are the FNN coordination numbers of A and X, n_i is the number of moles of species i in the solution, and $n_{i/j}$ is the number of moles of FNN (i-j) pairs. Let

$$\frac{1}{z_A} = \left(\frac{n_{A/X}}{Z^A_{A/X}} + \frac{n_{A/Y}}{Z^A_{A/Y}} + \frac{n_{A/Z}}{Z^A_{A/Z}} + \cdots\right) \times \left(\frac{1}{n_{A/X} + n_{A/Y} + n_{A/Z} + \cdots}\right) \qquad [5]$$

$$\frac{1}{z_X} = \left(\frac{n_{A/X}}{Z^X_{A/X}} + \frac{n_{B/X}}{Z^X_{B/X}} + \frac{n_{C/X}}{Z^X_{C/X}} + \cdots\right) \times \left(\frac{1}{n_{A/X} + n_{B/X} + n_{C/X} + \cdots}\right) \qquad [6]$$

Combining Eqs. [3] through [6] gives

$$n_A = n_{A/X}/Z^A_{A/X} + n_{A/Y}/Z^A_{A/Y} + n_{A/Z}/Z^A_{A/Z} + \cdots \qquad [7]$$

$$n_X = n_{A/X}/Z^X_{A/X} + n_{B/X}/Z^X_{B/X} + n_{C/X}/Z^X_{C/X} + \cdots \qquad [8]$$

The composition dependence of Eqs. [5] and [6] was chosen because it gives rise to the simple relationships of Eqs. [7] and [8]. The "site fractions" (X_i), "pair fractions" ($X_{i/j}$), and "coordination equivalent site fractions" (Y_i) are defined as

$$X_A = n_A/(n_A + n_B + \cdots)$$
$$X_X = n_X/(n_X + n_Y + \cdots) \qquad [9]$$

$$X_{i/j} = n_{i/j}/\sum n_{i/j} \qquad [10]$$

$$Y_A = z_A n_A/(z_A n_A + z_B n_B + \cdots)$$
$$Y_X = z_X n_X/(z_X n_X + z_Y n_Y + \cdots) \qquad [11]$$

Substitution into Eqs. [7] and [8] gives

$$Y_A = X_{A/X} + X_{A/Y} + X_{A/Z} + \cdots \qquad [12]$$

$$Y_X = X_{A/X} + X_{B/X} + X_{C/X} + \cdots \qquad [13]$$

Restrictions on Z_{ij}

The restrictions on Z_{ij} for a solid solution were given in Eqs. [1] and [2]. For a molten salt solution, these equations need not apply. However, it is necessary that

$$Z^A_{A/X}/Z^X_{A/X} = q_A/q_X \qquad [14]$$

where q_A and q_X are the absolute cationic and anionic charges, respectively. For example, in CaF_2, $Z^{Ca}_{Ca/F}/Z^{F}_{Ca/F} = 2/1$. Substitution of Eq. [14] into Eqs. [7] and [8] gives

$$(q_A n_A + q_B n_B + \cdots) = (q_X n_X + q_Y n_Y + \cdots) \qquad [15]$$

which is the necessary charge-neutrality condition.

B. *Gibbs Energy Equation*

We now define

$$g^\circ_{A/X} = \left(\frac{q_A}{Z^A_{A/X}}\right) g^\circ_{A_{1/qA}X_{1/qX}} = \left(\frac{q_X}{Z^X_{A/X}}\right) g^\circ_{A_{1/qA}X_{1/qX}} \qquad [16]$$

where $g^\circ_{A_{1/qA}X_{1/qX}}$ is the standard Gibbs energy of the pure component. In the case of a salt, if q_A and q_X are the absolute cationic and anionic charges, respectively, then $g^\circ_{A_{1/qA}X_{1/qX}}$ is the standard Gibbs energy per charge equivalent. For Al_2O_3, for example,

$$g^\circ_{Al/O} = (3/Z^{Al}_{Al/O})g^\circ_{Al_{1/3}O_{1/2}} = (2/Z^{O}_{Al/O})g^\circ_{Al_{1/3}O_{1/2}} = (2/Z^{O}_{Al/O})\,\frac{g^\circ_{Al_2O_3}}{6} \qquad [17]$$

That is, $g^\circ_{Al/O}$ is the standard Gibbs energy of Al_2O_3 per mole of Al-O pairs.

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

$$\begin{aligned} G = {} & (n_{A/X}g^\circ_{A/X} + n_{A/Y}g^\circ_{A/Y} + n_{B/X}g^\circ_{B/X} + \cdots) - T\Delta S^{\text{config}} \\ & + \left(\sum n_{i/j}\right)\left(\frac{X_{A/X}X_{B/X}}{Y_X}\,\Delta g_{AB/X} + \frac{X_{A/Y}X_{B/Y}}{Y_Y}\,\Delta g_{AB/Y} \right. \\ & \left. + \frac{X_{A/X}X_{A/Y}}{Y_A}\,\Delta g_{A/XY} + \frac{X_{B/X}X_{B/Y}}{Y_B}\Delta g_{B/XY} + \cdots\right) \\ & + (\text{Reciprocal ternary terms}) \end{aligned} \qquad [18]$$

where $\Sigma\, n_{i/j}$ is the total number of moles of pairs, and ΔS^{config} is the configurational entropy of mixing, given by

$$\begin{aligned} \Delta S^{\text{config}} = {} & -R(n_{A/X} \ln X_{A/X} + n_{A/Y} \ln X_{A/Y} \\ & + n_{B/X} \ln X_{B/X} + \cdots) + R(n_{A/X} \ln Y_A Y_X \\ & + n_{A/Y} \ln Y_A Y_Y + n_{B/X} \ln Y_B Y_X + \cdots) \\ & - R(n_A \ln X_A + n_B \ln X_B + \cdots + n_X \ln X_X \\ & + n_Y \ln X_Y + \cdots) \end{aligned} \qquad [19]$$

In Eq. [18], the parameter $\Delta g_{AB/X}$ is related to the interaction of SNN *A*-*B* pairs on lattice I when lattice II is occupied only by *X*, (a "cation-cation" interaction, in the case of a salt solution). This parameter can be evaluated from experimental data for the *AX*-*BX*-*CX* . . . (abbreviated as *ABC* . . . /*X*) subsystem. This is discussed in detail in Section II–D. The "reciprocal ternary terms" in Eq. [18] are discussed in Section II–E; these should be small, and, in the first approximation, they are equal to zero.

The configurational entropy expression in Eq. [19], for the distribution of the pairs over pair positions, is exact for a one-dimensional lattice and approximate for a three-dimensional lattice. Consider the limiting case of no SRO (that is, random mixing), when the interactions are very weak. The *A*, *B*, *C*, . . . species and the *X*, *Y*, *Z*, . . . species will then be randomly distributed over the sites of sublattices I and II, respectively. Hence, $X_{i/j} = Y_i Y_j$, and the first two terms of Eq. [19] cancel each other, leaving only the third term, which is indeed the correct expression for a random mixture of *A*, *B*, *C*, . . . species on sublattice I and *X*, *Y*, *Z*, . . . species on sublattice II, according to the Temkin[8] model for liquids, in which the number of sites on a sublattice can vary with composition.

Minimization of G to give the equilibrium pair distribution

The numbers of moles ($n_{i/j}$) of the pairs at equilibrium at a given overall composition are calculated by numerical minimization of G, subject to the constraints of Eqs. [7] and

[8]. To illustrate how this results in SRO, consider a simple case of a reciprocal ternary system *AX-AY-BX-BY* (abbreviated as *AB*/*XY*) when the last two terms in Eq. [18] are equal to zero. Setting $\partial G/\partial n_{i/j} = 0$, subject to the constraints of Eqs. [7] and [8], then gives the following "quasi-chemical equilibrium constant."

$$\frac{X_{A/Y}X_{B/X}}{X_{A/X}X_{B/Y}} = \exp\left(-\Delta g^{\text{exchange}}/\mathrm{R}T\right) \qquad [20]$$

for the pair-exchange reaction

$$(A\text{-}X) + (B\text{-}Y) = (A\text{-}Y) + (B\text{-}X) \qquad [21]$$

where

$$\Delta g^{\text{exchange}}_{AB/XY} = g^{\circ}_{A/Y} + g^{\circ}_{B/X} - g^{\circ}_{A/X} - g^{\circ}_{B/Y} \qquad [22]$$

If $\Delta g^{\text{exchange}}$ is negative, for example, then reaction [21] is shifted to the right, and (*A-Y*) and (*B-X*) pairs predominate. If $\Delta g^{\text{exchange}}$ is zero, then the solution of Eqs. [7], [8], and [20] gives $X_{i/j} = Y_iY_j$, which is the limiting case for random mixing, as discussed previously. From Eqs. [16] and [22], $\Delta g^{\text{exchange}}$ can be calculated solely from the standard Gibbs energies of the pure components.

C. *Limiting Case of Random Mixing*

Let us assume that the values of $\Delta g^{\text{exchange}}$ for all the pair-exchange reactions are sufficiently small for the distribution of species on the sublattices to be nearly random. Setting all values of $X_{i/j} = Y_iY_j$ in Eq. [18] then gives

$$\begin{aligned} G = {} & \left(\textstyle\sum n_{i/j}\right)\left(Y_AY_Xg^{\circ}_{A/X} + Y_AY_Yg^{\circ}_{A/Y} + Y_BY_Xg^{\circ}_{B/X} + \cdots\right) \\ & + \mathrm{R}T(n_A \ln X_A + n_B \ln X_B + \cdots \\ & + n_X \ln X_X + n_Y \ln X_Y + \cdots) \qquad [23] \\ & + \left(\textstyle\sum n_{i/j}\right)\left(Y_AY_BY_X\,\Delta g_{AB/X} + Y_AY_BY_Y\,\Delta g_{AB/Y}\right. \\ & \left. + Y_AY_XY_Y\,\Delta g_{A/XY} + Y_BY_XY_Y\,\Delta g_{B/XY} + \cdots\right) \\ & + (\text{reciprocal ternary terms}) \end{aligned}$$

If Eq. [23] is normalized per charge equivalent and if it is assumed, as was done previously,[3] that $z_i = q_iz$, where z is a constant, then Eq. [23] is identical to the expression given previously[3] for a molten salt solution with random mixing.

D. *SNN Interaction Terms*

As mentioned in Section II–B, the third term in Eq. [18] is related to the interactions of SNN pairs on the same sublattice. In the *ABC* . . . /*X* subsystem, sublattice II is occupied only by *X* species; hence, $Y_X = 1$ and $Y_Y = Y_Z = \ldots = 0$. Furthermore, $X_{A/X} = Y_A$, $X_{B/X} = Y_B$, *etc.*; $n_{A/X} = Z^{A}_{A/X}n_A$, $n_{B/X} = Z^{B}_{B/X}n_B$, *etc.*: while $n_{A/Y} = 0$, $X_{A/Y} = 0$. *etc.* Substitution into Eq. [18] gives

$$\begin{aligned} G = {} & \left(n_Ag^{\circ}_{AX_{q_X/q_A}} + n_Bg^{\circ}_{BX_{q_X/q_B}} + \cdots\right) \\ & + \mathrm{R}T(n_A \ln X_A + n_B \ln X_B + \cdots) \qquad [24] \\ & + \left(\textstyle\sum n_{i/j}\right)\left(Y_AY_B\,\Delta g_{AB/X} + Y_BY_C\,\Delta g_{BC/X}\right. \\ & \left. + Y_AY_C\,\Delta g_{AC/X} + \cdots\right) \end{aligned}$$

where $g^{\circ}_{AX_{q_X/q_A}}$ is the standard Gibbs energy of the pure component per mole of *A*.

Equation [24] is identical to the expression given previously[2] for the Gibbs energy of the *ABC* . . . /*X* solution when there is random mixing on sublattice I. If the parameters $\Delta g_{AB/X}$, $\Delta g_{BC/X}$, . . . are independent of composition, for example, then Eq. [24] is simply the expression for a regular solution.

The parameter $\Delta g_{AB/X}$ in Eq. [24] may be equated[1] to the energy of the following SNN pair-exchange reaction:

$$(A\text{-}X\text{-}A) + (B\text{-}X\text{-}B) = 2(A\text{-}X\text{-}B) \qquad [25]$$

and may be expanded as a polynomial such as[2]

$$\begin{aligned} \Delta g_{AB/X} = {} & \Delta g^{\circ}_{AB/X} + \sum_{(i+j)\geq 1} q^{ij}_{AB/X}\left(\frac{Y_{\mathrm{A}}}{Y_A + Y_B}\right)^{i}\left(\frac{Y_B}{Y_A + Y_B}\right)^{j} \qquad [26] \\ & + \sum_{\substack{j\geq 0\\ k\geq 1}} \left(\frac{Y_B}{Y_A + Y_B}\right)^{j} \left(q^{0jk}_{AB(C)/X}Y^{k}_{C} + q^{0jk}_{AB(D)/X}Y^{k}_{D} + \cdots\right) \end{aligned}$$

where $\Delta g^{\circ}_{AB/X}$ and $q^{ij}_{AB/X}$ are composition-independent (although possibly temperature-dependent) coefficients obtained from fitting experimental data for binary *AX-BX* solutions. The remaining terms in Eq. [26] are "ternary terms," which are all zero in the *AX-BX* binary system and which give the effect of the presence of *C*, *D*, . . . upon the energy of reaction [25]. The constant coefficients $q^{0jk}_{AB(C)/X}$, for example, can be obtained from fitting experimental data for the *A*,*B*,*C*/*X* ternary subsystem. For further discussion of the expansions of $\Delta g_{AB/X}$ as polynomials, refer to References 1 and 2.

Although Eq. [24] is identical to the expression for *G* given previously,[2] in the previous equation, Z_A and Z_B in the equivalent fraction expressions $Y_A = Z_A/(n_AZ_A + n_BZ_B + \cdots)$ were SNN coordination numbers. The present model, thus, requires that the ratios Z_B/Z_A, Z_C/Z_B, *etc.*, of SNN coordination numbers be the same as for the ratios z_B/z_A, z_C/z_B, *etc.*, of corresponding FNN coordination numbers. (Only the ratios need to be the same. The actual values of z_i for FNNs and Z_i for SNNs can be different, as long as the parameters $\Delta g_{AB/X}$, *etc.*, in Eq. [24] are expressed per mole of FNN pairs.)

In the limit of random mixing, as shown in Eq. [23], the term $Y_AY_B\,\Delta g_{AB/X}$ in Eq. [24] for the *ABC* . . . /*X* subsystem is simply multiplied by Y_X. That is, the contribution of reaction [25] to the Gibbs energy is decreased by the factor Y_X, which is the probability, in a random mixture, that $i = X$ in an (*A-i-B*) configuration. However, in the general nonrandom case when there is SRO, this is no longer true. Suppose that the value of $\Delta g^{\text{exchange}}$ for reaction [25] is negative. The reaction is, thus, displaced to the right, with a resultant clustering of (*A-Y*) and (*B-X*) pairs. Hence, the probability of an (*A-X-B*) configuration is less than in a random mixture, and so the contribution of the (*A-X-B*) SNN term to the Gibbs energy is less than in a random mixture. It was shown previously[7] that this effect can become very important when the absolute value of $\Delta g^{\text{exchange}}$ exceeds about 50 kJ. The use of the random-mixing approximation in such cases can result in calculated phase diagrams that are greatly in error.

To account for this effect, the term $Y_AY_BY_X\,\Delta g_{AB/X}$ in Eq. [23] for the *AB* . . . /*X* subsystem is replaced by $(X_{A/X}X_{B/X}/Y_X)\,\Delta g_{AB/X}$ in Eq. [18]. That is, $X_{A/X}$ is the probability that a given pair is an (A-X) pair, and $(X_{B/X}/Y_X)$ is the conditional probability that a neighboring pair is a (B-X) pair, given that one member of this pair is an X. In a random mixture, where $X_{A/X} = Y_A Y_X$ and $X_{B/X} = Y_B Y_X$, this expression reduces to the limiting value, $Y_A Y_B Y_X \ \Delta g_{AB/X}$, as given in Eq. [23].

Previously,[7] the expression for $\Delta g_{AB/X}$ from Eq. [26] (or a similar polynomial) was substituted directly into Eq. [18]. That is, it was assumed that $\Delta g_{AB/X}$ is constant along a surface of constant Y_A, Y_B, Y_C . . . . In the present model, this has been modified somewhat. The factors Y_A, Y_B, . . . in Eq. [26] are first replaced by $X_{A/X}/Y_X$, $X_{B/X}/Y_X$, . . . which are equal to Y_A, Y_B, . . . in the ABC . . . $/X$ subsystem). Then, Eq. [26] is substituted into Eq. [18]. From Eq. [13], it can be seen that this is equivalent to assuming that $\Delta g_{AB/X}$ is a constant along a surface of constant $X_{m/X}/(X_{A/X} + X_{B/X} + \cdots)$, where $m = A, B, C$ . . . . This is very similar to the previous[7] assumption, but has been found to give somewhat better results.

E. *Reciprocal Ternary Terms*

If the model is good, then Eq. [18] should give a reasonable prediction of the Gibbs energy of the solution, with no reciprocal ternary terms. However, if experimental data such as a phase diagram are available for an AB/XY reciprocal ternary subsystem, then these can be used to determine the empirical coefficients of reciprocal ternary terms. The following very simple form is proposed.

$$\begin{aligned}&(\text{Reciprocal ternary } AB/XY \text{ terms})\\&\quad = \left(\sum n_{m/n}\right) \sum_{\substack{i,j\neq 0\\ \text{or } k,l\neq 0}} q^{ijkl}_{AB/XY} X^{i}_{A/X} X^{j}_{B/Y} X^{k}_{A/Y} X^{l}_{B/X}\end{aligned} \qquad [27]$$

where the $q^{ijkl}_{AB/XY}$ terms are empirical coefficients. In order that these terms be zero in all binary subsystems, it is necessary either that i and j be both nonzero, or that k and l be both nonzero.

A more physically justifiable form for the reciprocal ternary terms could be proposed. This will be discussed with respect to the more general model in the next article of the present series.

F. *The Lattice Stability Term*

In Gibbs energy expressions such as Eq. [18], the first term is often called the "lattice stability term." In Eq. [18], the standard Gibbs energy $g^{\circ}_{A/X}$ is weighted by the factor $n_{A/X}$, the number of FNN pairs. The lattice stability term, thus, depends upon the degree of SRO. At the other extreme, one might propose replacing this term by $(\Sigma n_{i/j})(Y_A Y_X g^{\circ}_{A/X} + Y_B Y_X g^{\circ}_{B/X} + \cdots)$, which is independent of the SRO. If this were done, then minimizing G would simply involve maximizing the entropy, and a random mixture would always result. However, experience has shown that, at least in the case of molten salts, the lattice stability term of Eq. [18] yields predictions that agree closely with measurements.

Nevertheless, a more flexible equation could be proposed, in which the lattice stability term is written as

$$\begin{aligned}&(n_{A/X}(g^{\circ}_{A/X} - g^{*}_{A/X}) + n_{A/Y}(g^{\circ}_{A/Y} - g^{*}_{A/Y}) + \cdots)\\&\quad + \left(\sum n_{i/j}\right)(Y_A Y_X g^{*}_{A/X} + Y_A Y_Y g^{*}_{A/Y} + \cdots)\end{aligned} \qquad [28]$$

where the $g^{*}_{i/j}$ terms are additional adjustable parameters. In the ABC . . . $/X$ subsystem, $n_{A/X} = (\Sigma n_{i/j}) Y_A Y_X$, and so all terms in $g^{*}_{i/j}$ disappear. However, within the reciprocal system, it is now the term $(\Delta g^{\text{exchange}} - \Delta g^{*\text{exchange}})$ which appears in the exponential of Eq. [20] and which affects the degree of SRO. Note also that in a random mixture, $n_{A/X} = (\Sigma n_{i/j}) Y_A Y_X$, and all terms in $g^{*}_{i/j}$ disappear.

For molten salt systems, such as those presented in Section III, good results have been obtained with all $g^{*}_{i/j}$ terms set to zero (*i.e.*, by using Eq. [18]). However, the use of the lattice stability term of Eq. [28] may find application in solid solutions such as Ag-Au alloys, in which Ag and Au can occupy both sublattices. In this case, it can be shown that, in the first approximation, the SRO depends upon $(\Delta g^{\text{exchange}} - \Delta g^{*\text{exchange}})$, while the long-range ordering depends upon $\Delta g^{*\text{exchange}}$.

G. *Discussion*

If Eq. [18] is divided by $\Sigma n_{i/j}$ and if, furthermore, only the first term in Eq. [19] for ΔS^{config} is used, then

$$\begin{aligned}&g \text{ (per mole of bonds)}\\&\quad = \sum X_{i/j} g^{\circ}_{i/j} + \mathrm{R}T \sum X_{i/j} \ln X_{i/j} + g^{E}\end{aligned} \qquad [29]$$

where g^E can be written as a function only of $X_{i/j}$ as

$$\begin{aligned}g^E &= \left(\frac{X_{A/X} X_{B/X}}{Y_X} \Delta g_{AB/X} + \frac{X_{A/Y} X_{B/Y}}{Y_Y} \Delta g_{AB/Y} + \cdots\right)\\&\quad + \sum q^{ijkl}_{AB/XY} X^{i}_{A/X} X^{j}_{B/Y} X^{k}_{A/Y} X^{l}_{B/X}\end{aligned} \qquad [30]$$

with Y_i given as functions of $X_{i/j}$ by Eqs. [12] and [13].

Equation [29] is identical to the Gibbs-energy expression commonly used for a simple solution of the "species" (ij) with random mixing on a single lattice. That is, if the pairs (i-j) are formally considered to be the "components" of the solution, then the quasi-chemical model can be treated using currently available and relatively simple software. Only the two additional entropy terms of Eq. [19] need to be added, and these can both be written as functions only of $X_{i/j}$ through the use of Eqs. [9] through [13]. A further computational simplification can be achieved by formally treating the pairs (A-X) as the "associates" or "molecules" $A_{1/Z^{A}_{A/X}} X_{1/Z^{X}_{A/X}}$. For example, if we chose $Z^{\text{Na}}_{\text{Na/Cl}} = Z^{\text{Cl}}_{\text{Na/Cl}} = 6$ for NaCl, then the "component" becomes $\text{Na}_{1/6}\text{Cl}_{1/6}$. In this case, the quasi-chemical mass balances of Eqs. [7] and [8] become "true" chemical mass balances, in that the number of moles of Na and Cl on each side of the equations are equal.

Furthermore, by considering the pairs as components, the calculation of partial Gibbs energies and chemical activities is simplified. If $\mu_{A/X}$ is the "chemical potential of the A-X pairs,"

$$\mu_{A/X} = (\partial G/\partial n_{A/X})_{n_{i/j}} \qquad [31]$$

then, substitution of Eq. [18] into Eq. [31] gives

$$\mu_{A/X} = g^{\circ}_{A/X} + \mathrm{R}T\left(\frac{\ln X_A}{Z^{A}_{A/X}} + \frac{\ln X_X}{Z^{X}_{A/X}} + \ln \frac{X_{A/X}}{Y_A Y_X}\right) + g^{E}_{A/X} \qquad [32]$$

where the partial excess term $g^{E}_{A/X}$ is calculated from the polynomial expression for g^E in Eq. [30] in the usual way:

$$g^{E}_{A/X} = g^E + (\partial g^E/\partial X_{A/X}) - \sum_{(i,j \neq A,X)} X_{i/j}(\partial g^E/\partial X_{i/j}) \qquad [33]$$

where Eqs. [12] and [13] are used to express Y_i in terms of $X_{i/j}$.

The chemical potential of the actual pure component can then be calculated by the following equation, which is similar to Eq. [16]:

$$\mu_{A_{1/q_A}X_{1/q_X}} = (Z^A_{A/X}/q_A)\mu_{A/X} = (Z^X_{X/A}/q_X)\mu_{A/X} \qquad [34]$$

The influence of $\Delta g^{\text{exchange}}$ (Eq. [22]) upon the chemical potentials arises through the term ln $(X_{A/X}/Y_AY_X)$ in Eq. [32]. If $\Delta g^{\text{exchange}}$ is positive, then reaction [21] is shifted to the left, and $X_{A/X}$ becomes larger than Y_AY_X, which is its value in a random mixture. This makes a positive contribution to $\mu_{A/X}$ that will be greatest along the *AX-BY* "stable diagonal" of the composition square of the *AB*/*XY* reciprocal system, resulting in a tendency to immiscibility along this diagonal, as illustrated in Section III.

III. OPTIMIZATION OF THE Li, Na, K/F, Cl, SO_4 SYSTEM

The model was applied to the liquid phase of the Li,Na, K/F,Cl,SO_4 system. This system was chosen because of the high exchange Gibbs energy (~−61 kJ/mol at 700 °C) of the reaction

$$\text{LiCl(l)} + \text{KF(l)} = \text{LiF(l)} + \text{KCl(l)} \qquad [35]$$

which will result in significant FNN SRO in liquid Li, K/F,Cl solutions, and furthermore because deviations from ideal behavior in the binary common-ion subsystems are not large so that SNN cation-cation and anion-anion SRO is small, and because all binary and most common-ion ternary subsystems have been previously evaluated and optimized.[9,10,11]

All coordination numbers $Z^i_{i/j}$ and $Z^j_{i/j}$ (i = Li, Na, and K, and j = F, Cl, and SO_4) were set to 5.0, except for $Z^{SO_4}_{i/SO_4}$ (i = Li, Na, and K), which were set to 10.0.

The thermodynamic properties ($H°$, $S°$, C_p) of the nine pure solid and liquid salts and of the compounds K_3FSO_4, $LiNaSO_4$, and $LiKSO_4$ were taken from previous publications.[9,10,11] Slight adjustments were made to the H°_{298} values of NaF, NaCl, KF, and KCl, as discussed in Section III–B–1. The properties of Na_3FSO_4 were modified slightly from the earlier work.[11] The revised value of the Gibbs energy of formation of Na_3FSO_4 from 2NaF(l) and Na_2SO_4 (l) is $\Delta G° = (-57{,}134.4 + 42.179\ T)$ J/mol.

All available thermodynamic and phase-diagram data for all common-ion binary subsystems were critically evaluated previously[9,10,11] and optimized model coefficients were determined, with a random (Bragg–Williams) configurational entropy and polynomial expansions for the excess Gibbs energies. For example, the optimized[9] expression for the excess Gibbs energy of the LiF-Li_2SO_4 liquid solution is:

$$g^E = Y_F Y_{SO_4}(-629 - 2.352T - 718Y_{SO_4}) \quad \text{J/charge equivalent} \qquad [36]$$

(where a "charge equivalent" is defined, as usual, as one mole of LiF or 0.5 moles of Li_2SO_4), where

$$Y_{SO_4} = \frac{Z_{SO_4}n_{SO_4}}{Z_{SO_4}n_{SO_4} + Z_F n_F} = \frac{10n_{SO_4}}{10n_{SO_4} + 5n_F} = \frac{2X_{SO_4}}{2X_{SO_4} + X_F} \qquad [37]$$

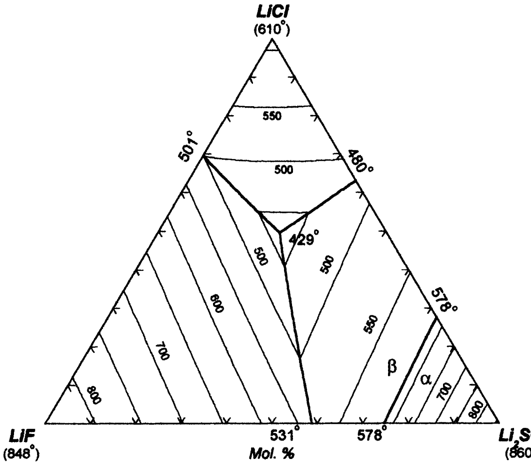


Fig. 1—Calculated liquidus projection of the LiCl-LiF-Li_2SO_4 system (predicted).

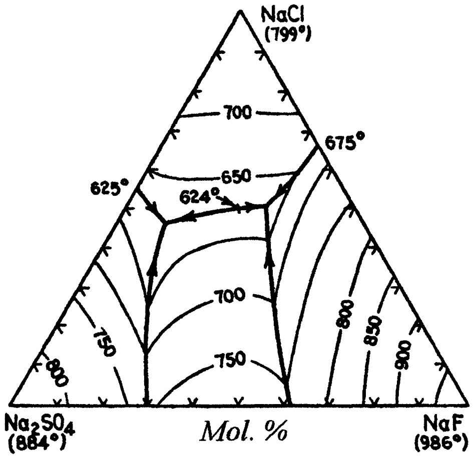


Fig. 2—Measured NaCl-NaF-Na_2SO_4 liquidus projection of Wolters.[13]

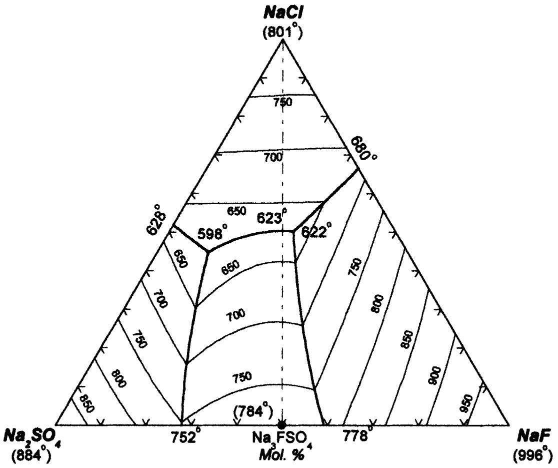


Fig. 3—Calculated NaCl-NaF-Na_2SO_4 liquidus projection.

Since $\Sigma n_{i/j}$ = 5 moles of pairs per charge equivalent, the parameter $\Delta g_{\text{Li}/\text{FSO}_4}$ in Eq. [18] is given by

$$\Delta g_{\text{Li}/F\text{SO}_4} = (-629 - 2.352T - 718Y_{SO_4})/5 \qquad [38]$$

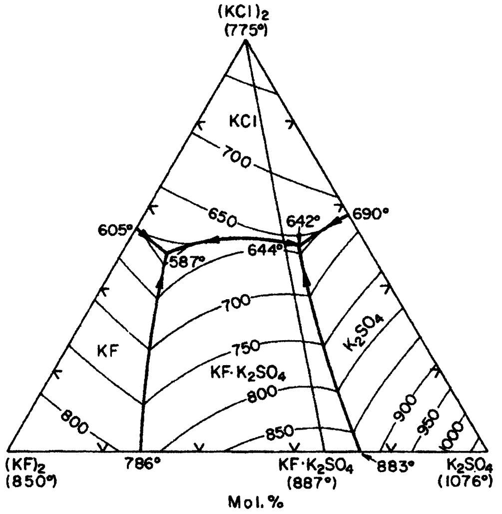


Fig. 4—Measured K_2Cl_2-K_2F_2-K_2SO_4 liquidus projection of Mukimov.[14]

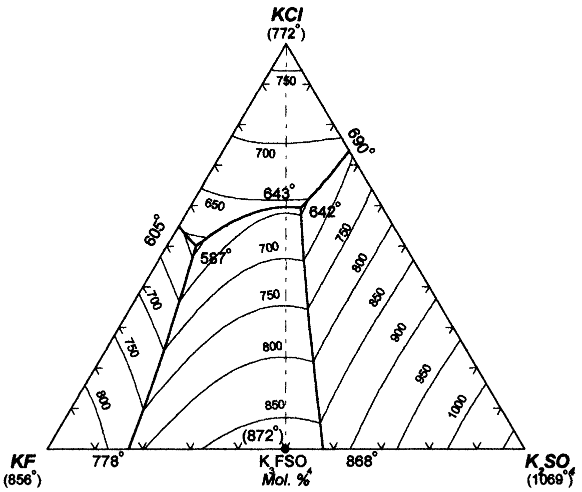


Fig. 5—Calculated KCl-KF-K_2SO_4 liquidus projection.

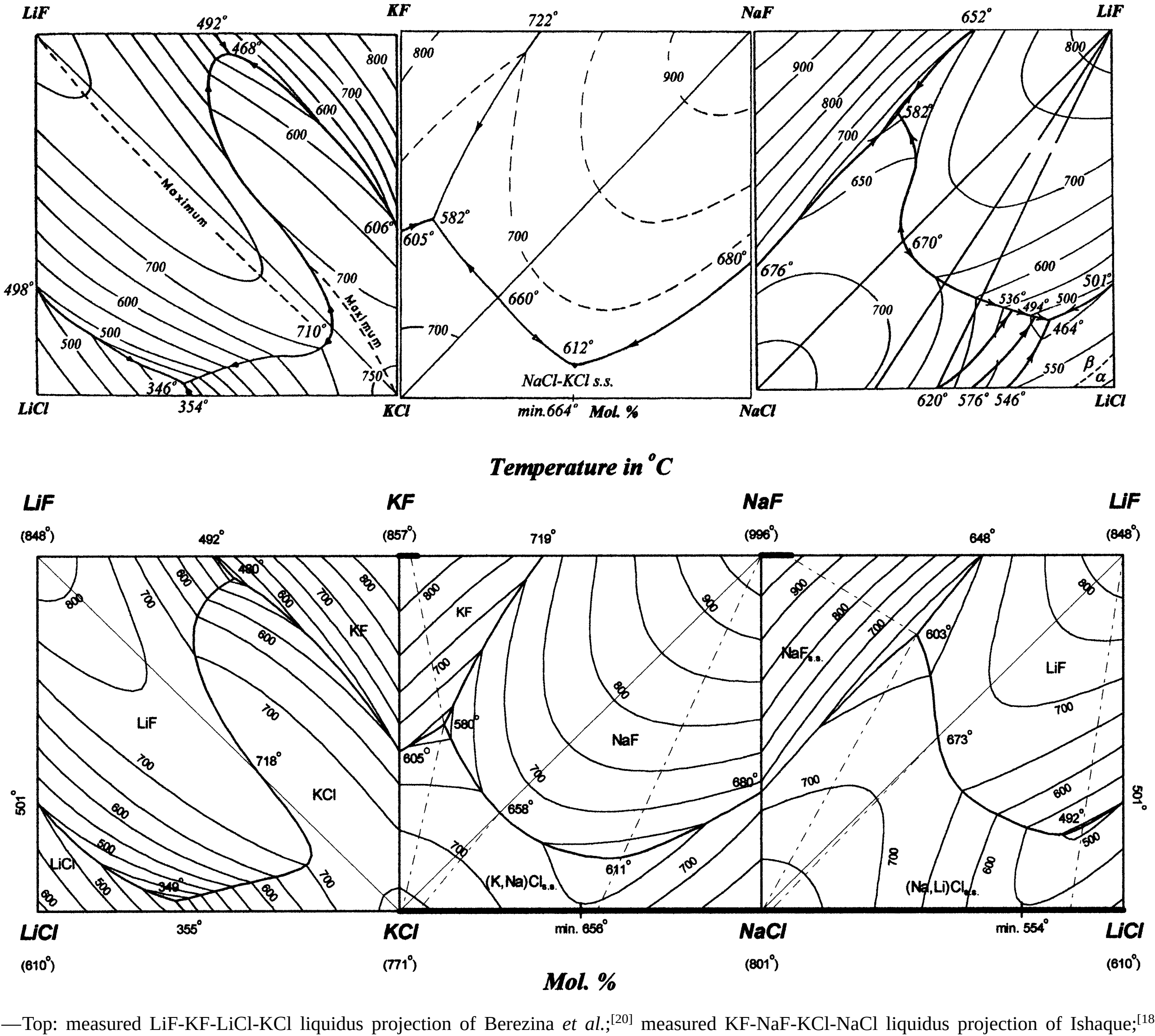


Fig. 6—Top: measured LiF-KF-LiCl-KCl liquidus projection of Berezina *et al.*;[20] measured KF-NaF-KCl-NaCl liquidus projection of Ishaque;[18] and measured NaF-LiF-NaCl-LiCl liquidus projection of Bergman *et al.*[16] Bottom: calculated liquidus projections.

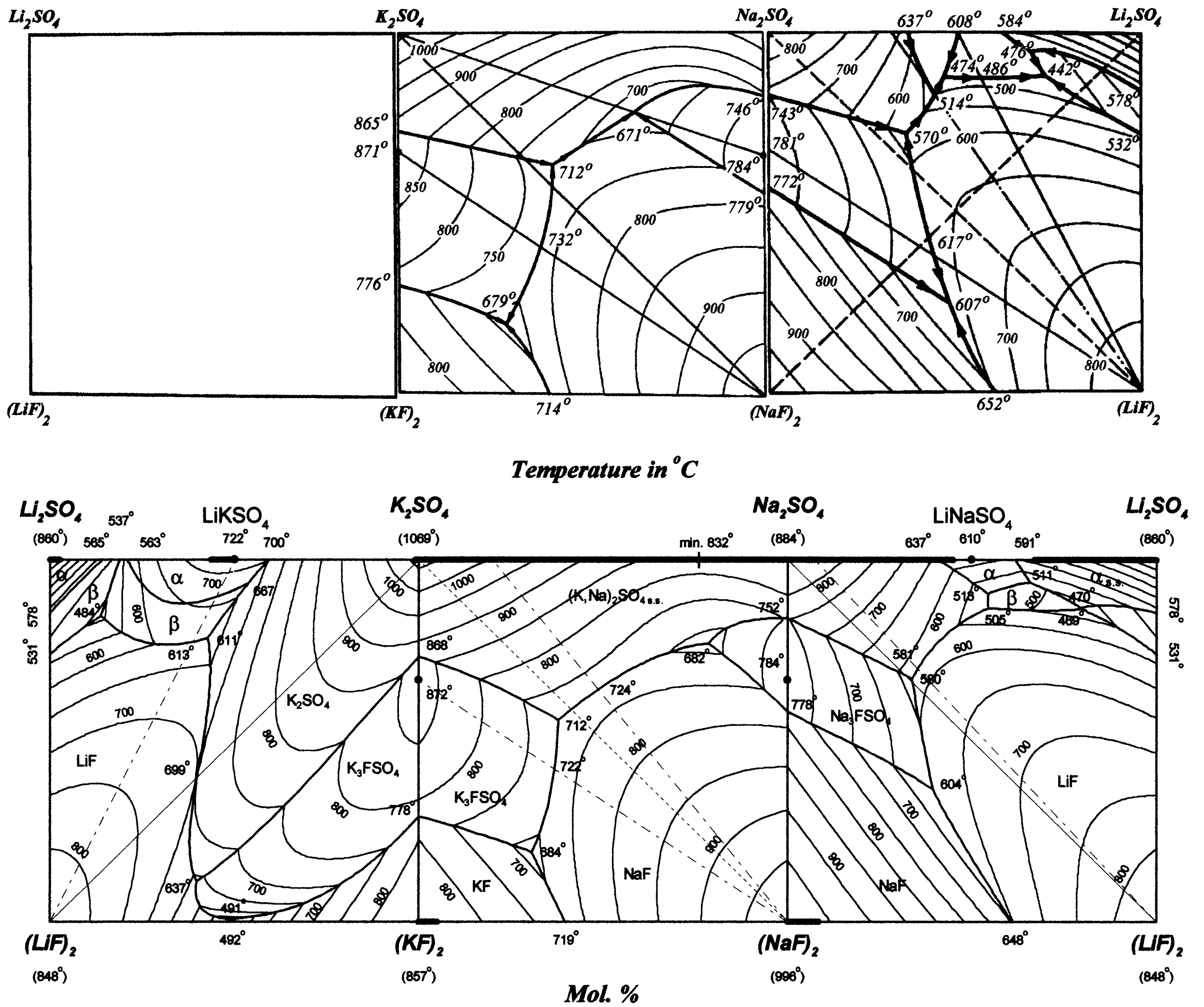


Fig. 7—Top: measured K_2SO_4-Na_2SO_4-$(KF)_2$-$(NaF)_2$ liquidus projection of Bergman and Rubleva;[23] and measured Na_2SO_4-Li_2SO_4-$(NaF)_2$-$(LiF)_2$ liquidus projection of Sperenskaya and Bergman.[24] Bottom: calculated liquidus projections.

or, in the notation of Eq. [26], $\Delta g^{\circ}_{\mathrm{Li/FSO_4}} = (-125.8 - 0.470\ T)$ and $q^{01}_{\mathrm{Li/FSO_4}} = -143.6$. Similarly, expressions for the thermodynamic properties of all solid solutions were also obtained by optimization.[9,10,11]

A. *Common-Ion Ternary Subsystems*

For the common-ion ternary subsystems, a symmetric (Kohler) model was used when all three components were halides or sulfates, and an asymmetric (Toop) model was used when two components were halides and the third was a sulfate, as described previously.[2]

The LiF-NaF-KF and LiCl-NaCl-KCl subsystems were discussed previously.[12] No additional ternary parameters were required to reproduce the experimental ternary-phase diagrams.

1. *LiF-LiCl-Li_2SO_4 system*

There is no reported experimental liquidus projection. It was assumed that no ternary terms are required for the liquid phase and that there are no ternary solid solutions. The calculated (predicted) liquidus projection is shown in Figure 1.

2. *NaF-NaCl-Na_2SO_4 system*

Liquidus projections are reported from two studies.[13,14] That of Wolters[13] is shown in Figure 2. It was assumed that there are no ternary solid solutions. A small ternary parameter, $q^{001}_{\mathrm{Na/FCl(SO_4)}} = 1674$ J (Eq. [26]), was required in order to give the calculated liquidus surface shown in Figure 3. From Eq. [18], it can be estimated that this term will give a maximum contribution of approximately 300 J/mol to the Gibbs energy of the liquid. That is, this is a very small term.

3. *KF-KCl-K_2SO_4 system*

The reported liquidus projection of Mukimov[14] is shown in Figure 4, and the calculated projection is shown in Figure 5. Ternary solid solubility was assumed to be negligible. A small ternary term, $q^{001}_{\mathrm{K/FCl(SO_4)}} = -2343$ J, was required. Note that the composition scales of Figures 4 and 5 are different.

4. *Li_2SO_4-Na_2SO_4-K_2SO_4 system*

The liquidus projection was measured by Akopov and Bergman,[15] who reported eight ternary crystallization fields of unknown phases. The calculated liquidus surface of the $(Na,K)_2SO_4$ solid solution and the Li_2SO_4-rich solid solution

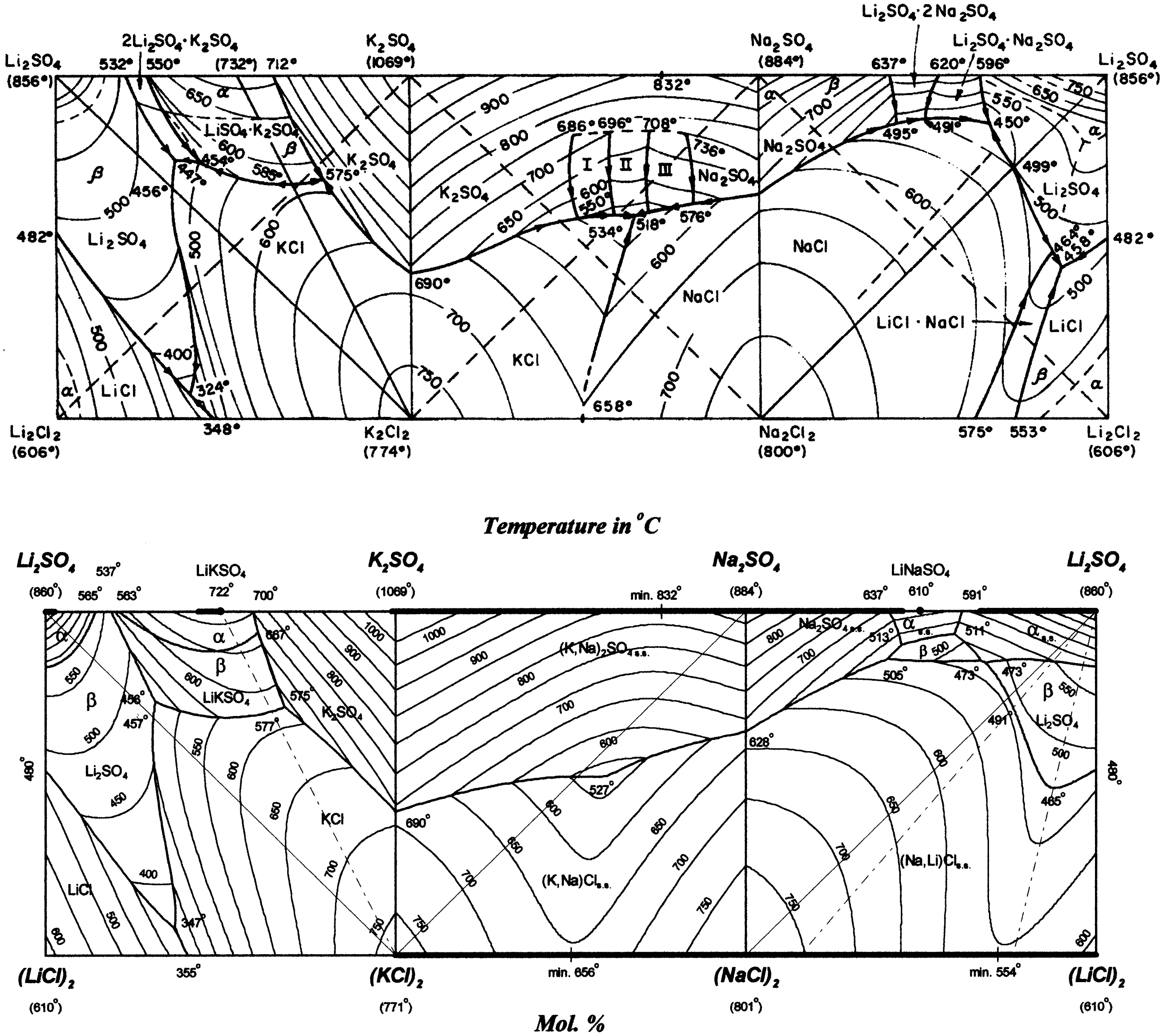


Fig. 8—Top: Measured Li,Na,K/Cl,SO_4 liquidus projections of Akopov and Bergman.[23] Bottom: calculated liquidus projections.

agree well with the measurements without the introduction of any ternary parameters for the liquid.

B. *Reciprocal Ternary Subsystems*

1. *The Li,Na/F,Cl; Li,K/F,Cl; and Na,K/F,Cl systems*

The liquidus projection of the Li,Na/F,Cl system, as reported by Bergman *et al.*,[16] is shown in Figure 6. Gabcova and Malinovsky[17] reported the liquidus in the NaCl-NaF-LiF triangle, giving the eutectic at 604 °C rather than at 582 °C, and the LiF-NaCl pseudobinary eutectic at 686.5 °C rather than at 670 °C.

The liquidus surface of the Na,K/F,Cl system was measured in two studies.[18,19] That of Ishaque[18] is shown in Figure 6.

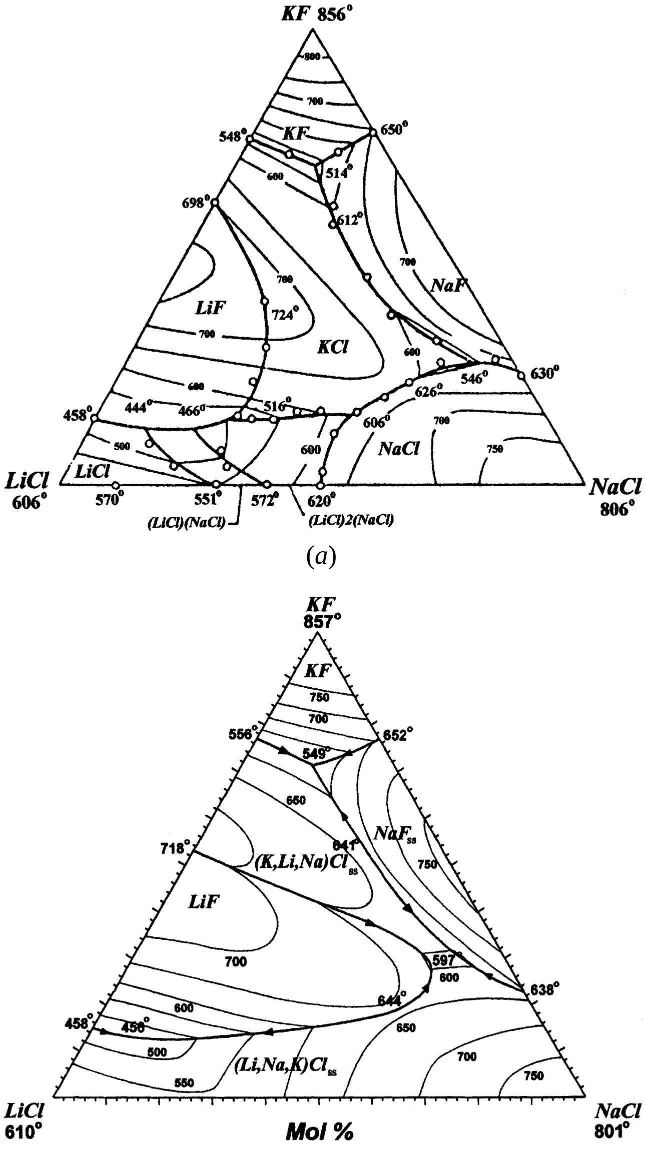
The liquidus projection of the Li,K/F,Cl system, as reported by Berezina *et al.*,[20] is shown in Figure 6. Gabcova *et al.*[21] measured the liquidus along the LiF-KCl join, reporting the pseudobinary eutectic at 719 °C rather than at 710 °C.

The calculated liquidus surfaces are also shown in Figure 6. It was assumed that there is no ternary solid solubility. No reciprocal ternary parameters were required. However, in order to reproduce the reported liquidus surfaces, small adjustments of +250 J/mol were made to the H°_{298} values of NaCl and KCl and of −250 J/mol to the H°_{298} values of NaF and KF. These are all within the stated error limits,[22] which vary from ±340 J/mol for NaCl to ±800 J/mol for NaF and KCl. The effect of these adjustments is to increase the $\Delta g^{\text{exchange}}$ value of the exchange reactions [35] and [39] by 500 J/mol, while leaving the $\Delta g^{\text{exchange}}$ value of reaction [40] unchanged.

$$\text{LiCl(l)} + \text{NaF(l)} = \text{LiF(l)} + \text{NaCl(l)} \qquad [39]$$

$$\text{NaCl(l)} + \text{KF(l)} = \text{KCl(l)} + \text{NaF(l)} \qquad [40]$$

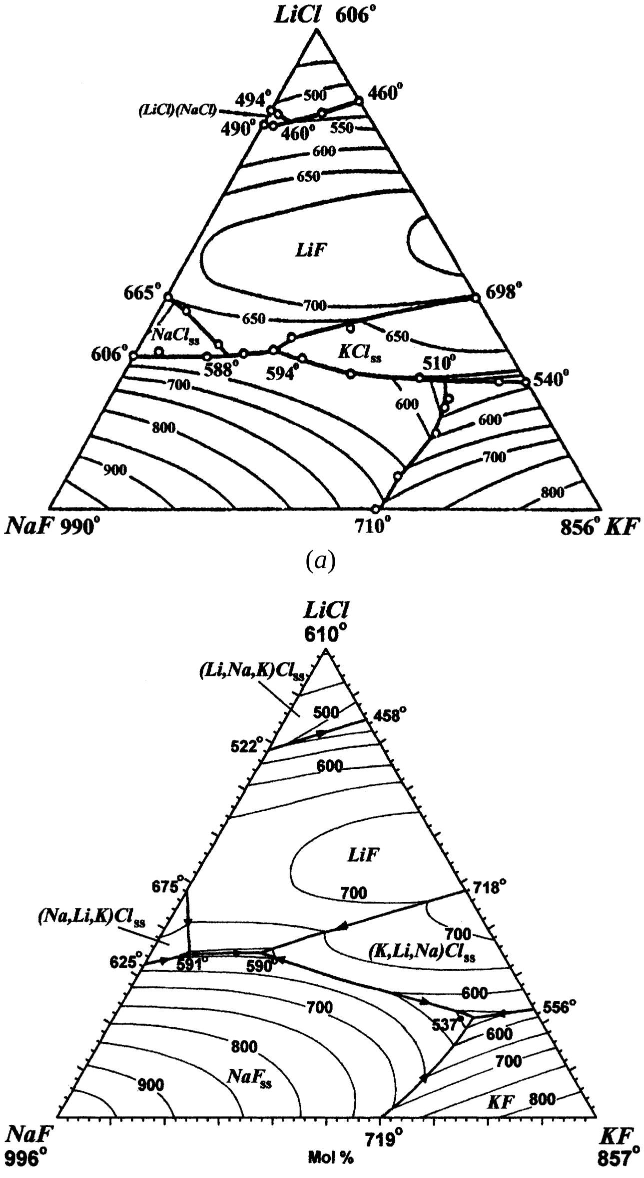
As can be seen from Figure 6, the reported liquidus surfaces are reproduced within experimental error limits except near the LiF-KCl join of the Li,K/F,Cl system, which is the system with the largest $\Delta g^{\text{exchange}}$ value. It is believed that



(*a*)

(*b*)

Fig. 9—(*a*) Measured KF-LiCl-NaCl liquidus projection from Bergman *et al.*[27] (*T* in °C). (*b*) Calculated KF-LiCl-NaCl liquidus projection (*T* in °C).



(*a*)

(*b*)

Fig. 10—(*a*) Measured LiCl-NaF-KF liquidus projection from Bergman *et al.*[27] (*T* in °C). (*b*) Calculated LiCl-NaF-KF liquidus projection (*T* in °C).

this is due to the fact that the present model neglects SNN cation-cation SRO and its coupling with the FNN ordering. This will be treated in the following article of the present series.

2. *The Li,Na/F,SO$_4$; Li,K/F,SO$_4$; and Na,K/F,SO$_4$ systems*

The liquidus surfaces of the Na,K/F,SO$_4$ and Li,Na/F,SO$_4$ systems, as reported by Bergman and Rubleva[23] and by Sperenskaya and Bergman,[24] are shown in Figure 7. No liquidus surface of the Li,K/F,SO$_4$ system has been reported.

The liquidus surface was calculated by assuming no ternary solid solubility and with the following reciprocal ternary parameters, as defined in Eq. [27]:

$$q^{0011}_{\mathrm{NaK/FSO_4}} = -335\ \mathrm{J} \qquad q^{2100}_{\mathrm{LiNa/FSO_4}} = 3347\ \mathrm{J} \qquad [41]$$

The calculated liquidus surfaces in Figure 7 agree with the measured surfaces, within the experimental error limits.

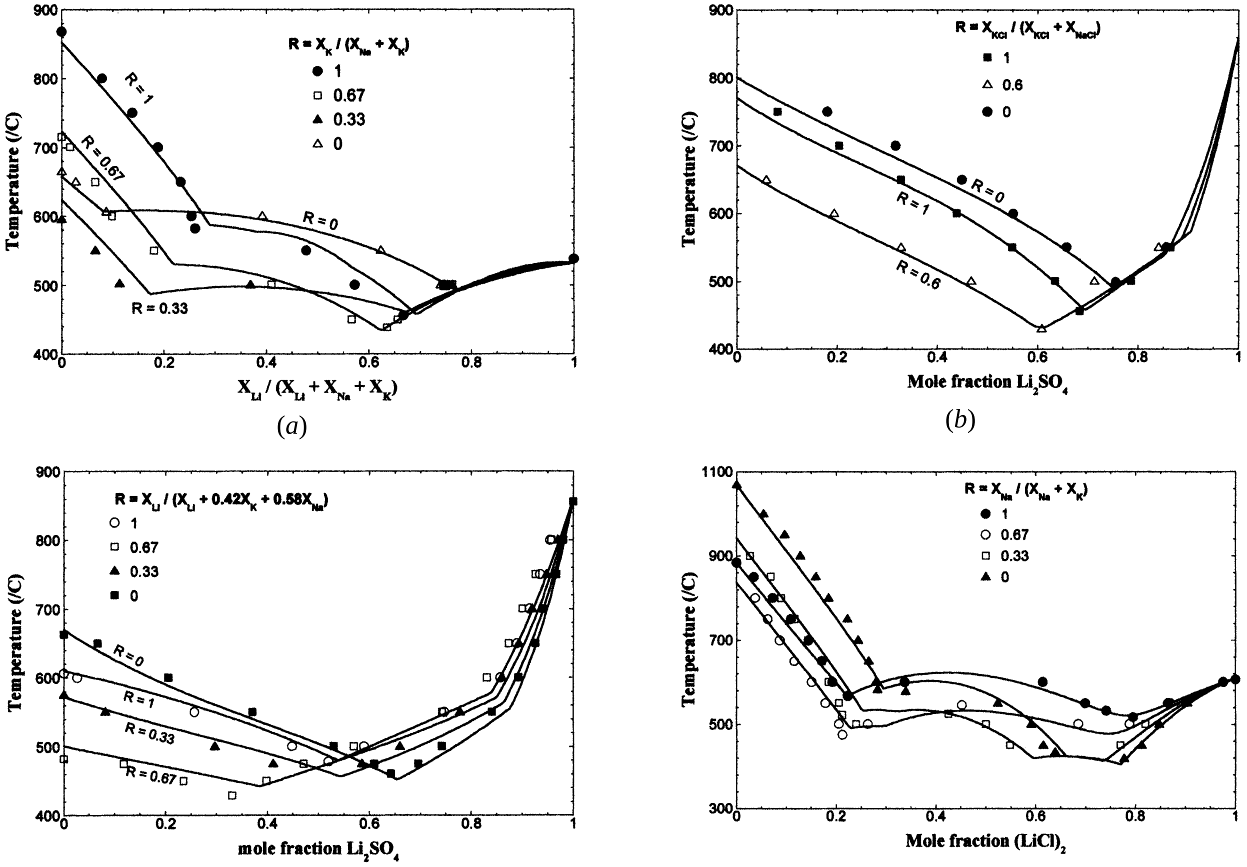
3. *The Li,Na/Cl,SO$_4$; Li,K/Cl,SO$_4$; and Na,K/Cl,SO$_4$ systems*

The liquidus projections of all three reciprocal ternary subsystems, as reported by Akopov and Bergman,[25] are shown in Figure 8. Phases I, II, and III in the Na,K/Cl,SO$_4$ system were reported as "unknown phases." Rowe *et al.*[26] measured the NaCl-K$_2$SO$_4$ join of this system and reported a crystallization field of K$_3$ClSO$_4$. None of these compounds were considered in the calculations, which assumed no ternary solid solubility and which included the two ternary reciprocal parameters of Eq. [42]. Agreement is within the experimental error limits.

$$q^{0021}_{\mathrm{LiK/ClSO_4}} = -1674\ \mathrm{J} \qquad q^{1100}_{\mathrm{NaK/ClSO_4}} = -1255\ \mathrm{J} \qquad [42]$$

C. *Quaternary Reciprocal Subsystems*

Reported[27] liquidus surface projections along the KF-LiCl-NaCl and LiCl-NaF-KF joins are compared with the



(*a*) (*b*) (*c*) (*d*)

Fig. 11—(*a*) Calculated 0.3 Li_2SO_4-0.7$(LiCl)_2$-0.3Na_2SO_4-0.7$(NaCl)_2$-0.3K_2SO_4-0.7$(KCl)_2$ liquidus at different K/Na ratios with experimental points from Akopov and Bergman.[20] (*b*) Calculated Li_2SO_4-$(NaCl)_2$-$(KCl)_2$ liquidus at different KCl/NaCl ratios with experimental liquidus points from Akopov and Bergman.[29] (*c*) Calculated Li_2SO_4-$(LiCl)_2$-(0.42KCl)-(0.58NaCl)$_2$ liquidus at different Li/(Na + K) ratios with experimental points from Akopov and Bergman.[28] (*d*) Calculated $(LiCl)_2$-Na_2SO_4-K_2SO_4 liquidus at different Na/K ratios with experimental points from Akopov and Bergman.[20]

calculated projections in Figures 9 and 10. Agreement is within the experimental error limits. It is believed that the reported eutectic temperatures of 546 °C and 514 °C, shown in Figure 9(a), may be in error, since these are inconsistent with the spacing of the isotherms at higher temperatures and indicate an unlikely precipitous drop in the liquidus just near the eutectic.

Liquidus points along four composition planes in the Li,Na,K/Cl,SO_4 reciprocal quaternary subsystem were reported by Akopov and Bergman.[25,28,29] These are compared with calculations in Figures 11(a) through (d). Excellent agreement is obtained.

IV. CONCLUSIONS

A very general quasi-chemical model has been proposed for solutions with two sublattices. Short-range ordering of FNN is treated in the pair approximation. The effect of SNN interactions upon this ordering is taken into account. Optimized parameters of the model are determined from the evaluation of available experimental data for the binary and ternary subsystems.

The model has been used to calculate liquidus surfaces of ternary, ternary reciprocal, and quaternary reciprocal subsystems of the Li,Na,K/F,Cl,SO_4 system. Quantitative agreement with measurements is obtained with only a very few small ternary parameters.

The model is suitable for liquid solutions, where the ratio of the numbers of sites on the two sublattices can vary with composition. However, the model also applies to solid solutions if the numbers of lattice sites and the coordination numbers are kept constant. The model can, thus, be combined with the compound-energy formalism[30,31] to treat a wide range of solution types (slags, mattes, salts, ceramics, and alloys), order-disorder phenomena, nonstoichiometric phases, point defects, *etc.* For a discussion of applications of the compound-energy formalism, refer to References 32 and 33.

By formally treating the nearest-neighbor pairs 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. A new proposal for the lattice stability term in this and similar models is proposed, which may help in separating the driving forces for long-range ordering and SRO.

Simultaneous SRO of FNNs and SNNs is not treated by the present model, since this is not possible within a pair approximation. This will be the subject of the next article in the present series.

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