

# The Modified Quasichemical Model I—Binary Solutions

A.D. PELTON, S.A. DEGTEROV, G. ERIKSSON, C. ROBELIN, and Y. DESSUREAULT

Further improvements to the modified quasichemical model in the pair approximation for short-range ordering in liquid and solid solutions are presented. The energy of pair formation is expanded in terms of the pair fractions rather than the component fractions, and coordination numbers are permitted to vary with composition. A formalism is introduced whereby the quasichemical equations are shown to be equivalent to the equations of an associate model if the pairs are formally treated as fractional associates. The model is applied to the liquid phase in a new optimization of the KCl-MgCl<sub>2</sub> system.

## I. INTRODUCTION

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

The present article is the first in a series describing further modifications and extensions to the model. Following a suggestion by Blander, the energy of pair formation has been expanded as a polynomial in the pair fractions rather than the component fractions. Furthermore, the coordination numbers are permitted to vary with composition. Both these modifications provide greater flexibility and ease of fitting. Finally, a formalism is introduced whereby the pairs are treated as fractional “associates.” This formalism permits calculations involving the quasichemical model to be made with currently available and relatively simple software.

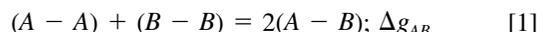
As an example, the quasichemical model with these modifications is used for the liquid phase in a new optimization of the KCl-MgCl<sub>2</sub> system.

Subsequent articles in this series will treat the extensions to multicomponent systems and to liquids with two “sublattices.”

## II. THEORY

In the modified quasichemical model in the pair approximation, as proposed by Pelton and Blander<sup>[1,2,3]</sup> for a liquid

binary solution, atoms or molecules *A* and *B* are distributed over the sites of a quasilattice. The following pair exchange reaction is considered:



where (*i* - *j*) represents a first-nearest-neighbor pair. The non-configurational Gibbs energy change for the formation of 2 moles of (*A* - *B*) pairs is  $\Delta g_{AB}$ . (There has been a minor change in notation. In our original<sup>[1,2,3]</sup> formulation, we let  $(\omega - \eta T)$  be the energy of Reaction [1] per mole of components.) Let  $n_A$  and  $n_B$  be the number of moles of *A* and *B* and  $n_{ij}$  be the number of moles of (*i* - *j*) pairs. ( $n_{AB}$  and  $n_{BA}$  represent the same quantity and can be used interchangeably.) Let  $Z_A$  and  $Z_B$  be the coordination numbers of *A* and *B*. Then

$$Z_A n_A = 2n_{AA} + n_{AB} \quad [2]$$

$$Z_B n_B = 2n_{BB} + n_{AB} \quad [3]$$

(Clearly, in the case of solid solutions,  $Z_A = Z_B$  necessarily.) We also introduce pair fractions  $X_{ij}$ :

$$X_{ij} = n_{ij}/(n_{AA} + n_{BB} + n_{AB}) \quad [4]$$

overall mole (or site) fractions:

$$X_A = n_A/(n_A + n_B) = 1 - X_B \quad [5]$$

and “coordination-equivalent” fractions.

$$\begin{aligned} Y_A &= Z_A n_A / (Z_A n_A + Z_B n_B) \\ &= Z_A X_A / (Z_A X_A + Z_B X_B) \\ &= 1 - Y_B \end{aligned} \quad [6]$$

Substitution of Eqs. [2] and [3] into Eqs. [4] and [6] gives

$$Y_A = X_{AA} + X_{AB}/2 \quad [7]$$

$$Y_B = X_{BB} + X_{AB}/2 \quad [8]$$

The Gibbs energy of the solution is given by

$$G = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{\text{config}} + (n_{AB}/2) \Delta g_{AB} \quad [9]$$

where  $g_A^\circ$  and  $g_B^\circ$  are the molar Gibbs energies of the pure components, and  $\Delta S^{\text{config}}$  is the configurational entropy of mixing given by randomly distributing the (*A*-*A*), (*B*-*B*), and (*A*-*B*) pairs.

$$\begin{aligned} \Delta S^{\text{config}} &= -R (n_A \ln X_A + n_B \ln X_B) \\ &- R [n_{AA} \ln(X_{AA}/Y_A^2) + n_{BB} \ln(X_{BB}/Y_B^2) \\ &+ n_{AB} \ln(X_{AB}/2Y_A Y_B)] \end{aligned} \quad [10]$$

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Because no exact expression is known for the entropy of this distribution in three dimensions, Eq. [10] is an approximate equation. However, it can be shown<sup>[1]</sup> to be an exact expression for a one-dimensional lattice (Ising model). Furthermore, when  $\Delta g_{AB}$  is equal to zero, then  $A$  and  $B$  should be randomly distributed over the quasi lattice sites. That is,

$$X_{AA} = Y_A^2; X_{BB} = Y_B^2; X_{AB} = 2Y_A Y_B \text{ when } \Delta g_{AB} = 0 \quad [11]$$

In this case, the second term on the right of Eq. [10] equals zero, and the configurational entropy correctly reduces to the random mixing point approximation (Bragg-Williams) expression. To derive Eq. [11], consider that the total number of moles of pair bonds emanating from the  $A$  and  $B$  atoms or molecules, respectively, are  $Z_A n_A$  and  $Z_B n_B$ . The probability, in a random (Bragg-Williams) solution, that a given pair has both ends emanating from an  $A$  is, thus, equal to  $(Z_A n_A / (Z_A n_A + Z_B n_B))^2 = Y_A^2 = X_{AA}$  and similarly for  $X_{BB}$  and  $X_{AB}$ .

The equilibrium distribution is calculated by setting

$$\partial(G/\partial n_{AB})_{n_A, n_B} = 0 \quad [12]$$

at constant  $n_A$  and  $n_B$ , subject to the constraints of Eqs. [2] and [3]. This gives<sup>[1]</sup>

$$X_{AB}^2 / (X_{AA} X_{BB}) = 4 \exp(-\Delta g_{AB} / RT) \quad [13]$$

For a given value of  $\Delta g_{AB}$ , the solution of Eq. [13] together with Eqs. [2], [3], and [4] gives  $n_{AA}$ ,  $n_{BB}$ ,  $n_{AB}$ , which can then be substituted into Eqs. [9] and [10]. Equation [13] is the "equilibrium constant" for the "quasichemical reaction" of Eq. [1]. When  $\Delta g_{AB} = 0$ , Eq. [13] is satisfied by Eq. [11]. As  $\Delta g_{AB}$  becomes progressively more negative, reaction [1] is shifted progressively to the right, and the calculated enthalpy and configurational entropy of mixing assume, respectively, the negative  $V$  and  $m$  shapes characteristic of short-range ordering with minima at  $Y_A = Y_B = 1/2$ , as illustrated in Figure 1.

The composition,  $X_B$ , of maximum short-range ordering is determined by the ratio  $(Z_B/Z_A)$ . For example, in liquid Ni-S solutions, the maximum short-range ordering occurs at  $X_S = X_{Ni} = 1/2$  where Ni atoms are predominantly surrounded by S atoms and *vice versa*. Hence, we set  $Z_{Ni} = Z_S$ . In Cu-S solutions, on the other hand, maximum short-range ordering occurs at the composition corresponding to  $\text{Cu}_2\text{S}$  where  $X_S = 1/3$ . Hence, we set  $Z_S = 2Z_{Cu}$  so that  $Y_S = 1/2$  when  $X_S = 1/3$ . As a final example, liquid KCl-MgCl<sub>2</sub> solutions exhibit a negative V-shaped enthalpy and m-shaped entropy of mixing with minima near  $X_{\text{MgCl}_2} = 1/3$ ; this indicates maximum short-range ordering of  $\text{K}^+$  and  $\text{Mg}^{2+}$  ions on the cation lattice at this composition. Hence, we set  $Z_{\text{Mg}} = 2Z_{\text{K}}$  so that  $Y_{\text{Mg}} = 1/2$  when  $X_{\text{Mg}} = 1/3$ . In this example, all anion sites are occupied by Cl ions so the anion lattice can be ignored. The model then applies to the cation lattice, and  $Z_{\text{Mg}}$  and  $Z_{\text{K}}$  are the cation-cation coordination numbers.

Finally, in order to permit the model to be used for fitting data in real systems, Pelton and Blander introduced additional empirical parameters by expanding  $\Delta g_{AB}$  as a polynomial in the component fractions:  $Y_i$ :

$$\Delta g_{AB} = (\omega_{AB}^0 - \eta_{AB}^0 T) + \sum_{(i+j \geq 1)} (\omega_{AB}^i - \eta_{AB}^i T) Y_A^i Y_B^j \quad [14]$$

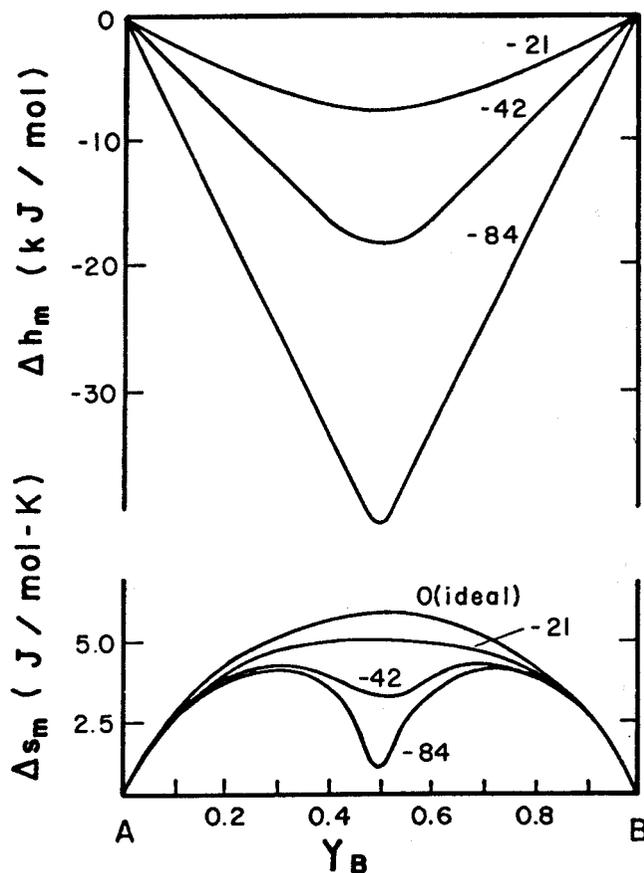


Fig. 1—Molar enthalpy and entropy of mixing for a system  $A-B$  calculated at 1000 °C with  $Z_A = Z_B = 2$  from the quasichemical model for short-range ordering with  $\Delta g_{AB} = \text{constant} = 0, -21, -42, \text{ and } -84 \text{ kJ}$ .

where  $\omega_{AB}^0$ ,  $\eta_{AB}^0$ ,  $\omega_{AB}^i$ , and  $\eta_{AB}^i$  were the adjustable parameters of the model, and  $T$  is temperature (K). Alternatively, the expansion could be written using Redlich-Kister polynomials  $(Y_B - Y_A)^i$ , Legendre polynomials, *etc.*

The quasichemical model has been applied extensively to molten sulfide solutions<sup>[6,7]</sup> molten alloys,<sup>[7,8,9]</sup> and oxide slags/glasses<sup>[9-21]</sup> such as molten silicates.

#### A. Bragg-Williams (Point Approximation) Limit When $\Delta g_{AB}$ Is Small

The total number of pairs in the solution ( $n_{AA} + n_{BB} + n_{AB}$ ) is equal to  $(Z_A n_A + Z_B n_B)/2$  from Eqs. [2] and [3]. Hence, from Eq. [11], when  $\Delta g_{AB}$  is small,  $n_{AB}$  is approximately equal to  $[(Z_A n_A + Z_B n_B)/2] 2 Y_A Y_B$ . Also in this case, as discussed previously, the configurational entropy is approximately equal to the random-mixing Bragg-Williams value. Substitution into Eq. [9] then gives, in the Bragg-Williams limit for small  $\Delta g_{AB}$

$$G \approx (n_A g_A^0 + n_B g_B^0) + RT (n_A \ln X_A + n_B \ln X_B) + \frac{(n_A Z_A + n_B Z_B)}{2} Y_A Y_B \Delta g_{AB} \quad [15]$$

or, per mole of solution ( $n_A + n_B = 1$ ),

$$g \approx (X_A g_A^\circ + X_B g_B^\circ) + RT (X_A \ln X_A + X_B \ln X_B) + \frac{(X_A Z_A + X_B Z_B)}{2} Y_A Y_B \Delta g_{AB} \quad [16]$$

(For a rigorous proof, it must be shown that the ratio of the last term in Eq. [10] to the last term in Eq. [9] approaches zero as  $\Delta g_{AB}$  goes to zero. By setting  $X_{AB} = (2X_A X_B + y)$ , expanding the logarithmic terms in Eq. (10) as Taylor series, and letting  $y \rightarrow 0$ , this ratio can be shown to be of the order of  $(Y_A Y_B \Delta g_{AB}/RT)$ ).

When  $Z_A = Z_B$ , then  $Y_A = X_A$ . If, as well,  $\Delta g_{AB} = (\omega_{AB}^\circ - \eta_{AB}^\circ T) = \text{constant}$ , then Eq. [16] is the well-known regular solution expression. If  $Z_A = Z_B$  and if  $\Delta g_{AB}$  is expanded as a polynomial as in Eq. [14], then Eq. [16] becomes the commonly used expression for the Gibbs energy of a binary solution with the “excess molar Gibbs energy,”  $g^E$ , expressed as a polynomial in the mole fractions.

When  $Z_A \neq Z_B$ , and  $\Delta g_{AB}$  is small and independent of composition, then from Eq. [16] a plot of  $[g^E/(X_A Z_A + X_B Z_B)]$  vs  $Y_B$  will exhibit a minimum near  $Y_B = 0.5$ . Many years ago, Blander<sup>[22]</sup> plotted curves of  $(g^E/Y'_A Y'_B)$  vs  $Y'_B$  for many common-anion binary molten salt systems such as KCl-MgCl<sub>2</sub>, where  $g^E = g^E/(q_A X_A + q_B X_B)$  is the excess Gibbs energy per charge equivalent,  $q_A$  and  $q_B$  are the cationic charges (e.g.,  $q_K = 1$ ,  $q_{Mg} = 2$ ), and where  $Y'_A$  and  $Y'_B$  are the charge-equivalent fractions  $Y'_B = (1 - Y'_A) = q_B X_B / (q_A X_A + q_B X_B)$ . He observed that these curves are generally flatter and smoother than plots of  $(g^E/X_A X_B)$  vs  $X_B$  and are well fitted by polynomial expansions with fewer terms. He, thus, founded the common practice of expressing excess Gibbs energies of molten salt solutions in terms of charge-equivalent fractions rather than mole fractions. If, taking the example of KCl-MgCl<sub>2</sub> solutions, we replace the charges  $q_K = 1$  and  $q_{Mg} = 2$  by the coordination numbers  $Z_K$  and  $Z_{Mg}$  with  $Z_{Mg} = 2Z_K$  as discussed previously, we see that Blander’s observation results from the fact that  $g^E$  exhibits a minimum near  $X_{Mg} = 1/3$  due to short-range ordering.

### B. Expansion of $\Delta g_{AB}$ in Terms of Pair Fractions

Following a suggestion by Blander,<sup>[23]</sup> we now propose a further modification to the quasichemical model: namely, the expansion of  $\Delta g_{AB}$  as a polynomial in terms of the pair fractions  $X_{AA}$  and  $X_{BB}$  rather than in terms of the equivalent fractions, as in Eq. [14].

That is,

$$\Delta g_{AB} = \Delta g_{AB}^\circ + \sum_{i \geq 1} g_{AB}^{i0} X_{AA}^i + \sum_{j \geq 1} g_{AB}^{0j} X_{BB}^j \quad [17]$$

where  $\Delta g_{AB}^\circ$ ,  $g_{AB}^{i0}$ , and  $g_{AB}^{0j}$  are the parameters of the model that can be functions of temperature. In the words of Blander,<sup>[23]</sup>  $\Delta g_{AB}$  is now “configuration dependent” rather than simply composition dependent, as in Eq. [14].

This presents a significant practical advantage for solutions with a large degree of short-range ordering (that is solutions for which  $\Delta g_{AB}$  is very negative.) When  $Y_B < 1/2$ ,  $X_{BB}$  is very small in such solutions. Hence, the terms  $(g_{AB}^{0j} X_{BB}^j)$  have little effect on the Gibbs energy, and so, in this composition region, only the parameters  $g_{AB}^{i0}$  are important. Similarly, for  $Y_B > 1/2$ , only the terms  $g_{AB}^{0j}$  are important. Hence, for curve-fitting purposes, the solution

can effectively be split into two nearly independent subsystems. We have found that this results in significantly improved fits with fewer coefficients.

Cross terms  $\sum g_{AB}^{ij} X_{AA}^i X_{BB}^j$  with  $i \geq 1$  and  $j \geq 1$  can also be included in Eq. [17]. Generally, however, this provides no advantage in practice.

When  $\Delta g_{AB}$  is small, Eq. [11] applies, and Eq. [17] reduces to Eq. [14] in the limit. For example, if we set  $g_{AB}^{10} = -g_{AB}^{01}$  and set all coefficients for  $i \geq 2$  and  $j \geq 2$  equal to zero, then from Eq. [11], for small  $\Delta g_{AB}$ ,

$$\Delta g_{AB} \approx \Delta g_{AB}^\circ + g_{AB}^{01} (Y_B^2 - Y_A^2) = (\Delta g_{AB}^\circ - g_{AB}^{01}) + 2g_{AB}^{01} Y_B \quad [18]$$

This is equivalent to Eq. [14] for a two-coefficient (“subregular”) expansion.

### C. Composition-Dependent Coordination Numbers

The next new modification to be introduced into the quasichemical model is composition-dependent coordination numbers. There are a number of drawbacks to the use of constant coordination numbers. If a solution exhibits a high degree of short-range ordering at, for example  $X_B = 1/3$ , then  $Z_B$  must equal  $2Z_A$  near this composition. However, this does not mean that  $Z_B$  in pure liquid  $B$  need necessarily be equal to  $2Z_A$  in pure  $A$ . Furthermore, from a more practical standpoint for the development of databases for multicomponent solution, consider a ternary system  $A$ - $B$ - $C$  in which we have chosen the ratios  $(Z_B/Z_A)$  and  $(Z_C/Z_B)$  to correspond to the observed compositions of maximum short-range ordering in the  $A$ - $B$  and  $B$ - $C$  binary subsystems. If we are restricted to constant coordination numbers, then the ratio  $(Z_C/Z_A)$  is now fixed. However, this may not correspond to the observed composition of maximum short-range ordering in the  $C$ - $A$  subsystem.

Finally, as discussed previously, Eq. [10] is an approximate expression for the configurational entropy, which is only exact one-dimensionally. Consider the case when  $Z_A = Z_B = Z$  and  $\Delta g_{AB} = -\infty$ . The solution is then completely ordered at  $X_A = X_B = 1/2$  (where  $X_{AB} = 1$ ), and the configurational entropy should be zero at this composition. However, substitution into Eq. [10], along with Eqs. [2] and [3] gives  $\Delta S^{\text{config}} = -R n_{AB} (1 - 2/Z) \ln 2$ , which is only equal to zero if  $Z = 2$ , as is the case in a one-dimensional lattice. Therefore, for highly ordered solutions, better results are expected if coordination numbers approximately equal to 2 are used, even though this value is nonphysical in three dimensions. This expectation has been confirmed in practice by the optimization of a great many binary systems.<sup>[6-21]</sup> On the other hand, for solutions with only a small degree of ordering, and particularly for solutions with  $\Delta g_{AB} > 0$ , which exhibit clustering and immiscibility, larger values of  $Z_A$  and  $Z_B$  of the order of 6 have been found necessary to yield good fits. That is, one is forced by the approximate nature of Eq. [10] to use nonphysical values of the coordination numbers. If one is restricted to constant coordination numbers, then a problem again arises for multicomponent solutions. If solutions  $A$ - $B$  are highly ordered, while solutions  $B$ - $C$  exhibit a tendency to immiscibility, then we should choose  $Z_B \approx 2$  in the  $A$ - $B$  systems, but  $Z_B \approx 6$  in the  $B$ - $C$  system. However, with constant coordination numbers, this is not possible if

we want one consistent set of parameters for the *A-B-C* ternary solution.

Accordingly, the model has been modified to permit  $Z_A$  and  $Z_B$  to vary with composition as follows:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left( \frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left( \frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \quad [19]$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left( \frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left( \frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \quad [20]$$

where  $Z_{AA}^A$  and  $Z_{AB}^A$  are the values of  $Z_A$  when all nearest neighbors of an *A* are *A*s, and when all nearest neighbors of an *A* are *B*s, and where  $Z_{BB}^B$  and  $Z_{BA}^B$  are defined similarly. Note that  $Z_{AB}^A$  and  $Z_{BA}^B$  represent the same quantity and can be used interchangeably. Substitution into Eqs. [2] and [3] gives

$$n_A = 2n_{AA}/Z_{AA}^A + n_{AB}/Z_{AB}^A \quad [21]$$

$$n_B = 2n_{BB}/Z_{BB}^B + n_{AB}/Z_{BA}^B \quad [22]$$

Equations [6] [7] and [8] remain unchanged. The composition dependence of Eqs. [19] and [20] was chosen because it results in the simple relationships of Eqs. [21] and [22]. This simplifies subsequent calculations, particularly calculations of chemical potentials and calculations in multicomponent solutions.

The composition of maximum short-range ordering is determined by the ratio ( $Z_{BA}^B/Z_{AB}^A$ ). Values of  $Z_{BA}^B$  and  $Z_{AB}^A$  are unique to the *A-B* binary system, while the value of  $Z_{AA}^A$  is common to all systems containing *A* as a component.

Clearly, in the case of solid solutions,  $Z_{AA}^A = Z_{BB}^B = Z_{AB}^A = Z_{BA}^B$  necessarily.

### III. OPTIMIZATION OF THE KCl-MgCl<sub>2</sub> SYSTEM

The application of the model will be illustrated by a thermodynamic optimization of the KCl-MgCl<sub>2</sub> system.

Experimental liquidus and eutectic temperatures of the phase diagram from three studies<sup>[24,25,26]</sup> are shown in Figure 2. Two compounds, K<sub>2</sub>MgCl<sub>4</sub> and KMgCl<sub>3</sub>, have been reported<sup>[26]</sup> to exist in equilibrium with the liquid. One other reported compound,<sup>[26]</sup> K<sub>3</sub>Mg<sub>2</sub>Cl<sub>7</sub>, has no, or virtually no, effect on the liquidus and so was ignored in the present optimization. The limiting slopes of the liquidus curves at  $X_{KCl} = 1.0$  and  $X_{MgCl_2} = 1.0$  are consistent with Raoult's law under the assumption of negligible terminal solid solubility. Also, there is no evidence for appreciable nonstoichiometry of K<sub>2</sub>MgCl<sub>4</sub> and KMgCl<sub>3</sub>. Therefore, all four solid phases were assumed to be stoichiometric line compounds in the present optimization.

Activities of KCl in the liquid phase, as reported in two studies<sup>[27,28]</sup> employing galvanic cells with K<sup>+</sup>-conducting glass electrolytes, are shown in Figure 3. Activity coefficients of MgCl<sub>2</sub>, as reported in two studies<sup>[29,30]</sup> employing galvanic formation cells, are reproduced in Figure 4. Enthalpies of mixing measured by direct mixing calorimetry at 800 °C<sup>[31]</sup> are shown in Figure 5.

The thermodynamic properties (*H*, *S*, *C<sub>p</sub>*) of pure solid and liquid KCl and MgCl<sub>2</sub> were taken from the F\*A\*C\*T database.<sup>[32]</sup> These data are reproduced in Table I. The heat capacities of K<sub>2</sub>MgCl<sub>4</sub> and KMgCl<sub>3</sub> were measured<sup>[33]</sup> over

the temperature ranges 594 < *T* < 693 K and 696 < *T* < 749 K, respectively, by drop calorimetry as *C<sub>p</sub>* = 263.05 and *C<sub>p</sub>* = 157.65 J/mol. K, respectively. These values were used in the present optimization and were assumed to be constant from 298 K to the melting points.

The modified quasichemical model was used for the liquid. Letting *A* = KCl and *B* = MgCl<sub>2</sub>, the parameters  $Z_{AA}^A$  and  $Z_{BB}^B$  were both set equal to 6. The tendency to maximum short-range ordering near the composition K<sub>2</sub>MgCl<sub>4</sub> ( $X_{MgCl_2} = 1/3$ ) was modeled by setting  $Z_{AB}^A = 3.0$  and  $Z_{BA}^B = 6.0$ .

All the data in Figures 2 through 5 were optimized simultaneously by a least-squares technique, to obtain the parameters of the quasichemical model as well as  $H_{298}^\circ$  and  $S_{298}^\circ$  for K<sub>2</sub>MgCl<sub>4</sub> and KMgCl<sub>3</sub>. The resulting optimized quasichemical parameters of Eq. [17] are

$$\Delta g_{AB} = -17,497 - 1026X_{AA} - 14,801X_{BB} \text{ J/mol} \quad [23]$$

The optimized properties of the compounds are listed in Table I. The calculated enthalpy of formation of K<sub>2</sub>MgCl<sub>4</sub> from solid KCl and MgCl<sub>2</sub> at 298.15 K is -35,030 J/mol, which may be compared to values of -7750 J/mol obtained<sup>[34]</sup> by solution calorimetry and -35,560 J/mol obtained<sup>[35]</sup> by combining enthalpy of fusion, heat capacity, and enthalpy of mixing data in a thermodynamic cycle. For KMgCl<sub>3</sub>, the calculated enthalpy of formation from solid KCl and MgCl<sub>2</sub> at 298.15 K is -22,620 J/mol, while reported values are -9900 J/mol from solution calorimetry<sup>[34]</sup> and -15,480 J/mol from combining enthalpy of fusion, heat capacity, and enthalpy of mixing data. Calculated entropies of formation of K<sub>2</sub>MgCl<sub>4</sub> and KMgCl<sub>3</sub> from solid KCl and MgCl<sub>2</sub> at 298.15 K are -37.9 and -9.9 J/mol K, respectively. These values are reasonable.

The phase diagram shown in Figure 2 and the curves plotted in Figures 3 through 5 are calculated from the optimized parameters. All the data are reproduced by only three quasichemical parameters in Eq. [23]. It is also to be noted that these parameters are temperature independent. That is, the entropy of the liquid is well represented by the configurational terms of the model with no need for additional nonconfigurational entropy terms. It is, of course, possible to reproduce the experimental points even more closely by the use of more parameters; however, it is not clear that this is justified by the precision of the available data. Attempts to optimize this system satisfactorily with a simple Bragg-Williams configurational entropy (*i.e.*, without using the quasichemical model) were unsuccessful even with a large number of temperature-dependent parameters in a polynomial expansion of  $g^E$ .

### IV. THE QUASICHEMICAL MODEL IN AN ASSOCIATE FORMALISM

It is very useful to compare the quasichemical model to so-called associate models of short-range ordering in liquids. As well as showing the similarities and differences of the two approaches, this comparison also suggests a particularly simple algorithm for solving the quasichemical model equations.

For a binary system *A-B* with short-range ordering about the composition  $X_B = 1/3$ , for example, an associate model might consider the solution to be a random mixture of *A*

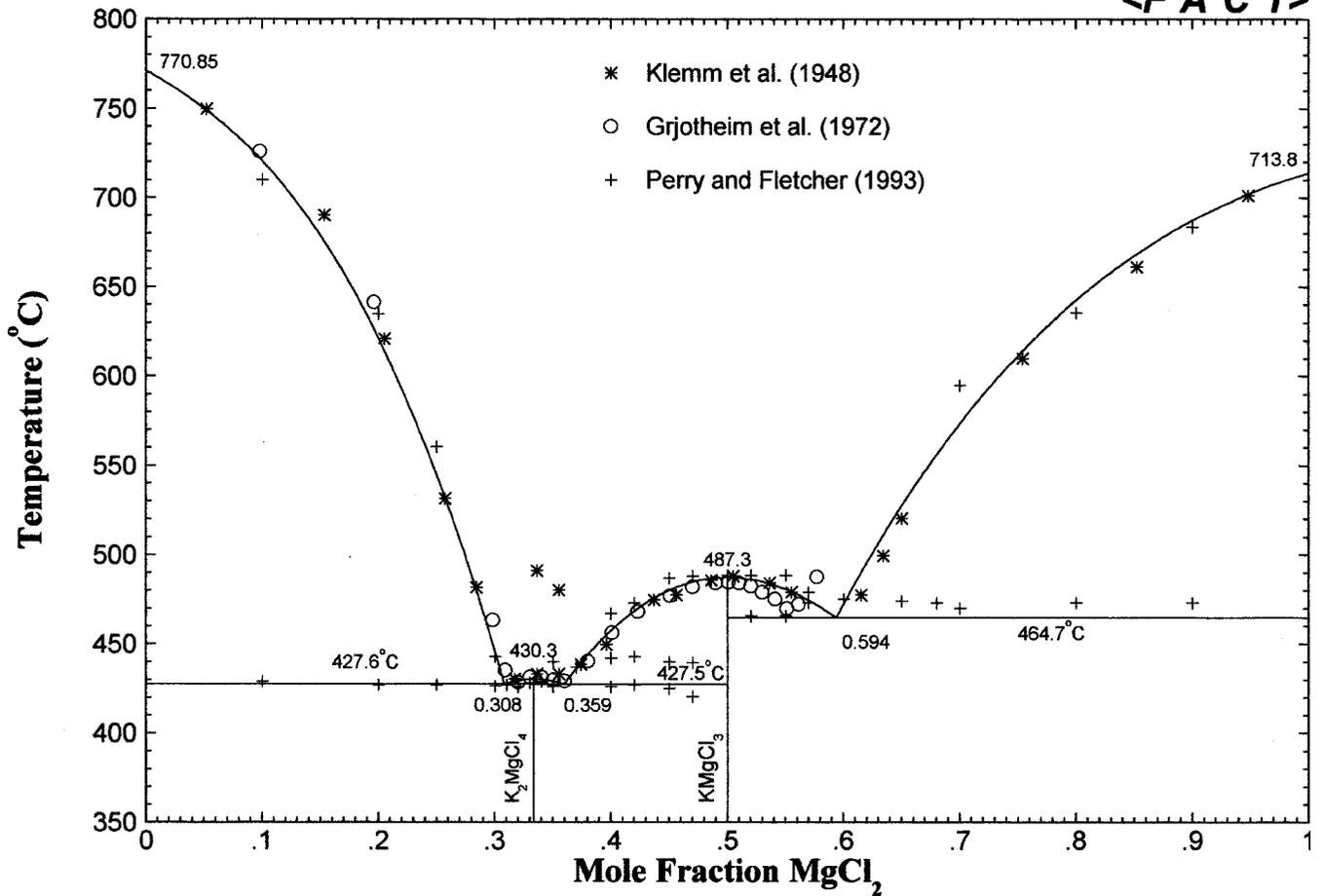


Fig. 2—Calculated KCl-MgCl<sub>2</sub> phase diagram and experimental points.<sup>[24,25,26]</sup>

atoms, *B* atoms, and *A*<sub>2</sub>*B* “molecules” distributed on a quasi-lattice. The Gibbs energy can be written

$$G = (n'_A g_A^\circ + n'_B g_B^\circ + n'_{A_2B} g_{A_2B}^\circ) + RT (n'_A \ln X'_A + n'_B \ln X'_B + n'_{A_2B} \ln X'_{A_2B}) + (n'_A + n'_B + n'_{A_2B}) g^E (X'_A, X'_B, X'_{A_2B}) \quad [24]$$

where *n*'<sub>*A*</sub>, *n*'<sub>*B*</sub>, and *n*'<sub>*A*<sub>2</sub>*B*</sub> are the numbers of moles of the species (*i.e.*, *n*'<sub>*A*</sub> is the number of moles of unassociated *A* atoms that are not part of the *A*<sub>2</sub>*B* associates), and *X*'<sub>*A*</sub>, *X*'<sub>*B*</sub>, and *X*'<sub>*A*<sub>2</sub>*B*</sub> are the corresponding species fractions. The following mass balances apply:

$$n_A = n'_A + 2n'_{A_2B} \quad [25]$$

$$n_B = n'_B + n'_{A_2B} \quad [26]$$

The standard Gibbs energy “pure” *A*<sub>2</sub>*B* is *g*<sub>*A*<sub>2</sub>*B*</sub><sup>°</sup>. This is a parameter of the model. The association reaction can be written:



with

$$\Delta G^\circ = g_{A_2B}^\circ - 2g_A^\circ - g_B^\circ = -RT \ln K \quad [28]$$

The excess molar Gibbs energy *g*<sup>*E*</sup> in Eq. [24] is generally

written as a polynomial function of the species fractions. If *g*<sup>*E*</sup> = 0, then Eq. [24] is identical to that of a gas. Otherwise, Eq. [24] is identical to the expression commonly used for the Gibbs energy of a “ternary” system *A*-*B*-*A*<sub>2</sub>*B* with an explicit polynomial expression for *g*<sup>*E*</sup>.

As well as being physically unrealistic, the associate model suffers from the disadvantage that it does not reduce to an ideal (Bragg–Williams) solution model. When Δ*G*<sup>°</sup> of Reaction [27] equals zero, then *K* = 1, and the equilibrium number of associates *A*<sub>2</sub>*B* is not zero. The number of associates is only zero when Δ*G*<sup>°</sup> = ∞. This was referred to by Lück *et al.*<sup>[36]</sup> as an “entropy paradox.” The quasichemical model, on the other hand, does reduce to an ideal solution model when Δ*g*<sub>*AB*</sub> = 0 as discussed previously.

Another problem with the associate model occurs in dilute solutions. For the present example of *A*<sub>2</sub>*B* associates, when the liquid is highly ordered, solutions rich in component *B* consist primarily of *B* and *A*<sub>2</sub>*B* species. That is, *A* atoms enter solution paired. Hence, at high *X*<sub>*B*</sub>, the chemical activity of *B* varies as (1 - *X*<sub>*A*</sub>/2) rather than (1 - *X*<sub>*A*</sub>) as is the case with the quasichemical model.

The quasichemical equations can be written in a form very similar to the equations of an associate model as follows. We consider the binary solution to contain three associates, *A*<sub>1/*Z*<sub>AA</sub></sub><sup>*A*</sup>, *A*<sub>1/*Z*<sub>AB</sub></sub><sup>*A*</sup>, *B*<sub>1/*Z*<sub>BB</sub></sub><sup>*B*</sup>, *B*<sub>1/*Z*<sub>BA</sub></sub><sup>*B*</sup>, and *A*<sub>1/*Z*<sub>AB</sub></sub><sup>*B*</sup>, *B*<sub>1/*Z*<sub>BA</sub></sub><sup>*A*</sup>. For example, if *Z*<sub>*AA*</sub><sup>*A*</sup> = 6, *Z*<sub>*BB*</sub><sup>*B*</sup> = 6, *Z*<sub>*AB*</sub><sup>*A*</sup> = 3, and *Z*<sub>*BA*</sub><sup>*B*</sup> = 6, then the three

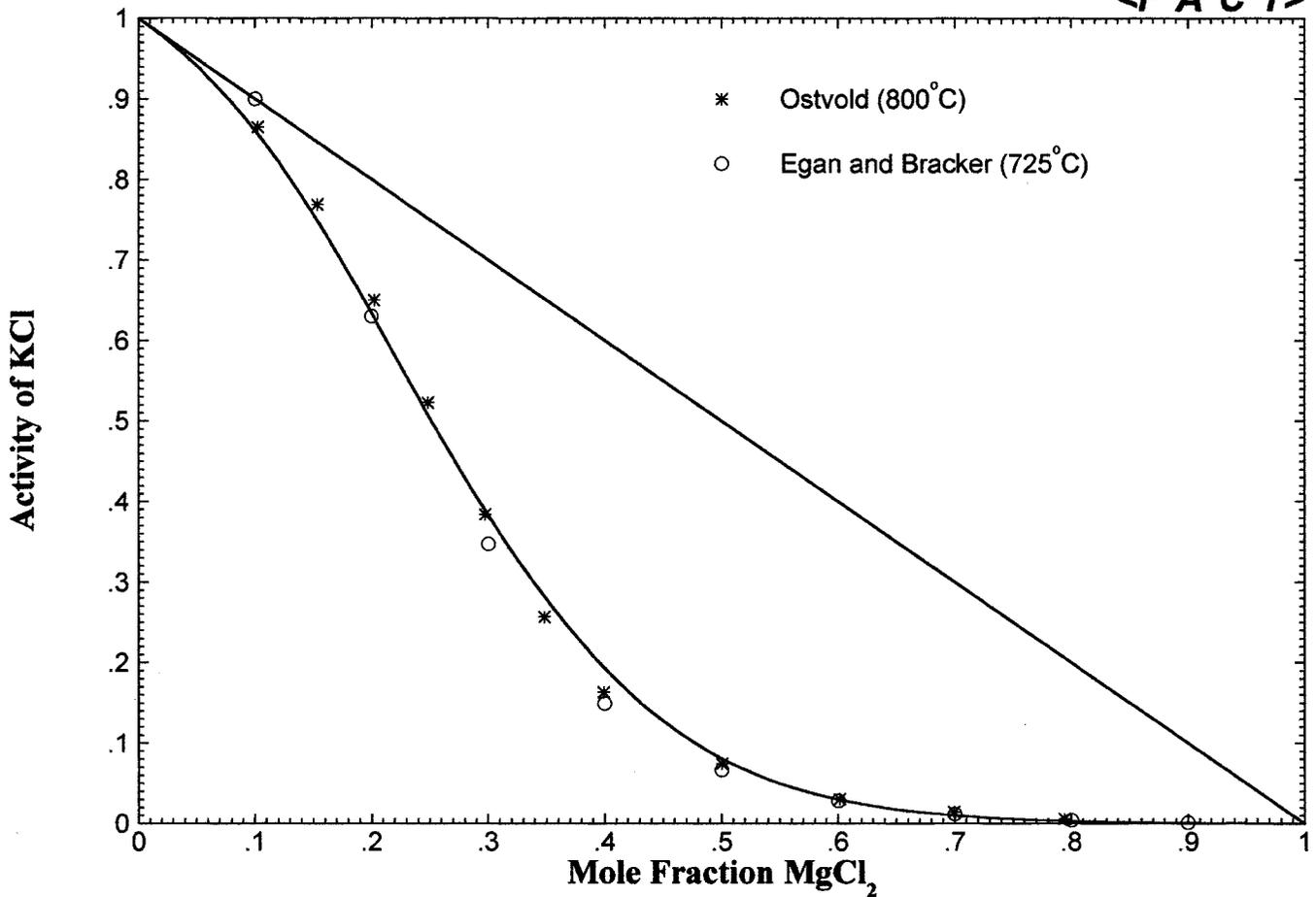


Fig. 3—Calculated activity of KCl (liquid standard state) at 800 °C in liquid KCl-MgCl<sub>2</sub> solutions and experimental<sup>[27,28]</sup> points from emf studies.

“species” are  $A_{2/6}$ ,  $B_{2/6}$ , and  $A_{1/3}B_{1/6}$ . We let the numbers of moles of the three species be equal to the numbers of moles of the pairs. That is,

$$n_{A_{1/3}A_{1/3}} = n_{AA}; n_{B_{1/3}B_{1/3}} = n_{BB}; n_{A_{1/3}B_{1/3}} = n_{AB} \quad [29]$$

The mass balance Eqs. [21] and [22] now become

$$n_A = (2/Z_{AA}^A) n_{A_{1/3}A_{1/3}} + (1/Z_{AB}^A) n_{A_{1/3}B_{1/3}} \quad [30]$$

$$n_B = (2/Z_{BB}^B) n_{B_{1/3}B_{1/3}} + (1/Z_{BA}^B) n_{A_{1/3}B_{1/3}} \quad [31]$$

Note that Eqs. [30] and [31] are “true” chemical mass balances in that the numbers of moles of A and B are equal on both sides of the equations as in Eqs. [25] and [26] for the associate model. We define

$$g_{AA}^\circ = g_{A_{1/3}A_{1/3}}^\circ / Z_{AA}^A = 2g_{AA}^\circ / Z_{AA}^A; g_{BB}^\circ = g_{B_{1/3}B_{1/3}}^\circ / Z_{BB}^B = 2g_{BB}^\circ / Z_{BB}^B \quad [32]$$

$$g_{AB}^\circ = g_{A_{1/3}B_{1/3}}^\circ / Z_{AB}^A = \Delta g_{AB}^\circ / 2 + g_{A_{1/3}}^\circ / Z_{AB}^A + g_{B_{1/3}}^\circ / Z_{BA}^B \quad [33]$$

where  $\Delta g_{AB}^\circ$  from Eq. [17] is the constant term in the expansion of  $\Delta g_{AB}$ , the Gibbs energy change of the quasicheical Reaction. [1]. Substitution of Eqs. [16] and [29] through [33] into Eq. [9] and rearrangement of terms then gives

$$G = (n_{AA} g_{AA}^\circ + n_{BB} g_{BB}^\circ + n_{AB} g_{AB}^\circ) + RT(n_{AA} \ln X_{AA} + n_{BB} \ln X_{BB} + n_{AB} \ln X_{AB}) + RT(n_A \ln X_A + n_B \ln X_B - n_{AA} \ln Y_A^2 - n_{BB} \ln Y_B^2 - n_{AB} \ln (2Y_A Y_B)) + G^E \quad [34]$$

where

$$G^E = \frac{(n_{AA} + n_{BB} + n_{AB})}{2} \quad [35]$$

$$\left[ X_{AA} X_{AB} \sum_{i \geq 1} g_{AB}^{i0} X_{AA}^{i-1} + X_{BB} X_{AB} \sum_{j \geq 1} g_{AB}^{0j} X_{BB}^{j-1} \right]$$

Apart from the second configurational entropy term, Eq. [34] is of the same form as an associate model equation like Eq. [24]. It is this second entropy term which resolves the “entropy paradox”<sup>[36]</sup> of the associate model and allows the quasicheical model to reduce to an ideal solution in the limit. The final term in Eq. [34] is an excess Gibbs energy expressed as a polynomial in the species fractions  $X_{AA}$ ,  $X_{BB}$ , and  $X_{AB}$ . The parameters of the model are  $g_{AB}^\circ$  and the polynomial coefficients  $g_{AB}^{i0}$  and  $g_{AB}^{0j}$ .

The same existing algorithms and computer subroutines that are commonly used for polynomial and associate solution models with polynomial expansions for  $G^E$  can, thus,

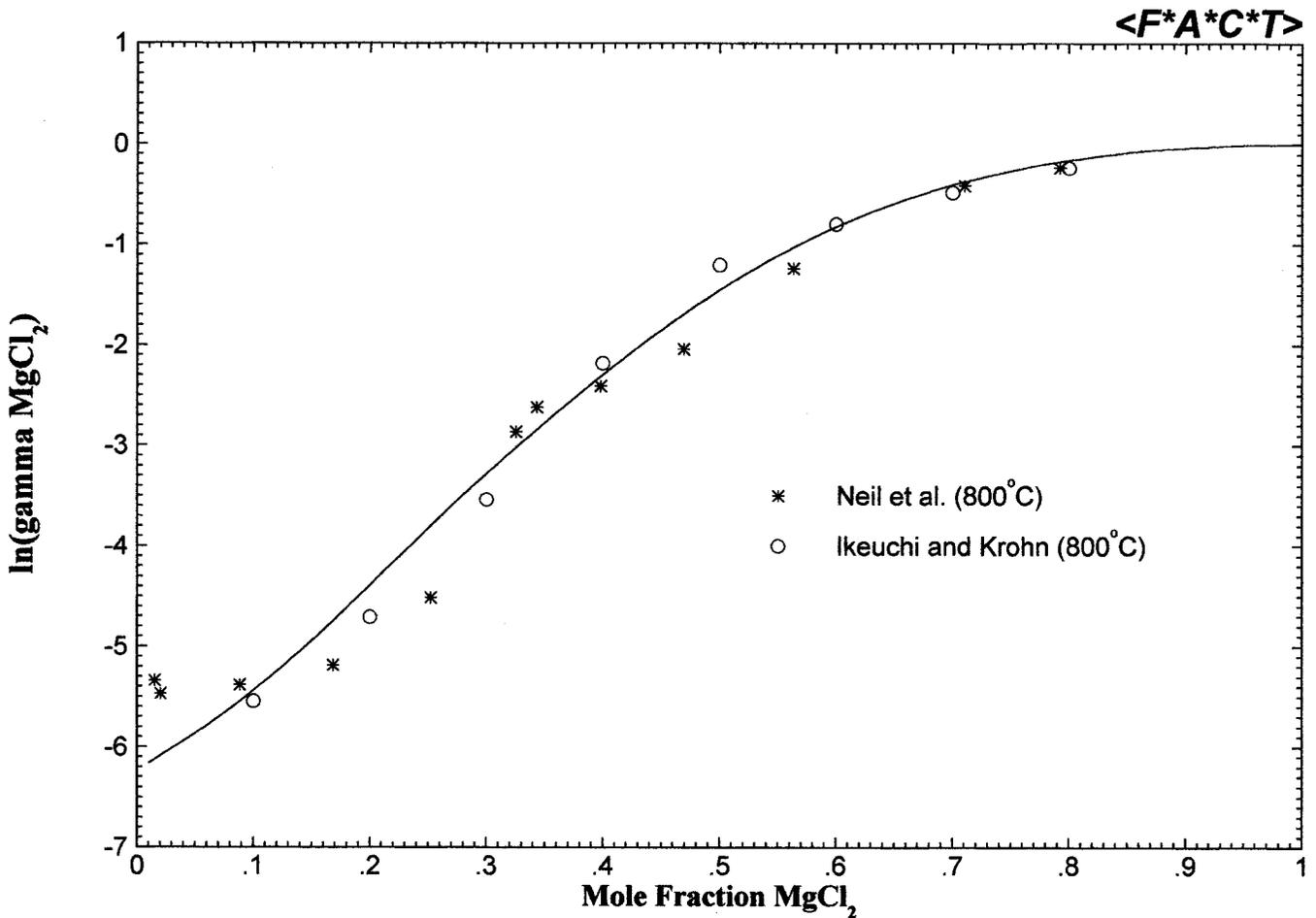


Fig. 4—Calculated activity coefficient of  $\text{MgCl}_2$  (liquid standard state) at  $800^\circ\text{C}$  in liquid  $\text{KCl-MgCl}_2$  solutions and experimental<sup>[29,30]</sup> points from emf studies.

be used directly for the quasichemical model with the simple addition of the extra entropy term. The extension to multi-component solutions is greatly simplified by this formalism as will be discussed in a later article in this series.

Finally, chemical potentials are easily calculated:

$$\begin{aligned} \mu_A &= (\partial G / \partial n_A)_{n_B} = (\partial G / \partial n_A)_{n_B, n_{AB}} + (\partial G / \partial n_{AB})_{n_A, n_B} \times \\ &\quad \times (\partial n_{AB} / \partial n_A)_{n_B} = (\partial G / \partial n_{AA})_{n_{BB}, n_{AB}} (\partial n_{AA} / \partial n_A)_{n_B, n_{AB}} [36] \\ &\quad + (\partial G / \partial n_{BB})_{n_{AA}, n_{AB}} (\partial n_{BB} / \partial n_A)_{n_B, n_{AB}} + (\partial G / \partial n_{AB})_{n_{AA}, n_{BB}} \times \\ &\quad \times (\partial n_{AB} / \partial n_A)_{n_B, n_{AB}} = (Z_{AA}^A / 2) (\partial G / \partial n_{AA})_{n_{BB}, n_{AB}} \end{aligned}$$

where Eqs. [12], [21], and [22] have been used. Hence,

$$\begin{aligned} \mu_A &= (Z_{AA}^A / 2) g_{AA} [37] \\ &= g_A^\circ RT \ln X_A + \left( \frac{Z_{AA}^A}{2} \right) \left( RT \ln \frac{X_{AA}}{Y_A^2} + g_{AA}^E \right) \end{aligned}$$

(and similarly for  $\mu_B$ ) where the partial excess Gibbs energy  $g_{AA}^E$  can be calculated from the polynomial expression in Eq. [35] in the usual way:

$$g_{AA}^E = (\partial G^E / \partial n)_{n_{BB}, n_{AB}} [38]$$

## V. CONCLUSIONS

Expanding the energy of pair formation,  $\Delta g_{AB}$ , as a polynomial in the pair fractions, rather than the component fractions, is physically more realistic and provides greater

flexibility and ease of optimization because, for systems with a large degree of short-range ordering, the binary system is thereby effectively split into two nearly independent subsystems.

The introduction of composition-dependent coordination numbers also provides greater flexibility and permits the compositions of maximum short-range ordering in each binary subsystem of a multicomponent system to be chosen independently.

Activity data for both components in the liquid, enthalpy of mixing data in the liquid, and the phase diagram for the  $\text{KCl-MgCl}_2$  binary system were optimized quantitatively with only three coefficients of the model for the liquid phase. Furthermore, these coefficients were independent of temperature, showing that the entropy of the liquid is well represented by the configurational entropy expression of the model. Attempts to optimize this solution using a random Bragg-Williams entropy and a polynomial excess Gibbs energy expression were unsuccessful, even when a large number of temperature-dependent coefficients were used.

A formalism has been introduced whereby nearest-neighbor A-A, B-B, and A-B pairs are represented as associates  $A_{1/Z_{AA}^A} A_{1/Z_{AA}^A}$ ,  $B_{1/Z_{BB}^B} B_{1/Z_{BB}^B}$ , and  $A_{1/Z_{AB}^A} B_{1/Z_{BA}^B}$  where  $Z_{ij}$  are the coordination numbers. The quasichemical equations are then identical, apart from a configurational entropy term, to the equations of an associate model with random Bragg-Williams mixing of the associates. This formalism permits

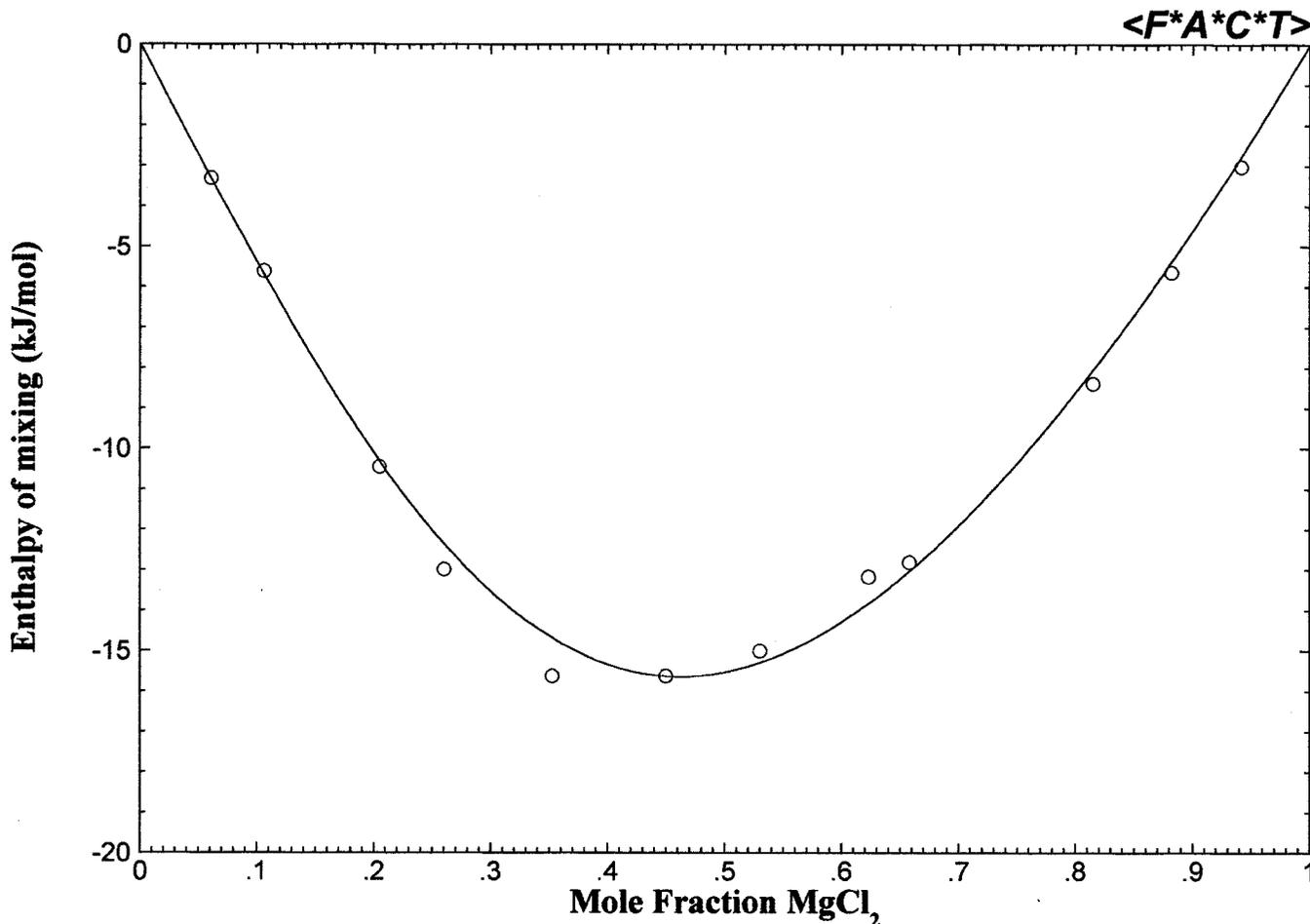


Fig. 5—Calculated enthalpy of liquid-liquid mixing in KCl-MgCl<sub>2</sub>, solutions at 800 °C and experimental<sup>[31]</sup> points from direct mixing calorimetry.

Table I. Thermodynamic Properties (H Relative to Elements at 298.15 K)

$$H(\text{J} \cdot \text{mol}^{-1}) = A + \int_{298.15}^T C_p dT$$

$$S(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = B + \int_{298.15}^T (C_p/T) dT$$

$$C_p(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = a + b(10^{-3})T + c(10^5)T^{-2} + dT^{-1/2} + e(10^{-6})T^2$$

Compound	T range	A	B	a	b	c	d	e
KCl (solid)	298 to 2500 K	-436,684.1	82.55032	40.01578	25.46801	3.64845	—	—
KCl (liquid)	298 to 2500 K	-421,824.9	86.52250	73.59656	—	—	—	—
MgCl <sub>2</sub> (solid)	298 to 2000 K	-641,616.0	89.62900	54.58434	21.42127	-11.12119	399.1767	-2.356672
MgCl <sub>2</sub> (liquid)	660 to 2500 K	-606,887.4	117.29708	92.04800	—	—	—	—
K <sub>2</sub> MgCl <sub>4</sub> (solid)	298 to 703 K	-1,550,013.0	216.8	263.05	—	—	—	—
KMgCl <sub>3</sub> (solid)	298 to 761 K	-1,100,924.0	162.3	157.65	—	—	—	—

the quasichemical model to be treated with currently available and relatively simple software. This presents a significant advantage, particularly for multicomponent solutions.

Although the model has been developed primarily for liquid solutions, it can be applied to solid solutions with short-range ordering. In this case,  $Z_{AA}^A = Z_{BB}^B = Z_{AB}^A = Z_{BA}^B$  necessarily.

Subsequent articles in the present series will describe extensions to multicomponent solutions and to solutions with two quasisublattices such as reciprocal molten salt solutions.

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