

Contribution to the quasichemical model of reciprocal molten salt solutions

Y Dessureault, AD Pelton

*Centre de Recherche en Calcul Thermochimique, École Polytechnique de Montréal, PO Box 6079,
Station «A» Montréal, Québec, Canada H3C 3A7*

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ABSTRACT

The Gibbs energy of a reciprocal ternary molten salt solution may be estimated from the Gibbs energies of the pure components and of the constituent binary subsystems by means of solution models. The standard sublattice model often gives unsatisfactory results for systems with a large exchange Gibbs energy due to its neglect of the effect of non-random mixing upon the second-nearest-neighbor interactions. An extended quasichemical model is proposed to account for this effect without the introduction of adjustable parameters. Several reciprocal salt phase diagrams are calculated as examples.

RÉSUMÉ

En utilisant des modèles, on peut estimer l'enthalpie de Gibbs d'une solution ternaire réciproque de sels fondus à partir des enthalpies de Gibbs des composants purs et des sous-systèmes binaires. Pour un système dans lequel l'enthalpie de Gibbs de la réaction d'échange est grande, le modèle usuel de sous-réseaux donne souvent des résultats peu satisfaisants, parce que ce modèle néglige l'influence de la distribution non-aléatoire des ions sur les interactions des deuxièmes voisins. On propose un modèle quasichimique élargi qui tient compte de cet effet sans introduire des paramètres ajustables additionnels. Des exemples de calculs de quelques diagrammes d'équilibre de systèmes réciproques sont données.

INTRODUCTION

In recent years we, along with other groups, have been involved in the coupled evaluation of thermodynamic and phase diagram data and in the computation of the phase diagrams of multicomponent systems. (See, for example, ref. 1.).

In this approach, all available thermodynamic and phase diagram data for a set of binary systems are optimized in order to obtain equations for the Gibbs energies of the various phases as functions of composition and temperature. These expressions can then be used, with appropriate solution models, to predict the Gibbs energies of multicomponent solutions. From these Gibbs energy expressions, the multicomponent phase diagrams can be calculated. Extensive computer databases are being developed in this way for alloys, ceramic systems, organic systems, etc.

As part of the "Phase Diagrams for Ceramists" project of the American Ceramic Society, we have systematically optimized over 100 binary salt systems involving halides, nitrates, carbonates, sulfates and hydroxides (2-6). We have then used established models to predict the thermodynamic properties and phase diagrams of ternary and multicomponent molten salts solutions from the optimized binary parameters (7-10). For ternary common-ion systems, the calculated phase diagrams agree very well with the measured phase diagrams (9,10). (A ternary common-ion system is one such as LiCl-NaCl-KCl with a common anion, or LiNO_3 -LiF-LiOH with a common cation). The same models can then be used with confidence in calculations involving quaternary and higher-order common-ion systems (7,8).

However, when we attempted to calculate the phase diagrams of reciprocal ternary salt systems (systems containing two different cations and two different anions), we found that the standard sublattice model (11-13) for reciprocal molten salt solutions gave unsatisfactory results in many cases.

We believe that the problem arises from the neglect of the effect of non-random mixing upon second-nearest-neighbor interactions. In the present article we propose an extended quasichemical model which accounts for this effect without introducing any adjustable parameters and which reduces to the standard model in the limit of weak interactions.

QUASICHEMICAL THEORY OF TERNARY RECIPROCAL SALT SOLUTIONS

A reciprocal ternary molten salt solution A,B/X,Y is one involving two cations, A⁺ and B⁺, and two anions, X⁻ and Y⁻. The model will be developed for systems in which all ions are monovalent. The extension to systems with polyvalent ions will be treated in the discussion section.

It is assumed that the cations reside on a cation sublattice and that the anions reside on an anion sublattice. The cationic and anionic site fractions are denoted by X_i :

$$X_A = n_A / (n_A + n_B) = 1 - X_B \quad [1]$$

$$X_X = n_X / (n_X + n_Y) = 1 - X_Y \quad [2]$$

where n_i is the number of moles of ion i in solution.

The composition of a reciprocal ternary system is usually plotted on a square as in Fig. 1, with cationic fractions along one axis and anionic fractions along the other. The pure salts are found at the corners of the square, and the edges represent compositions in binary common-ion subsystems.

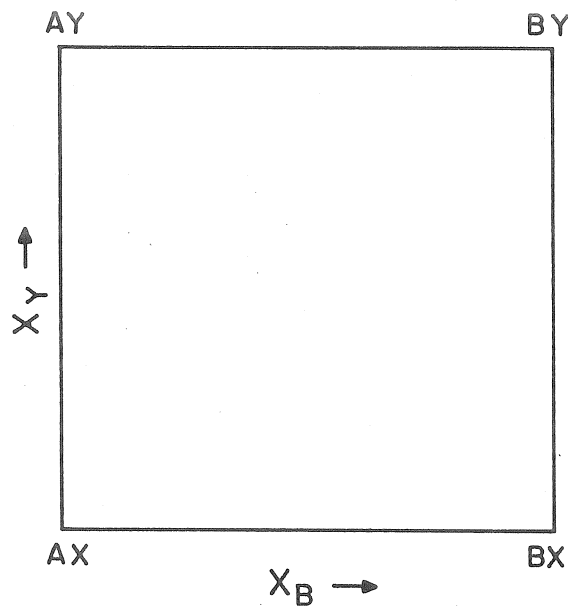


FIG. 1: Composition square of the A,B/X,Y reciprocal ternary system.

Binary common-ion subsystems

In the binary common-anion system AX-BX, which forms the bottom edge of the square in Fig. 1, the molar Gibbs energy of the liquid solution can be written as:

$$g_{AX-BX} = (X_A g_{AX}^{\circ} + X_B g_{BX}^{\circ}) + RT (X_A \ln X_A + X_B \ln X_B) + X_A X_B w_{A,B/X} \quad [3]$$

where g_{AX}° and g_{BX}° are the standard molar Gibbs energies of the pure salts and the cationic fractions, X_A and X_B , are equal, in this common-anion system, to the component mole fractions X_{AX} and X_{BX} . The second term on the right in Eq. [3] represents the ideal mixing of the cations on the cation sublattice.

The final term in Eq. [3] is the excess Gibbs energy. If the parameter $w_{A,B/X}$ is constant, independent of composition, then the binary liquid is a regular solution. In general, however, $w_{A,B/X}$ is a function of composition in the AX-BX binary system. For example, $w_{A,B/X}$ could be expressed as a polynomial in the cationic fractions.

Similar expressions can be written for the Gibbs energies of the common-ion binary systems on the other three edges of the composition square:

$$g_{AY-BY} = (X_A g_{AY}^{\circ} + X_B g_{BY}^{\circ}) + RT (X_A \ln X_A + X_B \ln X_B) + X_A X_B w_{A,B/Y} \quad [4]$$

$$g_{AX-AY} = (X_X g_{AX}^{\circ} + X_Y g_{AY}^{\circ}) + RT (X_X \ln X_X + X_Y \ln X_Y) + X_X X_Y w_{A/X,Y} \quad [5]$$

$$g_{BX-BY} = (X_X g_{BX}^{\circ} + X_Y g_{BY}^{\circ}) + RT (X_X \ln X_X + X_Y \ln X_Y) + X_X X_Y w_{B/X,Y} \quad [6]$$

where $w_{A,B/Y}$ is a function of the cationic fractions and where $w_{A/X,Y}$ and $w_{B/X,Y}$ are functions of the anionic fractions.

The parameter $w_{A,B/X}$ in Eq.[3] can, in a quasichemical approach, be considered to be the energy of formation of second-nearest-neighbor $A^+ - B^+$ pairs from $A^+ - A^+$ and $B^+ - B^+$ pairs according to:



where A-X-A, B-X-B and A-X-B represent second-nearest-neighbor cation pairs in a solution in which the only anions are X⁻ anions.

Similarly, the parameter $w_{A,B/Y}$ in Eq.[4] may be considered to be the energy of formation of A-Y-B pairs from A-Y-A and B-Y-B pairs in the presence of Y^- anions.

The parameter $w_{A/X,Y}$ in Eq.[5] is considered to be the energy of formation of second-nearest-neighbor anion pairs in the presence of A^+ cations according to:



and the parameter $w_{B/X,Y}$ of Eq.[6] is interpreted similarly.

Reciprocal System

In the reciprocal ternary molten salt solution, the molar Gibbs energy is commonly expressed by the following equation:

$$\begin{aligned} g = & (X_A X_X g_{AX}^{\circ} + X_B X_X g_{BX}^{\circ} + X_A X_Y g_{AY}^{\circ} + X_B X_Y g_{BY}^{\circ}) \\ & + RT (X_A \ln X_A + X_B \ln X_B + X_X \ln X_X + X_Y \ln X_Y) \\ & + (X_A X_B X_X w_{A,B/X} + X_A X_B X_Y w_{A,B/Y} + X_A X_X X_Y w_{A/X,Y} + X_B X_X X_Y w_{B/X,Y}) \\ & - X_A X_B X_X X_Y \Lambda \end{aligned} \quad [9]$$

It was shown by Blander and Yosim (11) that an equation of this form results from second-order Conformal Ionic Solution Theory. The equation can also be derived from quasichemical theory (12,13) as follows.

The first term on the right-hand-side of Eq.[9] contains the standard molar Gibbs energies, g° , of the pure salts. This term varies linearly with cationic fraction between its values in the AX-BX and AY-BY binary systems (Eqs.[3,4]). It also varies linearly with anionic fraction between its values in the AX-AY and BX-BY binary systems (Eqs.[5,6]).

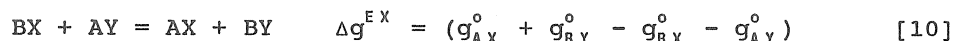
The second term on the right in Eq.[9] is the Gibbs energy of mixing for an ideal random solution of A and B cations on the cation sublattice and of X and Y anions on the anion sublattice.

In quasichemical terms, the third term on the right in Eq.[9], which involves the binary excess terms, states that the energy of

formation of second-nearest-neighbor A-B cation pairs varies linearly with the anionic fractions X_X and X_Y between the value $w_{A,B/X}$ for the formation of A-X-B groupings in the AX-BX binary system and the value $w_{A,B/Y}$ for the formation of A-Y-B grouping in the AY-BY system. Also, the energy of formation of second-nearest-neighbor X-Y anion pairs varies linearly with the cationic fractions X_A and X_B between the values $w_{A/X,Y}$ and $w_{B/X,Y}$ for X-A-Y and X-B-Y groupings respectively in the AX-AY and BX-BY binary systems.

The last term in Eq.[9] is a non-ideal mixing term which will be discussed shortly.

The standard molar Gibbs energies g_{AX}^o , g_{BX}^o , g_{AY}^o and g_{BY}^o in Eq.[9] are related by the Gibbs energy change, Δg^{EX} , of the "exchange reaction" among the pure salts:



By differentiation of Eq.[9], expressions for the activities of the neutral salts AX, AY, BX and BY can be obtained (7,8,13). For example, a_{BY} , the activity of BY, is given by:

$$RT \ln a_{BY} = - X_A X_X \Delta g^{EX} + RT \ln(X_B X_Y) + (\text{excess terms}) \quad [11]$$

If $\Delta g^{EX} < 0$, then AX and BY are called the "stable pair". It can be seen from Eq.[11] that, for a member of the stable pair, there is a positive contribution to $RT \ln a$ which varies directly with Δg^{EX} . For a member of the unstable pair, there will be a corresponding negative contribution.

Liquidus isotherms are shown on the reported (14) phase diagram of the Na,K/F,Cl system in Fig. 2a. In this system, NaF and KCl form the stable pair as can be seen from the sign of Δg^{EX} in Table 1. The resultant positive deviations in the activities of NaF and KCl are manifested by flat liquidus surfaces with widely spaced isotherms, while the negative deviations in the case of KF and NaCl are manifested by steep liquidus surfaces. Similar effects can be seen in the phase diagram (15) of the Li,K/F,Cl system in Fig. 3a.

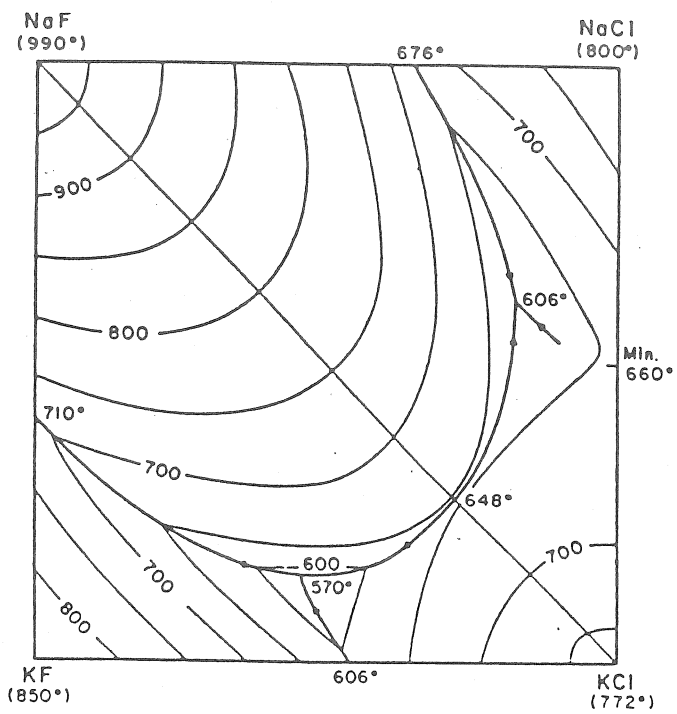
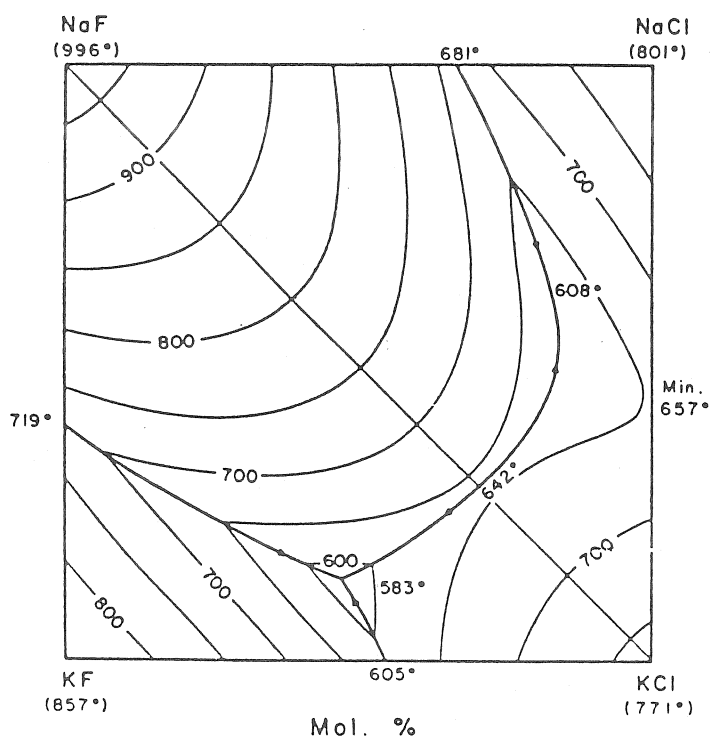


Fig. 2: Liquidus of the Na, K/F, Cl system

(a) As reported (15)



(b) Calculated

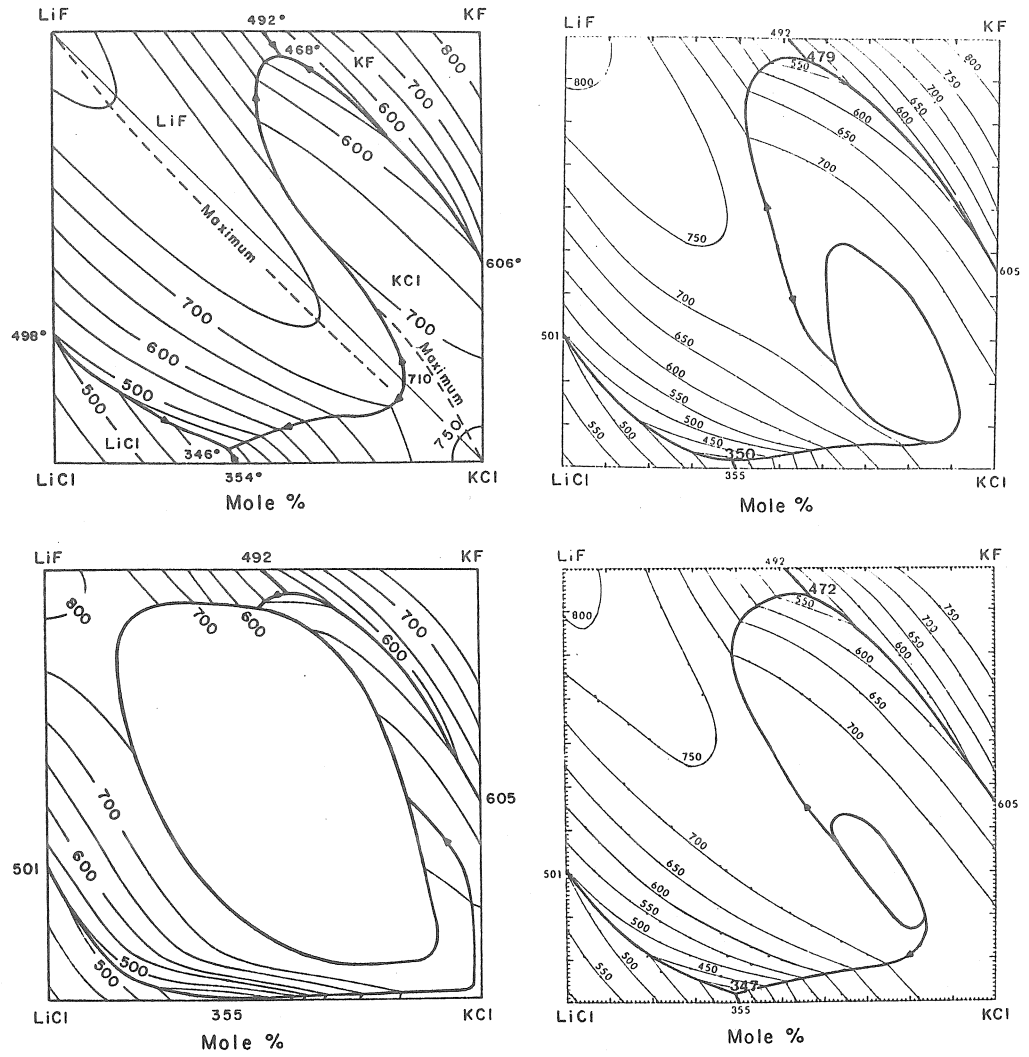


Fig. 3 The Li,K/F,Cl phase diagram

- (a) As reported by (15)
- (b) Calculated from Eqs. [9] and [13]
- (c) Calculated from Eqs. [9] and [14]
- (d) Calculated from the extended quasichemical model

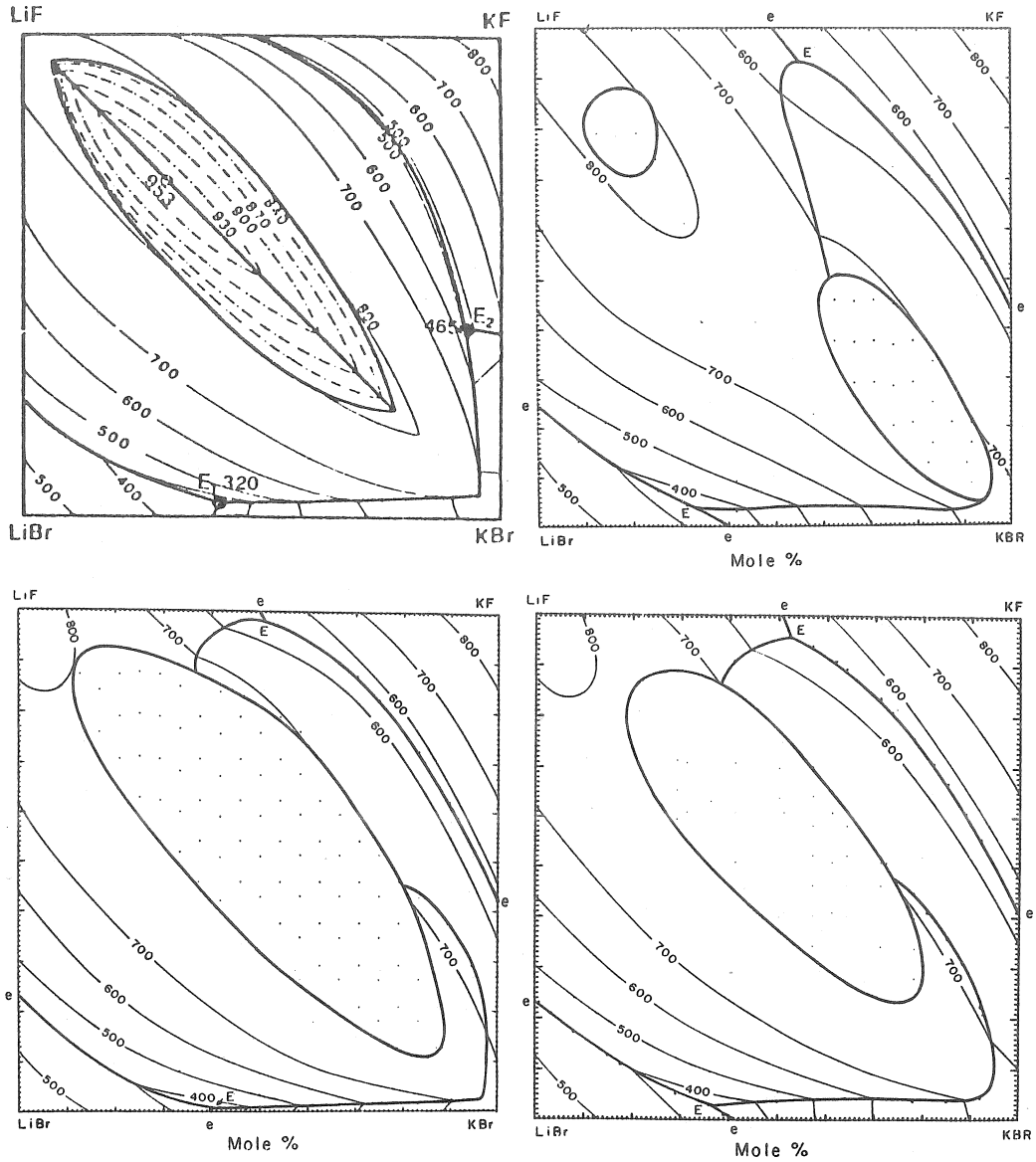


Fig. 4 The Li, K/F, Br phase diagram

- | | |
|---------------------------------------|--|
| (a) As reported by (16) | (b) Calculated from Eqs. [9] and [13] |
| (c) Calculated from Eqs. [9] and [14] | (d) Calculated from the extended quasichemical model |

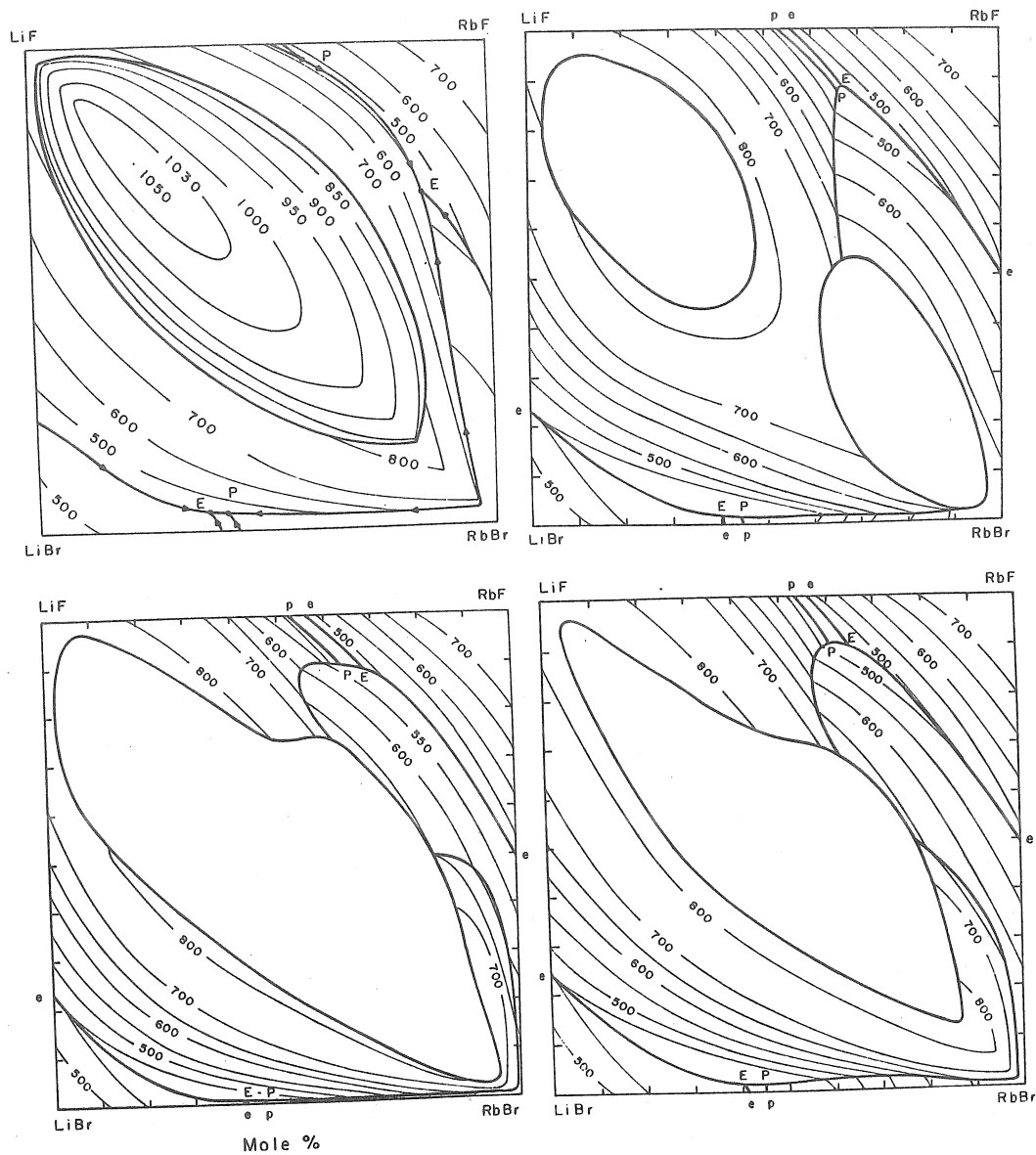


Fig. 5 The Li, Rb/F, Br phase diagram

- (a) As reported by (17) (b) Calculated from Eqs. [9] and [13].
 (c) Calculated from Eqs. [9] and [14] (d) Calculated from the extended
 quasichemical model

In the Li,K/F,Br system in Fig 4a (16), Δg^{EX} is so large (see Table 1) that a liquid miscibility gap is formed along the "stable diagonal" joining the stable pair, LiF and KBr. A similar effect is seen in the phase diagram (17) of the Li,Rb/F,Br system in Fig. 5a. Many molten salt systems exhibit such liquid miscibility gaps directed along the stable diagonal.

In quasichemical terms, if $\Delta g^{EX} < 0$, then a configuration with $A^+ - X^-$ and $B^+ - Y^-$ nearest-neighbors is energetically favorable to one with $A^+ - Y^-$ and $B^+ - X^-$ nearest neighbors. When the pure salts AX and BY which form the stable pair are mixed, some energetically unfavorable $B^+ - X^-$ and $A^+ - Y^-$ pairs are formed at the expense of the more favorable $A^+ - X^-$ and $B^+ - Y^-$ pairs. Hence, this process is energetically unfavorable and positive deviations occur along the stable diagonal. On the other hand, mixing of the pure salts AY and BX, which form the unstable pair, results in the formation of energetically favorable $A^+ - X^-$ and $B^+ - Y^-$ pairs in solution, and so negative deviations are observed along the unstable diagonal.

From these considerations it can also be seen that there will be a tendency to non-random mixing, with $A^+ - X^-$ and $B^+ - Y^-$ pairs tending to predominate. The degree to which such clustering occurs will vary as Δg^{EX} .

This non-randomness was treated by Blander and Braunstein (12,13) who considered the following pair exchange reaction:



where B-X represents a nearest-neighbor $B^+ - X^-$ cation-anion pair in solution, and similarly for the other terms. The Gibbs energy change of reaction [12] should be approximately equal to Δg^{EX} . If $\Delta g^{EX} < 0$ then reaction [12] is displaced to the right. By expanding the equilibrium constant of the quasichemical reaction [12] in a first-order Taylor series, Blander and Braunstein derived the final term in Eq. [9] which is valid for small deviations from randomness. In this approximation they showed that:

$$\Lambda = (\Delta g^{EX})^2 / 2ZRT \quad [13]$$

where Z is a coordination number usually taken as 6.

Phase diagram calculations

The phase diagrams of the four systems shown in Fig. 2-5 were calculated thermodynamically with Eq.[9] for the Gibbs energy of the liquid phase and Eq.[13] for Δg^{EX} with $Z = 6$. Values of Δg^{EX} and the Gibbs energies of melting of the pure salts were taken from thermodynamic tables (18). The values of Δg^{EX} are listed in Table 1. Values of $w_{A,B/X}$, $w_{A,B/Y}$, $w_{A/X,Y}$ and $w_{B/X,Y}$ were obtained earlier (2,3) from optimization of thermodynamic and phase diagram data in the binary common-ion systems. These are listed in Table 2. All solid phases were taken to be the pure stoichiometric salts as indicated by the binary phase diagrams (2,3) except for the NaCl-KCl solid solution for which optimized thermodynamic parameters were taken from (2,3) and except for the dilute solid solution of NaF in KF for which the Henrian activity coefficient was also taken from (2,3). The computations were performed with the RECIPFIG program of the F*A*C*T thermodynamic computer system (19).

TABLE 1
Gibbs energy changes (18) for exchange reactions
among pure liquid salts

<u>Exchange Reaction</u>	<u>Δg^{EX} (J/mol)</u>	<u>Δg^{EX} at 700°C</u> <u>(J/mol)</u>
NaCl+KF = NaF+KCl	-32323 + 9.0868T	-23482
LiCl+KF = LiF+KCl	-73404 + 15.429T - 3.2893x10 ⁻³ T ²	-61444
LiBr+KF = LiF+KBr	-85304 + 11.433T - 1.056x10 ⁻³ T ²	-75179
LiBr+RbF = LiF+RbBr	-97906 + 11.172T	-87036

The calculated phase diagrams, from Eqs.[9] and [13], are shown in Figs. 2b,3b,4b and 5b.

The calculated liquidus for the Na,K/F,Cl system, Fig. 2b, is in very good agreement with the measured diagram, Fig. 2a. For the Li,K/F,Cl system, Figs. (3a,3b), the agreement is not as good. A small miscibility gap appears in the calculated diagram.

TABLE 2

Excess Gibbs energy functions of binary
common-ion liquid solutions (2,3)

Common-anion systems:

$$w_{A,B/X}(\text{J/mol}) = [a_0 + a_1(2X_B - 1) + a_2(6X_B^2 - 6X_B + 1)] - T[b_0 + b_1(2X_B - 1) + b_2(6X_B^2 - 6X_B + 1)]$$

<u>System</u>	<u>a₀</u>	<u>a₁</u>	<u>a₂</u>	<u>b₀</u>	<u>b₁</u>	<u>b₂</u>
<u>AX-BX</u>						
LiF-KF	-18275	1765	789	-2.948	1.573	
LiF-RbF	-20292	3138		-8.991	7.512	-5.663
NaF-KF	-335			-2.541		
LiCl-KCl	-17758	189		-5.148	-2.479	
NaCl-KCl	-2186	136				
LiBr-KBr	-14428	878	327	-1.441	-1.819	
LiBr-RbBr	-18857	2009	781			

Common-cation systems

$$w_{A/X,Y}(\text{J/mol}) = [a_0 + a_1(2X_Y - 1) + a_2(6X_Y^2 - 6X_Y + 1)] - T[b_0 + b_1(2X_Y - 1) + b_2(6X_Y^2 - 6X_Y + 1)]$$

<u>System</u>	<u>a₀</u>	<u>a₁</u>	<u>a₂</u>	<u>b₀</u>	<u>b₁</u>	<u>b₂</u>
<u>AX-BX</u>						
LiF-LiCl	-1000					
NaF-NaCl	2057	-642				
KF-KCl	798	749	1521			
LiF-LiBr	5960	-4284		9.837	-0.406	
KF-KBr	-833	-200				
RbF-RbBr	-2583	1330	-376			

For the Li,K/F,Br and Li,Rb/F,Br systems, Figs. 4 and 5, agreement between measured and calculated diagrams is poor. The calculated miscibility gaps in Figs. 4b and 5b are split in two.

As can be seen from Table 1, the agreement is poorest for those systems which have the largest values of Δg^{EX} . We have calculated phase diagrams for several other systems for which Δg^{EX} is large. In some cases, agreement with the experimental diagram was reasonable. In other cases, agreement was poor. For all the cases for which agreement was poor, it was observed that $w_{A,B/X}$ and $w_{A,B/Y}$ were also large and negative. This is the case for the Li,K/F,Br and Li,Rb/F,Br systems as can be seen from Table 2.

To summarize, then, it was found that whenever Δg^{EX} is large enough to give rise to a miscibility gap and, at the same time, $w_{A,B/X}$ and $w_{A,B/Y}$ are quite negative, poor results are obtained from the calculations, with the miscibility gap tending to split in the middle.

Clearly, the model is predicting a Gibbs energy, g , of the liquid which is too negative in the centre of the composition square. This appears to be related to the terms $X_A X_B X_C w_{A,B/X}$ and $X_A X_B X_C w_{A,B/Y}$ in Eq.[9] giving too negative a contribution to g since, when $w_{A,B/X}$ and $w_{A,B/Y}$ are small, the problem does not arise. (It may be noted that in the majority of simple common-anion molten salts, $w_{A,B/X}$ is negative, while in the majority of simple common-cation molten salts, $w_{A/X,Y}$ is very small).

A similar observation was made by Saboungi and Blander (20,21) who proposed to correct the model by calculating Λ as:

$$\Lambda = (|\Delta g^{EX}| + (w_{A,B/X} + w_{A,B/Y} + w_{A/X,Y} + w_{B/X,Y})/2)^2 / 2ZRT \quad [14]$$

The phase diagrams of the Li,K/F,Br and Li,Rb/F,Br systems, recalculated with Eq.[14], are shown in Figs. 4c and 5c. Results are improved. However, for the Li,K/F,Cl system, Fig. 3c, agreement with the measured diagram is much worse when Eq. [14] is used.

Eq.[14] is not based upon a clearly defined theoretical model. Its use leads to some improvement in the majority of cases, but it can also often make things worse.

AN EXTENDED QUASICHEMICAL MODEL FOR RECIPROCAL TERNARY SYSTEMS

In order to understand why the standard model fails, the following explanation is proposed.

$w_{A,B/X}$ and $w_{A,B/Y}$ are the energies of formation of A-X-B and A-Y-B second-nearest-neighbor pairs. In Eq.[9], a random distribution of cations and anions on their respective sites is assumed such that the probability of A-X-B and A-Y-B groupings are $X_A X_B X_X$ and $X_A X_B X_Y$ respectively. However, when Δg^{EX} is large, there is a tendency to form A-X and B-Y clusters through displacement of reaction [12] to the right. This reduces the number of A-X-B and A-Y-B groupings and increases the number of A-X-A and B-Y-B groupings. This effect is greatest near the middle of the composition square. The terms $X_A X_B X_X w_{A,B/X}$ and $X_A X_B X_Y w_{A,B/Y}$ in Eq.[9] are thus too negative in this composition region, and so Eq.[9] overestimates the stability of the liquid.

In the case of a random distribution of cations and anions on their respective sublattices, the probability that a given nearest-neighbor cation-anion pair is an $A^+ - X^-$ pair is equal to $X_A X_X$. In the non-random mixture, following the notation of Fjørland (13), this probability is increased to $(X_A X_X + y)$ where y is a positive number. Similarly, the probabilities of B-Y, A-Y and B-X pairs are $(X_B X_Y + y)$, $(X_A X_Y - y)$ and $(X_B X_X - y)$.

The molar Gibbs energy of the solution is written as follows:

$$\begin{aligned}
 g = & (X_A X_X g_{AX}^0 + X_B X_X g_{BX}^0 + X_A X_Y g_{AY}^0 + X_B X_Y g_{BY}^0) \\
 & + y \Delta g^{EX} - T \Delta S^{config} \\
 & + X_X (X_A + y/X_X) (X_B - y/X_X) w_{A,B/X} + X_Y (X_A - y/X_Y) (X_B + y/X_Y) w_{A,B/Y} \\
 & + X_A (X_X + y/X_A) (X_Y - y/X_A) w_{A/X,Y} + X_B (X_X - y/X_B) (X_Y + y/X_B) w_{B/X,Y} \quad [15]
 \end{aligned}$$

The term $y \Delta g^{EX}$ arises because reaction [12] is now displaced to the right and because the Gibbs energy change of reaction [12] is assumed to be approximately equal to Δg^{EX} .

For the second-nearest-neighbor interactions, the energy of forming an A-B-X grouping, $w_{A,B/X}$, is now multiplied by the probability, $P(AXB)$, of finding such a grouping. This probability is given by:

$$P(AXB) = P(X) P(A|X) P(B|X) = X_X \left(\frac{X_A X_X + Y}{X_X} \right) \left(\frac{X_B X_X - Y}{X_X} \right) \quad [16]$$

where $P(X)$ is the probability that an anion site is occupied by an X^- ion, $P(A|X)$ is the conditional probability that a cation site is occupied by an A^+ cation given that the neighboring anion site is occupied by an X^- ion, and $P(B|X)$ is defined similarly.

ΔS^{config} is the molar configurational entropy. This is given by the following approximate expression (exact for a one-dimensional lattice) for the distribution of the A-X, A-Y, B-X and B-Y "bonds" over the Z bond positions in one mole of solution:

$$\begin{aligned} \Delta S^{\text{config}} = & -R (X_A \ln X_A + X_B \ln X_B + X_X \ln X_X + X_Y \ln X_Y) \\ & -RZ [(X_A X_X + Y) \ln \frac{X_A X_X + Y}{X_A X_X} + (X_B X_X + Y) \ln \frac{X_B X_X + Y}{X_B X_X} \\ & + (X_A X_Y - Y) \ln \frac{X_A X_Y - Y}{X_A X_Y} + (X_B X_Y - Y) \ln \frac{X_B X_Y - Y}{X_B X_Y}] \quad [17] \end{aligned}$$

Note that for random mixing, when $y = 0$, Eq. [17] reduces to the ideal entropy expression in Eq. [9].

In order to solve Eq. [15], we must calculate y . The value of y adopted by the system will be that which minimizes the Gibbs energy. Setting $dg/dy = 0$ we obtain the following expression:

$$\frac{(X_A X_X + Y) (X_B X_Y + Y)}{(X_B X_X - Y) (X_A X_Y - Y)} = e^{-(\Delta g^{\text{EX}} + Q)/ZRT} \quad [18]$$

where:

$$\begin{aligned} Q = & (X_B - X_A - 2Y/X_X) w_{A,B/X} + (X_A - X_B - 2Y/X_Y) w_{A,B/Y} \\ & + (X_Y - X_X - 2Y/X_A) w_{A/X,Y} + (X_X - X_Y - 2Y/X_B) w_{B/X,Y} \quad [19] \end{aligned}$$

Equations [18,19] can be solved for y by an iterative technique. On the first pass, Q is assumed equal to zero and Eq. [18], which is now quadratic, is solved for y . This value is then substituted into Eq. [19] to obtain a second estimate for Q , and so on. Although the equations are lengthy, their solution with a computer is straightforward.

When Δg^{EX} is small, Eq. [15] reduces Eq. [9]. The phase diagram of the Na,K/F,Cl system, calculated with the extended model, is virtually identical to Fig. 2b.

For the other three example systems, the phase diagrams calculated with the extended model are shown in Figs 3d, 4d and 5d. In all cases, agreement with the measured diagram is better than that obtained with Eq. [9] using either Eq. [13] or Eq. [14].

Equally good results have been obtained for several other ternary reciprocal molten salt solutions. In all cases, the extended quasichemical model provides the best agreement with the measured diagram.

It must be stressed that no new adjustable parameters are introduced in the extended model. As was the case with Eq. [9], only values of Δg^{EX} and of the binary excess terms $w_{A,B/X}$, etc. are required.

DISCUSSION

Approximate solution

The logarithm of the equilibrium constant, Eq. [18], may be expressed as:

$$\begin{aligned} & \ln (1+y/X_A X_X) + \ln (1+y/X_B X_Y) - \ln (1-y/X_B X_X) - \ln (1-y/X_A X_Y) \\ & = - (\Delta g^{EX} + Q)/ZRT \end{aligned} \quad [20]$$

Expanding the logarithmic terms as Taylor series in y and taking only the first order terms, we obtain the following approximate expression for y :

$$y = - X_A X_B X_X X_Y (\Delta g^{EX} + Q)/ZRT \quad [21]$$

Taking Q from Eq. [19] and substituting into Eq. [21] yields:

$$y = \frac{-X_A X_B X_X X_Y (\Delta g^{EX} + (X_B - X_A)w_{A,B/X} + (X_A - X_B)w_{A,B/Y} + (X_Y - X_X)w_{A/X,Y} + (X_X - X_Y)w_{B/X,Y})}{ZRT - 2(X_A X_B X_Y w_{A,B/X} + X_A X_B X_X w_{A,B/Y} + X_B X_X X_Y w_{A/X,Y} + X_A X_X X_Y w_{B/X,Y})} \quad [22]$$

Eq. [22] is an explicit expression for y which can be substituted back into Eq. [15] to give an explicit expression for g. The model equations can thus be solved without the necessity of iterating.

As a rule of thumb, Eq. [22] should give satisfactory results as long as $|\Delta g^{EX}| < 50$ kJ.

It might also be noted that the logarithmic terms in Eq. [17] for ΔS^{config} can also be expanded as Taylor series to the second power in y, yielding the following approximate expression:

$$\Delta S^{config} = -R(X_A \ln X_A + X_B \ln X_B + X_X \ln X_X + X_Y \ln X_Y) - RZy^2 / 2X_A X_B X_X X_Y \quad [23]$$

If all the binary terms $w_{A,B/X}$, etc., are set to zero, Eqs. [15,22,23], when combined, reduce to Eqs. [9,13].

Extensions to charge-asymmetric and multicomponent systems

Saboungi and Blander (22) have extended Eq. [9] to charge-asymmetric systems (systems for which all ions do not have the same charge) through the expedient of replacing all ionic fractions by equivalent ionic fractions except in the ideal entropy terms. A similar approach can be used in the extended quasichemical model. The model can also be extended to quaternary and higher-order systems. These topics will be discussed in a forthcoming article.

CONCLUSIONS

With the extended quasichemical model, ternary reciprocal salt phase diagrams can be calculated with satisfactory precision from the thermodynamic properties of the pure salts and from optimized parameters for the binary subsystems. Thus it is now possible to set up databases of such parameters for purposes of calculating the

thermodynamic properties and phase diagrams of multicomponent salt systems.

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