

# Thermodynamic modeling of simple and complex melts

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,  
in honour of his 60th birthday*

Thermodynamic modeling of melts is of great importance in many industrial applications involving these high-temperature liquids. Very often, melts are multicomponent systems and experimentation becomes more expensive and time-consuming with each component beyond binary mixtures. It is therefore crucial to use or to develop suitable models for such mixtures; of course, for the sake of selfconsistency, the suitability should be relative first to the binary systems limiting the multicomponent melt.

Several models are reviewed for those most simple melts only involving either simple ionic species or nonionized components. They are relative to binary mixtures and to additive and reciprocal molten salt mixtures, including either ions of the same valency or ions of different valency.

Complex melts are generally obtained from the mixing of an ionic salt with a nonionized component; they are characterized by the formation of associates contributing to the excess thermodynamic quantities. An ideal associated model is reported for mixtures involving two complex species.

For years the chemical industry has recognized the importance of the thermodynamic and physical properties of solution in design calculations in involving chemical separations, fluid flow and heat transfer. The development of calorimetry, mass spectrometry and potentiometry has enabled the experimental determination of excess enthalpies and heat capacities of melts with convenience and accuracy. But even with modern instrumentation, experimental measurements of thermodynamic properties have become progressively more expensive and time-consuming with each additional component beyond binary mixtures. In the chemical literature, knowledge of binary systems is relatively abundant, ternary systems are scarce and higher-order multicomponent systems are virtually nonexistent. Naturally, one of the primary goals of research in the area of solution thermodynamics has been the development of expressions for predicting the thermodynamic properties of multicomponent mixtures.

## Modeling of high-temperature melts

High-temperature melts can be liquid mixtures of metals, of molten salts or of metals and molten salts. The main problem when modeling is to account the actual nature of the solution. In most cases thermodynamic models are of interest when the melts involved are multicomponent systems; complete experimental studies are time-consuming and/or cannot be performed on the entire composition range. The strategy generally adopted to obtain the thermodynamics of such systems is:

- either purely estimative; prediction from the properties of lower-order systems (components and binary limiting systems),
- or “estimation-assisted” experimental; a restricted number of selected experiments is decided from the afore-mentioned *a priori* estimations.

In both cases it is therefore crucial to develop or to use a suitable model. Of course, for the sake of self-consistency, the suitability should be first relative to the binary mixtures limiting the multicomponent system.

Though metallic alloys and molten salt mixtures are generally described separately, most phenomenological models are not very different and the main distinction between these liquid inorganic melts can be considered as dependent on: *a*) the nature of the species present in the melt, neutral or ionic, atoms, ions or associates, *b*) the magnitude of the interactions between these species.

For ionic solutions, several kinds of *additive* and *reciprocal* molten salt solutions can be defined according to the nature and the number of involved components. A schematic classification is given in Table 1 for charge symmetrical systems and, obviously, it also holds for charge unsymmetrical mixtures. Additive systems and reciprocal systems not only represent two distinct types of molten salt solutions, but are parallel to two distinct types of metallic systems. The first type belongs to the class of additive systems in which either the types of positive ions differ and there is one type of anions (*e.g.*  $A^+$ ,  $B^+//X^-$ ) or the types of anions differ and there is one type of cation (*e.g.*  $A^+//X^-$ ,  $Y^-$ ). This class parallels substitutional alloys (*e.g.*  $Na + K$ ). This can be readily seen if one considers that electrons, at least in a formal sense, are like anions, *e.g.*  $Na + K \approx Na^+$ ,  $K^+//e^-$ . The second type is a member of the class of reciprocal systems which are systems containing at least two types of cations and two types of anions (*e.g.*  $A^+$ ,  $B^+//X^-$ ,  $Y^-$ ). The simplest member of this class are ternary systems. Reciprocal systems are equivalent to interstitial alloys (*e.g.*  $Fe^{2+}$ ,  $Cr^{2+}//O^{2-}$ ,  $e^-$ ).

Taking into account the nature of these different mixtures, appropriate relationships have been proposed for the ideal entropy of mixing. These are of primary importance for measuring the deviation from ideality of the other

Table 1

## Schematic classification of ionic mixtures

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

Table 2

## Formal analogies between symmetrical and asymmetrical binary mixtures

| Symmetrical mixtures<br>AX + BX        | Asymmetrical mixtures<br>AX <sub>2</sub> + BX |
|--|---|
| $x_A = \frac{n_{AX}}{n_{AX} + n_{BX}}$ | $x'_A = \frac{2n_{AX_2}}{2n_{AX_2} + n_{BX}}$ |
| $\Delta H$                             | $\Delta H' = \frac{\Delta H}{1 + x}$          |

functions of mixing. We give in the following the relationships expressing the ideal entropy in some typical ionic mixtures.

Another distinction among ionic melts lies in the possibly different valencies of the ions involved; in the previously quoted systems, all cations, and also anions, had the same charge while a mixture like NaCl—CaCl<sub>2</sub> includes at the same time monovalent and bivalent cations. Also those solutions obtained from at least one covalent salt have different features, generally characterized by complex species (*e.g.* AlCl<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Cl<sub>7</sub><sup>2-</sup>, in the aluminium chloride-based mixtures).

A considerable amount of experimental thermodynamic investigations revealed that those different classes of melts do not behave identically and,

therefore, it is evident that specific thermodynamic models should be developed and used to describe their features [1].

## Simple melts

### *Binary mixtures*

#### Symmetrical mixtures

Binary alloys (A + B) and common-ion molten salt symmetrical mixtures (AX + BX or AX<sub>2</sub> + BX<sub>2</sub>) are often described by quasi-lattice models, the main distinction lying in the interaction range of species of the same nature, atoms A and B or cations A<sup>+</sup> and B<sup>+</sup>

For an ideal solution, the energetic interactions of A (or A<sup>+</sup>) and B (or B<sup>+</sup>) with their environments are the same and these species mix randomly. Then the molar Gibbs energy of mixing is  $-T \Delta S_{\text{mix}}$  and the ideal entropy of mixing is

$$\Delta S_{\text{mix, id}} = -R(x_A \ln x_A + x_B \ln x_B) \quad (1)$$

where  $n_A$ ,  $n_B$  are the amounts of substances of atoms (or ions) in the mixture and the  $x$ 's are the mole (or ionic) fractions defined as

$$x_A = n_A/(n_A + n_B) \quad \text{and} \quad x_B = n_B/(n_A + n_B) \quad (2)$$

For molten salt mixtures, this relationship was proposed by *Temkin* [2] for the ideal entropy of mixing and the  $x_i$ 's are the so-called (Temkin) ionic fractions.

Deviations from ideality ( $\Delta G^{\text{ex}} \neq 0$ ,  $\gamma_i \neq 1$ ) arise from a lack of balance in the interatomic (or interionic) forces between the different species. If the components are similar in chemical nature (*i.e.* Na + K or NaCl + KCl), the mixture is nearly ideal. If they differ, the forces are usually greater between the atoms (or the cations). For those melts exhibiting small deviations from ideality, *e.g.* weak interactions, in principle any simple model can be used and regular or quasi-regular models are generally sufficient. For a great many simple binary solutions, simple polynomial expansions in the mole (or ionic) fractions provide a good representation of the excess Gibbs energy.

The surrounded ion model (SIM) [3—5], which is a statistical model of ionic mixtures, gives a more realistic description of a melt since it takes into account all the possible energetic interactions of A<sup>+</sup> and B<sup>+</sup>, depending on the local environment of each ion. Each "surrounded ion" has nearest neighbours of the opposite charge on its first coordination shell (X<sup>-</sup>) and next-nearest neighbours of the same charge on the second coordination shell (A<sup>+</sup> and B<sup>+</sup>). The same result is found for the ideal entropy of mixing which is given by a relationship

identical to eqn (1). The most interesting features of this model lie in the fact that it is able to take into account the asymmetry of the thermodynamic excess functions with only two energetic parameters with a physical meaning. The previous models, which were based on a pair-wise interaction concept, failed in the description of such asymmetries which are observed experimentally. At this stage most authors arbitrarily assumed a linear dependence of the "interaction parameter" against composition (Hardy's [6] quasi-regular model) or arbitrarily used polynomial expansions with parameters without any physical meaning. Also the more elaborated Guggenheim's "quasichemical model" [7], though able to account for the temperature dependence of the thermodynamic excess functions, was unable to account for experimental asymmetries. The SIM, which is the most general model, and was also found successful in describing the thermodynamics of other kinds of molten salt mixtures, allows the previously quoted models to be deduced as particular cases. A quite similar approach had been proposed for alloys in terms of "surrounded atom model" [8].

### Asymmetrical mixtures

In asymmetrical molten salt mixtures of the type  $AX_2 + BX$ , the same lattice description of the melt implies that the substitution of the  $A^{2+}$  bivalent cation by the  $B^+$  monovalent cation creates one vacancy on the corresponding sublattice. Several relationships have been proposed for the ideal entropy; they differ in the assumptions made on the vacancies.

If the number of vacancies is assumed to be negligible, *e.g.* changing a bivalent cation with a monovalent cation does not induce a local disorganization of the corresponding sublattice, the same result (1) is found for the ideal entropy of mixing.

If the number of vacancies is not negligible and if no particular association exists between the bivalent ion and the vacancy, *Førland* [9] found the following relationship for the ideal entropy of mixing

$$\Delta S_{\text{mix, id}} = -R[2x_A \ln x'_A + (1 - x_A) \ln(1 - x'_A)] \quad (3)$$

where

$$x_A = n_A/(n_A + n_B) \quad \text{and} \quad x'_A = 2n_A/(2n_A + n_B) \quad (4)$$

The  $x_i$ 's have been defined by eqn (2), and the  $x'_i$ 's are the so-called equivalent ionic fractions.

If the number of vacancies is not negligible and if the bivalent ion and the vacancy are assumed to constitute a dimer, *Flory* [10] proposed for the ideal entropy of mixing the relation

$$\Delta S_{\text{mix, id}} = -R[x_A \ln x'_A + (1 - x_A) \ln(1 - x'_A)] \quad (5)$$

The SIM [11, 12] provides, from different theoretical grounds, a relationship for the ideal entropy which is identical to the one (3) found by Førland.

It should be stressed that many authors do not take into account this charge-dependent expression for the ideal entropy of mixing but arbitrarily use equivalent ionic fractions (4) in the relationships expressing the other functions of mixing and Temkin's ideal entropy (eqn (1)). It has been shown [13] that this may lead to some inconsistencies.

The SIM already mentioned for melts including ions of the same valency, was extended to asymmetrical mixtures of the kind  $AX_2$ — $BX$ . For these binary common-ion mixtures  $AX_2$ — $BX$ , the surrounded ion model enabled some formal analogies to be evidenced between symmetrical and asymmetrical binary common-ion mixtures (Table 2).

### *Ternary mixtures*

#### Additive ternary mixtures

Models have been developed enabling to calculate the properties of ternary systems (alloys or common-ion [14, 15] and reciprocal [16, 17] molten salt solutions) from the binary coefficients. Empirical ternary coefficients may also be included in these equations.

As was discussed earlier, a binary molten salt system contains three kinds of ions, e.g.  $A^+$ ,  $B^+//X^-$ . Of the three ionic components, only two are independently variable because of the constraint imposed by electroneutrality  $n_{A^+} + n_{B^+} = n_{X^-}$ . Ternary ionic systems contain four ions which can be constituted in three different ways  $A^+$ ,  $B^+$ ,  $C^+//X^-$  or  $A^+//X^-$ ,  $Y^-$ ,  $Z^-$  or  $A^+$ ,  $B^+//X^-$ ,  $Y^-$ . The first two are additive ternary systems and the last is a ternary reciprocal molten salt mixture. There are only three independent component salts from which one can make up the solution.

Ternary, quaternary, ...,  $N$ th-order additive molten salt mixtures are ionic systems containing 3, 4, ...,  $N$  ions of the same species (cations or anions) and one ion of the other species (anion or cation). Of the 4, 5, ...,  $(N + 1)$  ionic constituents, only 3, 4, ...,  $N$  are independent because of the constraint imposed by electroneutrality  $n_{A^+} + n_{B^+} + n_{C^+} + \dots = n_{X^-} + n_{Y^-} + \dots$

The binary models provide reasonable estimates for several systems of practical importance and they also address the problem of how to report experimental data. Enthalpies of mixing, vapour pressures and other solution properties are worthless unless they are transmitted from the experimentalist to the design

engineer. Mathematical representation provides a convenient method to reduce extensive tables of experimental data into a few equations and this is of crucial importance for multicomponent systems.

This section will be devoted to several of the empirical equations or models that have been suggested for parametrizing and predicting mixture data.

*Redlich and Kister* [18] proposed an expression for the excess Gibbs energy of mixing of a ternary mixture

$$\begin{aligned} \Delta G^{\text{ex}} = & x_1 x_2 \sum_i (G_i^{\text{ex}})_{1,2} (x_1 - x_2)^{f_i} + x_1 x_3 \sum_i (G_i^{\text{ex}})_{1,3} (x_1 - x_3)^{f_i} + \\ & + x_2 x_3 \sum_i (G_i^{\text{ex}})_{2,3} (x_2 - x_3)^{f_i} \end{aligned} \quad (6)$$

which provisions for additional ternary parameters. The initial popularity of the Redlich—Kister equation arose because the first parameter  $(G_0^{\text{ex}})_{1,2}$  could be determined conveniently from the experimental data at  $x_1 = 0.50$  as  $4 \Delta G_{1,2}^{\text{ex}}$ . Remember that the computers were not available during the 1940s and the majority of experimental data were graphically presented in the literature. The Redlich—Kister equation provided a means to transmit data from the experimentalists to the chemical engineer designing distillation columns. It is common to predict the properties of a ternary solution phase by a simple summation of the binary expressions, when they obey the regular solution model. Several “geometric” models have been proposed which differ in the geometric weighting factors of the binary contributions.

*Kohler* [19] proposed an equation for the excess Gibbs energy of mixing of a ternary solution

$$\Delta G^{\text{ex}} = (x_1 + x_2)^2 \Delta G_{1,2}^{\text{ex}} + (x_1 + x_3)^2 \Delta G_{1,3}^{\text{ex}} + (x_2 + x_3)^2 \Delta G_{2,3}^{\text{ex}} \quad (7)$$

in which  $\Delta G_{i,j}^{\text{ex}}$  refers to the excess Gibbs energies of the binary mixtures at a composition  $(x_i^0, x_j^0)$  such that  $x_i^0 = 1 - x_j^0 = x_i/(x_i + x_j)$ . Kohler’s equation is symmetrical in that all three binary systems are treated identically. Its numerical predictions do not depend on the arbitrary designation of component numbering.

*Colinet* [20] established a slightly more complex relationship for expressing the thermodynamic excess properties of multicomponent systems

$$\Delta G^{\text{ex}} = \sum_i \sum_j x_i (1 - x_j)^{-1} (\Delta G_{i,j}^{\text{ex}}) x_j \quad (8)$$

in which  $(\Delta G_{i,j}^{\text{ex}}) x_j$ ’s are calculated from the binary data at constant mole fraction  $x_j$ . This equation, although perfectly symmetrical, requires the addition of the thermodynamic properties at six different binary compositions for a ternary mixture.

*Muggianu* [21] also developed a geometric model with different weightings of the binary contributions

$$\Delta G^{\text{ex}} = \sum_i \sum_j x_i(1 - x_j)^{-1} (\Delta G_{i,j}^{\text{ex}})_{x_1, x_2} \quad (9)$$

So far all the three methods that have been discussed treat the components in the same way and may thus be characterized as symmetric methods. However, sometimes there may be a physical reason to divide the component elements into different groups. For instance, if components 2 and 3 are similar to each other and differ markedly from component 1, then one should expect the binary systems 1—2 and 1—3 to be similar and it may be advantageous to describe the ternary 1—2—3 system in such a way that the expression would reduce to the binary expressions if one could make 2 and 3 identical. A numerical method has been proposed by *Toop* [22], which has this asymmetric property. It yields the following equation for the excess Gibbs energy of mixing

$$\Delta G^{\text{ex}} = x_2(1 - x_1)^{-1} \Delta G_{1,2}^{\text{ex}} + x_3(1 - x_1)^{-1} \Delta G_{1,3}^{\text{ex}} + (1 - x_1)^2 \Delta G_{2,3}^{\text{ex}} \quad (10)$$

in which the  $\Delta G_{i,j}^{\text{ex}}$  refer to the excess Gibbs energies for the binary mixtures at compositions  $(x_i^0, x_j^0)$  such that  $x_i^0 = x_1$  for the 1—2 and 1—3 binary systems and  $x_2^0 = x_2/(x_2 + x_3)$  for the 2—3 binary system. Eqn (10) possesses a desirable mathematical form since it is independent of binary parametrization  $\Delta G_{i,j}^{\text{ex}}$ .

Other asymmetric “geometric” numerical methods have been proposed by *Hillert* [23]. Very recently, *Wang et al.* [24] reviewed nine regular-type ternary models with different weight factors and proposed a new generalized model. The analytical expression of this general model may be given by

$$\Delta G_{\text{mix}}^{\text{ex}}(x_A, x_B, x_C) = \sum_i \sum_j \sum_{l_{ij}} \beta_{ij}^{(l_{ij})} \frac{x_i x_j}{x_{i(ij)}^{(l_{ij})} x_{j(ij)}^{(l_{ij})}} G_{ij}^{\text{ex}}(x_{i(ij)}^{(l_{ij})}, x_{j(ij)}^{(l_{ij})}) \quad (11)$$

where  $i = A, j = B, k = C$ ;  $i = B, j = C, k = A$  or  $i = C, j = A, k = B$ .  $l_{ij} = 1, 2, \dots, l'_{ij}$ ;  $x_i$  and  $\Delta G_{\text{mix}}^{\text{ex}}(x_A, x_B, x_C)$  are respectively the mole fraction of component  $i$  in the A—B—C ternary system and the ternary excess molar Gibbs energy;  $x_{i(ij)}^{(l_{ij})}$  and  $G_{ij}^{\text{ex}}(x_{i(ij)}^{(l_{ij})}, x_{j(ij)}^{(l_{ij})})$  are the corresponding binary properties at the  $l_{ij}$ -th point along the  $i$ — $j$  binary composition line (Fig. 1). Here

$$x_{i(ij)}^{(l_{ij})} = 1 - x_{j(ij)}^{(l_{ij})} = \frac{1 + x_i + x_j + \lambda_{ij}^{(l_{ij})} x_k}{2} \quad (12)$$

The weight factors of  $\lambda_{ij}^{(l_{ij})}$  still depend on the regular solution assumption, while those of  $\beta_{ij}$  are independent of it and only follow the conditions  $0 \leq \beta_{ij} \leq 1$ ,

$$\sum_{l_{ij}} \beta_{ij}^{(l_{ij})} = 1.$$



This proliferation of similar expressions becomes confusing especially when the equations are encountered for the first time. There is no preferred way of knowing which method will provide the best predictions for a given system. The fact that so many empirical equations have been developed suggests that no single equation can describe all types of systems encountered.

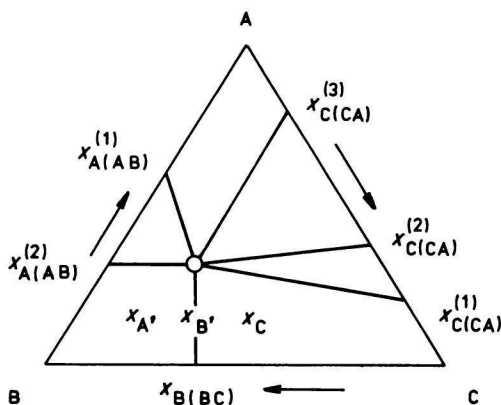


Fig. 1. Geometric illustration of the binary compositions used in the Wang model to calculate thermodynamic properties at a particular ternary composition.

Differing from the previous empirical equations in that they are based on a physical description of the melt and on statistical mechanics principles, some models also provide expressions able to predict multicomponent properties in terms of lower-order interactions.

The SIM [15, 16] yields an equation for the excess enthalpy of mixing of the ternary mixture AX—BX—CX (or AX<sub>2</sub>—BX<sub>2</sub>—CX<sub>2</sub>)

$$\Delta H = x_A x_B [x_A \Delta H_{B(A)} + (1 - x_A) \Delta H_{A(B)}] + x_A x_C [x_A \Delta H_{C(A)} + (1 - x_A) \Delta H_{A(C)}] + x_B x_C [x_C \Delta H_{B(C)} + (1 - x_C) \Delta H_{C(B)}] \quad (13)$$

where  $\Delta H_{A(B)}$  is the limiting partial enthalpy of AX in the AX—BX binary mixture and the ideal Gibbs energy of mixing is always

$$\Delta G_{\text{mix, id}} = RT(x_A \ln x_A + x_B \ln x_B + x_C \ln x_C) \quad (14)$$

For additive asymmetrical ternary mixtures (AX<sub>2</sub> + BX + CX), taking into account the analogies shown in Table 2, eqn (13) obtained for symmetrical additive ternary mixtures becomes

$$\frac{\Delta H}{1 + x_A} = x'_A x'_B \left[ x'_B \frac{\Delta H_{A(B)}}{2} + (1 - x'_B) \Delta H_{B(A)} \right] x'_A x'_C [x'_C \Delta H_{B(C)} + (1 - x'_C) \Delta H_{C(B)}] x'_C x'_A [x_A \Delta H_{C(A)} + (1 - x'_A) \Delta H_{A(C)}] \quad (15)$$

with

$$x'_A = \frac{2x_A}{1 + x_A}; \quad x'_B = \frac{x_B}{1 + x_A}; \quad x'_C = \frac{x_C}{1 + x_A}$$

The conformal ionic solution model [25] also gives a relationship for the excess enthalpy of mixing of a ternary solution

$$\Delta H = \sum_i \sum_j a_{i,j} x_i x_j + \sum_j \sum_j b_{i,j} x_i^2 x_j + \sum_j \sum_j c_{i,j} x_i^2 x_j^2 + P x_A x_B x_C + \sum_i \sum_j \sum_k Q_i x_i^2 x_j x_k \quad (16)$$

The coefficients  $a_{i,j}$ ,  $b_{i,j}$ , and  $c_{i,j}$  are evaluated from data on the three binary subsystems. The coefficients  $P$  and  $Q_i$  of the "ternary" terms are calculated from the binary data.

Very recently, *Hoch* and *Arpshofen* developed a model which is applicable to binary, ternary and larger systems [26, 27]. It was derived originally by considering complexes in the solution, and the A—B bond strength (between species A and B) was made dependent on the presence of other atoms in the complex. The model was applied to metal—salt [28], metal—metal oxide [29, 30], silicate [31, 32], metallic [33] systems and  $ZrF_4$ -based fluoride mixtures [34]. For a binary system the basic equation for the enthalpy of mixing is

$$\Delta H = W N (x - x^N) \quad (17)$$

The term  $N$  is an integer (2, 3, 4, etc.),  $W$  is the interaction parameter and  $x$  is the mole fraction of the component so that the maximum of  $\Delta H$  (either positive or negative) is at  $x > 0.5$ . The quantity  $N$  is chosen such that  $W$ , determined from the thermodynamic data, is independent of the composition.

The signs of the limiting partial enthalpies obtained from eqn (17) are determined by  $W$ . In other words, one interaction parameter describes one type of interaction or reaction in a system. If two reactions exist in the binary system such as the  $MgO$ — $SiO_2$  [35], where a strong compound-forming tendency exists on the magnesia-rich side ( $Mg_2SiO_4$ ) and a miscibility gap exists on the  $SiO_2$ -rich side, then two interaction parameters, an attractive  $W$  and repulsive  $U$ , are needed. Each has its major effect at different compositions with different dependence on composition ( $N_W$  and  $x$  in one case,  $N_U$  and  $y$  in the other). Thus

$$\Delta H = W N_W (x - x^{N_W}) + U N_U (y - y^{N_U}) \quad (18)$$

$W$  and  $U$  are determined by least-square analysis; confidence limit and error in  $W$  and  $U$  are also calculated.

This model was extended to ternary or larger system by evaluating the effect of each limiting binary system in the multicomponent mixture. Up to this point the primary emphasis has been on predicting multicomponent properties from binary data; several of the empirical expressions proposed during the past 40 years were summarized. These expressions also served as the point-of-departure for the mathematical representation of multicomponent excess properties. Differences between the predicted values and experimentally determined values are expressed as

$$(\Delta Z_{1,2,3}^{\text{ex}})_{\text{exp}} - (\Delta Z_{1,2,3}^{\text{ex}})_{\text{calc}} = x_1 x_2 x_3 Q_{1,2,3} \quad (19)$$

with  $Q$ -functions of varying complexity. The abbreviations **exp** and **calc** indicate experimental and calculated, respectively. For most systems commonly encountered, the experimental data can be adequately represented by the power series expansion

$$Q_{1,2,3} = A_{1,2,3} + \sum_i B_{1,2}^i (x_1 - x_2)^i + \sum_j B_{1,3}^j (x_1 - x_3)^j + \sum_k B_{2,3}^k (x_2 - x_3)^k \quad (20)$$

though it is unlikely that the data for multicomponent systems will be obtained with sufficient precision to warrant more than a few parameters.

### Reciprocal mixtures

The  $A^+$ ,  $B^+//X^-$ ,  $Y^-$  reciprocal mixture is also a ternary mixture; there are four constituent salts ( $AX$ ,  $BX$ ,  $AY$ ,  $BY$ ), but only three of them can be chosen as independent components:  $AX$ ,  $BX$ ,  $AY$  or  $AX$ ,  $BX$ ,  $BY$  or  $BX$ ,  $AY$ ,  $BY$  or  $AY$ ,  $BX$ ,  $BY$ . Therefore a solution which contains a given amount of  $A^+$ ,  $B^+$ ,  $X^-$  and  $Y^-$  ions can be made in four different ways.

Reciprocal systems must be represented by a square while the composition of usual ternary systems is obtained from a triangle representation. The addition of any component to a solution varies the composition linearly towards the corner of that component.

Consider a mixture inside the two triangles  $AX$ — $BX$ — $BY$  and  $AY$ — $BX$ — $BY$  (Fig. 2): it can be made up of positive quantities of each of these three. On the other hand, to make up this composition from  $AX$ ,  $AY$ , and  $BX$  and to get out of the triangle  $AX$ — $AY$ — $BX$  one must subtract  $AX$  from an  $AY + BX$  mixture. The activity and chemical potential of all four salts, however, are defined and are the same no matter how the three components were chosen.

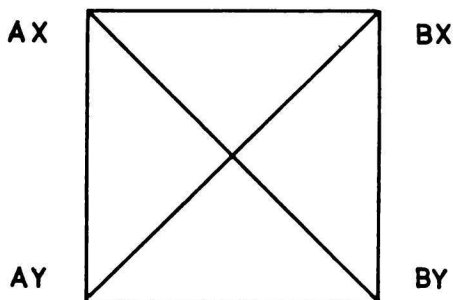


Fig. 2. Composition diagram of the  $A^+, B^+//X^-, Y^-$  ternary reciprocal system.

The Gibbs energy of mixing of such systems was first deduced by *Flood, Førland, and Grjotheim* [36]

$$\Delta G_{\text{mix}} = RT(x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y) \pm x_i x_j \Delta G^0 \quad (21)$$

where  $\Delta G^0$  is the standard Gibbs energy change for the metathetical reaction



and  $ij$  is the salt which is not a component. This last term expresses the idea that the three components, in effect, “react” to form the last constituent. The + sign is for the case when  $ij$  is  $AY$  or  $BX$  and the – sign is for  $AX$  or  $BY$ . Everything beyond the last term given in eqn (21) is the same no matter how the solution was made up.

*Førland* [9] improved the original FFG theory by including four binary interaction terms in (21)

$$\begin{aligned} \Delta G_{\text{mix}} = & RT(x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y) \pm \\ & \pm x_i x_j \Delta G^0 + x_A x_B x_X \lambda_X + x_A x_B x_Y \lambda_Y + x_X x_Y x_A \lambda_A + x_X x_Y x_B \lambda_B \end{aligned} \quad (22)$$

with the interaction parameter  $\lambda_i$  in the  $i$ -common-ion binary mixture.

Later, *Blander and Yosim* [25] generalized the conformal ionic solution theory [37, 38] which had been applied to binary molten salt mixtures by *Reiss, Katz and Kleppa* [39]. They found for the Gibbs energy of mixing a relationship identical to (22) and added a nonrandom term to this equation; this correction term was only taken by analogy with the one obtained from the quasi-lattice theory [40] developed for binary mixtures.

$$\begin{aligned} \Delta G_{\text{mix}} = & RT(x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y) \pm \\ & \pm x_i x_j \Delta G^0 + x_A x_B x_X \lambda_X + x_A x_B x_Y \lambda_Y + x_X x_Y x_A \lambda_A + x_X x_Y x_B \lambda_B + x_A x_B x_X x_Y \Lambda \end{aligned} \quad (23)$$

with  $\Lambda = -(-\Delta G^0)^2/zRT$  ( $z$  is the cation—anion coordination number).

The SIM was also applied to ternary reciprocal mixtures [11, 12]. The equation found for the Gibbs energy of mixing is

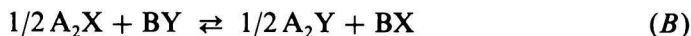
$$\Delta G_{\text{mix}} = RT(x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y) \pm x_i x_j \Delta G^0 + x_A \Delta G_A^{\text{ex}} + x_B \Delta G_B^{\text{ex}} + x_X \Delta G_X^{\text{ex}} + x_Y \Delta G_Y^{\text{ex}} + x_A x_B x_X x_Y \Lambda \quad (24)$$

with the excess energy of mixing  $\Delta G_i^{\text{ex}}$  in the *i*-common-ion binary mixture,  $\Lambda = -(-\Delta G^0)^2/2zRT$ . It should be stressed that eqn (24) is able to take into account experimental asymmetries in binary systems and contains the nonrandom term  $\Lambda$  which has been calculated and not estimated, by formal analogy, as previously.

The SIM has been applied to asymmetrical ternary reciprocal mixtures ( $A^{2+}$ ,  $B^+//X^-, Y^-$ ) [41]. By using the same analogies aforementioned, the equation found for the molar enthalpy of mixing is

$$\Delta H = x'_B x'_X (1 + x_A) \Delta H^0 + x'_X \Delta H_X + x'_Y \Delta H_Y + x_B \Delta H_B + x_A \Delta H_A + x'_A x'_B x'_X x'_Y (1 + x_A) \Lambda \quad (25)$$

where  $\Delta H^0$  is the enthalpy change for the metathetical reaction



$\Delta H_i$  is the excess enthalpy in the *i*-common-ion binary mixture and  $\Lambda = -(\Delta H^0)^2/2zRT$ .

The SIM has also been extended to quaternary reciprocal molten salt systems [42].

### Complex melts

Under this category we have classified those mixtures in which the mixing process gives rise to species different from those in the pure components. For instance, alloys like Cs—Au or Li—Pb fall into this category since the melt includes ionic species different from the metallic components; also the molten salt mixtures made from a ionic salt and of a covalent salt, for instance KCl—AlCl<sub>3</sub>, are characterized by complexes, for instance AlCl<sub>4</sub><sup>-</sup> and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>.

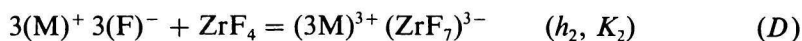
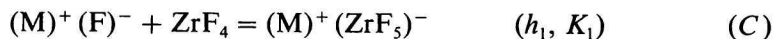
Very few exists on the thermodynamics of such systems. The reason is two-fold since, due to very different physical and chemical properties between the components of the mixtures, experimental investigations are not easy and also theoretical approaches not simple. Some experimental investigations and some theoretical approaches were recently performed or are in progress; in the molten salt field, for instance, advances are being made for systems containing alkali halides and halides of aluminium, rare earth, niobium, tantalum, bismuth,

zirconium and also for the very novel low-melting systems containing aluminium chloride and organic chlorides. Most of these investigations are related to industrial interests and are parts of national research programs in France, China, Germany, India, Norway, Poland, USA. The applications fields are mainly the production of the metals by electrolysis of the melts, fabrication of glasses in relation with optical fibres, elaboration of new materials, *etc.*

A proper description of the features of such melts can be given by models based on "associated solution" concepts. Very similar models have been developed recently and independently in Marseille [43] and in Trondheim [44] which are equally successful in describing the thermodynamics of  $\text{BiCl}_3$ - and  $\text{AlCl}_3$ -based mixtures.

Melts including at least one covalent salt may be either partially ionic or nonionic. Mixtures obtained from alkali halides  $\text{AX}$  (*e.g.* fully ionic salts) and transition, rare-earth, actinide, metal halides  $\text{M}_i\text{X}_j$  (*e.g.* covalent salts, generally) are examples of such melts, generally characterized by the formation of heterogeneous ionic complexes such as  $\text{M}_i\text{X}_{(j+1)}^q$ ,  $\text{M}_{(i+1)}\text{X}_{(j+1)}^{(p+q)}$ , *etc.* ( $p$  ( $> 0$ ) and  $q$  ( $< 0$ ) are the electrovalencies of  $\text{M}$  and  $\text{X}$ , respectively). The existence of complexes in molten salt mixtures has been the subject of lively discussions in the molten salt community [45]. Development of investigation methods of structure brought new arguments to the controversy. These complexes contribute to the entropy of the mixture and should be taken into account to model the solution.

We recently have proposed an ideal associated model to describe mixtures of alkali chlorides with bismuth chloride or mixtures of alkali fluorides with zirconium fluoride [46]. The excess thermodynamic quantities of the melt are assumed to arise only from the formation of complex ionic species. For the  $\text{ZrF}_4$ -based mixtures, for instance, the enthalpies  $h_i$  and the equilibrium constants  $K_i$  refer to the reactions



For a mixture made from  $n_1$  and  $n_2$  of  $\text{ZrF}_4$  and  $\text{MF}$ , respectively, the amount of substances of the species  $\text{ZrF}_4$ ,  $\text{M}^+$ ,  $\text{F}^-$ ,  $\text{ZrF}_5^-$ , and  $\text{ZrF}_7^{3-}$  in reactions (C) and (D) is denoted by  $n_1^*$ ,  $n_2^*$ ,  $n_3^*$ ,  $n_4^*$ , and  $n_5^*$ , respectively. Mass and electroneutrality balances introduced in the above complex formation reactions establish the following relation between the initial melt composition  $x(\text{MF})$  and the melt composition at equilibrium  $x^*(\text{MF})$

$$x = x^* \frac{1 + K_1 + K_2 x^{*2} (3 - 2x^*)}{1 + K_1 x^* (2 - x^*) + K_2 x^{*3} (4 - 3x^*)} \quad (26)$$

$$\text{with } x = \frac{n_2}{n_1 + n_2} \text{ and } x^* = \frac{n_3^*}{n_3^* + n_4^* + n_5^*}.$$

The enthalpy of mixing is obtained as

$$\Delta H = \frac{n_4^*}{n_1 + n_3} h_1 + \frac{n_5^*}{n_1 + n_3} h_2 \quad (27)$$

$$\Delta H = x^*(1 - x^*) \frac{K_1 h_1 + K_2 h_2 x^{*2}}{1 + K_1 x^*(2 - x^*) + K_2 x^{*3}(4 - 3x^*)} \quad (28)$$

The four parameters  $K_1$ ,  $K_2$ ,  $h_1$ , and  $h_2$  are obtained by numerical calculation. From the experimental enthalpy data it is possible to evaluate two approximate values for  $h_1$  and  $h_2$ ; they are used as the initial parameters  $h_{1,0}$  and  $h_{2,0}$  in the iterative procedure. Two arbitrary values are set for the initial parameters  $K_{1,0}$  and  $K_{2,0}$ . For each experimental data set  $[x, \Delta H(x)]$ , the program solves eqn (26) and calculates the solutions  $x^*$ .

A nonlinear regression program, applied to eqn (28), yields optimized values of the parameters  $h_{1,1}$ ,  $h_{2,1}$ ,  $K_{1,1}$ , and  $K_{2,1}$ . If these values differ from the initial values, the program iterates with  $h_{1,1}$ ,  $h_{2,1}$ ,  $K_{1,1}$ , and  $K_{2,1}$  as initial values. Convergence is attained after a few iterations.

## Conclusion

Suitable modeling of high-temperature melts has a crucial importance in the present context of thermochemical databanks and information systems. A few groups have developed such services which are currently used by scientists but also by industrial engineers. The service provided is first of all the data relative to a system but also an assessment of these data, through suitable modeling and numerical procedures, which result in thermodynamically consistent data and phase diagrams and in quantitative prediction of phase equilibria in multicomponent melts.

The principle of phase diagram calculation is the minimization of the Gibbs energy of the mixture under investigation. Several numerical calculation programs exist so far in Europe and North-America. These programs, developed by specialized research groups, differ in the method of description of the envisaged system (thermodynamic functions of mixing are described either by empirical polynomial expansions or by equations deduced from theoretically based models) and the mathematical methods worked out in the search of a minimum.

For metallic systems, for instance, a very efficient program has been elab-

orated, and successively improved, by Lukas [47] (Max-Planck-Institute, Stuttgart). Least-square methods were developed, which enable all the thermodynamic and phase diagram data to be simultaneously optimized and thus to provide optimized coefficients in polynomial expansions of thermodynamic functions of mixing.

We have developed in Marseille THERMOSALT [48, 49] which is a thermodynamic databank for molten salt mixtures. The previous optimization program has been satisfactorily used to calculate the phase diagrams of common-ion binary [50] or multicomponent [51] molten salt mixtures.

Modifications revealed indispensable in order to perform such calculations with asymmetrical ionic systems. Those were made according to the previously quoted theoretical developments; phase diagrams calculations were made for systems like  $\text{CaCl}_2$ — $\text{CsCl}$  or  $\text{Na}$ ,  $\text{K//F}$ ,  $\text{SO}_4$  [52, 53]. Advances are being made in the numerical procedures for complex systems.

## References

1. Gaune-Escard, M., *Pure Appl. Chem.* 55, 105 (1983).
2. Temkin, M., *Acta Physicochim. URSS* 20, 411 (1945).
3. Gaune-Escard, M., Mathieu, J. C., Desré, P., and Doucet, Y., *J. Chim. Phys.* 69, 1390 (1972).
4. Gaune-Escard, M., Mathieu, J. C., Desré, P., and Doucet, Y., *J. Chim. Phys.* 69, 1397 (1972).
5. Gaune-Escard, M., Mathieu, J. C., Desré, P., and Doucet, Y., *J. Chim. Phys.* 70, 1666 (1973).
6. Hardy, H. K., *Acta Metall.* 1, 202 (1953).
7. Guggenheim, E. A., *Mixtures*. Clarendon Press, Oxford, 1952.
8. Mathieu, J. C., Durand, F., and Bonnier, E., *J. Chim. Phys.* 62, 1289 (1965).
9. Førland, T., in *Fused Salts*. (Sundheim, B. R., Editor.) McGraw Hill, New York, 1964.
10. Flory, J. P., *J. Chem. Phys.* 49, 3919 (1971).
11. Hatem, G. and Gaune-Escard, M., *J. Chim. Phys.* 74, 754 (1977).
12. Hatem, G. and Gaune-Escard, M., *J. Chim. Phys.* 77, 925 (1980).
13. Hatem, G. and Gaune-Escard, M., *Thermochim. Acta* 57, 351 (1982).
14. Gaune-Escard, M., *J. Chim. Phys.* 71, 1167 (1974).
15. Gaune-Escard, M., *J. Chim. Phys.* 71, 1175 (1974).
16. Gaune-Escard, M., Mathieu, J. C., Desré, P., and Doucet, Y., *J. Chim. Phys.* 70, 1003 (1973).
17. Gaune-Escard, M., Mathieu, J. C., Desré, P., and Doucet, Y., *J. Chim. Phys.* 70, 1033 (1973).
18. Redlich, O. and Kister, A. T., *Ind. Eng. Chem.* 40, 341 (1948).
19. Kohler, F., *Monatsh. Chem.* 91, 738 (1960).
20. Colinet, C., *D.E.S. Fac. des Sci., Univ. Grenoble*, France, 1967.
21. Muggianu, Y.-M., Gambino, M., and Bros, J.-P., *J. Chim. Phys.* 72, 83 (1975).
22. Toop, G. W., *Trans. Metal. Soc. AIME* 233, 850 (1965).
23. Hillert, M., *CALPHAD* 4, 1 (1980).
24. Wang, Z. C., Lück, R., and Predel, B., *Proc. CALPHAD XVIII*. Stockholm, May 28—June 2, 1989.
25. Blander, M. and Yosim, S. J., *J. Chem. Phys.* 39, 2610 (1963).
26. Hoch, M. and Arpshofen, I., *Z. Metallkd.* 75, 23 (1984).



27. Hoch, M., *CALPHAD* 11, 219 (1987).
28. Hoch, M., *CALPHAD* 9, 59 (1985).
29. Babelot, J. F., Ohse, R. W., and Hoch, M., *J. Nucl. Mater.* 137, 144 (1986).
30. Hoch, M., *CALPHAD* 11, 224 (1987).
31. Hoch, M., *CALPHAD* 12, 43 (1988).
32. Hoch, M., *Proc. Int. Conf. on User Applications of Alloy Phase Diagrams 129*, ASM INTERNATIONAL, Metal Park, OH 44073, 1987.
33. Hoch, M., *CALPHAD* 11, 237 (1987).
34. Gaune-Escard, M., Hatem, G., Gaune, P., and Hoch, M., *Proc. 6th International Symposium on Halide Glasses*. Clausthal, FRG, October 1—5, 1989.
35. Huron, E. and Hoch, M., *Proc. 1984 International Symposium on Metallurgical Slags and Fluxes*. (Gaskell, D. F. and Fine, H. A., Editors.) P. 305—318. AIME, 1984.
36. Flood, H., Førland, T., and Grjotheim, K., *Z. Anorg. Allg. Chem.* 276, 289 (1954).
37. Longuet-Higgins, H. C., *Proc. R. Soc. London, A* 205, 247 (1951).
38. Brown, W., *Proc. R. Soc. London, A* 240, 561 (1957).
39. Reiss, H., Katz, J. L., and Kleppa, O. J., *J. Chem. Phys.* 36, 144 (1962).
40. Blander, M. and Braunstein, J., *Ann. N. Y. Acad. Sci.* 79, 838 (1967).
41. Hatem, G., de Gasquet, B., and Gaune-Escard, M., *J. Chem. Thermodyn.* 11, 927 (1979).
42. Gaune-Escard, M., *CALPHAD* 3, 119 (1979).
43. Gaune-Escard, M., Tabariès, F., and Hatem, G., Molten Salts Discussion Group. London, 1986.
44. Øye, H. A., Molten Salts Discussion Group. London, 1986.
45. EUCHEM Conferences (Europe) and Gordon Conferences (USA) from 1966.
46. Hatem, G., Tabariès, F., and Gaune-Escard, M., *Thermochim. Acta* 149, 15 (1989).
47. Dorner, P., Henig, E. Th., Krieg, K., Lukas, H. L., and Petzow, G., *CALPHAD* 4, 4, 241 (1980).
48. Hatem, G., Fouque, Y., Bros, J. P., and Gaune-Escard, M., *Proc. 1st International Symposium of Molten Salt Chemistry and Technology*. Kyoto, Japan, April 1983.
49. Gaune-Escard, M., Hatem, G., Fouque, Y., and Bros, J. P., *CODATA Bulletin* 58, 104 (1985).
50. Gaune-Escard, M., Gambino, M., Hatem, G., Bros, J. P., Fouque, Y., and Juhem, P., *Proc. CALPHAD XVI. IRSEE (RFA)* 24—29 May, 1987.
51. Juhem, P., Hatem, G., Bros, J. P., Fouque, Y., and Gaune-Escard, M., *14èmes Journées d'équilibre entre phases*, p. 143. Montpellier, 1988.
52. Hatem, G., Gaune-Escard, M., and Pelton, A. D., *J. Phys. Chem.* 86, 3039 (1982).
53. Gaune-Escard, M. and Hatem, G., High Temperature Materials Conference. Gaithersburg, USA, April 3—7, 1989.