FUNDAMENTAL ASPECTS OF TERNARY MOLTEN SALT SOLUTIONS AND THEIR APPLICATIONS IN TECHNOLOGY

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ABSTRACT

Theoretical concepts for additive and reciprocal ternary molten salt systems are reviewed and the limitations of theory discussed. In reciprocal salt systems, the a priori prediction of solubility products and of liquidus phase diagrams appears to be reliable. Thermodynamic measurements on additive ternary molten salt systems are in accord with a recent statistical mechanical calculations. Specific applications to nuclear fuel processing and to battery electrolytes illustrate the use of the theories in technology.

I. INTRODUCTION

A large variety of electrochemical and metallurgical processes utilize multicomponent molten salt systems. Recently, considerable advances have been made in understanding the thermodynamic properties of multicomponent systems. Consequently, much of the chemistry of such systems is now understood well enough to make technologically useful predictions concerning their thermodynamic behavior. We will review the chemistry of ternary systems, the simplest member of the class of multicomponent systems, and illustrate how it might be applied to practical problems. The extension of the principles we discuss to higher order systems is straightforward.

Because of the necessity for electroneutrality, a ternary system, with three independent components contains four kinds of ions. Reciprocal ternary systems are those containing two kinds of cations and two kinds of anions, e.g., A⁺,B⁺/X⁻,Y⁻;Li⁺,Na⁺/F⁻,Cl⁻;Ag⁺,K⁺/Cl⁻,NO₃⁻. If one formally considers electrons (e⁻) to be analogous to anions, then reciprocal ternary systems are equivalent to interstitial ternary alloys; e.g., Fe⁺⁺,Ni⁺⁺/e⁻,O²⁻. Additive ternary systems either contain three different kinds of cations and one kind of anion (e.g., A⁺,B⁺,C⁺/X⁻; Li⁺,Na⁺,K⁺/NO₃⁻) or three different kinds of anions and one kind of cation (e.g., A⁺/X⁻,Y⁻,Z⁻;Li⁺/F⁻,Cl⁻,Br⁻). The thermodynamic formalism for such systems is equivalent to substitutional metallic alloys (e.g., Fe⁺⁺,Ni⁺⁺,Cu⁺⁺/e⁻).
Fundamental concepts for the thermodynamic properties of these systems have been developed to an extent sufficient for making many predictions a priori in both dilute and concentrated solutions. There are several prior reviews which cover some of the earlier work on this subject.1-5 We will discuss these concepts with emphasis on recent developments and will indicate potential technological uses.

II. DILUTE SOLUTIONS

A. Insoluble Salts in Reciprocal Systems

One of the most useful concepts permits the calculation of solubility products, $K_{sp}$, and enthalpies of solution, $\Delta H_{soln}$, of relatively insoluble salts in reciprocal systems. The calculation is based on a cycle first proposed by Flood, Pórland and Grjotheim8 which can similarly be applied to interstitial alloys. For a solid salt AX in the solvent BY, the cycle consists of the three steps7,8

$$AX(\text{sol}) + BY(\text{liq}) \rightarrow BX(\text{liq or sol}) + AY(\text{liq or sol}) \quad (1)$$

$$AY(\text{liq or sol}) \rightarrow AY(\text{ci dilution in BY}) \quad (2)$$

$$BX(\text{liq or sol}) \rightarrow BX(\infty \text{ dilution in BY}) \quad (3)$$

Using available data on the free energies and enthalpies of formation of the pure constituents in Eq. (1) and the thermodynamic mixing properties for the two binary solutions [Eqs. (2) and (3)], one may calculate the solubility product ($K_{sp}$) and the enthalpy of solution ($\Delta H_{soln}$) from the equations

$$\Delta G_1 + \Delta G_2^{ST} + \Delta G_3^{ST} = -RT \ln K_{sp} = -RT \ln a_{BX}^A a_{AY} \quad (4)$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{soln} \quad (5)$$

where $\Delta G_2^{ST}$ and $\Delta G_3^{ST}$ ($\Delta H_2$ and $\Delta H_3$) are the standard Gibbs free energies (enthalpies) of solution at infinite dilution of the two solutes in the two binaries in Eqs. (2) and (3), respectively; $\Delta G_1$ ($\Delta H_1$) is the Gibbs free energy (enthalpy) accompanying reaction (1); and $a_i$ refers to the activity of the $i$th salt. The activities of the solutes, $a_{BX}^A$ and $a_{AY}$, are defined so as to be equal to the mole fractions at very high dilutions. The use of available thermodynamic data to calculate $\Delta G_1$ or $\Delta H_1$ thus reduces the problem in the ternary reciprocal system to the much simpler one in the binary systems AY-BY and BX-BY. As the total number of possible binary systems is far smaller than the total number of ternaries, far less information is needed overall. Furthermore, for insoluble salts the contribution from Eq. (1) is generally much larger than from Eqs. (2) and (3). Thus, even relatively inaccurate data on the binaries can suffice for making estimates. In general, adequate data for binary mixtures are often available or can be estimated with reasonable accuracy. This exact cycle has been successfully tested for solutions of solid silver halides in alkali nitrates.7,8
Recently, this cycle has been applied to solve a problem in pyrometallurgy. In the reduction of the nuclear fuel $\text{U}_2\text{Pu}_2$ using alkaline earth metals, the kinetics of fluxing the products $\text{CaO}$ and $\text{MgO}$ with molten $\text{CaCl}_2$ slowed the process. A calculation of the solubility product of $\text{MgO}$ in the $\text{CaCl}_2$ flux was made using the cycle

$$\text{MgO}(\text{sol}) + \text{CaCl}_2(\text{liq}) \rightleftharpoons \text{CaO}(\text{sol}) + \text{MgCl}_2(\text{liq})$$ (6)

$$\text{CaO}(\text{sol}) \rightleftharpoons \text{CaO}(\text{dilution in CaCl}_2)$$ (7)

$$\text{MgCl}_2(\text{liq}) \rightleftharpoons \text{MgCl}_2(\text{dilution in CaCl}_2)$$ (8)

The Gibbs free energy change for Eq. (6), 28.3 kcal mol$^{-1}$, was calculated from thermodynamic tables. The standard Gibbs free energy change for Eq. (7), 3.7 kcal mol$^{-1}$, was estimated from the binary phase diagram; and that for Eq. (8), 0 kcal mol$^{-1}$, was estimated from known enthalpies of solution. At 860°C, the calculated solubility product was $10^{-6.2}$ indicating a very small solubility of $\text{MgO}$ in the flux. This prediction was confirmed by experimental measurements. The calculations not only guided modifications of the process so as to eliminate $\text{MgO}$ and speed the fluxing but also suggested a potential means for recovery of the spent flux by adding $\text{MgCl}_2$ which precipitates the oxide ions. Analogous cycles should be useful in metallurgical systems. For example, calculations can be made for the deoxygenation or desulfurization of iron by the addition of a metal which forms a very stable oxide or sulfide.

B. Ionic Associations

Solubility products in reciprocal systems are related to the activities of the solutes. In order to evaluate solubilities from the solubility product, the activity coefficients of the solutes must be determined. Since most ionic species when dilute (<5 mol %) in a molten salt solvent generally obey Henry's law, one may relate the deviations of solute components from Henry's law to the formation of associated species. In general, at extremely low concentrations of the two solutes (<10$^{-3}$ mol %) such deviations are negligible and the activity products are also equal to the products of ion fractions. In more concentrated solutions, associations of solute ions can be significant. Consequently, activity coefficients are less than unity and the products of the ion fractions are larger than the solubility products. In such a case, the solubilities are larger than would be predicted for an ideal solution.

For a dilute solution of $\text{AY}$ and $\text{BX}$ in $\text{BY}$, the associations can be written as

$$\text{A}^+ + \text{X}^- \rightleftharpoons \text{AX} \quad K_1$$ (9)

$$\text{AX} + \text{X}^- \rightleftharpoons \text{AX}_2^- \quad K_2 \text{ etc...}$$ (10)

where the $K_i$'s are the association constants for the corresponding equilibrium. When properly defined and evaluated, the $K_i$'s have
According to the quasi-lattice theory, the $K_i$'s are related to $\Delta A_i$, the specific free energy for forming the $i$th bond in the species $AX_i$, through the equations:

$$K_1 = Z(\beta_1 - 1)$$

$$K_1K_2 = \frac{Z(Z-1)}{2!} (\beta_1\beta_2 - 2\beta_1 + 1) \text{ etc...}$$

where $Z$ is a coordination number ($\approx 6$ for molten salts) and $\beta_i = \exp(-\Delta A_i/RT)$.

Quantitative predictions for $\Delta A_i$ cannot be made; only crude estimates are possible. For silver halides, values of $\Delta A_i$ can be approximated, to within a factor of 2, by the equation

$$\Delta A_i \approx \frac{\Delta G_i}{Z}$$

$\Delta G_i$ is the standard Gibbs free energy change for a reaction as in Eq. (1). The assumption in Eq. (13) is that the specific bond free energies are additive.

A significant observation is that values of $\Delta A_i$ are temperature independent for the association of spherical ions. In such cases, the theory permits one to use measurements at one temperature to calculate association constants at any other temperature. For non-spherical ions, $\Delta A_i$ appears to be temperature dependent.

Associations may also occur in additive ternary systems. For example, in dilute solutions of $AX$ and $CX$ in the solvent $BX$, one may have associations such as

$$A^+ + C^+ \leftrightarrow [A^+C^+] \quad K_1$$

$$[A^+C^+] + C^+ \leftrightarrow [A^+C^+^+] \quad K_2 \text{ etc...}$$

where the brackets denote that the $C^+$ ions are next nearest neighbors to the $A^+$ ions. Equations (11) and (12) apply to these two equilibria. However, the coordination number will be larger with values of $Z$ between 8 and 12 since the cations must be next nearest neighbors. Analogous equations also apply to interstitial and substitutional alloys.

C. Solutions Dilute in One Component

Associations to form species are also important in solutions dilute in only one component. However, the thermodynamic significance and quantitative evaluation of the association constants are model dependent. The activity coefficients of the component $AX$ in dilute solutions in the binary solvents $BX$-$BY$ or $BX$-$CX$ are given by the expression

$$96$$
\[ \left[ \frac{\gamma_{AX}}{\gamma_{AX}(BX)} \right] = \left[ \sum_{i=0}^{Z} \frac{Z!}{1!(Z-1)!} x_k^i (1-x_k)^{Z-i} \beta_0 \ldots \beta_1 \right]^{-1} \] (16)

where \( \beta_0 = 1 \); the \( x_k \)'s are ion fractions of the \( k \) ions (in the binary BX-BY, \( k = Y \), and in BX-CX, \( k = C \)); \( \gamma_{AX} \) is the activity coefficient of AX based on pure molten AX as standard state; and \( \gamma_{AX}(BX) \) is the activity coefficient at infinite dilution in pure molten BX.

The use of Eq. (16) has never been fully explored for molten salts. However, this equation has been recently rederived for ternary alloy systems\(^{14,18}\) and compared with data fairly successfully when one makes a heuristic approximation for \( \Delta A_i \) as a linear function of \( i \).\(^{14,15}\) Such a linear dependence of \( \Delta A_i \) on \( i \) does not appear to be consistent with data on the first two association constants for silver with halide ions in molten nitrates.\(^1\) From a consideration of the cycle depicted in Eqs. (1), (2) and (3) and the definitions in Eq. (16), one can show that for reciprocal systems

\[ \sum_{i=1}^{Z} \Delta A_i = \Delta G_1 + \Delta G_2^ST + \Delta G_3^ST - \Delta G_{18}^ST \] (17)

where \( \Delta G_2^ST \) and \( \Delta G_3^ST \) are for the dissolution of pure liquids and \( \Delta G_{18}^ST \) the standard Gibbs free energy change for the following reaction:

\[ AX(\text{liq}) \rightleftharpoons AX(\text{dilution in BX}) \] (18)

III. CONCENTRATED SOLUTIONS - RECIPROCAL SYSTEMS

The conformal ionic solution (CIS) theory can be used to make predictions in more concentrated solutions. The CIS theory is a statistical mechanical perturbation theory first developed for binary solutions by Reiss et al.\(^{19}\) It has been extended to second order for reciprocal systems\(^20\) and to fourth order for additive ternary systems\(^{21}\) containing cations of the same positive charge and anions of the same negative charge. The extension to asymmetric systems containing ions of different valences (either cations and/or anions) has been made empirically.\(^3,22\) The CIS theory is only approximate in that it is restricted to conformal salts and some significant interactions between ions are not taken into account. This is compensated, at least in part, by relating the properties of the ternary systems in question to those of the lower order systems - the subsidiary binaries or the pure one component constituents. Thus, a large fraction of the uncertainties resulting from omitting certain interactions are cancelled since the uncertainties for the lower order systems (where the same approximations are made) are analogous to those for the ternary systems.

An additional imprecision for reciprocal systems arises from the fact that the calculation has been carried out only to second order,
whereas even for binary systems third and fourth order terms appear to be necessary. Although the contribution from higher order terms is relatively small, leaving them out obviously reduces the accuracy of calculations in some cases. However, at high concentrations, equations up to second order are accurate enough since the contributions of higher order terms are smaller than in dilute solutions. Consequently, for reciprocal systems, the CIS theory should be adequate for the calculation of phase diagrams where the concentration of components are generally high at the liquidus.

As mentioned earlier, the electroneutrality of the solution reduces the number of independent components to three which can be chosen arbitrarily from the four constituents of the reciprocal system. In what follows, AX, BX and BY are considered as the components of the \((A^+_{i}B^+_{j}/X^-_{k}Y^-_{l})\) system. The total molar Gibbs free energy of mixing reads:

\[
\Delta G_m = RT \sum_{i} \ln x_i + \sum_{i,j} x_i x_j \Delta G^o_{i,j} + \sum_{i} x_i \Delta G^E_A + \sum_{i} x_i \Delta G^E_B 
\]

(19)

\[
+ \sum_{i,j,k} x_i x_j x_k \Delta G_{i,j,k}^E 
\]

The X's are ion fractions (e.g., \(x_A = \frac{n_A}{n_{A}^+ + n_{B}^+}\), \(x_X = \frac{n_X}{n_X^+ + n_Y^+}\)); \(\Delta G^o\) is the standard Gibbs free energy change for the metathetical reaction:

\[
AX(\text{lq}) + BY(\text{lq}) \rightleftharpoons AY(\text{lq}) + BX(\text{lq})
\]

(20)

When \(\Delta G^o\) is positive, AX and BY are designated as the stable pair and AY and BX as the unstable pair of salts. The term \(\Lambda\) is approximated by the expression:

\[
\Lambda = -\frac{(\Delta G^o)^2}{2ZRT}
\]

(21)

where \(Z\) is a parameter of the size of the coordination number; in most reported calculations, \(Z = 6\). The terms \(\Delta G^E_{i,j}\) are the excess Gibbs free energies of mixing of the binary system containing \(i\) as a common ion. For example, \(\Delta G^E_{A}\) is the excess Gibbs free energy of mixing of the system, AX-AY; \(\Delta G^E_{A}\) is given up to second order by the following equation:

\[
\Delta G^E_A = \sum_{i,j,k} x_i x_j x_k \lambda^A_{i,j,k}
\]

(22)

The term \(\lambda^A_{i,j,k}\) is an interaction coefficient which could be deduced either from thermodynamic data on binary systems or by methods developed for their estimation. For calculations of phase diagrams, it is more self-consistent to utilize the binary eutectic temperature in order to calculate \(\lambda^A_{i,j,k}\). The method is described in more detail elsewhere. The chemical potential and consequently the activity of any component in
The activity of the same component in the liquid at its liquidus temperature is also given by the equation:

$$\ln \alpha_{BY} = -T \int_{T_m(BY)}^T \frac{\Delta H_f(BY)}{T^2} \, d\frac{1}{T}$$

where $T_m(BY)$ and $\Delta H_f(BY)$ are the melting temperature and the enthalpy of fusion of BY, respectively. Equations analogous to Eqs. (23) and (24) can be derived for the other constituents by properly substituting the ion fractions and the sign for $\Delta G^\circ$ ($\Delta G^\circ$ is positive for the salts of the stable pair and negative for the salts of the unstable pair). Equations (23) and (24) combined with their analogues for the three other salts lead to predictions of the liquidus temperatures. The coefficients needed for these calculations are obtained from data on the four pure components (such as the Gibbs free energy of formation, the melting temperatures and the enthalpies of fusion) and from data on the four subsidiary binaries (such as the eutectic temperatures or the interaction coefficients). Calculations for a number of liquidus phase diagrams of reciprocal systems have been made. The agreement between measured and calculated phase diagrams has generally been very good with excellent correspondence of the general topological characteristics. Figures 1 and 2 exhibit comparisons between measured and calculated phase diagrams for the Li$^+$/Na$^+/F^-$,Cl$^-$ and the Na$^+/Cs^+/F^-$,Cl$^-$ systems, respectively. The small differences can be related to uncertainties in values of $\Delta G^\circ$ and, in some cases, to experimental uncertainties. In addition, the two compounds between LiCl and NaCl in Figure 1a are questionable and were not included in the calculations. The calculation has proved to be reliable enough to be an aid in screening potential low melting electrolytes for use in battery systems.

An empirical extension of the equations has been made for charge asymmetric systems in which the pair of cations or anions do not have the same charge, e.g., $A^+B^{++}/X^-,Y^-$ or $A^+,B^{+}/X, Y$. The equations were constructed so as to be consistent with the Gibbs-Duhem equation and with known limiting cases for dilute solutions. For the system $A^{+q}A,B^{+q}B/X^{q},Y^{q}$, the Gibbs free energy of mixing per equivalent can be empirically derived from Eq. (19) and reads as:
\[ \Delta G_m = RT \sum_i \frac{X_i}{A_i} \ln \frac{X_i}{A_i} + \frac{X_i}{A_i} X_i \Delta G^\circ + \frac{X_i}{A_i} X_i Y_i \Delta \lambda_i + \frac{X_i}{A_i} X_i Y_i \Delta A_i \]  \\
+ \frac{X_i}{A_i} X_i Y_i \Delta B_i + \frac{X_i}{A_i} X_i Y_i \Delta A_i \\
X_i A_i B_i X_i Y_i + \frac{X_i}{A_i} X_i Y_i \Delta B_i + \frac{X_i}{A_i} X_i Y_i \Delta A_i \\
X_i A_i B_i X_i Y_i \\
\]

The \( q_i \)'s are the charges on the ions, the \( X_i \)'s are equivalent fractions, e.g., \( X_i = \frac{q_A}{q_A + q_B} \), \( \Delta G^\circ \) is the standard free energy change per equivalent for the reaction

\[ (q_B y^1 B y^1 q_B + (q_A x^1 A x^1 q_A) \frac{1}{2} (q_B y^1 B y^1 B q_B + (q_A x^1 A x^1 A q_A}} \]

and \( A \) is defined as in Eq. (21). From Eq. (25) one may derive a general expression for the activity coefficients where, for example,

\[ (q_A x^1 A x^1 A q_A) \frac{1}{2} (q_B y^1 B y^1 B q_B + (q_A x^1 A x^1 A q_A} \]

The activities of components are related to the activity coefficients through the equation:

\[ a_A q_X x_A = \left( \gamma_A x^1 A q_A \right) \left( x_A^1 A \right) \left( x_A^1 A \right) \]  \\

Equations (25) and (27) presume a particular form for the representation of the deviations from ideality of the four binaries which has been shown to be consistent with a number of systems. These equations can be modified for systems in which other forms better represent excess Gibbs free energy of the binaries. For the stable pair \( A x^1 A q_A \) and \( B y^1 B q_B \), in Eq. (27), the sign of the coefficient of \( \Delta G^\circ \) is positive and for the unstable pair, negative. For a simple case in which \( q_A = q_X = q_Y = 1 \) and \( q_B = 2 \), Eq. (27) reduces to equations as
Combining Eq. (24) with Eqs. (27) - (30) and from their analogues for the other constituents, one can calculate liquidus phase diagrams using information on pure components and on the four subsidiary binaries; the same method as for the symmetrical charge systems is used to evaluate all the necessary coefficients (i.e., $\Delta G^\circ$, $\Delta H_f$, $T_m$ and $\lambda_1$). Calculations and experimental measurements for the two systems Na$^+$,Ba$^{2+}$/Cl$^-$,NO$_3^-$ Na$^+$,Ca$^{2+}$/Cl$^-$,F$^-$ are illustrated in Figures 3 and 4, respectively. Aside from the fact that the compound in the CaF$_2$-CaCl$_2$ binary was ignored to simplify the calculations, differences between the measured and calculated phase diagrams can be largely related again to uncertainties in $\Delta G^\circ$ and ambiguities in the measurements. Figure 3b illustrates the utility of the calculations which permit one to define liquidus temperatures in regions inaccessible to experiment. The calculated liquidus temperatures in the CaF$_2$ field in Figure 4b appear to be more consistent with thermodynamic principles than the measured temperatures. In addition, in cases where gross inconsistencies were obtained between measured and calculated phase diagrams, the measurements were found to be incorrect. Thus, one use of these calculations could be to double-check reported measurements. Another use could be as an aid in constructing phase diagrams a priori or from a minimum amount of data. In a sense, such equations also represent a tool for extrapolating from or interpolating between measured points.

These equations have been applied to calculate phase diagrams for systems as possible electrolytes in fuel cells. Figure 5 illustrates calculations for the system Li$^+$,Na$^+$/OH$^-$,CO$_3^2$. For simplicity, we have omitted the binary compounds and their phase fields, an omission which has no effect on our conclusions. This hydroxide-carbonate mixture has potential uses in fuel cells which utilize variable amounts of water in...
the gaseous reactants. In such a case, the equilibrium

\[ \text{H}_2\text{O} + \text{CO}_3^- \rightleftharpoons \text{CO}_2 + 2\text{OH}^- \]  

(31)

obtains and different ratios of \( \text{H}_2\text{O}/\text{CO}_2 \) in the gas contacting the melt will change the ratios of \( (\text{OH}_2)^2/\text{CO}_3^- \) in the solution. Figure 5 shows that a change of this ratio, starting with a eutectic of \( \text{Li}_2\text{CO}_3 \) and \( \text{Na}_2\text{CO}_3 \), does not lead to an increase in liquidus temperature and to the precipitation of any of the phases. Thus, the phase relations of this system are suitable for use in a fuel cell.

In addition to the calculation of liquidus temperatures, the CIS theory has also been used to calculate liquid-liquid immiscibility for charge symmetric systems. For the system \( \text{A}^+,\text{B}^+/\text{X}^-,\text{Y}^- \) in which \( \text{AX} \) and \( \text{BY} \) define the stable pair, an expression has been derived for the upper consolute temperature \( T_c \) along the pseudobinary \( \text{AX-BY} \)

\[
\frac{1}{X_A X_B} = \frac{\Delta G^o}{RT} + \frac{1}{2} \frac{\lambda_A + \lambda_B + \lambda_X + \lambda_Y}{RT} \\
+ 3 \left( \frac{1}{2} - X_A \right) \frac{\lambda_B + \lambda_Y + \lambda_A + \lambda_X}{RT} \\
+ (6 X_A X_B - 1) \frac{\lambda}{RT} 
\]  

(32)

with \( X_A = X_X \) and \( X_B = X_Y \). One may calculate the upper consolute temperature along the AX-BY pseudo-binary using Eq. (32). However, the calculation is somewhat cumbersome. A simple approximate expression can be derived for cases where the upper consolute composition is close to \( X_A = X_B = X_X = X_Y = \frac{1}{2} \). Thus, one obtains

\[ T_c \cong \frac{\Delta G^o}{5.5R} + \frac{\lambda_A + \lambda_B + \lambda_X + \lambda_Y}{11R} \]  

(33)

Equation (33) enables one to make predictions of miscibility gaps which occur when \( T_c \) is larger than the liquidus temperature. The predictions appear to be consistent with a large number of measurements. Three factors appear to be related to the presence of a miscibility gap; the relative value of \( \Delta G^o \), values of \( \lambda \) and the melting point of the highest melting member of the stable pair. Values of \( T_c \) are higher the higher the values of \( \Delta G^o \) and \( \lambda \). The higher the melting point, the higher the liquidus temperatures and the higher \( T_c \) must be in order to have a miscibility gap. Many of the correlations observed\(^{26-29}\) can be rationalized and understood in terms of these three factors and of the influence of fundamental ionic interactions of these factors.\(^{23-25}\)

In addition, one may calculate the complete extent of a miscibility gap. For the system \( \text{Na}^+,\text{Ti}^+/\text{Br}^-,\text{NO}_3^- \), the computed miscibility isotherms
In Table I are given values of the compositions of the measured and calculated isotherms along the NaN\textsubscript{03}-TlBr diagonal.

| T(°C) | Measured (Fig. 6a) | Calculated (Fig. 6b) |
|-------|--------------------|-----------------------|
| 440   | 0.10 0.95          | 0.10 0.93             |
| 480   | 0.13 0.92          | 0.14 0.90             |
| 520   | 0.19 0.88          | 0.20 0.87             |
| 560   | 0.28 0.80          | 0.30 0.80             |

The measured asymmetry along the diagonal is reproduced to within 2% by the calculations. These calculations are a sensitive test of the reliability of the theory which correctly predicts the extent of the miscibility gap (i.e., refer to Table I) and its asymmetric position (i.e., the displacement of the elliptical isotherms towards the TlBr and NaBr corners is similar to the reported data). In addition, the theory gives a relationship between details of the miscibility isotherms and the fundamental ionic interactions, since the asymmetry is related to differences in the binary interaction parameters.

IV. CONCENTRATED SOLUTIONS - ADDITIVE SYSTEMS

The CIS theory has been extended to fourth order for additive ternary systems.\textsuperscript{21} The total molar Gibbs free energy of mixing for the system AX-BX-CX is given by the expression (AX is referred to as salt 1, BX as salt 2 and CX as salt 3):

\[
\Delta G_m = RT \sum_{i=1}^{3} X_i \ln X_i + \sum_{i<j} \sum_{i<j<k}^{3} a_{i,j,k} X_i X_j X_k + \sum_{i=1}^{3} b_{i,j} X_i^2 X_j + \sum_{i<j}^{3} c_{i,j} X_i^2 X_j^2 + \sum_{i=1}^{3} \sum_{i<j<k}^{3} \theta_{i,j,k} X_i X_j X_k
\]  

(34)
The coefficients \( a_{ij} \), \( b_{ij} \) \((= -b_{ij})\) and \( c_{ij} \) can be evaluated from data on the three subsidiary binary systems \( ij \) \((ij = AX-BX, AX-CX and BX-CX)\). The ternary coefficients \( P \) and \( Q_i \) can be calculated from the binary data using the expressions:

\[
P = -(b_{12}^{1/3} + b_{13}^{1/3})(b_{23}^{1/3} + b_{21}^{1/3})(b_{31}^{1/3} + b_{32}^{1/3})
\]

and

\[
Q_i = 2(c_{ij}c_{ik})^{1/2}
\]

Equations (34) - (36) permit the exact calculation of properties of ternary conformal systems solely from data on the binaries. Predictions from these equations are in good agreement with measurements of the enthalpies of mixing of nitrate systems.\(^{21}\)

Phase diagrams of additive ternary systems have been calculated by Saboungi and Cerisier\(^{30}\) using terms up to only second order \((i.e.,\) only terms containing \( a_{ij} \)\). Figure 7 exhibits measurements and calculations for the LiF-NaF-KF system. Even with so few terms, it is clear that the calculations provide a very good representation of the phase diagram.

V. CONCLUSION

Theoretical concepts for molten salt solutions have advanced our understanding of solution properties to the point where many useful predictions can be made a priori. Theories can be used to solve many problems in technology and are important for analyzing data and for minimizing the amount of experimental data needed to solve technological problems.

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Figure 1. The Na\(^+\),Li\(^+\)/F\(^-\),Cl\(^-\) Phase Diagram
a. Measured  

Figure 2. The Na\(^+\),Cs\(^+\)/F\(^-\),Cl\(^-\) Phase Diagram
a. Measured  

b. Calculated\(^{23b}\)
Figure 3. The $\text{Na}^+\text{Ba}^{++}/\text{Cl}^-,\text{NO}_3^-$ Phase Diagram

a. Measured
b. Calculated$^{22}$

Figure 4. The $\text{Na}^+\text{Ca}^{++}/\text{F}^-,\text{Cl}^-$ Phase Diagram

a. Measured
b. Calculated$^{22}$
Figure 5. Calculated Phase Diagram of the Na⁺, Li⁺/OH⁻, CO₃⁻ System

Figure 6. The Na⁺, Tl⁺/Br⁻, NO₃⁻ Phase Diagram

a. Measured²⁷  
b. Calculated Miscibility Isotherms²⁵
Figure 7. The NaF-KF-LiF Phase Diagram

a. Measured  
b. Calculated$^{30}$