

## THERMODYNAMIC MODELS OF MOLTEN SALT MIXTURES

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**Abstract** - The thermodynamics of several classes of molten salt mixtures was considered. For the simplest systems, which are binary molten salt solutions, emphasis was given on the one hand to the correlation of the excess thermodynamic functions with the physico-chemical features of the constituting ions and on the other to the concentration dependence of these functions. For higher order systems, emphasis has been placed on the a priori calculations of the thermodynamic properties of these multicomponent mixtures from those of the binary constituting systems and of the pure components.

Molten salt mixtures are ionic liquids and hence various categories must be defined. No ambiguity is involved when the terms binary, ternary (or higher order) systems are used for molecular or metallic mixtures such as Au-Ag, Au-Ag-Pd. Such a classification for molten salt mixtures depends not only on the number of components but also on the number of ionic species of these components :

NaCl - KCl is a binary common ion system

NaCl-KBr is a ternary reciprocal system.

Another feature of these systems is the charge-symmetry of the ions :

NaCl-KCl is a charge symmetrical mixture

NaCl-CaCl<sub>2</sub> is a charge unsymmetrical one.

A schematic classification is given in table 1 for charge symmetrical systems and, obviously, holds also for charge unsymmetrical mixtures

TABLE 1. Schematic classification of molten salt mixtures

Ions	System	Basic components
3 ions	Binary	2 components
A <sup>+</sup> , B <sup>+</sup> , X <sup>-</sup>	Common ion	AX, BX
or A <sup>+</sup> , X <sup>-</sup> , Y <sup>-</sup>	-	or AX, AY
4 ions	Ternary	3 components
. A <sup>+</sup> , B <sup>+</sup> , C <sup>+</sup> , X <sup>-</sup>	. Additive	. AX, BX, CX
or A <sup>+</sup> , X <sup>-</sup> , Y <sup>-</sup> , Z <sup>-</sup>		or AX, AY, AZ
. A <sup>+</sup> , B <sup>+</sup> , X <sup>-</sup> , Y <sup>-</sup>	. Reciprocal	. Any 3 among AX, BX, AY, BY
5 ions	Quaternary	4 components
. A <sup>+</sup> , B <sup>+</sup> , C <sup>+</sup> , D <sup>+</sup> , X <sup>-</sup>	. Additive	. AX, BX, CX, DX
. A <sup>+</sup> , B <sup>+</sup> , C <sup>+</sup> , X <sup>-</sup> , Y <sup>-</sup>	. Reciprocal	. Any 4 among AX, BX, CX, AY, BY, CY
or A <sup>+</sup> , B <sup>+</sup> , X <sup>-</sup> , Y <sup>-</sup> , Z <sup>-</sup>		or AX, AY, AZ, BX, BY, BZ

In the following we will first report on binary mixtures and distinguish between charge symmetrical and unsymmetrical systems. The same procedure will be then followed for higher-order systems.

## I - BINARY MIXTURES

## a-Charge symmetric systems.

Many experimental thermodynamic data are available for molten salt mixtures ; they were obtained using mainly the following techniques : cryoscopy (Ref. 1), calorimetry (Ref. 2 & 3), potentiometry (Ref. 4), vapor pressure measurements (Ref. 5 & 6). The theoretical interpretation of such data should explain the order of magnitude of these thermodynamic quantities and their concentration dependence.

The ideality reference state used in defining excess thermodynamic quantities was introduced by Temkin (7) : the ionic melt was described as two interlocking lattices on which cations and anions were randomly distributed. The total entropy is related to the total number of possible equivalent and distinguishable configurations in the mixture : for the mixture AX-BX for instance, this entropy can be expressed as :

$$\Delta S = - R [n_A \ln x_A + n_B \ln x_B]$$

where  $n_A$ ,  $n_B$  are the number of moles of ions in the mixture and the x's are the ionic fractions defined as :

$$x_A = n_A / (n_A + n_B) \quad x_B = n_B / (n_A + n_B)$$

the ionic fraction of the common ion X, being equal to unity, does not appear in the previous equation for entropy nor in the following expressions derived for the chemical potential of one component (e.g. AX) and its activity

$$\Delta \mu_{AX} = RT \ln x_A$$

$$a_{AX} = x_A$$

Most molten salt mixtures are far from ideal : when two salts are mixed, exchange of ions of different size induce changes in ionic forces, mainly coulombic and polarization ones. This was first illustrated by Førland (8) using the simple linear model reported in figure 1.

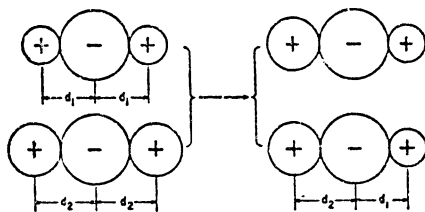


Fig. 1 Forland's linear model of the mixing of  $A^+ X^-$  and  $B^+ X^-$  salts.

The energy of mixing, evaluated from the Coulombic repulsive forces between the cations, was found negative and expressed as :

$$E_c = - 2e^2 (d_1 - d_2)^2 / (d_1 + d_2) (4d_1 d_2)$$

where  $e$  = electronic charge and  $d$  with suffix is the interionic distance.

From the same model, Lumsden (9) evaluated the other contributions to the energy of mixing : polarisation (negative) and dispersion (positive). So this rough description of the mixing process can explain some early results obtained from systematic investigations : for instance in the case of alkali-metal nitrates Kleppa and Hersh (10) reported that the enthalpy of mixing of the equimolar mixtures was negative and proportional of the size parameter  $\delta_{12} = (d_1 - d_2) / (d_1 d_2)^2$ , squared as suggested by the previous equation.

More recently during the last decade, computer simulations by the Monte-Carlo method were carried out (Ref. 11 to 15) in order to investigate the solution structure and the relative importance of the possible ionic interactions.

These results appear to be not decisive since the excess thermodynamic quantities are obtained as small differences between two large numbers (Ref. 11). Nevertheless, Lantelme and Turq (15) from numerical simulations of LiBr-KBr melts pointed out the dependence of the coordination numbers on the nature of the cations (and not only on their relative number e.g. the concentration of the mixture).

Computations of enthalpies of mixing were also performed from the conformal ionic solution theory (Ref. 16) (C.I.S.) where the thermodynamic properties of a binary mixture is obtained from those a reference salt by perturbation methods. These simulations indicated that the dependence of structure on concentration was not accounted for. Furthermore it appears that the magnitude (Ref. 11), and even the sign (Ref. 13), of the thermodynamic quantities is very sensitive to the choice of the pair potential.

Systematic investigations of molten salt mixtures evidenced that the excess thermodynamic quantities are not symmetrical functions of composition. The enthalpy of mixing, for

instance, is generally expressed by an equation of the form

$$\Delta H = x(1-x) [a + bx + cx(1-x)]$$

where  $x$  is the mole fraction of one component and  $a$ ,  $b$  and  $c$  are coefficients obtained by least-squares fit of the experimental data.

The interaction parameter

$$\lambda = \Delta H/x(1-x)$$

is a varying function of composition instead of a constant as in the regular solution model (Ref. 17).

The limiting values of the interaction parameter at  $x = 0$  and  $x = 1$  are of special interest since they are the partial enthalpies at infinite dilution of both components. In the mixture AX-BX ( $x = x_{AX}$ )

$$\lim_{x \rightarrow 0} \lambda = \Delta H_{AX}^{\infty}$$

and  $\lim_{x \rightarrow 1} \lambda = \Delta H_{BX}^{\infty}$

Therefore the parameters  $a$  and  $b$  used in the equation given for  $\Delta H$  can be related to physical quantities ( $a = \Delta H_{AX}^{\infty}$  and  $b = \Delta H_{BX}^{\infty} - \Delta H_{AX}^{\infty}$ ), but the parameter  $c$  (or other parameters if higher powers are used for a polynomial fit of  $\Delta H$ ) has no particular physical meaning. Many kinds of polynomial representations of enthalpy of mixing against mole fraction were proposed (power expansions, Legendre polynomials, centre d variables...). These procedures provide a useful tool for the representation of the data of a fully investigated system, but because of their purely empirical origin cannot be used in interpolation or prevision for mixtures for which data are scarce or impossible to obtain experimentally.

We developed a structural model (Ref. 18) which revealed successful in predicting the concentration dependence of the thermodynamic functions and accounting for the deviations from regular solution behaviour i.e. the order effects within the solution.

This model, "Surrounded Ion Model" (S.I.M.), has the same basic features as that developed by Guggenheim (19) (separation of the degrees of freedom, quasi-lattice structure of the liquid and no long-range interactions) but instead of considering the energetic interactions between pairs of ions we adopted as an elementary entity a central ion in the field of forces of its next neighbours i.e. its two first coordination shells (hence the name "surrounded ion").

All the possible neighbours of a specified ion, ranging from those corresponding to the pure salt AX to those corresponding to the second component BX, are considered for a description of the configuration of the solution. A probability and a configurational potential energy is then ascribed to each so defined "surrounded ion" and hence a partition function can be obtained.

Two statistical methods (Ref. 19 & 20) were used to estimate the partition functions of the solutions and the thermodynamic functions of mixing. Then hypothesis on the variation of the energies (see note a) allowed to obtain analytical expressions of these functions.

TABLE 2 : Results obtained from the surrounded ion model (S.I.M.) for the molar enthalpy of mixing  $\Delta H$  of binary symmetrical.

Statistical	Bragg and Williams (20)	Bragg and Williams (20)	Guggenheim (20)	Guggenheim (20)
Distribution	Random	Random	Quasichemical order	Quasichemical order
Variation of energies	Linear	Parabolic	Linear	Parabolic
Enthalpy of mixing	$\Delta H = x(1-x)W$ $W = z(\alpha + \beta)$	$\Delta H = x(1-x)(A + Bx)$ $A = z^2\alpha + z(2z-1)\beta$ $B = z(3z-1)(\alpha - \beta)$	$\Delta H = x(1-x)W$ [1st order [1-x(1-x)W/zRT]]	Numerical Treatment
Comparison with previous models	Regular solution (17)	Pseudo-regular solution (21)	Quasichemical (19)	

Note a : the energy difference  $U_j$  between an ion A in the mixture (i.e. with  $(z-j)$  ions A and  $j$  ions B as next-nearest neighbours) and an ion A in the pure reference salt AX (i.e. with  $z$  ions A as next nearest neighbours) is linear when  $U_j = j\alpha$ . It is parabolic when  $U_j = j(2z-j)\alpha$ .  $z$  and  $\alpha$  are respectively the coordination number and an energy parameter; the energetic parameter  $\beta$  is defined similarly for B ions.

In the more general case (quasichemical order and parabolic energies) the enthalpy of mixing (as well as the other thermodynamic functions) is not expressed as an analytical expression. Nevertheless an analytical solution can be obtained for the two limiting partial enthalpies which are identical to those obtained with a random distribution

$$\begin{aligned}\overline{\Delta H}_{AX}^{\infty} &= A = z^2\alpha + z(2z-1)\beta \\ \overline{\Delta H}_{BX}^{\infty} &= A + B = z^2\beta + z(2z-1)\alpha\end{aligned}$$

These values of the limiting enthalpies are used as an initial step of an iterative computing procedure of  $\Delta H$ . Figure 2 reports a typical example of application for the system LiCl - CsCl.

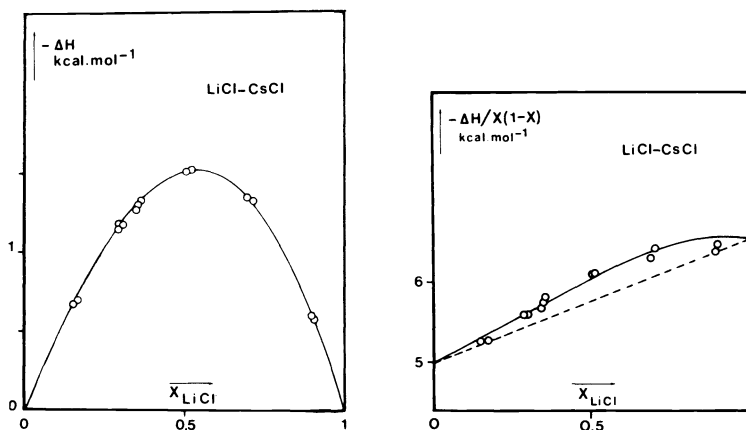


Fig. 2 a - Calculated and experimental enthalpy of mixing  $\Delta H$  for the LiCl-CsCl system.

b - Calculated and experimental interaction parameter  $\Delta H/x(1-x)$  for the same system.

Experimental points from Ref. 22, full line curve calculated from S.I.M.

A good agreement can be noticed between the experimental and calculated enthalpy curves (Fig. 2a). We represented in Fig. 2b the interaction parameter  $\lambda = \Delta H/x(1-x)$  versus  $x$  and it can be tested that the model is able to take into account the curvature of this interaction parameter (i.e. a short-range order). This point is noteworthy since only two energetic parameters  $\alpha$  and  $\beta$  with a physical meaning were used instead of three (or more) empirical coefficients as in polynomial fits of experimental data.

#### b-Charge-unsymmetrical systems.

The main difficulty in molten salt systems with ions of different valencies lies in the concentration dependence of the coordination number of each species (Ref. 8, 23, 24). Already the pure components of such mixtures have not the same coordination numbers: 2 and 1 respectively for the salts  $AX_2$  and  $BX$  (Ref. 25 & 26). Therefore a simple substitution model is irrelevant for such mixtures since electroneutrality is no more preserved.

These charge-unsymmetrical binary systems were examined using the S.I.M. In systems where the charge-asymmetry effect equally both components (i.e.  $CaCl_2$ - $BaCl_2$ ), the model (Ref. 27) is easily assimilated to that developed for symmetrical systems. In the case of the mixtures  $AX_2$ - $BX$ , a more specific description of the mixing process was given (Ref. 28).

Using the same concept of "surrounded ion" and the same basic hypothesis, we postulated that, in a mixture  $AX_2$  -  $BX$ , the A ions have as next-nearest neighbours:

- i) A and B ions in normal position
- ii) B ions and vacancies (vacant sites) in interstitial position.

Similarly, the B ions have normal and interstitial nearest neighbours.

The maximum number of configurations resulting from this description yielded for the ideal entropy of mixing:

$$\Delta S = -R[2x \ln x' + (1-x) \ln(1-x')]$$

in this expression  $x = x_{AX}$  are Temkin's ionic fraction and  $x'$  Forland's equivalent ionic fraction, respectively:

$$\begin{aligned}x &= n_A/n_A + n_B \\ x' &= 2n_A/2n_A + n_B\end{aligned}$$

It should be emphasized that many expressions have been proposed for the ideal entropy of mixing of a charge-unsymmetrical mixture (Ref. 7, 29, 30). The previous expression is

identical to that proposed by Førlund (29).

As previously for symmetrical systems, we obtained the partition function of the solution and then the thermodynamic functions of mixing in both cases of a random distribution and of a short range order.

We reported in the following some examples of application of this model. It must be emphasized before that most systems  $AX_2-BX$  have typical features : the enthalpy of mixing and, in a more marked way, the interaction parameter  $\lambda = \Delta H/x(1-x)$  exhibit an extremum in the vicinity of  $x = 0.33$ . Polynomial expression up to fifth power are generally used to account for the concentration dependence of the enthalpy of mixing :

$$\Delta H = x(1-x) [a + bx + cx^2 + dx^3]$$

and, as discussed above, no particular meaning is to ascribe to the  $a, b, \dots d$  coefficients. Here again only two parameters were sufficient to represent the enthalpy data of such systems. As previously, these two energetic parameters were deduced from the limiting partial enthalpies of both components. The comparison of the results obtained with the S.I.M. between symmetrical and unsymmetrical binary systems suggested the following formal analogy.

Symmetrical system	unsymmetrical
$\Delta H$	$\rightarrow \Delta H/(1+x)$
$x$	$\rightarrow x'$
$\lambda = \Delta H/x(1-x)$	$\rightarrow \Delta H/(1+x)/x'(1-x')$

Such a correspondance was used for the system  $SrCl_2-NaCl$  (see figure 3)

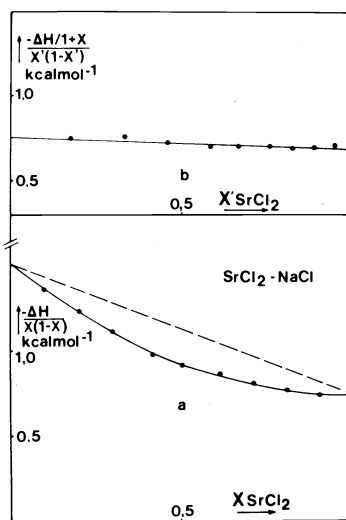


Fig. 3  $SrCl_2-NaCl$  system

a - Calculated and experimental interaction parameter  $\Delta H/x(1-x)$  versus  $x$

b - Calculated and experimental equivalent interaction parameter

$\Delta H/(1+x)x'(1-x')$  versus  $x'$ .

Experimental points from Ref. 31, full line curve calculated from S.I.M.

in the lower part (a) we reported the interaction parameter given by Østvold (31) as a polynomial expansion : the well-marked curvature suggested an order effect in the solution. This point was rather refuted by Lumsden (9) from the analysis of the phase diagram. We reported in the upper part of figure 3 (b), the "equivalent" interaction parameter defined above as  $\Delta H/(1+x)x'(1-x')$  against the equivalent ionic fraction  $x'$  and a straight line was obtained in agreement with a random distribution of ions.

In figure 4, we reported examples of unsymmetrical systems where a short-range order did exist and a good agreement was obtained between estimated and experimental values of both enthalpies of mixing and equivalent interactions parameters.

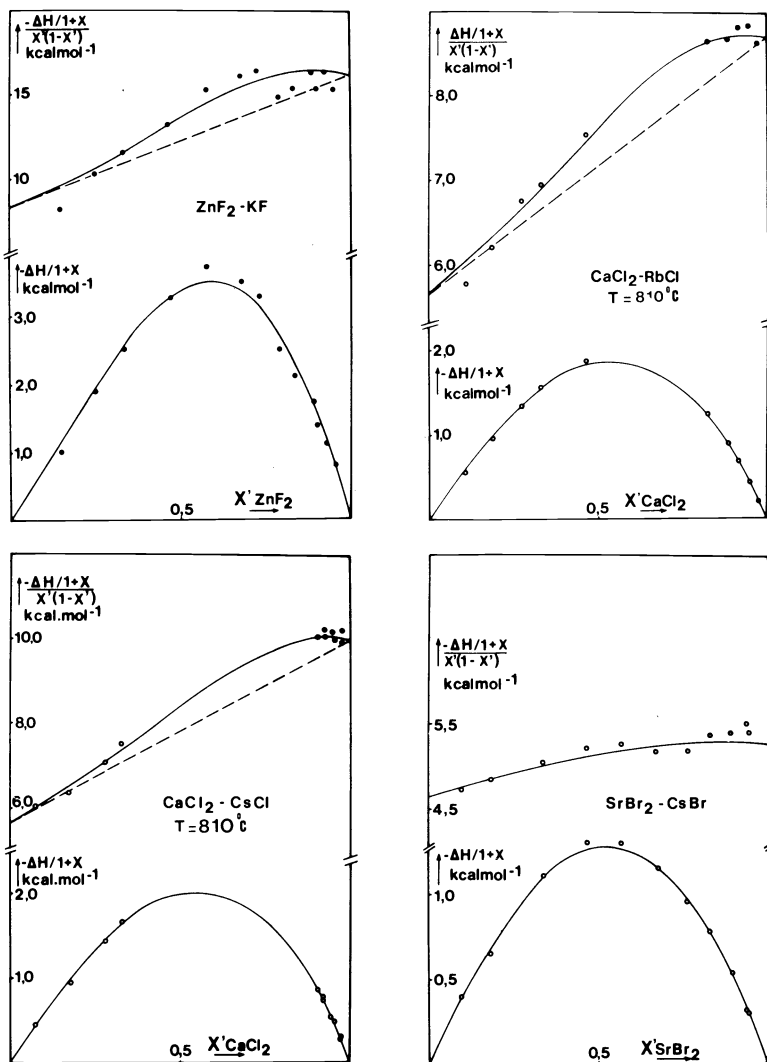


Fig. 4 Calculated and experimental equivalent enthalpy  $\Delta H/(1+x)$  and interaction parameter  $\Delta H/(1+x)x'(1-x')$  versus  $x'$  open circles from Ref. 31 black circles from Ref. 48 are experimental values ; full line curve is calculated from S.I.M.

As for symmetrical binary systems, some theories were developed to predict the order of magnitude of the excess thermodynamic quantities.

The Førlund model, already discussed for charge-symmetric mixtures, was used (Ref. 31) to illustrate the mixing process of the two salts  $AX_2$  and  $BX$ ; the charge in Coulomb repulsion energy of next-nearest neighbour cations  $\Delta E_c$  was found equal to :

$$\Delta E_c = e^2 \left[ \frac{1}{2d_1} - 2 \left( \frac{d_1 - d_2}{d_2(d_1 + d_2)} \right) \right]$$

where  $e$  = electronic charge and  $d$  with suffix is the interionic distance.

The principal variation in this equation is in the term  $(d_1 - d_2)$ . The first term on the right hand side is constant for a given univalent solvent, while the second term is roughly proportional to  $\delta_{12}$ .

Davis (32, 33) developed the Conformal Ionic Solution Theory (C.I.S.) for unsymmetrical systems. According to Davis the molar excess Gibbs energy or enthalpy interaction parameter developed to the first order in  $\delta_{12}$  will have the form

$$\lambda = \frac{\Delta H}{x(1-x)} = T A(x, z, \tau, v) + B(x, z, \tau, v) \delta_{12}$$

Both  $A$  and  $B$  are universal functions of the reduced temperature,  $\tau$ , and volume,  $v$ , Østvold (23) studied the dependence of the limiting interaction parameter  $\lambda_0$  on the distance parameter  $\delta_{12} = \frac{d_1 - d_2}{d_1 d_2}$

$$\lambda_0 = \lim_{x \rightarrow 0} (\Delta H/x(1-x)) = f(\delta_{12}) \quad (x = x_{AX_2})$$

for the alkali halide-alkaline earth halide mixtures. A rather "weak" connection was obtained between experimental data and the Davis theoretical equation postulating that the limiting interaction parameter  $\lambda_0$  varies linearly with  $\delta_{12}$ . Nevertheless, by plotting the enthalpy interaction parameter,  $\lambda$ , versus  $\delta_{12}$  for systems where either an alkali halide or an alkaline earth halide is a common salt a better agreement was obtained between theoretical predictions and the experimental results (figure 5 to figure 8)

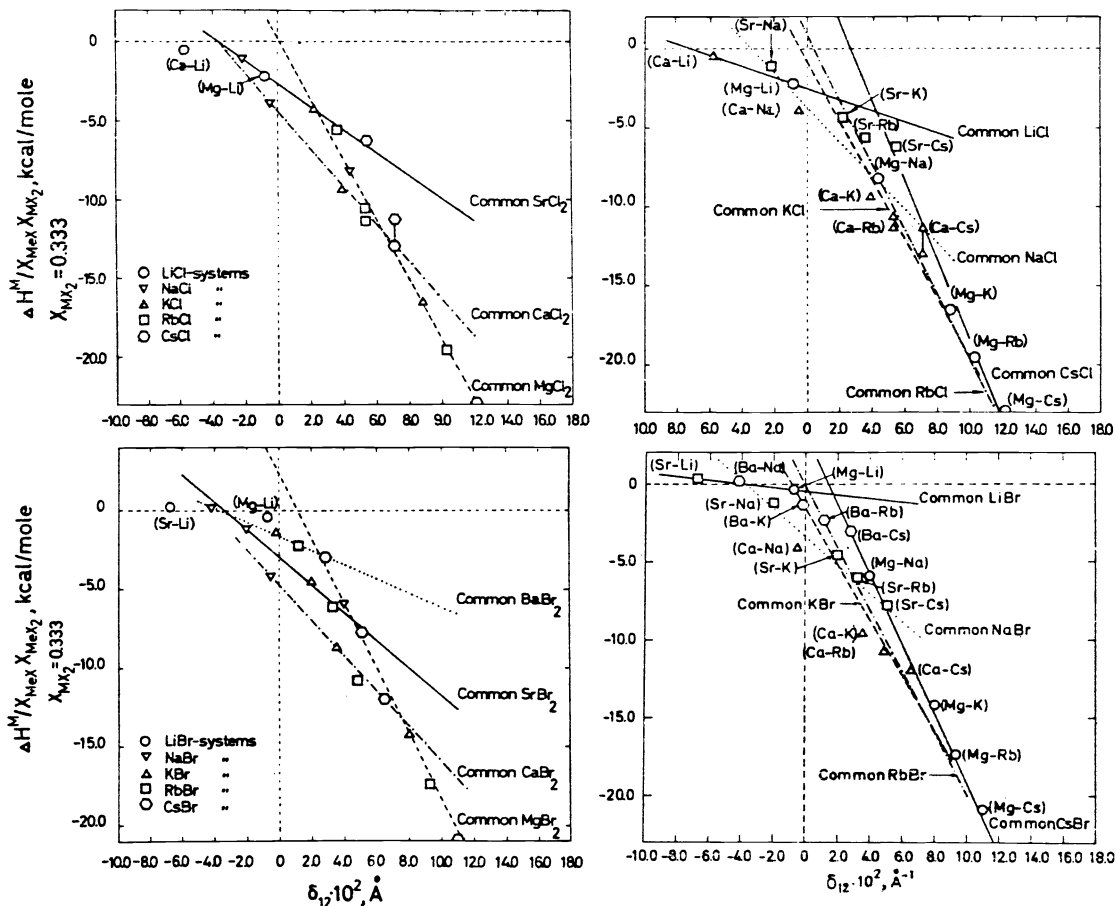


Fig. 5 to 8 (reproduced from Ref. 31). Interaction parameter,  $\Delta H/x(1-x)$ , in the alkali-alkaline earth chloride (bromide) mixtures versus the distance parameter,  $\delta_{12}$ , at  $X_{MX_2} = 0.333$ .

The first remark on these results is that the C.I.S. theory seems to be of restricted applicability to binary asymmetrical mixtures. Moreover, as underlined by Papatheodorou (49) this theory does not predict any explicit concentration dependence of the interaction parameter. Rather than taking into account only the distance parameter for correlation with the enthalpy of mixing, we thought were realistic to attempt to find the influence of both sizes and charge-asymmetry  $AX_2-BX_2$ .

We showed previously, from the S.I.M., that for such mixtures an "equivalent" interaction parameter  $\lambda'$  should be considered rather than the usual interaction parameter  $\lambda$

$$\lambda' = \Delta H/(1+x)x'(1-x')$$

where  $x'$  is the ionic equivalent fraction of the ions A.

On the other hand, it was shown that the definition for one given ion of its ions potential (Ref. 34&35)

$$I.P. = z/r$$

allows to take into account both its size ( $r$  = ionic radius) and its charge ( $z$  = valency). Therefore, the enthalpy of mixing, or any excess thermodynamic quantity, should be related to the difference of the ionic potentials  $\Delta IP$

$$\Delta IP = z_1/r_1 - z_2/r_2$$

Kleppa (36) plotted the interaction parameter  $\lambda_0$  versus this difference of the ionic potentials for the systems AX - MX<sub>2</sub>, reported in figure 9. Two straight lines were obtained which means that the chloride and bromide systems on the one hand and the fluoride systems on the other hand verified the theoretical prediction, but independently.

For the same systems, we represented in figure 10, the equivalent interaction parameter  $\lambda'$  versus the difference of the ionic potentials AIP.

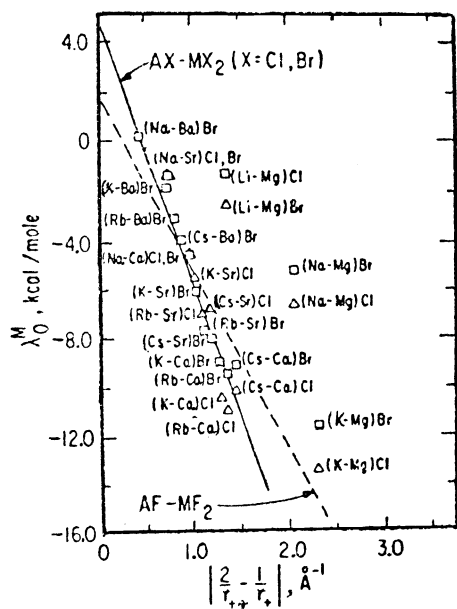


Fig. 9 Plot of the interaction parameter  $\lambda_0$  versus the difference of ionic potentials for the systems AX-MX<sub>2</sub> (reproduced from Ref. 36).

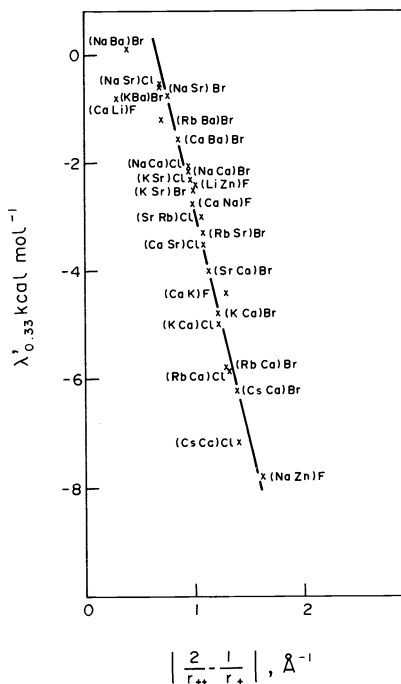


Fig. 10 Plot of the equivalent interaction parameter  $\lambda'_{0.33}$  versus the difference of ionic potentials for the systems AX-AX<sub>2</sub> (experimental values from Ref. 36).

It can easily be seen that the use of an equivalent interaction enables a generalization of the previous results since all experimental data are on a single straight line.

## II - TERNARY AND HIGHER - ORDER SYSTEMS

Thermodynamic models of ternary or higher order systems are mostly aimed to the a priori estimation of the functions of mixing from those of lower order systems.

### a - Charge - symmetric system.

Additive ternary systems have been examined using the C.I.S theory (Ref. 37). The thermodynamic functions, obtained from expansion up to the fourth order, include terms representing the thermodynamic properties of the three binary component systems and also ternary terms. Surprisingly these "ternary" terms are obtained from the binary data; the order of magnitude of ternary interactions being within the experimental uncertainty, definitive comparisons with experiment is rather difficult.

The S.I.M. was extended to this class of mixtures (Ref. 38). As for binary system, this model appeared as a generalization of previous models; ternary regular solution, quasi-regular solution. In the more general case, the thermodynamic functions can be obtained from a numerical iterative process. But, due to the previous remark, in most cases the properties of the ternary system can be evaluated only from those of the binary systems. Figure 11 shows as an example the enthalpy of mixing of a section of the ternary mixture AgCl-LiCl-KCl. Experimental values were obtained from direct calorimetry (Ref. 39) and calculated values yielded by the equation

$$\begin{aligned} \Delta H = & X_{Ag} X_{Li} \left[ X_{Li} \Delta \bar{H}_{Ag(Li)}^{\infty} + (1-X_{Li}) \Delta \bar{H}_{Li(Ag)}^{\infty} \right] \\ & + X_{Ag} X_{K} \left[ X_{Ag} \Delta \bar{H}_{K(Ag)}^{\infty} + (1-X_{Ag}) \Delta \bar{H}_{Ag(K)}^{\infty} \right] \\ & + X_{Li} X_{K} \left[ X_{K} \Delta \bar{H}_{Li(K)}^{\infty} + (1-X_{K}) \Delta \bar{H}_{K(Li)}^{\infty} \right] \end{aligned}$$

where the  $X'_i$  are ternary ionic fractions and  $\Delta \bar{H}_{i(j)}^{\infty}$  the limiting partial entropy of the i- chloride in the j-chloride.



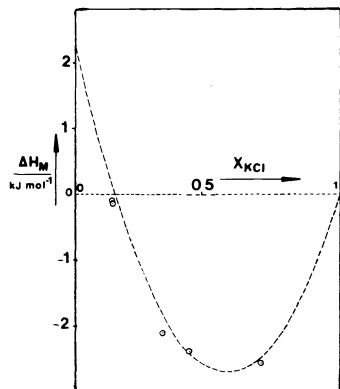


Fig. 11 Molar enthalpy of mixing of the ternary mixture AgCl-LiCl-KCl ( $X_{LiCl}/X_{AgCl} = 1/1$ ). Experimental points from ref. 39, dotted line calculated from SIM.

A good agreement can be observed between experimental and estimated values.

Reciprocal ternary and quaternary molten salt mixtures were also investigated using the S.I.M (Ref. 40 & 41).

The composition of a reciprocal ternary mixture  $A^+, B^+ / X^-, Y^-$  is conveniently plotted on a composition square as shown in figure 12.

The horizontal axis is the cationic mole fraction  $x = n_B/n_A + n_B$  and the vertical axis is the anionic mole fraction  $x_X = n_X/n_A + n_X$  (where  $n_i$  is the number of moles of ion  $i$ ). The SIM has been applied (Ref. 39) in the present case and the thermodynamic properties of the ternary reciprocal mixture were obtained. The molar enthalpy of mixing, for instance, relative to the components AX, BX and BY, is given by :

$$\Delta H = x_A x_Y \Delta H_0 + x_A \Delta H_{AX-AY} + x_B \Delta H_{BX-BY} + x_X \Delta H_{AX-BX} + x_Y \Delta H_{AY-BY} + x_A x_B x_X x_Y \Lambda$$

where the  $x_i$  are the ionic fractions and  $\Delta H_0$  is the enthalpy variation for the exchange reaction between the pure salts :



The binary terms such as  $\Delta H_{AX-AY}$  are the enthalpies of mixing in the binary sub-systems at the composition given on the square figure 12.

The factor  $\Lambda$  is a non-random term and is composition independent :

$$\Lambda = -(\Delta H_0)^2 / 2zRT$$

where the coordination number  $z$  is commonly taken as  $z = 6$ .

We have tested the validity of the equation obtained for the enthalpy of mixing on several reciprocal systems of alkali halides (Ref. 2) and of alkali nitrates and halides of hydroxydes (Ref. 42).

Similar expressions for the thermodynamic functions of mixing have been obtained from the C.I.S. theory (Ref. 43 & 44).

Quaternary reciprocal systems such as  $A^+, B^+, C^+ / X^-, Y^-$ , are much more complex since they include six pure salts and nine binary common-ion mixtures. A complete experimental study being rather time-consuming, if not impossible, it was of interest to obtain estimates of the thermodynamic functions. We obtained (Ref. 41), from the S.I.M., expressions which included binary interactions arising from the nine common-ion systems and also the properties of the pure salts through the possible exchange reactions.

#### b - Charge-asymmetric systems.

Ternary and quaternary additive systems will not be discussed here.

For ternary reciprocal mixtures, no rigorous theory exist at this time. We showed (Ref. 45) that the thermodynamics of the system  $(A^+ + B^+ + X^- + Y^-)$  can be deduced from results obtained for symmetrical systems of the same class. Using the concept of "equivalent salt" introduced by Lumsden (9) as

$$AY_{0.5} = 0.5 (A_2Y)$$

the ternary asymmetrical system reduces to the fictitious symmetrical mixture  $(A^+ + B^+ + X^- + Y^-)_{0.5}$ . Expressions for the thermodynamic functions were then obtained established for symmetrical reciprocal system from the S.I.M.. Similar equations were obtained from an empirical extension

of the C.I.S. theory. These results were compared with experimental calorimetric results obtained for reciprocal mixtures of alkali fluorides and sulphates (Ref. 46).

An example is given in figure 13 for the reciprocal ternary mixture  $Li^+, Rb^+ / F^-, SO_4^{2-}$  :

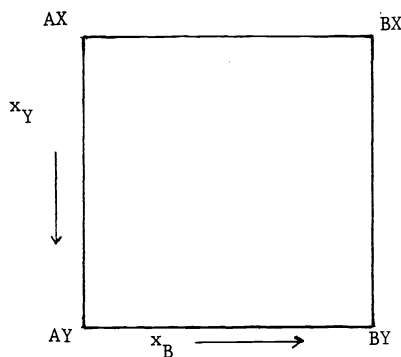


Fig. 12 Composition square of the reciprocal ternary system  $A^+, B^+ / X^-, Y^-$

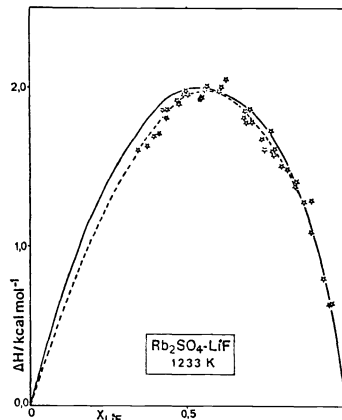


Fig. 13 Experimental (Ref. 46) and estimated values of enthalpies of mixing of one diagonal of the  $Li^+, Rb^+ / F^-, SO_4^{2-}$  mixture.

the experimental and calculated enthalpies of mixing were compared for the diagonal  $\text{Rb}_2\text{SO}_4 - \text{LiF}$ . A fairly good agreement can be observed between the calorimetric values (Ref. 46) and those a priori estimated from the S.I.M.

The calculations of the equilibrium phase diagrams of some of these systems provided another satisfactory test of the model (Ref. 47).

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