ABSTRACT

Most molten salt industrial processes, for instance electrolytic elaboration of metals from melts, involve compromise between several parameters to be optimized. Thermodynamic properties play an important role and the choice both of suitable electrolyte and molten salts to be electrolyzed is directly related to the operation temperature and to the "average valency" of the electrolytic bath. Experimental thermochemical investigations conducted by high temperature calorimetry, differential enthalpic analysis, differential scanning calorimetry can provide information on phase equilibria in the melt. From a theoretical point of view, the molten salt mixtures considered in those investigations are not simple since they involve i) ions with different valency, ii) ionic and non-ionic components and iii) several components. Classical models used for the most simple molten salt mixtures cannot be used and suitable modelling involving complex species, should be developed.

INTRODUCTION

For years the chemical industry has recognized the importance of the thermodynamic and physical properties of solution in design calculations involving chemical separations, fluid flow and heat transfer. The development of techniques has enabled the experimental investigation of melts with convenience and accuracy. But even with modern instrumentation, experimental measurement of thermodynamic properties has become progressively more expensive and time-consuming with each additional component beyond binary mixtures. In the chemical literature, properties for binary systems are relatively abundant, properties for ternary systems are scarce and properties for 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.

1. EXAMPLE OF APPLICATION

Most molten salt industrial processes, e.g. electrolytic elaboration of metals
from melts, involve compromise between several parameters to be optimized. Electrolysis has many advantages over conventional pyrometallurgical processes employing metallic reducing agents (C, Si, ..) :
- it is selective since potential, electrode overvoltages and valency state (complexing) of the electrolyte can be adjusted.
- it allows elements either very electropositive or very electronegative to be obtained
- it is a quasi-continuous process and can be easily automated.

These advantages outweigh some drawbacks such as high capital and operation costs related to energy use (electricity), limitation of productivity by current density. As a result, the design and engineering of an electrolytic process rises a number of technological challenges for the cell itself but also for the electrolyte and the salt to be electrolysed:

**ELECTROLYTE**
- Phase diagram
- stability/hygroscopy
- vapor pressure
- complexing ability
- viscosity
- conductivity
- etc...

**SALT**
- solubility
- stability/hygroscopy
- vapor pressure
- etc...

Thermodynamic properties play an important role and the choice of a suitable molten salt solvent is directly related to the operation temperature and also to the "average valency" of the electrolytic bath. For the elaboration of niobium, for instance, from NbCl₅ (m.p. 478 K, b.p. 520 K) the choice of a chloride melt as a solvent induces appreciable losses by evaporation (eutectic chloride mixtures generally melt at temperatures higher than 650 K). The problem is therefore to find a suitable solvent including anionic species, like F⁻, corresponding to a higher stability of the niobium species in the melt.

Another example is the production of rare earth metals. Neodymium, for instance, is used for the fabrication of magnets; alloys of neodymium can be obtained either by reduction with calcium or by electrolysis. In the electrolytic process a compromise had to be found between the following features:
- in molten chloride baths, a poor current efficiency is obtained because of the two coexisting valence states (II and III). Adding fluorides to the bath results in a stabilization of the III valence but also induces formation of neodymium oxycholorides and related operating problems.
- in molten fluoride melts, electrolysis of NdF₃ is easier but costs are higher; electrolysis of oxides would not pose any problem of anodic reaction but is not promoted by the low solubility.

Nevertheless a compromise had been found and a process successfully developed [1] : a derivative of the industrial product, hydrated neodymium carbonate, is dissolved and electrolysed in a mixture of molten fluorides at 900°C.

Refining of elements is also an important application in the molten salt area, e.g. aluminium electrorefining by the "3-layer" Gadeau process which is a
sequential refining employing more than one electrolyte \[2\]. This process uses chloride/fluoride melts, which involve lower energy consumption than required for fluoride-only melts and of adjustable complexing ability with respect to the impurities to be removed.

Experimental thermochemical investigations conducted by high temperature calorimetry, differential enthalpic analysis, differential scanning calorimetry can provide information on phase equilibria in the melt. From a theoretical point of view, the molten salt mixtures considered in those investigations are not simple since they involve i) ions with different valency, ii) ionic and non-ionic components and iii) several components. Classical models used for the most simple molten salts mixtures cannot be used so far and a suitable modeling involving complex species, should be developed.

2. MODELING OF HIGH TEMPERATURE MELTS

The main problem when modeling is to account for the actual nature of the solution. In most actual cases, 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: \textit{a priori} 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 \textit{a priori} estimations.

Suitable models should be used both for binary mixtures and multicomponent systems; of course, they have to take into account the nature of the species present in the melt and the magnitude of the interactions between these species.

A considerable amount of experimental thermodynamic investigations made evident that all melts do not behave identically and, therefore, also evident that specific thermodynamic models should be developed and used to describe their features[3].

Though any classification usually is somewhat arbitrary, for the sake of clarity it will be distinguished between simple melts and complex melts in the following. Simple mets are those molten salt mixtures in which no new species arise from the mixing of components. By opposition, complex melts include formation of new species (complexes) which did not exist in the constituting salts..

Two distinct types of molten salt solutions can be defined according to the nature and the number of involved components. These \textit{additive} and \textit{reciprocal} systems parallel two distinct types of metallic systems, \textit{substitutional} alloys and \textit{interstitial} alloys. 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 to measure the deviation from ideality of the other functions of mixing.

Another distinction among ionic melts lies in the possibly different valencies of the ions involved.
Also those solutions obtained from at least one covalent salt have different features, generally characterized by the formation of complex species (e.g. \( \text{AlCl}_4^- \), \( \text{Al}_2\text{Cl}_7^{2-} \), ...in the aluminum chloride-based mixtures).

3. SIMPLE MELTS

3.1. Binary mixtures

3.1.1. Symmetrical mixtures

Common-ion molten salt symmetrical mixtures (AX+BX or AX2+BX2) are often described by quasi-lattice models, the main distinction lying in the interaction range of the species of the same nature, cations A+ and B+.

For an ideal solution, the energetic interactions of A+ and B+ with their environments are the same and these species mix randomly. Then the molar free energy of mixing is

\[
\Delta S_{id}^{mix} = - RT \left[ x_A \ln x_A + x_B \ln x_B \right]
\]

(1)

where \( n_A \), \( n_B \) are the number of moles of atoms (or ions) in the mixture and the x's are the molar (or ionic) fractions defined as:

\[
x_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad x_B = \frac{n_B}{n_A + n_B}
\]

(2)

For molten salt mixtures, this relationship was proposed by Temkin [4] for the ideal entropy of mixing and the x's are the so-called (Temkin) ionic fractions.

Deviations from ideality (\( \Delta G^{ex} \neq 0 \), \( \gamma \neq 1 \)) arise from a lack of balance in the interionic forces between the different species. If the components are similar in chemical nature (e.g., sodium chloride + potassium chloride), the mixture is nearly ideal. If they differ, the forces are usually greater between the cations.

For those melts exhibiting small deviations from ideality, e.g. weak interactions, in principle any simple model, based on a pair-wise interaction concept, can be used (regular or quasi-regular models).

The Surrounded Ion Model (SIM) [5] [6] [7], which is a statistical model, gives a more realistic description of a melt since it takes into account all the possible energetic interactions of A+ and B+, depending on the local environment of each ion. The ideal entropy of mixing is given by a relationship identical to (1). The most interesting feature of this model lie in the fact that it is able to account for the asymmetry of the thermodynamic excess functions with only two energetic parameters having a physical meaning. The previous models based on a pair-wise interaction concept, generally 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 [8] quasi-regular model) or used polynomial expansions whose parameters have no physical meaning. Also the more elaborated Guggenheim's "quasichemical model" [9], though able to account for the temperature dependence of the thermodynamic excess functions, failed in describing experimental asymmetries. The SIM is generalization of the above binary models and has also been extended to other kinds of molten salt mixtures.

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3.1.2. Asymmetrical mixtures

In asymmetrical molten salt mixtures of the type $AX_2 + BX$, the same lattice description of the melt implies that the substitution to the A$^{2+}$ divalent cation of the B$^+$ monovalent cation creates one vacancy on the corresponding sublattice. Several relationships have been proposed for the ideal entropy [10] [11]; they differ in the assumptions made on the vacancies. The S.I.M. [12] [13] provides, from different theoretical grounds, a relationship for the ideal entropy which is identical to the one by Forland [10]:

$$\Delta S_{id}^{mix} = - R [2x_A \ln x_A + (1-x_A) \ln (1-x_A')]$$ (3)

where $x_A = n_A / (n_A + n_B)$ and $x_A' = 2n_A / (2n_A + n_B)$ (4)

The $x_i$'s have been defined previously and the $x_i$'s are the so-called equivalent ionic fractions. 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 the equivalent ionic fractions defined by Forland [10] in the relationships expressing the other functions of mixing and Temkin's ideal entropy (1). It has been shown [14] that this may lead to some inconsistencies.

3.2. Ternary mixtures

Models have been developed to permit the properties of common-ion and reciprocal ternary molten salt systems to be calculated from the binary coefficients. Empirical ternary coefficients may also be included in these equations.

3.2.1. Additive ternary mixtures

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 proposed which differ in the geometric weighting factors of the binary contributions. The binary models provide reasonable estimates for several systems of practical importance and they also address the problem of how to report experimental data.

This paragraph will be devoted to several of the empirical equations or models that have been suggested for parametrizing and predicting mixture data. Redlich and Kister [15] proposed an expression for the excess Gibbs free energy of mixing of a ternary mixture

$$\Delta G^{ex} = x_1 x_2 \sum (G_n^{ex})_{12} (x_1 - x_2)^n + x_1 x_3 \sum (G_n^{ex})_{13} (x_1 - x_3)^n$$

$$+ x_2 x_3 \sum (G_n^{ex})_{23} (x_2 - x_3)^n$$ (5)

which provisions for additional ternary parameters.

Kohler [16] proposed an equation for the excess Gibbs free energy of mixing
of a ternary solution
\[ \Delta G^{\text{ex}} = (x_1 + x_2)^2 \Delta G_{12}^{\text{ex}} + (x_1 + x_3)^2 \Delta G_{13}^{\text{ex}} + (x_2 + x_3)^2 \Delta G_{23}^{\text{ex}} \]  

(6)
in which \( \Delta G_{ij}^{\text{ex}} \) refers to the excess Gibbs free energies of the binary mixtures at a composition \((x_0^i, x_0^j)\) such that \( x_0^i = 1 - x_0^j = x_i / (x_i + x_j) \).
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 [17] established a slightly more complex relationship for expressing the thermodynamic excess properties of multicomponent systems
\[ \Delta G^{\text{ex}} = \sum \sum x_i (1 - x_j)^{-1} \left[ \Delta G_{ij}^{\text{ex}} \right] x_j \]  

(7)
in which \( \{\Delta G_{ij}^{\text{ex}}\} \) '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 [18] also developed a geometric model with different weightings of the binary contributions :
\[ \Delta G^{\text{ex}} = \sum \sum x_i (1 - x_j)^{-1} \left[ \Delta G_{ij}^{\text{ex}} \right] x_1 ; x_2 \]  

(8)
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. Other asymmetric "geometric" numerical methods have been proposed by Toop[19] and Hillert[20].
Very recently, Z.C. Wang et al.[21] 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 :
\[ W_{ABC} (x_A, x_B, x_C) = \sum \sum \sum \beta_{ij}^{(l)} \frac{x_i}{x_i(\{ij\})} \frac{x_j}{x_j(\{ij\})} \cdot W_{ij} (x_i(\{ij\}), x_j(\{ij\})) \]  

(9)
where
\[
\begin{align*}
i &= A & j &= B & k &= C \\
i &= B & j &= C & k &= A \\
i &= C & j &= A & k &= B
\end{align*}
\]
\( l_{ij} = 1, 2, ..., l'_{ij} \); \( x_i \) and \( W_{ABC} (x_A, x_B, x_C) \) are respectively the mole fractions of component \( i \) in the A-B-C ternary system and the ternary excess molar free energy or excess molar enthalpy ;
\( x_i(\{ij\}) \) and \( W_{ij} (x_i(\{ij\}), x_j(\{ij\})) \) are the corresponding binary properties at the \( l_{ij} \)th
point along the i-j binary composition line. Here:

\[ x^{(ij)}_{(ij)} = 1 - x^{(ij)}_{(ij)} = \frac{1 + x_i + x_j + \lambda_{ij}^{(ij)} x_k}{2} \]

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

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.

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 Surrounded Ion Model (SIM) [22][23] yields an equation for the excess enthalpy of mixing of the symmetrical ternary mixture AX-BX-CX (or AX_2-BX_2-CX_2):

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

(10)

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

\[ \Delta G_{mix}^{id} = RT \left\{ x_A \ln x_A + x_B \ln x_B + x_C \ln x_C \right\} \]

For additive asymmetrical ternary mixtures \((AX_2 + BX + CX)\), Equation (10) becomes:

\[ \frac{\Delta H}{1 + x_A} = x_A x_B \left\{ x_B \left\{ \Delta H_{B(A)} - \frac{2}{2} \Delta H_{A(B)} \right\} + (1 - x_B) \Delta H_{B(A)} \right\} \\
+ x_A x_C \left\{ x_C \Delta H_{C(A)} + (1 - x_C) \Delta H_{C(A)} \right\} \\
+ x_B x_C \left\{ x_A \Delta H_{A(C)} + (1 - x_A) \Delta H_{A(C)} \right\} \]

(11)

with

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

The Conformal Ionic Solution model [24] also gives a relationship for the
excess enthalpy of mixing of a ternary solution:

$$\Delta H = \sum a_{ij} x_i x_j + \sum b_{ij} x_i^2 x_j + \sum c_{ij} x_i x_j^2 + P x_A x_B x_C + \sum Q_j x_j^2 x_j x_k$$

(12)

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

Very recently, Hoch and Arpshofen developed a model which is applicable to binary, ternary and larger systems [25] [26]. It was derived originally by looking at the complexes in the solution, and the A-B bond strength (between species A and B) made dependent on the presence of other atoms in the complex. The model was applied to metal-salt [27], metal-metal oxide[28] [29], silicate[30] [31], metallic systems[32] and ZrF$_4$-based fluoride mixtures[33]. For a binary system the basic equation for the enthalpy of mixing is:

$$\Delta H = W n (x - x^n)$$

(13)

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 thermodynamic data, is independent of the composition.

The signs of the limiting partial enthalpies obtained from equation (13) 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$_2$ [34], where a strong compound- forming tendency exists on the magnesium-rich side (Mg$_2$SiO$_4$) and a miscibility gap exists on the SiO$_2$-rich side, then two interaction parameters, an attractive $W$ and repulsive $M$, are needed. Each has its major effect at different compositions with different dependency on composition ($n$ and $x$ in one case, $m$ and $y$ and the other). Thus

$$\Delta H = W n (x - x^n) + M m (y - y^m)$$

(14)

$W$ and $M$ are determined by least square analysis; confidence limit and error in $W$ and $M$ 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.

3.2.2. 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.
The free energy of mixing of such systems was first deduced by Flood, Førland, and Grjotheim [35].

\[
\Delta G_{\text{mix}} = RT \left( x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y \right) + x_i x_j \Delta G^0
\]

(15)

where \( \Delta G^0 \) is the standard free energy change for the metathetical reaction

\[
AX + BY \rightleftharpoons AY + BX
\]

(16)

and where \( i,j \) 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 \( i,j \) is \( AY \) or \( BX \) and the - sign is for \( AX \) or \( BY \). Everything beyond the last term given in Eq. (15) is the same no matter how the solution was made up.

Førland [36] improved the original FFG theory by including four binary interaction terms in (15)

\[
\Delta G_{\text{mix}} = RT \left( x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y \right) + x_i x_j \Delta G^0 + x_A x_B x_X x_Y + x_A x_B x_Y x_Y + x_X x_Y x_A x_A + x_X x_Y x_B x_B
\]

(17)

with \( \lambda_i \) the interaction parameter in the \( i \) common ion binary mixture.

Later, Blander and Yosim [26] generalized the Conformal Ionic Solution theory [37] [38] which has been applied to binary molten salt mixtures by Reiss, Katz and Kleppa [39]. They found for the free energy of mixing a relationship identical to (17) 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.

\[
\Delta G_{\text{mix}} = RT \left( x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y \right) + x_i x_j \Delta G^0 + x_A x_B x_X x_Y + x_A x_B x_Y x_Y + x_X x_Y x_A x_A + x_X x_Y x_B x_B
\]

(18)

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

The Surrounded Ion Model (SIM) was also applied to ternary reciprocal mixtures [41] [42]. The equation found for the Gibbs free energy of mixing is:

\[
\Delta G_{\text{mix}} = RT \left( x_A \ln x_A + x_B \ln x_B + x_X \ln x_X + x_Y \ln x_Y \right) + x_i x_j \Delta G^0 + x_A \Delta G_{\text{ex}}^{x_A} + x_B \Delta G_{\text{ex}}^{x_B} + x_X \Delta G_{\text{ex}}^{x_X} + x_Y \Delta G_{\text{ex}}^{x_Y}
\]

(19)

with \( \Delta G_{\text{ex}} \) the excess free energy of mixing in the \( i \) common ion binary mixture, \( \Lambda = -(-\Delta G^0^2) / 2 \) zRT and \( z \) the cation-anion coordination number.
It should be stressed that Eq.(19) is able to take into account experimental asymmetries in binary systems and contains the non-random term $\Lambda$ which has been calculated, and not estimated by formal analogy, as previously.

The Surrounded Ion Model has also been extended to quaternary reciprocal molten salt solutions [43] and to asymmetrical ternary reciprocal mixtures ($A^{2+}, B^+/X^-, Y^-$)[44].

4. 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, the molten salt mixtures made from an ionic salt and of a covalent salt. Mixtures obtained from alkali halides AX (e.g. fully ionic salts) and transition, rare-earth, actinide, ..., metal halides MX$_i$ (e.g. covalent salts), are examples of such melts, generally characterized by the formation of heterogeneous ionic complexes such as AlCl$_4^-$ and Al$_2$Cl$_7^{2-}$, etc.

Very few exists on the thermodynamics of such systems. The reason is two-fold: because of the very different physical and chemical properties of the components, experimental investigations of the mixture are not easy and, similarly, also the theoretical approaches are not simple. Some advances are being made for systems containing alkali halides and halides of aluminum, rare earth, niobium, tantalum, bismuth, zirconium and also for the very novel low melting systems containing aluminum 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 from electrolysis of the melts, fabrication of halide glasses for optical fibers, elaboration of new materials...

A proper description of such melts can be given by models based on "associated solution" concepts. Very similar models have been developed, recently and independently, in Marseille [45] and in Trondheim [46] which are equally successful in describing the thermodynamics of BiCl$_3^-$ and AlCl$_3$-based mixtures.

The existence of complexes in molten salt mixtures has been the subject of lively discussions in the molten salt community [47]. The development of investigation methods of structure brought new arguments to the controversy and provided bases for the structural description of melts. The complexes contribute to the entropy of the mixture and should be taken into account when modeling the solution.

We recently have proposed an ideal associated model to describe the mixtures of alkali chlorides with bismuth chloride [45] or the mixtures of alkali fluorides with zirconium fluoride [48]. The excess thermodynamic quantities of the melt are assumed to only arise from the formation of complex ionic species. For the ZrF$_4$-based mixtures, for instance, the enthalpies and the constants of formation refer to the reactions:
and the enthalpy of mixing is obtained as:

$$\Delta H = \frac{n_4}{n_1 + n_3} h_1 + \frac{n_5}{n_1 + n_3} h_2$$

(22)

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

(23)

with $x = x(MF)$:

$$x = x^* \left[ \frac{1 + K_1 + K_2 x^* 2 (3 - 2x^*)}{1 + K_1 x^* (2 - x^*) + K_2 x^* 3 (4 - 3x^*)} \right]$$

(24)

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 approximative values for $h_1$ and $h_2$; they are used as the initial parameters $h_{10}$ and $h_{20}$ in the iterative procedure. Two arbitrary values are set for the initial parameters $K_{10}$ and $K_{20}$.

For each experimental data set $[x, \Delta H(x)]$, the programme solves equation (24) and calculates the solutions $x^*$.

A non-linear regression programme, applied to equation (23), yield optimized values of the parameters $h_{11}$, $h_{21}$, $K_{11}$, and $K_{21}$. If these values differ from the initial values, the programme iterates with $h_{11}$, $h_{21}$, $K_{11}$, and $K_{21}$ 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 the access to all the data relative to a system but also the assessment of these data. Assessment is made through suitable modeling and numerical procedures, and results 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 free 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 system considered; the thermodynamic functions of mixing are described either by empirical polynomial expansions or by equations deduced from theoretically based models

- the mathematical methods worked out in the search of a minimum.

For metallic systems, for instance, a very efficient program has been elaborated, and successively improved, by H.L. Lukas [49] (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 [50] [51] which is a thermodynamic data bank for molten salt mixtures. The previous optimization program has been satisfactorily used to calculate the phase diagrams of common-ion binary [52] or multicomponent [53] molten salt mixtures. But modifications were necessary to deal with the less-simple melts. For instance, the numerical procedure has been adapted to asymmetrical ionic systems [54] [55] This was made according to the theoretical developments quoted above [12-13,44]. Advances are also being made in the numerical procedures for complex systems.

REFERENCES

[1] Pechiney - French Patent FR 2 494 725.
[2] R. Sevin, J. four électri e & indus. chim., 1964, 8, 79
[3] M. Gaune-Escard, Pure & Applied Chemistry, 1983, 55, 105
[4] M. Temkin, Acta Physicochim USSR, 1945, 20, 411.
[5] M. Gaune-Escard, J.C. Mathieu, P. Desré and Y. Doucet, J. Chim. Phys., 197 n°9, 1390.
[6] M. Gaune-Escard, J.C. Mathieu, P. Desré and Y. Doucet, J. Chim. Phys., 197 9, 1397.
[7] M. Gaune-Escard, J.C. Mathieu, P. Desré and Y. Doucet, J. Chim. Phys., 197 11-12, 1666.
[8] H.K. Hardy, Acta Metallurgica, 1, 202, 1953.
[9] E.A. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.
[10] T. Førland, in "Fused Salts", B. R. Sundheim. Ed., McGraw Hill, 1964.
[11] Flory, J. P., J. Chem. Phys., 49, 3919, 1971.
[12] G. Hatem and M. Gaune-Escard, J. Chim. Phys., 7-8, 754, 1977.
[13] G. Hatem and M. Gaune-Escard, J. Chim. Phys., 77, 925, 1980.
[14] G. Hatem and M. Gaune-Escard, Thermochimica Acta, 57, 351, 1982.
[15] O. Redlich and A. T. Kister, Ind. Eng. Chem., 40, 341, 1948.
[16] F. Kohler, Monatsh. Chemie, 91, 738, (1960).
[17] C. Colinet, D. E. S. Univ. Grenoble, France (1967).
[18] Y.-M. Muggianu, M. Gambino and J.-P. Bros, J. Chim. Phys., 72, 83, 1975.
[19] G. W. Toop, Trans. TMS-AIME, 233, 850, 1965.
[20] M. Hillert, CALPHAD, 4, 1, 1980.
[21] Z. C. Wang, R. Lück and B. Predel, in Proc. CALPHAD XVIII, May 28-June 2 1989, Stockholm (Sweden).
[22] M. Gaune-Escard, J. Chim. Phys., 9, 1167, 1974.
[23] M. Gaune-Escard, J. Chim. Phys., 9, 1175, 1974.
[24] M. Blander and S. J. Yosim, J. Chem. Phys., 39, 2610, 1963.
[25] M. Hoch and I. Arpshofen, Z. Metallkd., 75, 23, 1984.
[26] M. Hoch, I. Arpshofen and B. Predel, Z. Metallkd., 75, 30, 1984.
[27] M. Hoch, CALPHAD, 9, 59, 1985.
[28] J. F. Babelot, R. W. Ohse and M. Hoch, J. Nucl. Mat., 137, 144, 1986.
[29] M. Hoch, CALPHAD, 11, 1987.
[30] M. Hoch, CALPHAD, 11, 1987.
[31] M. Hoch, in Proc. ASM Meeting, Orlando, 1986.
[32] M. Hoch, CALPHAD, 11, 1987.
[33] M. Gaune-Escard, G. Hatem, P. Gaune and M. Hoch, in Proc. 6th Int. Symp. on Halide Glasses, Clausthal, FRG, October 1-5, 1989.
[34] E. Huron and M Hoch, in Proc. 1984 Int. Symp. On Metallurgical Slags and Fluxes, D. F. Gaskell and H. A. Fine, Ed.;(pp. 305-318), AIME 1984.
[35] H. Flood, T. Førland and K. Grjotheim, Z. Anorg. Allg. Chem., 276, 289, 1954.
[36] T. Førland, in "Fused Salts", B.R. Sundheim. Ed., Mc Graw Hill, 1964.
[37] H.C. Longuet-Higgins, Proc. Roy. Soc. (London), A 205, 247, 1951.
[38] W. Brown, Proc. Roy. Soc. (London), A 240, 561, 1957.
[39] H. Reiss, J.L. Katz and O.J. Kleppa, J. Chem. Phys., 36, 144, 1962.
[40] M. Blander and J. Braunstein, Ann. New York Acad. Sci., 79, 838, 1967.
[41] M. Gaune-Escard, J.C. Mathieu, P. Desré and Y. Doucet, J. Chim. Phys., n°6 1003, 1973.
[42] M. Gaune-Escard, J.C. Mathieu, P. Desré and Y. Doucet, J. Chim. Phys., n°7-8 1033, 1973.
[43] M. Gaune-Escard, CALPHAD.
[44] G. Hatem, B. de Gasquet and M. Gaune-Escard, J. Chem. Thermodynamics 11, 927, 1979.
[45] M. Gaune-Escard, F. Tabariès and G. Hatem, Molten Salts Discussion Group London, December 1986.
[46] H.A. Øye, Molten Salts Discussion Group, London, December 1986.
[47] EUCHEM Conferences (Europe) and Gordon Conferences (USA) from 1966.
[48] G. Hatem, F. Tabariès and M. Gaune-Escard, Thermochimica Acta, 149, 15, 1989.
[49] P. Dorner, E. Th. Henig, K. Krieg, H.L. Lukas and G. Petzow, CALPHAD, 4, 241 1980.
[50] G. Hatem, Y. Fouque, J.P. Bros and M. Gaune-Escard, in Proc. 1st Int. Symp. o Molten Salt Chemistry and Technology, Kyoto, Japan, April 1983.
[51] M. Gaune-Escard, G. Hatem, Y. Fouque and J.P. Bros, CODATA Bulletin, 58 104, 1985
[52] M. Gaune-Escard, M. Gambino, G. Hatem, J.P. Bros, Y. Fouque and P. Juhem, in Proc. CALPHAD XVI, May 24-29, Irsee, FRG, 1987.
[53] P. Juhem, G. Hatem, J.P. Bros, Y. Fouque and M. Gaune-Escard, in Proc. XIV Journées d'équilibre entre phases, Montpellier, 1988,
[54] G. Hatem, M. Gaune-Escard and A.D. Pelton, J. Phys. Chem., 1982, 86, 3039.
[55] M. Gaune-Escard and G. Hatem, in Proc. High Temp. Mat. Conference, April 3-7, Gaiththersburg, USA, 1989.