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NOUVEAUX MODÈLES THERMODYNAMIQUES POUR SOLUTIONS LIQUIDES

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ÉCOLE POLYTECHNIQUE DE MONTRÉAL

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POUR SOLUTIONS LIQUIDES

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Dédicace

Cette thèse est dédiée aux membres de ma famille, Isabelle, Pascal, Nicole et André, et à mes grands-parents Yvette, Gilles, Solange et Vitalien.

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RÉSUMÉ

La prédiction des propriétés thermodynamiques et des équilibres de phases impliquant les solutions liquides joue un rôle important dans le développement et la compréhension des procédés métallurgiques. L'importance croissante de la simulation numérique des procédés métallurgiques oblige à développer des modèles thermodynamiques qui donnent de meilleures prédictions des équilibres de phases et des propriétés thermodynamiques. Les liquides utilisés en métallurgie à haute température sont des liquides de type ionique avec certaines tendances covalentes, et de type métallique. Cette thèse porte sur l'amélioration et le développement de modèles thermodynamiques qui permettent de mieux reproduire et de mieux prédire les données thermodynamiques des propriétés et des équilibres des phases impliquant ces liquides.

Concrètement, les nouveaux modèles thermodynamiques pour solutions liquides de cette thèse ont été intégrés à un système informatique reconnu mondialement en métallurgie, le système FACT (développé à l'École Polytechnique de Montréal). Le système FACT permet, à l'aide de son interface Windows, de calculer des équilibres de phases dans des systèmes métallurgiques et chimiques complexes où les énergies de Gibbs de ces phases sont représentées par des modèles thermodynamiques (dont les nouveaux modèles de cette thèse). Le système FACT accède directement les bases de données de paramètres des modèles thermodynamiques des phases pour effectuer ces calculs chimiques complexes. Une base de données complète de paramètres des nouveaux modèles appliqués aux solutions de sels fondus de chlorures et de fluorures alcalins et alcalino-terreux, très utilisés en métallurgie, a été produite dans cette thèse en plus d'une base de données sur les mélanges fondus d'oxydes alcalins avec la silice et l'alumine . Ces bases de données représentent le condensé et la synthèse de centaines, voire de milliers d'expériences de laboratoire du dernier siècle qui ont permis d'obtenir des mesures des propriétés thermodynamiques et d'équilibres des mélanges de sels et d'oxydes utilisés

en métallurgie. La modélisation thermodynamique d'un système chimique complexe passe par l'obtention de paramètres pour chaque modèle qui représente l'énergie de Gibbs d'une phase du système. Ces paramètres sont obtenus par optimisation, c'est-à-dire que ces paramètres sont ceux qui donnent le meilleur lissage (par les moindres carrés) des données thermodynamiques expérimentales reliées à ces phases. Il ne s'agit pas d'un lissage "statistique" des données (approche empirique), mais d'une obtention des paramètres de modèles théoriques qui permettent de calculer ces données. Cette base théorique permet de bien meilleures prédictions. L'intégration des nouveaux modèles de cette thèse et des paramètres de ces modèles appliqués aux mélanges de sels LiF-LiCl-(Li_2SO_4)-NaF-NaCl-(Na_2SO_4)-KF-KCl-(K_2SO_4)-(RbCl-CsCl)-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$-($SrCl_2$-$BaCl_2$), permet aux ingénieurs et chercheurs du domaine métallurgique et chimique de calculer les équilibres de phases et leurs propriétés thermodynamiques, nécessaires à la compréhension et à la quantification des procédés métallurgiques reliés à la production et à la purification des métaux réactifs (Mg, Al, Na, Sr, etc...), au soudage des ces métaux, à l'électro-déposition des métaux réfractaires (Nb, Ta, etc...), à la corrosion et à plusieurs autres phénomènes et procédés. Ces ingénieurs et chercheurs ont donc maintenant accès, à l'aide de l'interface logicielle FACT, à la capacité de calculer et de prédire les équilibres de phases pour ces applications. Cette capacité de calcul est accessible dès maintenant.

Le modèle quasichimique modifié a été développé et appliqué par notre groupe (Centre de Recherche en Calcul Thermochimique, École Polytechnique de Montréal) aux solutions liquides d'oxydes fondus, aux mattes et aux métaux liquides. Le modèle quasichimique modifié permet d'évaluer l'ordonnement premiers-voisins des atomes (liquides métalliques et mattes) ou l'ordonnement seconds-voisins (oxydes fondus) à partir de l'énergie de formation des paires d'atomes :

$$[A-Y]_{paire} + [B-X]_{paire} \Leftrightarrow [A-X]_{paire} + [B-Y]_{paire} \qquad \Delta g^{o}_{A,B//X,Y}$$

$$[A-(X-)A]_{paire}+[B-(X-)B]_{paire} \Leftrightarrow 2[A-(X-)B]_{paire} \qquad \Delta g^{o}_{A,B(//X)}$$

Le modèle ne peut cependant pas évaluer les deux types d'ordonnement simultanément. De ce fait, les systèmes réciproques montrant un fort ordonnement premiers-voisins (cation-anion) et un ordonnement seconds-voisins cationiques ne pouvaient, au début de cette thèse, être évalués avec satisfaction. Il était donc impératif d'obtenir un nouveau modèle pouvant faire de bonnes prédictions pour les systèmes à fort ordonnement premiers et seconds-voisins. Il est aussi nécessaire que les bases de données existantes de paramètres optimisés avec le modèle quasichimique modifié puissent être facilement utilisables avec le nouveau modèle, ce qui implique que le nouveau modèle doit être une amélioration du modèle quasichimique actuel.

De nombreuses améliorations ont été apportées au modèle quasichimique pour solutions liquides dans cette thèse, et elles ont été appliquées à la solution de sels fondus LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$-[LiF-NaF-KF-MgF_2-CaF_2]-[Li_2SO_4-Na_2SO_4-K_2SO_4] et au liquide Na_2O-K_2O-Al_2O_3-SiO_2. Ces améliorations portent principalement sur une meilleure évaluation de l'ordonnement des ions premiers et seconds-voisins dans les solutions réciproques, sur une meilleure représentation de la variation compositionnelle de l'énergie de formation des complexes dans la solution et des nombres de coordination des espèces; sur l'intégration du modèle d'association au modèle quasichimique afin de traiter l'effet structural de compensation de charge dans les laitiers (Na_2O-K_2O-Al_2O_3-SiO_2); et d'une généralisation et extension des principaux modèles géométriques d'estimation des propriétés thermodynamiques des systèmes multicomposants à partir des paramètres du modèle des sous-systèmes binaires.

Les équations du modèle quasichimique amélioré ont été dérivées du modèle quasichimique modifié en un premier temps, avec les variations compositionnelles des énergies des paires et des nombres de coordination. Le modèle a été codé dans le programme de calcul d'équilibre de phases EQUILIB du système FACT, et le code a été

testé avec des systèmes hypothétiques contenant tous les types d'interactions permises par le modèle. Le modèle a été testé avec la solution liquide LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$, ce qui pemet d'évaluer la capacité du modèle a reproduire les propriétés thermodynamiques et les équilibres de phases d'une solution multicomposante multivalente d'intérêt industriel avec propriétés acide/base, et avec des tendances à l'ordonnement s'étendant sur une large gamme énergétique. Pour les mêmes raisons, la solution liquide LiF-NaF-KF-MgF_2-CaF_2 a été aussi optimisée avec le nouveau modèle. Dans le but d'éventuellement traiter avec un modèle à venir, le système réciproque LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$, les systèmes binaires LiF-LiCl, NaF-NaCl, KF-KCl, MgF_2-$MgCl_2$ et CaF_2-$CaCl_2$ ont aussi été optimisés. Pour tous ces systèmes, les données thermodynamiques disponibles (diagrammes de phases, projections du liquidus, activités, enthalpies et capacités thermiques) ont toutes été reproduites avec une bonne précision à l'aide d'un ensemble de paramètres consistant et montrant une certaine linéarité dans leurs valeurs tel qu'attendu pour les mélanges de sels alcalins et alcalino-terreux. Ceci est aussi valide pour les paramètres obtenus pour les solutions solides (perovskites, etc...) et pour les composés purs associés à ces systèmes. Les paramètres des modèles ont été obtenus par optimisation des propriétés thermodynamiques et des équilibres de phases.

La méthode d'optimisation consiste à trouver, à l'aide de la méthode des moindres carrés, l'ensemble de paramètres des modèles de toutes les phases d'un système chimique qui minimise les erreurs entre les calculs des propriétés thermodynamiques et les équilibres de phases effectués à l'aide de ces paramètres et les données thermodynamiques expérimentales obtenues dans la littérature. Les paramètres des modèles pour les phases des sous-systèmes binaires sont d'abord obtenus à l'aide des données expérimentales binaires (et parfois ternaires). Ensuite cet ensemble de paramètres binaires est utilisé, à l'aide du modèle, pour calculer les propriétés et les équilibres de phases des sous-systèmes ternaires. De petits paramètres ternaires peuvent être ajoutés afin d'améliorer les calculs ternaires si nécessaire. L'ensemble des

paramètres binaires et ternaires est ensuite utilisé, à l'aide du modèle, pour calculer les propriétés thermodynamiques et les équilibres de phases multicomposants. Étant donné le faible nombre de données expérimentales pour les systèmes multicomposants, ces calculs sont souvent des prédictions, qui sont utiles pour des calculs industriels (justement à cause du manque de données).

Une nouvelle approche quasichimique qui remplace le traitement des paires d'espèces par un traitement de quadruplets d'espèces a été développée avec toutes les équations d'énergie de Gibbs. Ce nouveau modèle quasichimique a été développé de sorte que le modèle des paires (traitement quasichimique classique) puisse être un sous-système exact du traitement par quadruplets. Les concentrations de quadruplets à l'équilibre permettent d'évaluer les concentrations de paires premiers et seconds-voisins dans la solution, d'où le fait que pour une solution à ion-commun le modèle se réduise exactement au modèle quasichimique amélioré. Les équations du nouveau modèle ont été codées dans le programme de minimisation de l'énergie de Gibbs EQUILIB de FACT, et le code a été testé sur un système hypothétique qui inclut toutes les interactions possibles traitables par le modèle. Ensuite le modèle a été appliqué à la solution réciproque LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ pour vérifier sa capacité à reproduire les équilibres de phases multicomposants. Toutes les projections du liquidus des sous-systèmes ternaires reciproques ont été reproduites à l'aide du modèle; et la plupart des données du liquidus des sous-systèmes réciproques quaternaires et multicomposants ont été reproduites avec satisfaction par le modèle. Ces résultats sont très satisfaisants sachant que le système étudié montre de très fortes tendances à l'ordonnement des atomes tant pour les premiers que pour les seconds voisins.

L'effet de compensation de charge sur l'énergie de Gibbs des laitiers riches en SiO_2 et contenant Al_2O_3 avec des oxydes alcalins (Na_2O et K_2O) a été modélisé par l'intégration d'espèces associées $NaAlO_2$ et $KAlO_2$ (issues du modèle d'association) au modèle

quasichimique appliqué aux oxydes fondus. Ainsi, le système quaternaire SiO_2-Al_2O_3-Na_2O-K_2O a été étendu pour fin de modélisation à un système à 6 composants SiO_2-Al_2O_3-Na_2O-K_2O-$NaAlO_2$-$KAlO_2$ afin de reproduire les liquidus de la silice et de la mullite qui montrent que les cations Al^{3+} et Na^+/K^+ penètrent dans le réseau tétraédrique de la silice fondue sans le détruire en étant couplés sous la forme d'une seule particule.

Pour les modèles thermodynamiques en général, et pour les modèles des liquides en particulier, les méthodes d'estimation « géométriques » des propriétés thermodynamiques de systèmes ternaires et multicomposants à partir des paramètres binaires du modèle ont été revues, critiquées, améliorées et généralisées dans cette thèse dans le but d'obtenir les meilleures reproductions et prédictions possibles des propriétés thermodynamiques et des équilibres de phases.

Cette thèse donne au domaine de la modélisation thermodynamique, celle des liquides ioniques et des sels fondus en particulier, de meilleurs outils de calcul et de prédiction des propriétés thermodynamiques et des équilibres de phases. Ces outils permettent le calcul et la prédiction des propriétés thermodynamiques et des équilibres de phases dans des systèmes réciproques multicomposants à fortes tendances d'ordonnement des ions premiers et seconds-voisins, ce qui n'était pas possible avant. De plus, une base de données complète et consistante sur les systèmes de sels de chlorures alcalins et alcalino-terreux a été produite, qui inclut plusieurs fluorures, et qui peut servir de base à l'analyse et l'optimisation de la thermodynamique d'un grand nombre de systèmes de sels fondus utilisés comme électrolytes ou flux dans le secteur métallurgique pour la production, la déposition, le soudage et l'affinage de métaux réactifs (Al, Mg, Li, Na, K, La, Ce, Nd, Ta, Nb, etc...).

ABSTRACT

The prediction of thermodynamic properties and phase equilibria related to liquid solutions can play an important role in the development and understanding of metallurgical processes. The importance of numerical simulation of metallurgical processes is increasing, and the thermodynamic models must follow and be able to calculate and predict phase equilibria and thermodynamic properties of complex mixtures. The liquids used in high temperature metallurgical processes are generally ionic liquids with some covalent bonding, or metallic liquid solutions. The subject of this thesis is the improvement and the development of thermodynamic models, in order to obtain better fits and predictions of thermodynamic properties and phase equilibria related to these liquid phases.

The new thermodynamic models for liquid solutions developed in this thesis were integrated to the well-known FACT system (developed at l'École Polytechnique de Montréal). The FACT system, with its Windows interface, can calculate phase equilibria in complex metallurgical and chemical systems with the help of thermodynamic models describing the Gibbs energy of every phase in the system. FACT directly access databases containing the models parameters of these phases. New databases have been integrated for the parameters of the new models applied to the molten salt solutions of alkali alkaline-earth chlorides and fluorides (used commonly in metallurgical processes) and Na_2O-K_2O-Al_2O_3-SiO_2 melts. These databases represent the synthesis of hundreds of experiments accumulated in the last century on thermodynamic properties and phase equilibria related to these systems. The thermodynamic modelling of a complex chemical system starts by finding a set of model parameters for all phases in the system. These parameters are obtained by optimization of all available literature data related to the phases of the system. In these optimizations, a single set of parameters is found that minimizes the errors between the

model calculations and the experimental data. It is not a purely statistical method because the models are derived from physical and chemical theories, so predictions are possible outside the range of experimental data. The integration in the FACT system of the new models and the new databases of parameters related to the mixtures of LiF-LiCl-(Li_2SO_4)-NaF-NaCl-(Na_2SO_4)-KF-KCl-(K_2SO_4)-(RbCl-CsCl)-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$-($SrCl_2$-$BaCl_2$) salts gives the metallurgical and chemical engineers and researchers the capacity to calculate and predict the phase equilibrium and the thermodynamic properties of this system. This is of great importance for the understanding of industrial processes related to the production of reactive metals (Mg, Al, Na, Sr, ...), the welding of these metals, the electroplating of refractory metals (Nb, Ta, ...), corrosion, and many other processes. Engineers and researchers can now calculate with FACT the thermodynamic properties and phase equilibria in these applications.

The modified quasichemical model has been developed and used by our group (Centre for Research in Computational Thermochemistry, École Polytechnique de Montréal) for the thermodynamics of slags, mattes and liquid metals. This model evaluates the ordering of atoms with 1st nearest-neighbor (liquid metals and mattes) or 2nd nearest-neighbor (slags) pairs as a function of the Gibbs energies of formation of the pairs :

$$[A-Y]_{pair} + [B-X]_{pair} \Leftrightarrow [A-X]_{pair} + [B-Y]_{pair} \qquad \Delta g^{o}_{A,B//X,Y}$$

$$[A-(X-)A]_{pair} + [B-(X-)B]_{pair} \Leftrightarrow 2[A-(X-)B]_{pair} \qquad \Delta g^{o}_{A,B(//X)}$$

However, the model cannot take into account both 1st and 2nd nearest-neighbor ordering simultaneously. No reliable thermodynamic model for reciprocal liquid solutions exhibiting both 1st and 2nd nearest-neighbor ordering was available for large database development at the beginning of this thesis. A new model able to make reliable

predictions in multicomponent reciprocal systems with variable 1st and 2nd nearest-neighbor ordering tendencies was therefore be developed. It was desired that the new model be able to incorporate current thermodynamic databases developed over the years with the modified quasichemical model. Therefore the new model was based upon the modified quasichemical model.

The modified quasichemical model for liquid solutions has been improved in this thesis and has been applied to a new optimisation of the molten salt phase of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$-[LiF-NaF-KF-MgF_2-CaF_2]-[Li_2SO_4-Na_2SO_4-K_2SO_4] system and to the Na_2O-K_2O-Al_2O_3-SiO_2 silica-rich liquid. The improvements are a simultaneous treatment of 1st and 2nd nearest-neighbor ordering, a better composition variation of the Gibbs energy of formation of liquid complexes and species coordination numbers, an integration of "chemical associates" from the association model into the quasichemical model for the thermodynamics of the structural charge compensation effect in SiO_2-Al_2O_3-alkali oxides melts, and an extended generalized "geometric" model for the estimation of ternary and multicomponent thermodynamic properties of a phase from optimized binary model parameters.

The Gibbs energy equations of the modified quasichemical model were improved by modifying the composition variation of the Gibbs energy of formation of pairs as a function of equilibrium pair mole fractions instead of species mole (or equivalent) fractions. The species coordination numbers were also made a function of composition. The model equations were coded into the Gibbs energy minimization program EQUILIB of the FACT system (Facility for the Analysis of Chemical Thermodynamics), and the coding was tested with a hypothetical system containing all possible interactions considered by the model. Then the model was applied to (and tested on) the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ molten salt solution. The application of the improved modified quasichemical model to this system of industrial interest permits an evaluation of the ability of the model to cope with a

large multicomponent multivalent acid/base solution with a wide range of ordering tendencies. For the same reasons, the model was applied to the thermodynamics of the liquid phase of the LiF-NaF-KF-MgF_2-CaF_2 system. In order to use the previous optimizations of common-ion systems in the evaluation of the thermodynamics of the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ reciprocal system with the new model, the common-cation LiF-LiCl, NaF-NaCl, KF-KCl, MgF_2-$MgCl_2$ and CaF_2-$CaCl_2$ binary systems were also optimized with the new model for the liquid phase. For all these systems, all the available binary, ternary and multicomponent thermodynamic data (phase diagrams, liquidus projections, activities, enthalpies, heat capacities) were accurately reproduced with a consistent set of parameters that also shows the expected trends. The optimizations also include modeling of the solid solutions (perovskites, etc...) with appropriate models, and optimized properties of the pure compounds. These parameters were obtained by optimization of thermodynamic properties and phase equilibrium data.

The optimization technique consists in finding (by least squares techniques) the set of models parameters that minimizes the errors between calculated thermodynamic properties and phase equilibria, and the same experimental data found in literature. The parameters of the binary subsystems are found first from binary (and possibly ternary) experimental data. Then the model is used to calculate the thermodynamic properties and phase equilibria in the ternary subsystems, and the results are compared with experimental data. If necessary, small ternary empirical parameters can be added to the model set of parameters in order to refine the calculations. The set of binary and ternary parameters is then used, with the model, to predict the thermodynamic properties (and related phase equilibria) of the multicomponent system where few experimental data exist.

A new quasichemical model using quadruplets instead of pairs of species has been developed. This new model has been developed in such a way that it reduces exactly to

the improved modified quasichemical model for common-ion systems. The use of quadruplets of species containing 2 cations and 2 anions permits the consideration of 1st nearest-neighbor cation-anion pairs and 2nd nearest-neighbors cation-cation and anion-anion pairs. Reciprocal solutions with 1st and 2nd nearest-neighbor ordering can be evaluated with this model. The Gibbs energy equations of the model were coded into the EQUILIB program of the FACT system and the code was tested with a hypothetical system containing all possible interactions that can be treated by the model. The model was then applied to the optimization of the reciprocal multicomponent multivalent solution LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ with success. The model reproduced all ternary reciprocal liquidus data, and most quaternary and multicomponent reciprocal liquidus data were satisfactorily reproduced considering that very strong 1st and 2nd nearest-neighbor interactions are present in this system.

The well known charge compensation effect in silica-rich SiO_2-Al_2O_3-Na_2O-K_2O slags has been treated by the integration of the associate species $NaAlO_2$ and $KAlO_2$ into the existing quasichemcial model database. The silica and mullite liquidus were fitted with good precision only by introducing these species in the liquid model as associate species in the association/quasichemical model. These new species shows that Al^{3+} and Na^+/K^+ ions enter the molten SiO_2 tetrahedral network as a single species replacing the Si^{4+} cation without destroying its quasi-lattice.

The "geometric" models for the estimation of the thermodynamic properties of ternary and multicomponent solutions from optimized binary model parameters were reviewed, analyzed, improved and generalized in this thesis in order to obtain a better fitting and predictions of phase equilibria and thermodynamic properties of phases in general, and of liquids in particular.

From a general point of view, this thesis contributes to the thermodynamic modeling of solutions, especially ionic liquids and molten salts, and provides new tools for the

development of large databases for thermodynamic properties and phase equilibrium calculations and predictions. Moreover, a full and self-consistent database for a chloride-based alkali-alkaline-earth liquid phase has been obtained, with some reciprocal fluoride additions, together with the Gibbs energies of all solid solutions and pure compounds. This new database can be used as a base and starting point for the development of databases related to the thermodynamics of molten high-temperature metallurgical electrolytes and fluxes for the production, deposition, welding and purification of reactive metals (Al, Mg, Li, Na, K, La, Ce, Nd, Ta, Nb, etc...).

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α	Proportion de complexes $MgCl_4^{2-}$
a_i	Activité de l'espèce *i*
∂	Dérivée partielle
δ_{ij}	Delta Kronecker (vaut 1 si $i=j$, vaut 0 si $i \neq j$)
c_p	Capacité thermique molaire (J/mol-K)
C_p	Capacité thermique (J/K)
ε_{ij}	Énergie d'une paire d'espèces *i-j* (J)
$\varepsilon_{ij...}$	Énergie adimensionnelle d'une interaction d'espèces *i-j*
$\Delta\varepsilon_{ij}$	Différence d'énergie de formation d'une paire d'espèces *i-j* (J)
$\Delta e^{ACl}_{MgCl_4^{2-}}$	Énergie de la réaction $Mg^{2+}+4\ Cl^- \Leftrightarrow MgCl_4^{2-}$ dans ACl liquide pur (J/mol)
$\Delta e^{MgCl_2}_{MgCl_4^{2-}}$	Énergie de la réaction $Mg^{2+}+4\ Cl^- \Leftrightarrow MgCl_4^{2-}$ dans $MgCl_2$ liquide pur (J/mol)
$\in$	Appartient à
η_{ij}	Différence d'entropie molaire de formation de paire d'espèces *i-j* (J/mol-K)
$f()$	Fonction
F_i	Énergie libre de Helmholtz de l'espèce *i* (J)
ΔF^m	Différence d'énergie d'Helmholtz totale de mélange (J)
g	Énergie de Gibbs molaire (J/mol)
g^E	Énergie de Gibbs molaire en excès (J/mol)
g^{mm}	Énergie de Gibbs molaire de mélange mécanique des espèces (J/mol)
g_i	Énergie de Gibbs molaire partielle de l'espèce *i* (J/mol)
g_{ca}	Ratio λ / λ_{ca} du cation *c* et de l'anion *a*
g_i^o	Énergie de Gibbs molaire standard de l'espèce *i* (J/mol)
Δg	Différence d'énergie de Gibbs molaire (J/mol)

Δg^m	Différence d'énergie de Gibbs molaire de mélange (J/mol)
$\Delta g^{éch}$	Différence d'énergie de Gibbs molaire d'échange d'ions premiers-voisins (J/mol)
Δg_{ij}	Différence d'énergie molaire de formation de paire d'espèces *i-j* (J/mol-K)
Δg_i^o	Différence d'énergie de Gibbs molaire standard de l'espèce *i* (J/mol)
G	Énergie de Gibbs totale (J)
G^E	Énergie de Gibbs totale en excès (J)
ΔG	Différence d'énergie de Gibbs totale (J)
ΔG^m	Différence d'énergie de Gibbs totale de mélange (J)
$\Delta G^{ass}_{A_aB_b}$	Différence d'énergie de Gibbs de formation du complexe associé A_aB_b (J)
γ_i	Coefficient d'activité de l'espèce *i*
γ_i^o	Coefficient d'activité Henrien de l'espèce *i*
h	Enthalpie molaire (J/mol)
Δh	Différence d'enthalpie molaire (J/mol)
Δh^m	Différence d'enthalpie molaire de mélange (J/mol)
H	Enthalpie totale (J)
H_i	Enthalpie "totale" partielle de l'espèce *i* (J)
ΔH	Différence d'enthalpie totale (J)
ΔH^m	Différence d'enthalpie totale de mélange (J)
k	Constante de Boltzmann (R/N_{Av} = 1.3805 x 10^{-23} J/mol-K)
K_{equ}	Constante d'équilibre
λ	Somme de référence des rayons cationique et anionique (m)
λ_{ca}	Somme des rayons du cation *c* et de l'anion *a* (m)
ln	Logarithme naturel
N_{Av}	Nombre d'Avogadro (6.023 x 10^{23} molécules/mol)
n_i	Nombre de moles de l'espèce *i*

N_i	Nombre d'espèces i
Ω	Nombre de permutations possibles (entropie)
$\Omega()$	Fonction de la température de Reiss, Katz et Kleppa (1962)
P	Pression (atm)
P_i	Pression partielle de l'espèce i (atm)
q	Charge ionique
$\Phi^{()}_{ij..}$	Paramètre énergétique d'un modèle (J/mol) – peut être une fonction de T
$q^{()}_{ij..}$	Paramètre énergétique d'un modèle (J/mol) – peut être une fonction de T
R	Constante des gas (8.31451 J/mol-K)
r_i	Rayon ionique de l'espèce i (m)
s	Entropie molaire (J/mol-K)
Δs	Différence d'entropie molaire (J/mol-K)
Δs^m	Différence d'entropie molaire de mélange (J/mol-K)
S	Entropie totale (J/K)
ΔS	Différence d'entropie totale (J/K)
ΔS^m	Différence d'entropie totale de mélange (J/K)
$\Delta S^{idéale}$	Différence d'entropie totale configurationnelle de Bragg-Williams (J/K)
T	Température absolue (K)
U	Énergie potentielle totale (J)
u_{ij}	Potentiel de paire ionique i-j (J)
μ_i	Potentiel chimique de l'espèce i
μ_i^o	Potentiel chimique de référence de l'espèce i
V	Volume (m^3)
υ	Nombre de particules
Va	Lacune
ΔV^m	Différence volumique de mélange (m^3)

ω_{ij}	Différence d'énergie (enthalpie) molaire de formation de paire d'espèces *i-j* (J/mol)
X_i	Fraction molaire de l'espèce *i*
X_{ij}	Fraction molaire de la paire d'espèces *i-j*
$X_{i/j}$	Fraction molaire de la paire d'espèces *i-j* (premiers-voisins)
y	Déviation au mélange aléatoire pour les concentrations de paires d'espèces
y_i	Fraction molaire du quasi-réseau de l'espèce *i*
Y_i	Fraction équivalente (de coordination) de l'espèce *i*
Z	Nombre de coordination (premiers ou seconds voisins)
Z	Intégrale volumique de configuration (fonction)
Z_i	Nombre de coordination de l'espèce *i* (premiers ou seconds voisins)
Z_i	Intégrale volumique de configuration (fonction)
Z_{ij}^{i}	Nombre de coordination de l'espèce *i* dans une solution hypothétique formée que de paires d'espèces *i-j*
ξ_i	Fraction compositionnelle du groupe auquel appartient l'espèce *i*
$\xi_{i.j}$	Fraction compositionnelle du sous-groupe *i* du groupe *j*

1. Introduction

Les phases liquides sont parties intégrantes d'une grande variété de procédés métallurgiques et chimiques. Qu'ils soient produits de réactions ou réactifs, simples solvants ou lubrifiants, les liquides, de par leurs propriétés physiques et chimiques, ont acquis une place de choix dans l'activité humaine, tout en conservant leur place dominante à la surface et au coeur de notre Terre. Tant pour l'activité humaine que pour la géophysique et la géochimie, l'eau a toujours été le liquide par excellence; celui qui est intrinsèquement au coeur de nos vies, mais aussi de notre industrie. C'est particulièrement vrai pour l'industrie métallurgique et chimique qui en consomme énormément. L'eau n'est cependant pas aussi dominante en métallurgie, lorsque les procédés nécessitent une température élevée, transformant l'eau en vapeur. À ces températures, d'autres liquides sont utilisés, en tant que réactifs ou produits, en tant que solvants ou lubrifiants, ou pour toute autre raison, souvent dans le but d'obtenir un quelconque produit (pas nécessairement fluide) qui inondera le marché. Il s'agit de ces liquides, employés en métallurgie à haute température, qui sont au coeur de la présente recherche, et particulièrement leurs propriétés énergétiques, intimement reliées aux équilibres de phases.

L'énergétique (ou la thermodynamique) des solutions liquides doit beaucoup à Willard Gibbs (1902) qui lui donna ses premières équations, dont l'équation dite de Gibbs :

$$G = H - TS \qquad [1]$$

Où G est l'énergie de Gibbs de la phase (liquide) ou le mélange de phases, H est l'enthalpie (chaleur interne), S est l'entropie (mesure du désordre) et T la température absolue. Cette équation générale a été explicitée au cours des années par des chercheurs qui ont développé les termes H et S en fonction de leur variation selon la température, la

composition, la structure ou tout autre paramètre significatif de la phase (liquide) qui affectent l'énergie de Gibbs (G).

La présente étude porte sur le développement d'un nouveau modèle thermodynamique qui explicite l'équation de Gibbs pour des solutions liquides qui comportent un certain ordonnement des atomes, selon leur différent type. Ce modèle, distant descendant du modèle des solutions régulières, est le modèle quasichimique modifié pour solutions réciproques. Les travaux de cette thèse ont donc porté sur la formulation des équations du modèle; le codage des ces équations sous un format informatique permettant des calculs multiples de propriétés thermodynamiques et d'équilibres de phases; le test informatique de ce codage; et la validation scientifique des résultats des équations (vérifier la capacité de reproduction et de prédiction du modèle), en particulier avec un type de liquide couramment utilisé en métallurgie : le sel fondu (de manière particulière les mélanges de chlorures et de fluorures alcalins et alcalino-terreux). La capacité du modèle à être appliqué à une base de données pour un système comprenant un grand nombre de composants à été testé. De fait le modèle à été appliqué à la solution liquide à ion commun LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ et à la solution liquide réciproque LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$. Il est cependant à noter que le modèle peut aussi s'appliquer aux solutions solides où il y a mélange des espèces sur deux sous-réseaux seulement (avec certaines restrictions sur les nombres de coordination).

Buts de cette thèse :

- Améliorer le modèle quasichimique modifié pour obtenir de meilleures reproductions/prédictions des équilibres de phase et des propriétés thermodynamiques pour les solutions liquides ionique à ion commun.
- Développer un modèle quasichimique réciproque pour reproduire/prédire les équilibres de phases et les propriétés thermodynamiques pour les solutions liquides

ioniques réciproques. Ce modèle doit se réduire au modèle quasichimique modifié avec les améliorations précédentes pour le cas limite d'une solution liquide ionique à ion commun.

Moyens utilisés :

- Développement des équations des deux modèles thermodynamiques; codage de ces équations dans le programme de minimisation d'énergie de Gibbs du système FACT et validation du code par des tests fictifs.
- Critique et amélioration des techniques de prédiction des équilibres de phases et des propriétés thermodynamiques de solutions multicomposantes à partir des paramètres binaires du modèle.
- Intégration du modèle d'association au modèle quasichimique modifié afin de mieux traiter un aspect structurel du liquide : application à l'effet de compensation de charge dans le système Na_2O-K_2O-Al_2O_3-SiO_2.
- Validation du modèle quasichimique modifié (avec améliorations) sur la solution de chlorures fondus LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ et sur la solution de fluorures fondus LiF-NaF-KF-MgF_2-CaF_2.
- Validation du modèle quasichimique réciproque sur la solution de sels fondus réciproque LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$.

Nouveautés de cette thèse :

- Un nouveau modèle thermodynamique est proposé, dérivé de la théorie quasichimique, qui permet de reproduire et de prédire les propriétés thermodynamiques et les équilibres de phases de solutions liquides réciproques multicomposantes à ions de charges multivalentes, montrant de fortes tendances à l'ordonnement premiers et seconds voisins.

- Intégration des modèles quasichimique et d'association pour le traitement simultané des tendances de complexation dans les silicates fondus et de l'effet de compensation de charge dans les alumino-silicates fondus contenant des oxydes alcalins.
- Intégration des méthodes Kohler/Toop/Muggianu dans un seul formalisme multigroupe flexible permettant une meilleure prédiction des équilibres de phases et des propriétés thermodynamiques des solutions multicomposantes avec constituants à tendances acides, basiques et amphotères, à partir des paramètres binaires du modèle.
- Développement d'une base de données pour toutes les phases condensées des mélanges de chlorures alkalins et alkalino-terreux LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$.
- Développement d'une base de données pour toutes les phases condensées des mélanges de fluorures LiF-NaF-KF-MgF_2-CaF_2.
- Développement d'une base de données pour toutes les phases condensées des mélanges de chlorures et fluorures LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$.
- Développement d'une base de données pour toutes les phases condensées des mélanges de sels LiF-LiCl-Li_2SO_4-NaF-NaCl-Na_2SO_4-KF-KCl-K_2SO_4.

<u>Note :</u>

Toutes les figures calculées, montrées dans cette thèse et dans les articles qui y sont associés, ont été produites grâce au logiciel ***FIGURE*** d'édition de figures. Ce logiciel a été programmé par l'auteur de cette thèse durant ses études doctorales afin de faciliter la production et la présentation de calculs thermodynamiques complexes sous forme de figures de grande qualité pour publications.

2. Revue de la littérature sur les modèles thermodynamiques pour solutions liquides

Les liquides

Il existe différents types de liquide. Il y a les liquides moléculaires, dont l'eau est un exemple bien connu, qui sont des molécules de stoechiométrie et de structure fixes et qui interagissent entre elles (contrairement au gaz) par des forces relativement faibles (van Der Waals); il y a les liquides métalliques monoatomiques, qui sont une distribution d'atomes plus ou moins aléatoire dans un nuage électronique; il y a les liquides ioniques, comme les sels fondus, dont les interactions principales sont reliées aux forces coulombiennes (charges électroniques et rayons des ions) et aux polarisations; et il y a les liquides à liaisons covalentes, comme la silice fondue, qui montrent un fort aspect structural. D'autres types de liquide peuvent aussi exister (polymères, cristaux liquides, etc...). Certains liquides montrent une structure mixte qui mélange deux des types mentionnés.

Le modèle qui décrit l'aspect thermodynamique d'un liquide peut être fonction de la structure de ce liquide. Il est tout à l'avantage du modèle d'intégrer dans ses équations les aspects structurels du liquide afin d'améliorer sa capacité de prédiction, mais malheureusement, cela est généralement associé à une complexité mathématique qui rend le modèle moins général, donc moins applicable au développement d'une base de données couvrant un large éventail de composants chimiques. Il y a donc un compromis à faire entre une reproduction fidèle de la physique du liquide par le modèle et la capacité du modèle à être appliqué à une base de données pour une vaste gamme de liquides.

Équation de base

L'équation de Gibbs pour l'énergie d'une phase est donnée par :

$$G = H - TS \tag{2.0.1}$$

où G est l'énergie de Gibbs, H est l'enthalpie (ou chaleur), S est l'entropie et T est la température absolue. L'énergie de Gibbs pour toute transformation de phase est donnée par :

$$\Delta G = \Delta H - T\Delta S \tag{2.0.2}$$

où ΔG est le changement (ou différence) d'énergie entre l'état final et l'état initial, ΔH est le changement d'enthalpie et ΔS est le changement d'entropie.

Lorsque deux espèces pures A et B se mélangent pour former une solution (du même état physique), le changement d'énergie de Gibbs devient :

$$\Delta G^m = \Delta H^m - T\Delta S^m \tag{2.0.3}$$

où ΔH^m et ΔS^m sont l'enthalpie et l'entropie de mélange de la solution. Les différents modèles qui suivent vont expliciter ces deux valeurs (après diverses approximations) et vont permettre d'obtenir l'énergie de Gibbs, G, de la solution à partir de l'énergie des constituants pures.

Utilité des modèles thermodynamiques

La connaissance de l'équilibre des phases présentes dans un système chimique donné permet de mieux comprendre le comportement et les limites de ce système. De nombreuses données expérimentales et industrielles ont été prises à ce jour dans le but d'améliorer cette connaissance. Cependant ces données demeurent limitées et permettent souvent mal de connaître les réactions d'un système chimique à quelque changement que ce soit.

La possibilité de reproduire mathématiquement les données thermodynamiques mesurées et de prédire les valeurs des proporiétés thermodynamiques et des équilibres de phase est souhaitable afin d'améliorer la connaissance d'un système chimique.

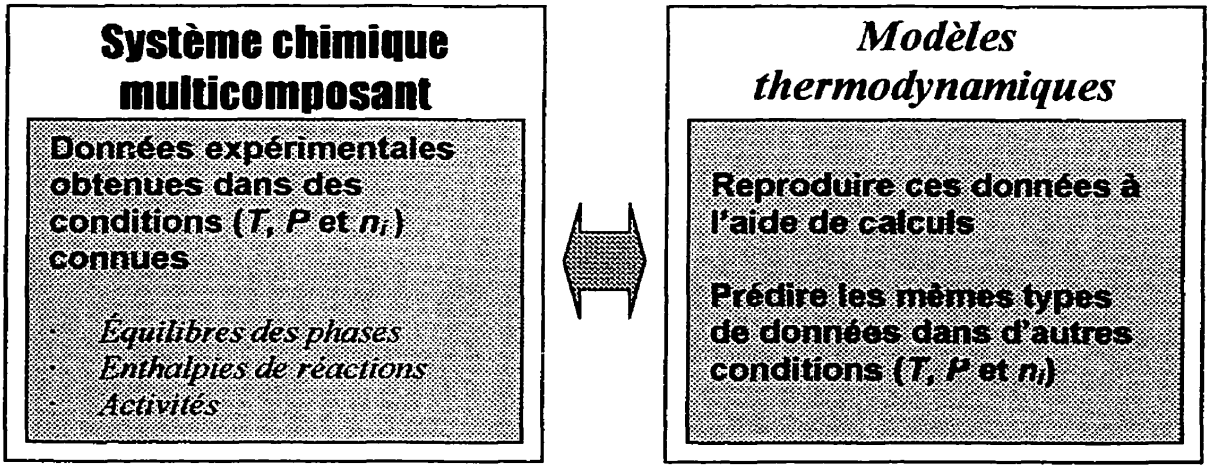


Figure 2.1 : Utilité des modèles thermodynamiques.

Les modèles thermodynamiques sont un outil mathématique qui permet de reproduire les données expérimentales portant sur les propriétés thermodynamiques et les équilibres de phases (stables ou métastables) et de prédire les valeurs similaires dans d'autres conditions opératoires. Le modèle est une fonction qui donne l'énergie de Gibbs d'une

phase ou d'un assemblage de phases selon certaines propriétés (T, P, n_i, etc...) qui peuvent inclurent des paramètres physico-chimiques de ces phases (r_i, Z_i, etc...). Cette fonction de G :

$$G = f(T, P, n_i, ...) \tag{2.0.4}$$

est reliée à l'équation 2.0.1, selon :

$$H = \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)} \right)_{P,n_i} \tag{2.0.5}$$

et

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i} \tag{2.0.6}$$

Ce qui permet d'obtenir la chaleur réactionnelle ou enthalpie (H) de même que le niveau de désordre ou entropie (S) d'une phase ou d'un assemblage de phases. De plus, la capacité calorifique (C_p – à pression constante) est obtenue selon :

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{P,n_i} \tag{2.0.7}$$

Enfin, le potentiel chimique d'un constituant i d'une solution peut être obtenu grâce à l'équation suivante :

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{2.0.8}$$

d'où son activité a_i peut être évaluée selon :

$$\mu_i - \mu_i^o = RT \ln a_i \qquad (2.0.9)$$

où μ_i^o est le potentiel chimique de l'espèce pure i dans son état de référence (appelé état standard de l'espèce i pour la solution évaluée). μ_i^o est aussi noté comme g_i^o, l'énergie de Gibbs molaire standard de l'espèce i. Il est aussi possible à partir de l'activité d'un constituant i d'une phase d'obtenir le coefficient d'activité de cette phase γ_i. Le coefficient d'activité relie l'activité a_i de l'espèce i à la concentration (X_i, $\%_i$, m_i, etc...) de cette espèce dans la phase évaluée. Cependant plusieurs définitions du coefficient d'activité existent selon les différentes réprésentations compositionnelles des modèles thermodynamiques. Pour une solution substitutionnelle où les concentrations sont les fractions molaires des constituants, l'expression suivante est souvent utilisée :

$$a_i = \gamma_i X_i \qquad (2.0.10)$$

Il est ainsi possible, à partir de la fonction mathématique du modèle qui représente le G d'une solution, de calculer des valeurs dérivées qui donnent des propriétés thermodynamiques mesurables expérimentalement (X_i, a_i, ΔH). Ces données permettent de vérifier la validité du modèle qui en retour permet de prédire ces mêmes types de valeur dans d'autres conditions.

Les équilibres de phases sont obtenus par la minimisation de l'énergie de Gibbs donnée par la fonction suivante :

$$G = \sum_{i=1}^{N_{phases}} n_i g_i \qquad (2.0.11)$$

où N_{phases} est le nombre de phases du système, n_i est le nombre de moles de la phase i et g_i est l'énergie de Gibbs molaire de cette même phase qui peut est elle-même être une fonction de sa composition interne. Mais cette minimisation de l'énergie de Gibbs totale, G, se fait sous la contrainte du bilan de masse atomique que doivent respecter les termes n_i de l'équation 2.0.11 et la composition chimique interne des phases. D'autres contraintes peuvent être exercées sur la fonction 2.0.11 pour trouver l'équilibre de phases dans des conditions particulières (par exemple un système adiabatique, $\Delta H = 0$). Pour le système *FACT*, développé par Pelton, Bale et Thompson (1999) depuis la fin des années 1970, la routine de minimisation de l'énergie de Gibbs utilisée est celle de *SOLGASMIX* développée par Eriksson (Eriksson et Rosen, 1973) qui utilise la méthode des multiplicateurs de Lagrange, où la fonction G est approximée à l'aide d'un polynôme de Taylor (où seule la première dérivée est utilisée) autour d'une composition d'équilibre estimée. La règle des phases de Gibbs doit toujours être respectée (voir Pelton, 1996) :

$$F = C - P + 2 \qquad (2.0.12)$$

où F est le nombre de paramètres (T, P, n_i, etc...) ou degrés de liberté qui doivent être spécifiés afin de complètement définir le système, C est le nombre de constituants du système et P est le nombre de phases à l'équilibre du système.

Il existe aussi d'autres manières d'obtenir l'équilibre des phases qu'en minimisant l'énergie de Gibbs. Par exemple, il suffit de stiasfaire les constantes d'équilibre de toutes les réactions chimiques possibles du système en respectant le bilan de masse.

Les modèles thermodynamiques qui explicitent les énergies de Gibbs des phases, g_i, de l'équation 2.0.11, permettent à l'industrie et aux chercheurs de comprendre le

comportement thermodynamique d'un procédé ou d'une réaction et d'optimiser les paramètres d'opération de ce procédé afin d'en améliorer le rendement (économique, environnemental, etc...). De plus, ces mêmes modèles sont des plus utiles lorsqu'un nouveau procédé est développé car la capacité prédictive du modèle est pleinement employée.

2.1. Modèle des solutions idéales

Lorsque les espèces A et B se mélangent substitutionnellement sur des sites d'espèces (positions spatiales), le terme entropique (relié au niveau de désordre de la solution) de changement de configuration (distribution des espèces) est donnée selon Boltzmann par:

$$\Delta S^{config} = k \ln \Omega \tag{2.1.1}$$

où k est la constante de Boltzmann et Ω est le nombre de permutations possibles lors du mélange. N_A espèces A et N_B espèces B sont distribuées sur $N=N_A+N_B$ sites d'espèces. Donc, on a :

$$\Omega = \frac{(N_A + N_B)!}{N_A! N_B!} \tag{2.1.2}$$

$$\Delta S^{config} = -k \ln \frac{N_A! N_B!}{(N_A + N_B)!} \tag{2.1.3}$$

Avec l'approximation de Stirling (Fraser, 1958) pour la factorielle de très grands nombres:

$$N_A! \approx (2\pi)^{\frac{1}{2}} e^{-N_A} N_A{}^{N_A + \frac{1}{2}} \tag{2.1.4a}$$

$$N_B! \approx (2\pi)^{\frac{1}{2}} e^{-N_B} N_B{}^{N_B + \frac{1}{2}} \tag{2.1.4b}$$

$$(N_A + N_B)! \approx (2\pi)^{\frac{1}{2}} e^{-(N_A + N_B)} (N_A + N_B)^{(N_A + N_B) + \frac{1}{2}} \tag{2.1.4c}$$

$$\ln N_A! = \tfrac{1}{2} \ln(2\pi) - N_A \ln e + \left(N_A + \tfrac{1}{2}\right) \ln N_A \tag{2.1.4d}$$

$$\ln N_B! = \tfrac{1}{2} \ln(2\pi) - N_B \ln e + \left(N_B + \tfrac{1}{2}\right) \ln N_B \tag{2.1.4e}$$

$$\ln[(N_A + N_B)!] = \tfrac{1}{2}\ln(2\pi) - (N_A + N_B)\ln e + \left(N_A + N_B + \tfrac{1}{2}\right)\ln(N_A + N_B) \quad (2.1.4f)$$

On obtient, en posant $n_A = N_A / N_{Av}$ et $n_B = N_B / N_{Av}$:

$$\Delta S^{config} = -N_{Av}k(n_A \ln X_A + n_B \ln X_B) - \frac{k}{2}\ln\left(\frac{2\pi N_{Av} n_A n_B}{n_A + n_B}\right) \quad (2.1.5)$$

où N_{Av} est le nombre d'Avogadro et les X_i sont les fractions molaires des espèces i données par :

$$X_i = \frac{n_i}{\sum_j n_j} \quad (2.6.1)$$

Sachant que $R = N_{Av}k$ (R est la constante des gaz), et que le second terme de l'équation 2.1.5 peut être négligé pour les très grands nombres, on a :

$$\Delta S^{config} = -R(n_A \ln X_A + n_B \ln X_B) \quad (2.1.7)$$

qui est le changement d'entropie dû au changement de configuration lors du mélange (aussi appelée entropie configurationnelle). Parce que cette entropie évalue le changement de configuration du mélange en supposant une substitution idéale des espèces sur les sites d'espèces, cette entropie configurationnelle est souvent appelée entropie idéale ou entropie de l'approximation ponctuelle. Ce type d'entropie est souvent référé comme étant l'approximation de Bragg-Williams (Ziman, 1965). Le changement vibrationnel des espèces lors du mélange, qui contribue au niveau de désordre de la solution, est négligé pour le modèle des solutions régulières, ce qui revient à dire :

$$\Delta S^m = \Delta S^{idéale} = \Delta S^{config} \tag{2.1.8}$$

Le modèle des solutions idéales suppose que l'enthalpie de mélange de la solution est nulle.

$$\Delta H^m = 0 \tag{2.1.9}$$

Cette supposition implique qu'aucune chaleur n'est échangée avec l'environnement ("l'univers") lorsque le mélange s'effectue. Ce qui est justifié par le fait qu'un mélange idéal d'espèces implique qu'aucune distinction n'est faite entre ces espèces en dehors de leur nature propre.

Les propriétés thermodynamiques molaires (par mole de solution) de mélange ($\Delta h^m, \Delta s^m$) pour le modèle des solutions idéales sont donc :

$$\Delta g^m = -T\Delta s^m \tag{2.1.10}$$

$$\Delta h^m = 0 \tag{2.1.11}$$

$$\Delta s^m = \Delta s^{idéale} \tag{2.1.12}$$

L'activité d'un constituant de la solution idéale, a_i, est simplement donnée par la fraction molaire de ce constituant dans la solution, X_i, car :

$$RT \ln a_i = \frac{\partial \Delta G^m}{\partial n_i} \tag{2.1.13}$$

$$RT \ln a_i = \frac{\partial \left(RT \left[n_i \ln X_i + n_j \ln X_j \right] \right)}{\partial n_i} = RT \ln X_i \tag{2.1.14}$$

L'énergie de Gibbs totale de la solution peut être calculée avec l'énergie de Gibbs de mélange, ΔG^m, et l'énergie de Gibbs molaire des constituants (purs) de la solution (g_A^o et g_B^o) selon :

$$G = n_A g_A^o + n_B g_B^o + \Delta G^m = n_A g_A^o + n_B g_B^o - T\Delta S^{idéale} \tag{2.1.15}$$

Pour une solution idéale multicomposante ($i = A, B, C, \ldots$), l'énergie de Gibbs est donnée par :

$$G = \sum_i n_i \left(g_i^o + RT \ln X_i\right) \tag{2.1.16}$$

Ce qui peut être relié à l'équation de Gibbs, $G = H - TS$, (équation 2.0.1) :

$$G = \sum_i n_i \left(h_i^o - T\left(s_i^o - R \ln X_i\right)\right) \tag{2.1.17}$$

$$H = \sum_i n_i h_i^o \tag{2.1.18}$$

$$S = \sum_i n_i \left(s_i^o - R \ln X_i\right) \tag{2.1.19}$$

avec

$$h_i^o = h_{298.15K}^o(i) + \int_{298.15K}^{T} c_p(i) dT \tag{2.1.20}$$

$$s_i^o = s_{298.15K}^o(i) - \int_{298.15K}^{T} \frac{c_p(i)}{T} dT \tag{2.1.21}$$

où $h_{298.15K}^o(i)$ est l'enthalpie molaire standard (constante), $s_{298.15K}^o(i)$ est l'entropie molaire standard (constante) et $c_p(i)$ est la capacité calorifique molaire (fonction de la température) du constituant i pur.

2.2. Modèle des solutions régulières

Lorsque les espèces A et B se mélangent substitutionnellement sur des sites d'espèces (positions spatiales), la différence d'enthalpie entre le mélange final et les mêmes quantités des espèces A et B pures dans le même état (solide, liquide, gas, etc...) est donnée par :

$$\Delta H^m = n_{solution} h_{solution} - n_A h_A - n_B h_B \tag{2.2.1}$$

où $n_{solution}$ est le nombre de moles de solution, n_i est le nombre de moles de l'espèce i (A ou B) et h_i est l'enthalpie molaire de l'espèce i pure, avec :

$$n_{solution} = n_A + n_B \tag{2.2.2}$$

La différence d'enthalpie molaire de mélange, Δh^m, est obtenue en divisant ΔH^m par le nombre de moles de solution.

$$\Delta h^m = \frac{\Delta H^m}{n_{solution}} = \frac{\Delta H^m}{n_A + n_B} = h_{solution} - X_A h_A - X_B h_B \tag{2.2.3}$$

L'enthalpie molaire de la solution peut être évaluée à partir de la réaction quasichimique suivante (car elle implique les paires d'espèces du mélange et non les espèces elles-mêmes) :

$$[A-A]_{paire} + [B-B]_{paire} \Leftrightarrow 2[A-B]_{paire} \tag{2.2.4}$$

dont l'énergie totale pour 2 paires est donnée par :

$$\Delta\varepsilon_{AB} = 2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB} \tag{2.2.5}$$

où les ε_{ij} sont les énergies des paires d'espèces (peuvent être fonction de la température). En supposant les ε_{ij} indépendantes de la température, l'enthalpie molaire de la solution est donc :

$$h_{solution} = \frac{N_{Av}Z}{2}\left(X_{AB}\varepsilon_{AB} + X_{AA}\varepsilon_{AA} + X_{BB}\varepsilon_{BB}\right) \tag{2.2.6}$$

où les X_{ij} sont les fractions molaires (proportions ou probabilités) des paires *i-j* dans le mélange. Le changement d'enthalpie molaire lors du mélange formant la solution à partir des espèces A et B pures est (en supposant $\varepsilon_{AA} = \varepsilon^{o}_{AA}$ et $\varepsilon_{BB} = \varepsilon^{o}_{BB}$ où ε^{o}_{ii} est l'énergie de la paire *i-i* dans *i* pure) :

$$\Delta h^{m} = \frac{N_{Av}Z}{2}\left(X_{AB}\varepsilon_{AB} + X_{AA}\varepsilon_{AA} + X_{BB}\varepsilon_{BB}\right) - X_{A}\frac{N_{Av}Z}{2}\varepsilon_{AA} - X_{B}\frac{N_{Av}Z}{2}\varepsilon_{BB} \tag{2.2.7}$$

Le modèle des solutions régulières suppose que le mélange des espèces A et B sur les sites d'espèce se fait de façon aléatoire (l'enthalpie dérivée de l'énergie des liaisons ε_{ij} n'influence pas la configuration du mélange). Cette approximation, suggérée par Bragg-Williams (Ziman, 1965), permet d'évaluer à partir des probabilités les fractions molaires des paires X_{AA}, X_{BB} et X_{AB} qui autrement seraient des inconnues. De cette façon, on obtient :

$$X_{AA} = X_{A}^{2} \tag{2.2.8a}$$

$$X_{BB} = X_{B}^{2} \tag{2.2.8b}$$

$$X_{AB} = 2X_{A}X_{B} \tag{2.2.8c}$$

Ces valeurs de X_{ij} donnent la probabilité globale (et non locale) que les espèces i et j soient des premiers voisins dans la solution. L'enthalpie molaire de mélange de la solution devient donc :

$$\Delta h^m = \frac{N_{Av}Z}{2}(2X_A X_B \varepsilon_{AB} + (X_A^2 - X_A)\varepsilon_{AA} + (X_B^2 - X_B)\varepsilon_{BB}) \tag{2.2.9}$$

$$\Delta h^m = \frac{N_{Av}Z}{2}(2X_A X_B \varepsilon_{AB} - X_A(1 - X_A)\varepsilon_{AA} - X_B(1 - X_B)\varepsilon_{BB}) \tag{2.2.10}$$

Sachant que dans un mélange binaire A-B on a que $X_A = 1\text{-}X_B$, alors :

$$\Delta h^m = \frac{N_{Av}Z}{2}[2X_A X_B \varepsilon_{AB} - X_A X_B \varepsilon_{AA} - X_A X_B \varepsilon_{BB}] \tag{2.2.11}$$

$$\Delta h^m = X_A X_B N_{Av} Z[\varepsilon_{AB} - \tfrac{1}{2}\varepsilon_{AA} - \tfrac{1}{2}\varepsilon_{BB}] \tag{2.2.12}$$

$$\Delta h^m = X_A X_B N_{Av} Z \Delta\varepsilon_{AB} \tag{2.2.13}$$

$$\Delta h^m = X_A X_B \omega_{AB} \tag{2.2.14}$$

Cette dernière expression donne le changement d'enthalpie lors de la formation de la solution à partir des espèces pures A et B dans le même état que la solution. Ayant maintenant le terme enthalpique de l'équation de Gibbs, le terme entropique (relié au niveau de désordre de la solution) doit être évalué. L'entropie du modèle des solutions régulières, qui suppose un mélange aléatoire des espèces sur les sites d'espèces, est donc la même que l'entropie idéale si le changement d'entropie vibrationelle est négligée.

Les propriétés thermodynamiques (molaires) de mélange ($\Delta h^m, \Delta s^m$) pour le modèles des solutions régulières sont donc (en supposant ε_{ij} indépendants de la température et $\varepsilon_{ii} = \varepsilon_{ii}^o$) :

$$\Delta g^m = \Delta h^m - T\Delta s^m \tag{2.2.15}$$

$$\Delta h^m = X_A X_B \omega_{AB} \tag{2.2.16}$$

$$\Delta s^m = \Delta s^{idéale} \tag{2.2.17}$$

Si le changement d'entropie vibrationelle n'est pas négligée ($\varepsilon_{ij} = f(T)$), l'enthalpie et l'entropie de mélange deviennent :

$$\Delta h^m = X_A X_B \left(\frac{\partial\left(\frac{\omega_{AB}}{T}\right)}{\partial\left(\frac{1}{T}\right)} \right)_{P,n_i} \tag{2.2.18}$$

$$\Delta s^m = \Delta s^{idéale} - X_A X_B \left(\frac{\partial \omega_{AB}}{\partial T} \right)_{P,n_i} \tag{2.2.19}$$

L'activité d'un constituant de la solution régulière, a_i, est calculée de la manière suivante :

$$RT \ln a_i = \frac{\partial \Delta G^m}{\partial n_i} \tag{2.2.20}$$

$$RT \ln a_i = \frac{\partial\left(RT\left[n_i \ln X_i + n_j \ln X_j\right] + \left(n_i + n_j\right) X_i X_j \omega_{ij}\right)}{\partial n_i} \tag{2.2.21}$$

$$RT \ln a_i = RT \ln X_i + X_j^2 \omega_{ij} \tag{2.2.22}$$

Pour les solutions de sels fondus (mélanges d'halogénures alcalins), Reiss, Katz et Kleppa (1962) ont montré, à l'aide d'intégrales de perturbation des ions, que l'enthalpie de mélange devrait suivre la relation suivante (pour un mélange de sels *AX-BX* monovalent) :

$$\Delta h^m = X_{AX} X_{BX} \Omega\left(T, P, r_{A^+}, r_{B^+}, r_{X^-}\right) \tag{2.2.23}$$

où Ω est une fonction de la température, de la pression et des rayons ioniques. Cette équation sera démontrée plus loin dans la section des solutions ioniques conformes. Cette conclusion donne une certaine validité au modèle des solutions régulières. De plus, de nombreux mélanges d'espèces chimiquement similaires (tant métalliques qu'ioniques) ont montré une enthalpie de mélange (mesurée calorimétriquement) très proche d'une fonction donnée par l'équation 2.2.16.

Pour un mélange de plusieurs espèces (A, B, C, ...), le modèle des solutions régulières s'applique de façon suivante :

$$\Delta g^m = \Delta h^m - T\Delta s^m \tag{2.2.24}$$

$$\Delta h^m = X_A X_B \omega_{AB} + X_A X_C \omega_{AC} + X_B X_C \omega_{BC} + \ldots \tag{2.2.25}$$

$$\Delta s^m = \Delta s^{idéale} = -R(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C + \ldots) \tag{2.2.26}$$

On obtient donc une simple sommation des termes en excès binaires réguliers en utilisant les fractions molaires des espèces de la solution multicomposante. L'énergie de Gibbs totale de la solution multicomposante est donc :

$$G = \sum_i n_i g_i^o + RT\sum_i n_i \ln X_i + \left(\sum_k n_k\right)\sum_i \sum_{j>i} X_i X_j \omega_{ij} \tag{2.2.27}$$

La dernière sommation de l'équation 2.2.27 est souvent appelée énergie de Gibbs en excès de la solution, G^E (g^E par mole de solution), qui peut être exprimée selon :

$$g^E = h^E - Ts^E \tag{2.2.28}$$

en utilisant les dérivées données à la section 2.0.

2.3. Expansions polynomiales de l'énergie en excès

Ce modèle, dérivé du modèle des solutions régulières (et qui peut aussi être obtenu en supposant un mélange aléatoire de triplets *AAA*, *AAB*, *BAA* et *BBB*, tout comme le modèle des solutions régulière est un mélange aléatoire de paires *AA*, *AB* et *BB*), suppose que l'énergie de formation de 2 liaisons (paires) *A-B* à partir d'une paire d'espèces *A-A* et d'une paire *B-B* est fonction de la composition globale du mélange. L'enthalpie de mélange de la solution pour une solution régulière :

$$\Delta h^m = h^E = X_A X_B \omega_{AB} \tag{2.3.1}$$

devient dans ce cas.

$$\Delta h^m = X_A X_B (f(X_A, X_B)) \tag{2.3.2}$$

L'entropie configurationnelle est la même que pour les solutions régulières. Plusieurs fonctions de la composition ont été proposées. Une fonction polynomiale générale est :

$$f(X_A, X_B) = \sum_{i,j} X_A^i X_B^j q_{AB}^{(ij)} \qquad (i, j \geq 0) \tag{2.3.3}$$

Si une des puissances i ou j vaut 0, alors le polynôme 2.3.3 est appelé polynôme de Margules.

L'entropie non-configurationnelle, ou entropie en excès, qui est fortement dépendante du changement vibrationnel des espèces lors du mélange, peut aussi être exprimée par une fonction du type 2.3.3.

L'article "Thermodynamic Optimization and Cryoscopic Measurements of the NaCl-$CaCl_2$-$MgCl_2$-CaF_2 System", montré en Annexe IX montre que tous les sous-systèmes binaires à ions communs de la solution de sels fondus (du système étudié) ont leurs propriétés thermodynamiques assez bien reproduites par une expansion polynomiale générale avec une entropie configurationnelle de type Bragg-Williams. Cependant, pour les systèmes binaires NaCl-$MgCl_2$ et NaF-MgF_2, les données thermodynamiques sont moins bien reproduites car la solution liquide a une certaine tendance à l'ordonnement des cations (cet ordonnement influence l'entropie configurationnelle diminuant ainsi la validité de la supposition d'un mélange aléatoire).

L'expansion de Redlich-Kister (1952) est souvent utilisée au lieu de l'équation 2.3.3 :

$$f(X_A, X_B) = \sum_i (X_A - X_B)^i q_{AB}^{(i)} \qquad (i \geq 0) \qquad (2.3.4)$$

Certains avantages sont reliés à l'utilisation d'un polynôme de Redlich-Kister au lieu du polynôme général. Le premier est que les paramètres $q_{AB}^{(i)}$-Redlich-Kister (2.3.4) de différentes puissances i sont moins fortement corrélés que les paramètres $q_{AB}^{(ij)}$-général (2.3.3). Une simplification mathématique peut aussi être obtenue par l'emploi de ce type d'expansion lors de l'estimation de l'enthalpie de mélange d'un système multicomposant dans certain cas. De plus, la forme des fonctions Redlich-Kister peut aider au lissage de certaines solutions, de par l'utilisation de puissances paires ou impaires uniquement. Quoiqu'il advienne, il est possible de convertir exactement les paramètres Redlich-Kister en paramètres généraux.

Pelton et Bale (1986) ont proposé l'utilisation de polynômes de Legendre qui sont moins fortement corrélés que le polynôme général et aussi moins fortement corrélés que le polynôme de Redlich-Kister.

L'entropie non-configurationnelle, ou entropie en excès, qui est dépendante du changement vibrationnel des espèces lors du mélange, peut aussi être exprimée par une fonction du même type que 2.3.4.

Pour une solution multicomposante, les propriétés en excès doivent être estimées à partir des paramètres polynomiaux des sous-systèmes binaires. Plusieurs méthodes d'estimation ont été suggérées. La figure 2.2 montre plusieurs de ces méthodes, dont les plus connues.

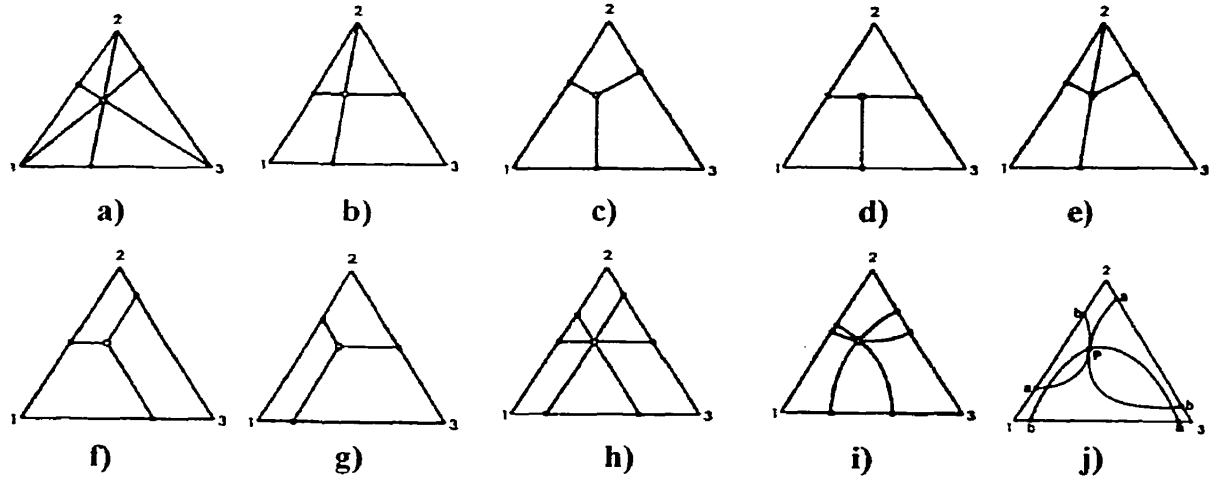


Figure 2.2 : Méthodes d'estimation des propriétés en excès d'une solution ternaire (1-2-3) à partir des paramètres polynomiaux des sous-systèmes binaires (1-2; 1-3; 2-3) : a) Kohler (1960); b) Toop (1965); c) Muggianu (1975); d) Hillert (1980); e) Li (1989); f) Chou (1987) "gauche"; g) Chou (1987) "droite"; h) Colinet (1967); i) Malakhov (1995); j) Ganesan (1997);

Les méthodes a) à g) sont des méthodes qui n'utilisent qu'une seule composition d'interpolation pour chaque sous-système binaire, alors que les méthodes h) à j) utilisent deux compositions d'interpolation. Les méthodes a), c) et f) à j) sont dites symétriques du fait que tous les paramètres binaires de la solution ont la même équation qui évalue leur contribution à l'énergie en excès totale de la solution. Les méthodes b), d) et e)

sont dites asymétriques car un paramètre des sous-systèmes binaires voit sa contribution à l'énergie en excès de la solution différemment exprimée. Une autre manière de présenter cette dualité "symétrique/asymétrique" est d'associer chacun des constituants de la solution à un groupe (qui peut être défini par la famille chimique, la charge ionique, etc...). Si les 3 constituants de la solution appartiennent au même groupe, une méthode symétrique est utilisée; si un des 3 constituants de la solution diffère des deux autres, alors une méthode asymétrique est utilisée.

Pour chacune de ces méthodes, seule la fonction $g^E/X_A X_B$ (équations 2.3.3 ou 2.3.4) est interpolée. Le type d'expansion (par exemple l'expansion de Redlich-Kister) peut simplifier la mathématique de certaine méthode d'estimation (voir commentaires dans l'article "On the Choice of "Geometric" Thermodynamic Models" (section "Kohler Versus Muggianu") en Annexe II). Une discussion de ces méthodes d'estimation est donnée à la section 3.1.

2.4. Solutions diluées

À partir de l'expansion polynomiale générale, il est possible d'obtenir des paramètres applicables pour les solutions diluées. Pour ce faire, on sait que l'activité d'un constituant d'une solution est donnée par :

$$a_A = \gamma_A X_A \tag{2.4.1}$$

Pour une solution régulière (équ. 2.2.21), on a :

$$RT \ln a_A = RT \ln X_A + RT \ln \gamma_A = RT \ln X_A + X_B^2 \omega_{AB} \tag{2.4.2}$$

Ce qui donne :

$$\ln \gamma_A = X_B^2 \frac{\omega_{AB}}{RT} \tag{2.4.3}$$

L'expansion polynomiale générale donne :

$$\frac{g^E}{RT} = \sum_i \sum_j X_A^i X_B^j \frac{\omega_{AB}^{(ij)}}{RT} = X_A \ln \gamma_A + X_B \ln \gamma_B \tag{2.4.4}$$

Ainsi, les coefficients d'activité, γ_A et γ_B, peuvent être reliés aux paramètres polynomiaux $\omega_{AB}^{(ij)}$. Cependant, pour une solution diluée, où A est le soluté et B est le solvant, la loi de Raoult dit que le coefficient d'activité de B tend vers l'unité quand X_B tend vers 1 ($\ln 1 = 0$). Avec l'ajout d'une terme Henrien, C_A, qui redéfini l'état standard du soluté, on obtient :

$$\ln \gamma_A = X_B^2 \frac{\omega_{AB}}{RT} + C_A \tag{2.4.5}$$

Cette approche est celle de Darken (1967) et est appelée "formalisme quadratique", où on a :

$$\frac{g^E}{RT} = X_A X_B \frac{\omega_{AB}}{RT} + X_A C_A \tag{2.4.6}$$

Pour une solution très diluée, le coefficient d'activité Henrien, γ_A^o, est obtenu quand $X_B \cong 1$, selon :

$$\ln \gamma_A^o = \frac{\omega_{AB}}{RT} + C_A \tag{2.4.7}$$

De plus, en effectuant le changement suivant :

$$\varepsilon_{AA} = -2\omega_{AB} \tag{2.4.8}$$

Pelton et Bale (1986) et Bale et Pelton (1990) obtiennent les relations suivantes pour un système binaire, reliées à leur modèle des paramètres d'interaction unifiés.

$$\ln \gamma_A = \ln \gamma_A^o + \varepsilon_{AA}\left(X_A - \frac{X_A^2}{2} \right) \tag{2.4.9}$$

$$\ln \gamma_B = -\frac{\varepsilon_{AA}}{2} X_A^2 \tag{2.4.10}$$

Pour une solution multicomposante, Wagner (1962) a proposé de faire dépendre le coefficient d'activité d'un soluté i dans un solvant B de la concentration des autres solutés p ($p = j, k, l, \ldots$) selon :

$$\ln \gamma_i = \ln \gamma_i^o + \sum_p \varepsilon_{ip} X_p \tag{2.4.11}$$

Cependant, Pelton (1997) donne que le formalisme de Wagner ne respecte pas l'équation de Gibbs-Duhem pour une solution non-infiniment diluée, ce que respecte le formalisme quadratique de Darken précédemment montré. Pelton et Bale (1986) et Bale et Pelton (1990) proposent pour une solution multicomposante, où A est le solvant, que les coefficients d'activité des espèces soient :

$$\ln \gamma_A = -\tfrac{1}{2}\sum_{j,k} \varepsilon_{jk} X_j X_k - \tfrac{2}{3}\sum_{j,k,l} \varepsilon_{jkl} X_j X_k X_l - \tfrac{3}{4}\sum_{j,k,l,m} \varepsilon_{jklm} X_j X_k X_l X_m - \ldots \tag{2.4.12}$$

$$\ln \gamma_i = \ln \gamma_i^o + \ln \gamma_A + \sum_j \varepsilon_{ij} X_j + \sum_{j,k} \varepsilon_{ijk} X_j X_k + \sum_{j,k,l} \varepsilon_{ijkl} X_j X_k X_l + \ldots \tag{2.4.13}$$

où i, j, k, l et m sont des solutés, et les paramètres ε_{ij}, ε_{ijk}, ε_{ijkl}, ... sont appelés paramètres d'interaction du premier, second, troisième,... ordre. La permutation des indices des paramètres d'interaction ne modifie pas la valeur du paramètre. En substituant les équations 2.4.12 et 2.4.13 dans l'équation 2.4.4 (sous sa forme multicomposante), on obtient :

$$\frac{g^E}{RT} = \sum_i X_i \ln \gamma_i^o + \tfrac{1}{2}\sum_{i,j} \varepsilon_{ij} X_i X_j + \tfrac{1}{3}\sum_{i,j,k} \varepsilon_{ijk} X_i X_j X_k + \ldots \tag{2.4.14}$$

Ce qui revient à l'expansion polynomiale générale lorsque i, j et k sont des solutés et que des « termes ternaires » sont ajoutés.

Les modèles des solutions diluées peuvent être plus complexes que le petit fragment présenté dans cette thèse. Ils peuvent inclure la présence de particules associées qui modifient grandement les propriétés de solutions diluées multicomposantes : généralement un atome non-métallique couplé à un atome métallique comme Al et O (voir Bouchard et Bale, 1995). De plus, les méthodes d'estimation des propriétés multicomposantes des solutions, telles que les méthodes de Kohler, Toop et Muggianu peuvent être intégrées aux formalismes des solutions diluées.

Contrairement aux liquides métalliques, que l'on tente généralement en métallurgie de produire avec une grande pureté, les sels fondus sont plus souvent utilisés comme des mélanges complexes des plusieurs sels de différentes familles chimiques. Le modèle des solutions diluées voit son utilité diminuée pour de telles solutions dans l'optique du développement d'une base de données de paramètres pour les applications métallurgiques.

2.5. Solutions aqueuses

Les modèles les plus répendus pour les solutions aqueuses sont le modèle de Pitzer (Pitzer, 1973) et de Helgeson (Helgeson, 1967). L'étude des solutions aqueuses n'est pas incluse dans cette thèse, mais de nombreux travaux permettent de mettre en valeur le modèle de Pitzer (entre autre, voir Kaasa, 1998).

Cependant, la dilution de l'eau dans d'autres types de solution doit être traitée par le modèle choisi pour cette solution. La dilution de l'eau dans une solution ionique de type sels fondus peut se faire en considérant la dissociation de l'eau en ions H_3O^+ et OH^-.

2.6. Modèle des complexes anioniques particuliers

Le modèle a été développé pour évaluer la complexation de certaines espèces dans les mélanges liquides. Pelton et Thompson (1970) ont développé ce modèle pour les solutions binaires de $MgCl_2$ et de $NiCl_2$ avec les sels monovalents LiCl, NaCl, KCl, RbCl, CsCl et AgCl (ou ACl). Le modèle suppose qu'une fraction des cations Mg^{2+} et Ni^{2+} vont former des « complexes anioniques » $MgCl_4^{2-}$ et $NiCl_4^{2-}$ qui fixent un certain nombre d'anions Cl^-; le reste des cations Mg^{2+} et Ni^{2+} sont considérés comme étant libres. Le modèle s'applique à toute concentration binaire ACl-$MgCl_2$ (ou ACl-$NiCl_2$), de ACl pur à $MgCl_2$ pur. Cela implique la réaction suivante pour le $MgCl_2$ pur :

$$2MgCl_2 \Leftrightarrow Mg^{2+} + MgCl_4^{2-} \tag{2.6.1}$$

Dans la solution, n_{ACl} et n_{MgCl_2} moles de ACl et $MgCl_2$ sont présentes (A = Li, Na, K, Rb, Cs ou Ag), ce qui permet de calculer les fractions molaires globales selon :

$$X_{ACl} = \frac{n_{ACl}}{n_{ACl} + n_{MgCl_2}} \tag{2.6.2}$$

$$X_{MgCl_2} = \frac{n_{MgCl_2}}{n_{ACl} + n_{MgCl_2}} \tag{2.6.3}$$

La proportion de Mg^{2+} complexée en $MgCl_4^{2-}$ est notée $\alpha/2$, ce qui laisse à $1-\alpha/2$ la proportion de Mg^{2+} sous forme libre. Le modèle évalue à une concentration globale ACl-$MgCl_2$ et à une température données quelle est la valeur de α par minimization de l'énergie de Gibbs.

Les cations présents dans la solution sont A^+ et Mg^{2+}; les anions présents dans la solution sont Cl^- et $MgCl_4^{2-}$. Les nombres de moles de ces ions par mole de solution sont :

$$X_{MgCl_2}\left(1-\frac{\alpha}{2}\right) \text{ moles de } Mg^{2+} \tag{2.6.4}$$

$$X_{ACl} \text{ moles de } A^+ \tag{2.6.5}$$

$$X_{MgCl_2}\left(\frac{\alpha}{2}\right) \text{ moles de } MgCl_4^{2-} \tag{2.6.6}$$

$$X_{ACl}+2X_{MgCl_2}(1-\alpha) \text{ ou } 1+X_{MgCl_2}-2\alpha X_{MgCl_2} \text{ moles de } Cl^- \tag{2.6.7}$$

Ce qui permet d'obtenir les fractions molaires ioniques suivantes :

$$X_{Mg^{2+}}=\frac{X_{MgCl_2}\left(1-\frac{\alpha}{2}\right)}{X_{ACl}+X_{MgCl_2}\left(1-\frac{\alpha}{2}\right)}=\frac{X_{MgCl_2}\left(1-\frac{\alpha}{2}\right)}{1-\frac{\alpha X_{MgCl_2}}{2}} \tag{2.6.8}$$

$$X_{A^+}=\frac{X_{ACl}}{X_{ACl}+X_{MgCl_2}\left(1-\frac{\alpha}{2}\right)}=\frac{X_{ACl}}{1-\frac{\alpha X_{MgCl_2}}{2}} \tag{2.6.9}$$

$$X_{MgCl_4^{2-}}=\frac{\alpha X_{MgCl_2}}{2\left(1+X_{MgCl_2}-1.5\alpha X_{MgCl_2}\right)} \tag{2.6.10}$$

$$X_{Cl^-}=\frac{1+X_{MgCl_2}-2\alpha X_{MgCl_2}}{2\left(1+X_{MgCl_2}-1.5\alpha X_{MgCl_2}\right)} \tag{2.6.11}$$

L'entropie configurationnelle, basée sur le modèle de Temkin (1945) de mélange aléatoire des cations sur les sites cationiques et des anions sur les sites anioniques voisins, est donnée par :

$$-\frac{\Delta S^{config}}{R} = \left[X_{ACl} + X_{MgCl_2}\left(1-\frac{\alpha}{2}\right)\right]\left(X_{A^+}\ln X_{A^+} + X_{Mg^{2+}}\ln X_{Mg^{2+}}\right) + \left[X_{MgCl_2}\left(\frac{\alpha}{2}-2\alpha+1\right)+1\right]\left(X_{Cl^-}\ln X_{Cl^-} + X_{MgCl_4^{2-}}\ln X_{MgCl_4^{2-}}\right) \quad (2.6.12)$$

Le modèle est basé sur 2 paramètres : $\Delta e^{MgCl_2}_{MgCl_4^{2-}}$ qui est l'énergie de formation des complexes $MgCl_4^{2-}$ selon la réaction 2.6.13 dans du $MgCl_2$ pur et $\Delta e^{ACl}_{MgCl_4^{2-}}$ qui est l'énergie de formation des complexes $MgCl_4^{2-}$ selon la réaction 2.6.13 dans du ACl presque pur ($MgCl_4^{2-}$ est infiniment dilué).

$$Mg^{2+} + 4Cl^- \Leftrightarrow MgCl_4^{2-} \quad (2.6.13)$$

L'énergie de formation d'une mole de complexes $MgCl_4^{2-}$ peut donc être interpolée à partir des termes $\Delta e^{MgCl_2}_{MgCl_4^{2-}}$ et $\Delta e^{ACl}_{MgCl_4^{2-}}$ comme étant :

$$\Delta e_{MgCl_4^{2-}} = X_{A^+}\Delta e^{ACl}_{MgCl_4^{2-}} + X_{Mg^{2+}}\Delta e^{MgCl_2}_{MgCl_4^{2-}} \quad (2.6.14)$$

Le travail dû à l'effet pression-volume étant négligeable au mélange, l'enthalpie de mélange peut être évaluée sachant qu'il y a $\alpha/2\, X_{MgCl_2}$ moles de complexe $MgCl_4^{2-}$ par mole de solution à la composition d'évaluation, 0 moles de complexe à $X_{ACl} = 1$ et $\alpha^o/2\, X_{MgCl_2}$ moles de complexe à $X_{MgCl_2} = 1$.

$$\Delta h^m = X_{MgCl_2}\left[\left(\frac{\alpha}{2}\right)\Delta e_{MgCl_4^{2-}} - \left(\frac{\alpha^o}{2}\right)\Delta e^{MgCl_2}_{MgCl_4^{2-}}\right] \quad (2.6.15)$$

L'énergie de Gibbs de mélange est donc :

$$\Delta g^m = \Delta h^m - T\Delta s^{config} \tag{2.6.16}$$

qui est une fonction de α.

Pelton et Thompson (1970) ont poussé plus loin le concept en évaluant le système binaire ACl-$MgCl_2$ comme un système réciproque $A^+,Mg^{2+}//Cl^-,MgCl_4^{2-}$ qui répond à l'équilibre de la réaction quasichimique d'échange d'ions premiers-voisins suivante :

$$\left[Mg^{2+} - MgCl_4^{2-}\right]_{paire} + \left[A^+ - Cl^-\right]_{paire} \Leftrightarrow \left[A^+ - MgCl_4^{2-}\right]_{paire} + \left[Mg^{2+} - Cl^-\right]_{paire} \tag{2.6.17}$$

Cette réaction répond à la constante d'équilibre suivante :

$$\frac{\left(X_{A^+}X_{MgCl_4^{2-}} + y\right)\left(X_{Mg^{2+}}X_{Cl^-} + y\right)}{\left(X_{Mg^{2+}}X_{MgCl_4^{2-}} - y\right)\left(X_{A^+}X_{Cl^-} - y\right)} = e^{\left(\frac{\Delta e^{MgCl_2}_{MgCl_4^{2-}} - \Delta e^{ACl}_{MgCl_4^{2-}}}{ZRT}\right)} \tag{2.6.18}$$

où Z est le nombre de coordination cation-anion de la solution et y est la déviation au mélange aléatoire des ions pour la concentration des paires d'ions premiers-voisins. La valeur de y peut être calculée (Førland, 1964) :

$$y = -X_{A^+}X_{Mg^{2+}}X_{Cl^-}X_{MgCl_4^{2-}}\left(\frac{\Delta e^{ACl}_{MgCl_4^{2-}} - \Delta e^{MgCl_2}_{MgCl_4^{2-}}}{ZRT}\right) \tag{2.6.19}$$

Des expressions entropique et enthalpique dérivées des équations ci-haut ont été obtenues pour définir l'énergie de Gibbs de la solution. Cette approche permet une meilleure reproduction des propriétés thermodynamiques expérimentales à partir d'exactement les mêmes deux paramètres car elle évalue une approximation de la contribution à l'énergie de Gibbs de mélange de l'ordonnement premiers-voisins des ions.

Davis et Thompson (1992) ont développé les équations pour le ternaire LiCl-NaCl-$MgCl_2$ en utilisant l'approximation du mélange aléatoire pour l'entropie et non l'approche quasichimique. Karakaya (1985) a appliqué le modèle (avec l'approximation du mélange aléatoire) au binaire $MgCl_2$-$CaCl_2$ où $CaCl_2$ peut aussi former des complexes, ce qui a été étendu aux ternaires NaCl-$CaCl_2$-$MgCl_2$ (Karakaya et Thompson, 1986) et KCl-$CaCl_2$-$MgCl_2$ (Zhu, Karakaya et Thompson, 1988). Davis (1994) a appliqué le modèle (avec approximation du mélange aléatoire) au quaternaire LiCl-NaCl-KCl-$MgCl_2$.

Østvold (1971) a développé un modèle très similaire à celui de Pelton et Thompson (1970), qui traite de la formation de complexes $MgCl_4^{2-}$.

2.7. Modèles quasichimiques

Le modèle quasichimique a été introduit par Fowler et Guggenheim (1939). Ce modèle évalue l'impact de l'énergie de liaison des espèces sur la configuration des espèces lors du mélange. L'entropie configurationnelle et l'enthalpie de mélange sont dépendantes de l'énergie des liaisons (paires d'espèces) pour ce modèle. Il permet donc d'évaluer l'ordonnement à courte distance d'une solution où la distribution des espèces s'écarte de la distribution aléatoire sur les sites d'espèces, telle qu'approximée par Bragg-Williams.

2.7.1. Modèle quasichimique (Fowler et Guggenheim, 1939)

Le modèle quasichimique de Fowler et Guggenheim (1939) évalue l'énergie de Gibbs d'une solution à partir des concentrations des paires d'espèces dans la solution au lieu des concentrations des espèces dans la solution, telles qu'utilisées pour les modèles dérivés des solutions régulières. Avec l'énergie de formation (Δg_{AB}) des paires dites binaires "*A-B*" à partir des paires dites unaires "*A-A*" et "*B-B*", tel que montrée à la réaction 2.7.1.1, le modèle évalue la configuration des espèces *A* et *B* qui minimise l'énergie de Gibbs.

$$[A-A]_{paire} + [B-B]_{paire} \Leftrightarrow 2[A-B]_{paire} \qquad \Delta g_{AB} = \omega_{AB} - \eta_{AB}T \qquad (2.7.1.1)$$

Un mélange aléatoire de paires d'espèces sur d'hypothétiques sites de paires formant une chaîne linéaire fermée (comme un collier) permet d'évaluer avec ce modèle un ordonnement des espèces sur les sites d'espèces. Ce modèle est le modèle d'Ising (voir Ziman, 1965) qui donne l'entropie configurationnelle.

N_A espèces A sont d'abord placées dans la chaîne linéaire fermée (collier) sur N_A sites. Tous les sites sont occupés par des espèces A formant N_A liaisons A-A. Ensuite, N_A-N_{AA} liaisons entre ces espèces A (choisies aléatoirement) sont coupées, ce qui donne :

- nombre total d'espèces A : N_A
- nombre total de liaisons initiales : N_A
- nombre total de liaisons non-coupées : N_{AA}
- nombre total de liaisons coupées : N_A-N_{AA}

Les permutations possibles associées à cette première étape de positionnement des espèces A est nommée Ω_A et vaut :

$$\Omega_A = \frac{(\text{liaisons initiales})\ !}{(\text{liaisons coupées})!\,(\text{liaisons non - coupées})!} = \frac{N_A!}{(N_A - N_{AA})!\,N_{AA}!} \qquad (2.7.1.2)$$

Suite à cette étape, les liaisons coupées sont remplacées par N_B-(N_A-N_{AA}) espèces B avec aucune restriction sur le nombre consécutif de B par liaison coupée.

- nombre total d'espèces B : N_B
- nombre de liaisons ajoutées par l'addition d'espèces B : N_B
- nombre de nouvelles liaisons B-B : N_{BB}
- nombre de liaisons A-B créées avec l'ajout de B : $2(N_A$-$N_{AA})$

Le nombre de liaisons B-B peut être calculé :

$$N_{AA} + N_{AB} + N_{BB} = N_A + N_B \qquad (2.7.1.3)$$

$$N_{AA} + 2(N_A - N_{AA}) + N_{BB} = N_A + N_B \qquad (2.7.1.4)$$

$$N_{BB} = N_B - (N_A - N_{AA}) \qquad (2.7.1.5)$$

Sachant que N_A-N_{AA} = N_B-N_{BB} par bilan de masse sur le collier, les permutations possibles associées à cette première étape de remplacement des liaisons coupées par des espèces B est nommée Ω_B et vaut :

$$\Omega_B = \frac{(\text{nouvelles liaisons créées})!}{(\text{liaisons } A\text{-}B)!\,(\text{liaisons } B\text{-}B)!} = \frac{N_B!}{(N_B - N_{BB})!N_{BB}!} \qquad (2.7.1.6)$$

Sachant que la différence d'entropie au mélange vaut selon Boltzmann :

$$\Delta S = k \ln \Omega \qquad (2.7.1.7)$$

et que l'on peut distribuer Ω selon :

$$\Omega = \Omega_A \Omega_B \qquad (2.7.1.8)$$

$$\Delta S = k \ln \frac{N_A! N_B!}{N_{AA}! N_{BB}! (N_A - N_{AA})! (N_B - N_{BB})!} \qquad (2.7.1.9)$$

Avec l'approximation de Stirling (voir Fraser, 1958) pour les factorielles de très grands nombres, on a :

$$N_A! \approx (2\pi)^{\frac{1}{2}} e^{-N_A} N_A^{N_A + \frac{1}{2}} \qquad (2.7.1.10a)$$

$$N_B! \approx (2\pi)^{\frac{1}{2}} e^{-N_B} N_B^{N_B + \frac{1}{2}} \qquad (2.7.1.10b)$$

et similairement pour les autres termes. Alors :

$$\ln N_A! = \tfrac{1}{2}\ln(2\pi) - N_A \ln e + \left(N_A + \tfrac{1}{2}\right)\ln N_A \qquad (2.7.1.11a)$$

$$\ln N_B! = \tfrac{1}{2}\ln(2\pi) - N_B \ln e + \left(N_B + \tfrac{1}{2}\right)\ln N_B \qquad (2.7.1.11b)$$

et similairement pour les autres termes. L'entropie devient donc :

$$\begin{aligned}\Delta S = {} & k(N_A \ln N_A + N_B \ln N_B) - k(N_{AA} \ln N_{AA} + N_{BB} \ln N_{BB}) \\ & - k((N_A - N_{AA})\ln(N_A - N_{AA}) + (N_B - N_{BB})\ln(N_B - N_{BB})) \\ & + \frac{k}{2}\ln\left(\frac{N_A N_B}{2\pi N_{AA} N_{BB}(N_A - N_{AA})(N_B - N_{BB})}\right)\end{aligned} \tag{2.7.1.12}$$

Pour de très grands nombres, le dernier terme peut être éliminé. Sachant que $R = N_{Av}\, k$, on obtient :

$$\begin{aligned}\Delta S = {} & R(n_A \ln N_A + n_B \ln N_B) - R(n_{AA} \ln N_{AA} + n_{BB} \ln N_{BB}) \\ & - R((n_A - n_{AA})\ln(N_A - N_{AA}) + (n_B - n_{BB})\ln(N_B - N_{BB}))\end{aligned} \tag{2.7.1.13}$$

Sachant que par bilan de masse (collier avec un nombre de coordination de 2) on a :

$$2n_A = 2n_{AA} + n_{AB} \tag{2.7.1.14}$$

$$2n_B = 2n_{BB} + n_{AB} \tag{2.7.1.15}$$

Et similairement pour N_A et N_B. Alors :

$$\begin{aligned}\Delta S = {} & R(n_A \ln N_A + n_B \ln N_B) - R(n_{AA} \ln N_{AA} + n_{BB} \ln N_{BB}) \\ & - R\left(\frac{n_{AB}}{2}\ln\frac{N_{AB}}{2} + \frac{n_{AB}}{2}\ln\frac{N_{AB}}{2}\right)\end{aligned} \tag{2.7.1.16}$$

Ce qui revient à :

$$\Delta S = R(n_A \ln N_A + n_B \ln N_B) - R\left(n_{AA} \ln N_{AA} + n_{BB} \ln N_{BB} + n_{AB} \ln\frac{N_{AB}}{2}\right) \tag{2.7.1.17}$$

En ajoutant 2 fois l'entropie de Bragg-Williams (idéale) du côté droit de l'équation 2.7.1.17 et en soustrayer 2 fois la même entropie aussi du même côté, on trouve :

$$\Delta S = R(n_A \ln N_A + n_B \ln N_B) - R\left(n_{AA} \ln N_{AA} + n_{BB} \ln N_{BB} + n_{AB} \ln \frac{N_{AB}}{2}\right)$$
$$- 2R(n_A \ln N_A + n_B \ln N_B) + 2R(n_A \ln N_A + n_B \ln N_B)$$

(2.7.1.18)

Et en réarrangeant, on a :

$$\Delta S = -R(n_A \ln N_A + n_B \ln N_B) - R\left(n_{AA} \ln N_{AA} + n_{BB} \ln N_{BB} + n_{AB} \ln \frac{N_{AB}}{2}\right)$$
$$+ 2R\left(\left(n_{AA} + \tfrac{1}{2} n_{AB}\right) \ln N_A + \left(n_{BB} + \tfrac{1}{2} n_{AB}\right) \ln N_B\right)$$

(2.7.1.19)

Ce qui donne :

$$\Delta S = -R(n_A \ln N_A + n_B \ln N_B) - R\left(n_{AA} \ln \frac{N_{AA}}{N_A^2} + n_{BB} \ln \frac{N_{BB}}{N_B^2} + n_{AB} \ln \frac{N_{AB}}{2N_A N_B}\right)$$

(2.7.1.20)

Avec l'addition suivante :

$$\Delta S = -R(n_A \ln N_A + n_B \ln N_B) - R\left(n_{AA} \ln \frac{N_{AA}}{N_A^2} + n_{BB} \ln \frac{N_{BB}}{N_B^2} + n_{AB} \ln \frac{N_{AB}}{2N_A N_B}\right)$$
$$- R\left(n_{AA} \ln \frac{(N_A + N_B)^2}{N_A + N_B} + n_{BB} \ln \frac{(N_A + N_B)^2}{N_A + N_B} + n_{AB} \ln \frac{(N_A + N_B)^2}{N_A + N_B}\right)$$
$$+ R(n_A \ln(N_A + N_B) + n_B \ln(N_A + N_B))$$

(2.7.1.21)

et sachant que $N_A+N_B = N_{AA}+N_{AB}+N_{BB}$ et que $n_A+n_B = n_{AA}+n_{AB}+n_{BB}$, alors l'entropie quasichimique configurationnelle vaut :

$$\Delta S = -R(n_A \ln X_A + n_B \ln X_B) - R\left(n_{AA} \ln \frac{X_{AA}}{X_A^2} + n_{BB} \ln \frac{X_{BB}}{X_B^2} + n_{AB} \ln \frac{X_{AB}}{2X_A X_B}\right)$$
$$= \Delta S^{config}$$

(2.7.1.21)

Le changement d'enthalpie molaire lors du mélange des espèces A et B pures est donné par :

$$\Delta h^m = \frac{N_{Av}Z}{2}(X_{AB}\varepsilon_{AB} + X_{AA}\varepsilon_{AA} + X_{BB}\varepsilon_{BB}) - X_A \frac{N_{Av}Z}{2}\varepsilon_{AA} - X_B \frac{N_{Av}Z}{2}\varepsilon_{BB}$$

(2.7.1.22)

Sachant que (à partir des équations 2.7.1.14 et 2.7.1.15):

$$X_A = X_{AA} + \tfrac{1}{2}X_{AB} \qquad (2.7.1.23)$$

$$X_B = X_{BB} + \tfrac{1}{2}X_{AB} \qquad (2.7.1.24)$$

En remplaçant, on obtient (en supposant $\varepsilon_{AA} = \varepsilon_{AA}^o$ et $\varepsilon_{BB} = \varepsilon_{BB}^o$):

$$\Delta h^m = \frac{N_{Av}Z}{2}\left(X_{AB}\varepsilon_{AB} + X_{AA}\varepsilon_{AA} + X_{BB}\varepsilon_{BB} - \left(X_{AA} + \tfrac{1}{2}X_{AB}\right)\varepsilon_{AA} - \left(X_{BB} + \tfrac{1}{2}X_{AB}\right)\varepsilon_{BB}\right)$$

(2.7.1.25)

Ce qui donne (si les ε_{ij} sont indépendants de la température) :

$$\Delta h^m = X_{AB}\frac{N_{Av}Z}{2}\left(\varepsilon_{AB} - \tfrac{1}{2}\varepsilon_{AA} - \tfrac{1}{2}\varepsilon_{BB}\right) = \frac{X_{AB}}{2}\omega_{AB} \tag{2.7.1.26}$$

Avec l'équation de Gibbs :

$$G = H - TS = n_A g_A^o + n_B g_B^o - T\Delta S^m + \Delta H^m \tag{2.7.1.27}$$

où

$$\Delta S^m = (n_A + n_B)(\Delta s^{config} + \Delta s^{non-config}) \tag{2.7.1.28}$$

L'entropie non-configurationnelle peut être évaluée si l'on pose que l'énergie des paires ε_{ij} est une fonction de la température. Alors, on a :

$$\Delta h^m = \frac{X_{AB}}{2}\left(\frac{\partial\left(\frac{\omega_{AB}}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P \tag{2.7.1.29}$$

$$\Delta s^{non-config} = -\frac{X_{AB}}{2}\left(\frac{\partial\omega_{AB}}{\partial T}\right)_P \tag{2.7.1.30}$$

Le modèle quasichimique donne que l'énergie de Gibbs d'une solution substitutionnelle binaire *A-B* est :

$$\begin{aligned} G = {} & n_A g_A^o + n_B g_B^o + RT(n_A \ln X_A + n_B \ln X_B) \\ & + RT\left(n_{AA}\ln\frac{X_{AA}}{X_A^2} + n_{BB}\ln\frac{X_{BB}}{X_B^2} + n_{AB}\ln\frac{X_{AB}}{2X_A X_B}\right) \\ & + \tfrac{1}{2}n_{AB}\omega_{AB} \end{aligned} \tag{2.7.1.28}$$

où n_{AA}, n_{BB} et n_{AB} sont les nombres de moles des liaisons (ou paires) d'espèces *A-A*, *B-B* et *A-B* respectivement, et reliés à la réaction 2.7.1.1. Ces nombres de moles doivent respecter le bilan de masse des espèces *A* et *B* selon les équations 2.7.1.14 et 2.7.1.15, et sont évalués à l'équilibre par minimisation de l'énergie de Gibbs.

Plus l'énergie des paires *A-B* est négative par rapport à la valeur interpolée des paires *A-A* et *B-B*, plus la concentration des paires *A-B* va augmenter au détriment des paires *A-A* et *B-B*. Les valeurs de ces concentrations X_{AB}, X_{AA} et X_{BB} vont donc s'éloigner de la valeurs de ces concentrations telles que prédites par un mélange aléatoire des espèces *A* et *B* sur un quasi-réseau de sites d'espèces (voir équations 2.2.8a) à c)). La configuration des espèces *A* et *B* devient donc dépendante de l'énergie d'interaction entre ces espèces, donc l'entropie configurationnelle est couplée à cette énergie contrairement à l'entropie idéale dite de Bragg-Williams. Pour des solutions dont l'écart à l'idéalité est grand, le modèle quasichimique, avec son approximation des paires, est donc en théorie plus approprié que l'entropie de Bragg-Williams et son approximation dite ponctuelle, car il évalue l'ordonnement à courte distance (complexation) des espèces. Pour des solutions proches de l'idéalité, la deuxième partie l'entropie de l'équation 2.7.1.21 devient nulle, ce qui fait que le modèle quasichimique tend vers le modèle des solutions régulières lorsque l'énergie de formation des paires « binaires » à partir des paires « unaires » tend vers 0. La figure 2.3 montre la variation de la dépendence compositionnelle de l'enthalpie et de l'entropie de mélange d'une solution *A-B* en fonction de l'énergie de formation des paires *A-B* à partir des paires *A-A* et *B-B*.

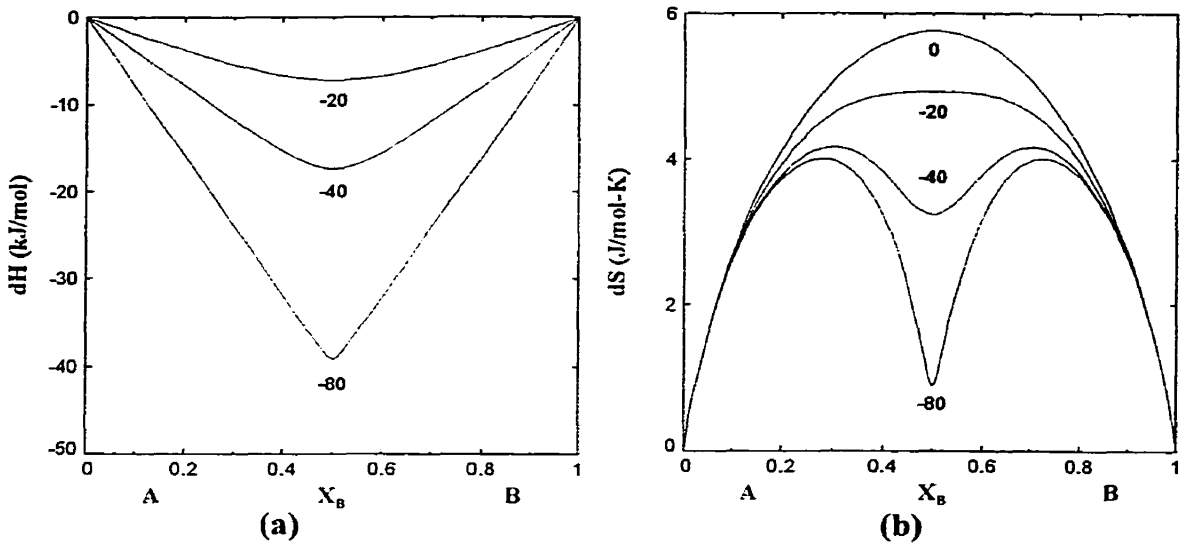


Figure 2.3 : Dependence compositionnelle de l'enthalpie et de l'entropie de mélange d'une solution *A-B* à 1000°C en fonction de l'énergie de formation des paires *A-B* à partir des paires *A-A* et *B-B* (0, -20, -40 et –80 kJ/mol) : a) enthalpie de mélange; b) entropie de mélange.

Cette forme en « V » de l'enthalpie de mélange lorsque l'énergie d'interaction *A-B* est très négative a été observée expérimentalement. La forme en « m » de l'entropie configurationnelle montre qu'à la composition du maximum de complexation ($X_B = 0.5$ où le nombre de paires *A-B* est maximisé) la solution est très ordonnée (faible désordre donc faible ΔS^{config}).

Le principal defaut de ce modèle vient du fait que le maximum d'ordonnement est fixé à un mélange équimolaire de *A* et de *B*, et que l'énergie de formation des paires n'est pas fonction de la composition.

2.7.2. Modèle quasichimique modifié (Pelton et Blander, 1984)

Pelton et Blander (1984 et 1986) ont modifié le modèle quasichimique de Fowler et Guggenheim (1939). La composition du maximum d'ordonnement (complexation) peut être ajustée dans le modèle quasichimique modifié de Pelton et Blander par l'utilisation de variables compositionnelles qui sont des fonctions des nombres de coordination des espèces. Ces variables compositionnelles, appelées fractions équivalentes (de coordination), remplacent les fractions molaires des espèces dans l'équation de l'énergie de Gibbs du modèle quasichimique modifié (sauf dans le terme entropique du mélange des espèces). Il s'agit de permettre un nombre de coordination différent mais constant pour les espèces qui se mélangent (Fowler et Guggenheim utilisent un nombre de coordination constant pour toutes les espèces). L'entropie quasichimique, dérivée du modèle d'Ising linéaire, n'est plus exacte, mais devient une approximation, si le nombre de coordination moyen de la solution est différent de 2.

La seconde modification de Pelton et Blander au modèle quasichimique original a été de rendre l'énergie de formation des liaisons (paires) dites "binaires" *A-B* à partir des liaisons dites "unaires", *A-A* et *B-B*, fonction de la composition de la solution. Une fonction des fractions équivalentes de coordination (fractions molaires pondérées par les nombres de coordination) a été choisie.

Pelton et Blander ont aussi modifié le modèle quasichimique de Guggenheim en explicitant un formalisme complet pour les solutions multicomposantes, incluant un traitement "acide/base" à l'aide des techniques d'interpolation similaires à celle de Kohler et de Toop.

Modification de la composition du maximum d'ordonnement

Le modèle quasichimique modifié de Pelton et Blander considère la réaction de paires suivante :

$$[A-A]_{paire} + [B-B]_{paire} \Leftrightarrow 2[A-B]_{paire} \qquad (2.7.2.1)$$

qui est la même que celle de Guggenheim. L'énergie de formation de 2 paires *A-B* à partir des paires *A-A* et *B-B* est donnée par :

$$\Delta\varepsilon_{AB} = 2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB} \qquad (2.7.2.2)$$

L'enthalpie de mélange de la solution lorsque les nombres de coordination des espèces *A* et *B* sont constants mais peuvent être différents est donnée par (en supposant ε_{ij} indépendant de la température) :

$$\Delta H^m = N_{Av}(n_{AA}\varepsilon_{AA} + n_{AB}\varepsilon_{AB} + n_{BB}\varepsilon_{BB}) - n_A \frac{N_{Av}Z_A}{2}\varepsilon_{AA} - n_B \frac{N_{Av}Z_B}{2}\varepsilon_{BB} \qquad (2.7.2.3)$$

où Z_A et Z_B sont les nombres de coordination respectifs des espèces *A* et *B*. Le bilan de masse des espèces devient :

$$Z_A n_A = 2n_{AA} + n_{AB} \qquad (2.7.2.4)$$

$$Z_B n_B = 2n_{BB} + n_{AB} \qquad (2.7.2.5)$$

Ce qui transforme l'équation 2.7.2.3 en :

$$\Delta H^m = N_{Av}\left(n_{AA}\varepsilon_{AA} + n_{AB}\varepsilon_{AB} + n_{BB}\varepsilon_{BB}\right) - \left(n_{AA} + \frac{n_{AB}}{2}\right)N_{Av}\varepsilon_{AA} - \left(n_{BB} + \frac{n_{AB}}{2}\right)N_{Av}\varepsilon_{BB} \tag{2.7.2.6}$$

$$\Delta H^m = n_{AB}N_{Av}\left(\varepsilon_{AB} - \tfrac{1}{2}\varepsilon_{AA} - \tfrac{1}{2}\varepsilon_{BB}\right) = \frac{n_{AB}}{2}N_{Av}\Delta\varepsilon_{AB} = \frac{n_{AB}}{2}\omega_{AB} \tag{2.7.2.7}$$

Si $\Delta\varepsilon_{AB}$ est une fonction de la température, avec :

$$\Delta g_{AB} = N_{Av}\Delta\varepsilon_{AB} = f(T) \tag{2.7.2.8}$$

alors l'équation 2.7.2.7 devient :

$$\Delta H^m = \frac{n_{AB}}{2}\left(\frac{\partial\left(\frac{\Delta g_{AB}}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_{P,n_i} \tag{2.7.2.9}$$

et l'entropie non-configurationnelle devient :

$$\Delta S^{non\text{-}config} = -\frac{n_{AB}}{2}\left(\frac{\partial\Delta g_{AB}}{\partial T}\right)_{P,n_i} \tag{2.7.2.10}$$

Avant de considérer l'expression entropique configurationnelle modifiée par les nombres de coordination différents, la définition mathématique des fractions équivalentes de coordination doit être faite avec l'aide des équations 2.7.2.4 et 2.7.2.5:

$$Y_A = \frac{Z_A n_A}{Z_A n_A + Z_B n_B} = \frac{2n_{AA} + n_{AB}}{2n_{AA} + 2n_{AB} + 2n_{BB}} = X_{AA} + \tfrac{1}{2}X_{AB} \tag{2.7.2.11}$$

$$Y_B = \frac{Z_B n_B}{Z_A n_A + Z_B n_B} = \frac{2n_{BB} + n_{AB}}{2n_{AA} + 2n_{AB} + 2n_{BB}} = X_{BB} + \tfrac{1}{2} X_{AB} \qquad (2.7.2.12)$$

L'entropie configurationnelle est obtenue en remplaçant les fractions molaires des espèces par les fractions équivalentes de coordination de ces mêmes espèces pour le terme de mélange aléatoire des paires de l'expression entropique configurationnelle du modèle d'Ising linéaire.

$$\Delta S = -R(n_A \ln X_A + n_B \ln X_B) - R\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right)$$
$$= \Delta S^{config} \qquad (2.7.2.13)$$

L'utilisation de nombres de coordination différents pour les espèces implique certaines différences entre le modèle quasichimique de Guggenheim et la version modifiée de Pelton et Blander :

- La composition du maximum d'ordonnement passe de la composition où $X_A = X_B$ à la composition où $Y_A = Y_B$, c'est-à-dire $X_B = Z_A(Z_A + Z_B)^{-1}$.

- La pondération de la contribution de l'enthalpie (H) et de l'entropie (S) à l'énergie de Gibbs (G) est affectée par la valeur moyenne du nombre de coordination de la solution. Plus ce nombre est grand, plus la contribution du terme entropique augmente par rapport au terme enthalpique (car pour un même nombre d'espèces, le nombre de liaisons augmente). De ce fait, la fonction $G = f(Y_i)$ devient de plus en plus arrondie (taux de changement de G en fonction de Y_i est plus faible près de la composition du maximum d'ordonnement), même pour un ordonnement prononcé, et la variation des activités des espèces en fonction de la composition est plus faible.

- Le terme entropique n'est exacte que lorsque que la valeur du nombre de coordination de toutes les espèces vaut 2 (de par le modèle d'Ising linéaire). Si le nombre de coordination de la solution est différent de 2, alors Z ne devrait plus être condidéré comme le nombre de coordination réel de la solution, mais plutôt comme un paramètre du modèle qui influence la distribution de l'énergie de Gibbs de mélange, Δg^m, entre le terme enthalpique, Δh^m, et le terme entropique, Δs^{config} (car il influence le nombre de liaisons totales pour un nombre d'espèces donné).

Systèmes multicomposants

Pelton et Blander (1984) ont décrit les équations pour un système multicomposant (A, B, C, ...). Chaque constituant (espèce) de la solution possède son propre nombre de coordination et le bilan de masse devient :

$$Z_i n_i = n_{ii} + \sum_j n_{ij} \tag{2.7.2.14}$$

Les fractions équivalentes sont donc :

$$Y_i = \frac{Z_i n_i}{\sum_j Z_j n_j} = \frac{n_{ii} + \sum_j n_{ij}}{\sum_k \left(n_{kk} + \sum_l n_{kl} \right)} = X_{ii} + \tfrac{1}{2} \sum_{\substack{j \\ j \neq i}} X_{ij} \tag{2.7.2.15}$$

L'expression de l'énergie de Gibbs de la solution devient :

$$G = \sum_i n_i g_i^o + RT \sum_i n_i \ln X_i + RT \left(\sum_i \sum_{j \geq i} n_{ij} \ln \frac{X_{ij}}{(2-\delta_{ij}) Y_i Y_j} \right) + \frac{1}{2} \sum_i \sum_{i>j} n_{ij} \Delta g_{ij} \tag{2.7.2.16}$$

où i et j sont des espèces et δ_{ij} est le delta Kronecker ($\delta_{ij} = 1$ si $i = j$ et $\delta_{ij} = 0$ si $i \neq j$). Les valeurs à l'équilibre des nombres de moles de paires sont celles qui minimisent l'énergie de Gibbs sous la contrainte du bilan de masse.

Dépendance compositionnelle de Δg_{AB}

Une importante modification apportée au modèle quasichimique par Pelton et Blander (1984) est la dépendance compositionnelle de l'énergie de formation des paires (liaisons) dites "binaires" *A-B*, à partir des paires dites "unaires" *A-A* et *B-B*. Pour une solution multicomposante (*A*, *B*, *C*, ...), la variation compositionnelle de Δg_{AB} oblige l'utilisation de méthodes d'estimation de cette énergie (d'un sous-système binaire) dans le champ compositionnel multicomposant. Pour ce faire, Pelton et Blander utilisent les méthodes de Kohler (1960) et de Toop (1965) qui on l'avantage de s'intégrer à une séparation des espèces de la solution en deux groupes distincts. L'utilisation de deux groupes divisant les espèces permet de lier le modèle quasichimique aux propriétés "acide/base" communément associées à plusieurs types de solutions liquides, dont plusieurs montrent des signes d'ordonnement à courte distance (laitiers métallurgiques, mattes et sels fondus). Pelton et Blander ont donc formulé la variation de l'énergie de formation des paires *A-B* en tenant compte des propriétés "acide/base" des liquides et de l'influence des autres espèces (*C*, *D*, ...) sur cette energie.

Si A et B appartiennent au même groupe chimique (acide ou base), alors la variation compositionnelle de Δg_{AB} , telle que donnée par Pelton et Blander, est une variation similaire à celle de Kohler pour un système polynomial:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{\substack{ij \\ i+j>0}} \left(\frac{Y_A}{Y_A + Y_B}\right)^{i} \left(\frac{Y_B}{Y_A + Y_B}\right)^{j} \left[q^{(ij)}_{AB} + \sum_{k>0} Y_C \left(1 - Y_A - Y_B\right)^{k-1} q^{(ijk)}_{AB(C)} \right] \tag{2.7.2.17}$$

où C est une espèce qui appartient à n'importe quel des deux groupes; $q^{(ij)}_{AB}$ est un paramètre binaire compositionnel et $q^{(ijk)}_{AB(C)}$ est un paramètre ternaire compositionnel qui évalue l'influence de C sur l'énergie de la liaison A-B. Ces paramètres sont obtenus par optimisation des données thermodynamiques expérimentales (voir section 2.13).

Si A est une espèce acide et B est une espèce basique, alors la variation compositionnelle de Δg_{AB} , telle que donnée par Pelton et Blander, est une variation similaire à celle de Toop pour un système polynomial:

$$\begin{aligned} \Delta g_{AB} &= \Delta g^{o}_{AB} \\ &+ \sum_{\substack{ij \\ i+j>0}} \xi^{i}_{acides} \xi^{j}_{bases} \left[q^{(ij)}_{AB} + \sum_{k>0} Y_C \left(1 - \xi_{acides}\right)^{k-1} q^{(ijk)}_{AB(C)} + \sum_{l>0} Y_D \left(1 - \xi_{bases}\right)^{l-1} q^{(ijl)}_{AB(D)} \right] \end{aligned} \tag{2.7.2.18}$$

où C est une espèce acide et D est une espèce basique. Les variables ξ_{acides} et ξ_{bases} sont définies comme :

$$\xi_{acides} = \sum_{\substack{j \\ j \in \text{acides}}} Y_j \qquad (2.7.2.19)$$

$$\xi_{bases} = \sum_{\substack{j \\ j \in \text{bases}}} Y_j \qquad (2.7.2.20)$$

avec

$$\xi_{acides} + \xi_{bases} = 1 \quad \text{(car il y a 2 groupes)} \qquad (2.7.2.21)$$

La technique d'interpolation des termes ternaires $q_{AB(C)}^{(ijk)}$ des équations 2.7.2.17 et 2.7.2.18 ont été proposées par Pelton. À l'équation 2.7.2.18, l'interpolation du terme ternaire $q_{AB(C)}^{(ijk)}$ se fait en utilisant une sous-fonction $Y_C(1-\xi_{acides})^{k-1}$ au lieu de Y_C^k afin de tenir compte de toutes les autres espèces qui appartiennent au même groupe acide/base que l'espèce C et qui devraient avoir un effet additif (similairement pour $q_{AB(D)}^{(ijl)}$). Pour plus de précision sur ce dernier point, le lecteur est invité à consulter la section « Ternary Terms » de l'article « On the Choice of « Geometric » Thermodynamic Models » en Annexe II.

<u>Examples d'utilisation du modèle quasichimique modifié</u>

Le modèle quasichimique modifié a été utilisé de manière extensive par le *CRCT* (École Polytechnique de Montréal) depuis plusieurs années pour le développement de bases de données de solutions liquides où la tendance à l'ordonnement à courte distance est forte.

Deux types d'interactions ont été étudiées avec ce modèle :

- les interactions premiers voisins;

- les interactions seconds voisins où A et B sont des espèces d'un même quasi-réseau intercalé avec un autre quasi-réseau totalement occupé par une seule espèce (disons X).

A) Interactions premiers-voisins :

Les solutions liquides métal-soufre, communément appelée mattes, ont été modélisées thermodynamiquement avec succès grâce aux travaux de Dessureault (1993), Kongoli (1995), Kongoli, Dessureault et Pelton (1998) et Kongoli et Pelton (1999). Ces solutions montrent un fort ordonnement premiers-voisins (par exemple Fe-S et Cu-S), bien qu'une certaine dissociation soit présente (les liaisons Cu-S et Cu-Cu prédominent dans l'intervalle de composition Cu-Cu_2S, mais certaines liaisons S-S y sont présentes). La prédiction des propriétés thermodynamiques (PS_2) dans les systèmes ternaires et quaternaires à partir des variations compositionnelles de type Kohler/Toop sont excellentes avec une utilisation minimale des termes "ternaires". L'utilisation de nombres de coordination différents et supérieurs à 2 pour les espèces ne semble pas causer de problème pour l'approximation entropique de l'ordonnement à courte distance.

Les propriétés des solutions métalliques liquides Al-Mg-Si-Sr-C ont été reproduites par ce modèle avec satisfaction dans les travaux de Bérubé (1993) et de Chartrand (1995). Les fortes enthalpies de mélange des sous-systèmes qui contiennent du Sr ont pu être reproduites avec succès grâce à des nombres de coordination avoisinant une valeur de 6.

Les avantages et inconvénients d'un nombre de coordination moyen différent de 2 ont été donnés à la section "Modification de la composition du maximum d'ordonnement" peu avant.

B) Interactions seconds-voisins :

L'énergie de Gibbs de la solution d'oxydes fondus du système FACT (Pelton, Bale et Thompson, 1998) est décrite par le modèle quasichimique modifié de Pelton et Blander (1984) avec les équations telles que données dans cette section. La réaction quasichimique suivante :

$$[M-O-M]_{paire}+[Si-O-Si]_{paire} \Leftrightarrow 2[M-O-Si]_{paire} \qquad (2.7.2.22)$$

est similaire aux réactions de formation de silicates à l'état fondu de Toop et Samis (1962) :

$$O^{2-}+O^{o} \Leftrightarrow 2O^{-} \qquad (2.7.2.23)$$

et permet d'évaluer l'ordonnement à courte-distance associé à la formation de complexes SiO_4^{4-}, SiO_3^{2-}, etc... dans les oxydes fondus constitués d'acides et de bases.

Un nombre considérable de systèmes binaires, ternaires et multicomposants ont vu leurs propriétés thermodynamiques de la phase liquide reproduites avec succès, ce qui permet de reproduire et de prédire les équilibres de phases liquide-solides. De nombreux exemples peuvent être trouvés dans les articles suivants : Wu (1992), Eriksson, Wu, Blander et Pelton (1994).

Pelton, Eriksson et Romero-Serrano (1993) ont aussi étendu le modèle quasichimique modifié aux calculs de capacités en sulfures des solutions d'oxydes fondus par l'utilisation de la réaction suivante qui est une modification du modèle de Reddy et Blander (1987) :

$$M^{2+}O + \tfrac{1}{2}S_2 \Leftrightarrow M^{2+}S + \tfrac{1}{2}O_2 \qquad (2.7.2.24)$$

À laquelle la constante d'équilibre suivante est associée :

$$K_{equ} = \frac{a_{MS}}{a_{MO}}\left(\frac{P_{O_2}}{P_{S_2}}\right)^{\frac{1}{2}} \qquad (2.7.2.25)$$

Le modèle quasichimique modifié appliqué aux oxydes fondus permet de calculer a_{MO}, et avec les pressions partielles d'O_2 et de S_2 provenant de la phase gazeuse, il est possible de calculer a_{MS} si la constante d'équilibre est connue. En supposant une activité idéale, la fraction molaire de MS est calculée suivant :

$$a_{MS} = \frac{X_{MS}}{X_{MO} - X_{SiO_2} + X_{MS}} \qquad (\text{pour } X_{SiO_2} \leq \tfrac{1}{3}) \qquad (2.7.2.26)$$

$$a_{MS} = \frac{X_{MS}}{X_{SiO_2} + X_{MS}}\left(\frac{2X_{SiO_2}}{1 - X_{SiO_2}}\right)^2 \qquad (\text{pour } X_{SiO_2} \geq \tfrac{1}{3}) \qquad (2.7.2.27)$$

Les cations de charge autre que 2^+ peuvent aussi être considérés de façon similaire. Ce modèle simple, couplé au modèle quasichimique modifié, permet de calculer avec satisfaction un grand nombre de dissolutions anioniques (S^{2-}, SO_4^{2-}, F^-, Cl^-, OH^-, etc..) en faible concentration dans les laitiers.

2.8. Modèle d'association

Le modèle d'association suppose la présence hypothétique d'espèces associées dans le liquide selon la réaction chimique suivante (pour un système binaire substitutionnel *A-B*) :

$$aA + bB \Leftrightarrow A_aB_b \qquad \Delta g^{ass}_{A_aB_b} \tag{2.8.1}$$

L'énergie de Gibbs de cette solution est donnée par :

$$G = n_A g^o_A + n_B g^o_B + n_{A_aB_b} g^o_{A_aB_b} + RT\left(n_A \ln X_A + n_B \ln X_B + n_{A_aB_b} \ln X_{A_aB_b}\right) + G^E \tag{2.8.2}$$

avec

$$g^o_{A_aB_b} = ag^o_A + bg^o_B + \Delta g^{ass}_{A_aB_b} \tag{2.8.3}$$

Ce qui est essentiellement la même expression que pour un modèle dit "polynomial" (section 2.3) avec l'entropie de Bragg-Williams, cependant qu'une nouvelle espèces A_aB_b indépendante (entropiquement) de A et de B, est considérée. Différentes expressions de G^E peuvent être utilisées. Le bilan de masse est dit "naturel" en ce sens qu'il s'agit d'un bilan de masse chimique normal :

$$n^{tot}_A = n_A + an_{A_aB_b} \tag{2.8.4}$$

$$n^{tot}_B = n_B + bn_{A_aB_b} \tag{2.8.5}$$

L'expression de G pour un système multicomposant est triviale et similaire à l'équation (2.2.26) où les espèces associées introduites sont traitées comme toute autre espèce i.

Certains problèmes de nature entropique sont reliés au modèle d'association. Par exemple, si une espèce associée AB_2 dont l'énergie de formation à partir de A et de B est négative, est présente dans une solution A_{solvant}-$B_{\text{soluté}}$, alors l'ajout d'atomes de B dans A pur se fera sous la forme de AB_2 au lieu d'atomes B individuels. Deux atomes de B sont donc dilués dans A sous la forme d'une seule particule. Pour corriger cet aspect entropique, il est proposé d'utiliser des espèces associées $A_{0.5}B$ au lieu de AB_2, au détriment de l'aspect "physique" du model.

Un autre problème apparaît lorsque l'énergie d'association $\Delta g^{ass}_{A_aB_b}$ est nulle. Dans ces conditions, on a que :

$$\frac{X_{A_aB_b}}{X_A^a X_B^b} = 1 \tag{2.8.6}$$

Ce qui implique que l'énergie de Gibbs devient (si G^E=0):

$$G = n_A^{tot} g_A^o + n_B^{tot} g_B^o + RT\left(n_A \ln X_A + n_B \ln X_B + n_{A_aB_b} \ln X_{A_aB_b}\right) \tag{2.8.7}$$

Ce qui n'est pas équivalent à une solution idéale de A et de B. Pour avoir une solution idéale avec le modèle d'association, il faut fixer $\Delta g^{ass}_{A_aB_b} = +\infty$ pour que le nombre de moles d'espèces associées soit nul. Cela implique que l'énergie entre A et B pour former un associé A_aB_b est infiniment positive avec que l'énergie d'interaction entre A et B est nulle! Dans ce cas le modèle devient purement mathématique.

Les travaux de Lück, Gerling et Predel (1989) sont suggérés comme référence.

2.9. Modèle cellulaire (Kapoor et Frohberg, 1971)

Le modèle cellulaire de Kapoor et Frohberg (1971) a été développé pour les solutions d'oxydes fondus contenant de la silice (SiO_2). Ce modèle considère la présence d'hypothétiques "cellules" dans le liquide qui définissent l'état de polarisation de l'oxygène qui y est associé selon la réaction 2.7.1.

$$O^{2-} + O^{o} \Leftrightarrow 2O^{-} \qquad (2.9.1)$$

La solution fondue M_2O-MO-SiO_2 contient des cellules de type $M^{+}OM^{+}$, $M^{2+}OM^{2+}$, $M^{+}OM^{2+}$, $SiOSi$, $M^{+}OSi$ et $M^{2+}OSi$, et les équilibres suivants sont respectés:

$$M^{+}OM^{+} + SiOSi \Leftrightarrow 2M^{+}OSi \qquad \Delta g^{o}_{M^{+}OSi} = 2\omega_{M^{+}Si} \qquad (2.9.2)$$

$$M^{2+}OM^{2+} + SiOSi \Leftrightarrow 2M^{2+}OSi \qquad \Delta g^{o}_{M^{2+}OSi} = 2\omega_{M^{2+}Si} \qquad (2.9.3)$$

$$M^{+}OM^{+} + M^{2+}OM^{2+} \Leftrightarrow 2M^{+}OM^{2+} \qquad \Delta g^{o}_{M^{+}OM^{2+}} = 2\omega_{M^{+}M^{2+}} \qquad (2.9.4)$$

où les termes ω_{ij} sont les énergies de formation des cellules iOj à partir des cellules iOi et jOj. Pour un nombre de moles d'oxydes M_2O, MO et SiO_2 donné, il existe une seule configuration de cellules (nombre de moles de chaque type de cellules) qui minimise l'énergie de Gibbs. L'énergie de mélange est donnée par :

$$\Delta G^{m} = -RT \frac{\ln \Omega}{n_{M_2O} + n_{MO} + 2n_{SiO_2}} \qquad (2.9.5)$$

où

$$\Omega = \sum_i g(E_i) e^{\left(-E_i/RT\right)} \tag{2.9.6}$$

avec

$$g(E_i) = f\left(n_{M_2O}, n_{MO}, n_{SiO_2}, n_{M^+OS}, n_{M^{2+}OS}, n_{M^+OM^{2+}}\right) \tag{2.9.7}$$

et

$$E_i = E_i^{\text{formation}} + E_i^{\text{interaction}} \tag{2.9.8}$$

où

$$E_i^{\text{formation}} = n_{M^+OM^{2+}} \Delta g^o_{M^+OM^{2+}} + n_{M^+OSi} \Delta g^o_{M^+OSi} + n_{M^{2+}OSi} \Delta g^o_{M^{2+}OSi} \tag{2.9.9}$$

et

$$E_i^{\text{interaction}} = f\left(\varepsilon_{M^+OSi-SiOSi}, \varepsilon_{M^{2+}OSi-SiOSi}, n_{M_2O}, n_{MO}, n_{SiO_2}, n_{M^+OS}, n_{M^{2+}OS}, n_{M^+OM^{2+}}\right) \tag{2.9.10}$$

Les termes $\varepsilon_{M^+OSi-SiOSi}$ et $\varepsilon_{M^{2+}OSi-SiOSi}$ définissent l'énergie de l'interaction des cellules associées et permettent de définir une tendance à la polymérisation. À partir de ces équations énergétiques, l'équilibre des phases peut être calculé.

Gaye et Welfringer (1984) ont exprimé l'énergie de Gibbs de solutions d'oxydes multicomposantes du modèle cellulaire. Récemment, Lehmann et Gaye (1999) ont aussi considéré la présence d'anions autres que O^{2-} dans les cellules en étendant à une seconde "couche" cellulaire leur modèle (application à l'addition de soufre aux laitiers).

Il existe des similitudes entre le modèle cellulaire et le modèle quasichimique. La réaction 2.9.1 ressemble en effet à la réaction quasichimique suivante :

$$[Base - O^{2-} - Base] + [Si - O^{o} - Si] \Leftrightarrow 2[Base - O^{-} - Si] \qquad (2.9.11)$$

Les équations 2.9.2 à 2.9.4 sont très similaires à l'équation 2.9.11. Le modèle quasichimique évalue l'énergie de Gibbs de la solution à l'aide d'une distribution aléatoire des paires de la réaction 2.9.11, alors que le modèle cellulaire utilise une distribution aléatoire des cellules. L'ordonnement cationique est évalué à partir de la minimisation de l'énergie de Gibbs selon l'énergie de formation et d'interaction des cellules, tout comme le modèle quasichimique évalue l'ordonnement des espèces à l'aide de l'énergie de formation des paires. L'entropie configurationnelle est donc modifiée tout comme c'est le cas pour le modèle quasichimique. Les deux modèles diffèrent cependant sur certains points : les tendances acides/bases des espèces n'influencent pas l'évaluation des énergies d'interactions entre les cellules dans le système multicomposant (comme c'est le cas pour le modèle quasichimique); le modèle cellulaire s'applique essentiellement à des interactions seconds-voisins car les cellules possède un ion commun (dans les laitiers l'oxygène), cependant que le modèle quasichimique est plus général et s'applique à des interactions premiers- ou seconds-voisins.

2.10. Modèle des solutions réciproques conformes

La théorie des solutions conformes a été développée par Longuet-Higgins (1951). Plusieurs autres auteurs, Førland (1964), Reiss, Katz et Kleppa (1962), Blander et Yosim (1963), Blander et Braunstein (1960), Saboungi et Blander (1974 et 1975) ont contribué au développement du modèle des solutions réciproques conformes qui est basé sur la théorie de perturbation de la mécanique statistique.

Reiss, Katz et Kleppa (1962) ont développé l'énergie libre de mélange d'Helmholtz pour un mélange de sels fondus *AX-BX* de charge symétrique et monovalente :

$$\Delta F^m = F_{A,B/X} - X_{AX}F_{AX} - X_{BX}F_{BX} \qquad (2.10.1)$$

en exprimant :

$$F_{AX} = -kT \ln Z(g_{AX}) \qquad (2.10.2)$$

et similairement pour F_{BX} et où Z est l'intégrale volumique de configuration qui est fonction du volume et de la température et est exprimée de manière générale comme étant :

$$Z = \iiint_V \exp^{-\frac{U}{kT}} (d\tau)^{2N} \qquad (2.10.3)$$

où U est l'énergie potentielle de $2N$ ions (N cations et N anions), et $(d\tau)^{2N}$ est le symbole utilisé pour décrire le volume combiné des éléments de $2N$ ions. Dans l'équation 2.10.2, on a g_{AX} qui est défini comme :

$$g_{AX} = \frac{\lambda}{\lambda_{AX}} \text{ et } g_{BX} = \frac{\lambda}{\lambda_{BX}} \tag{2.10.4}$$

où $\lambda_{AX} = r_{A^+} + r_{X^-}$, $\lambda_{BX} = r_{B^+} + r_{X^-}$ et λ est la même valeur exprimée pour une composition de référence de la solution *AX-BX* à partir de laquelle la perturbation est évaluée. On définit aussi :

$$Z_{AX} = Z(g_{AX}) \text{ et } Z_{BX} = Z(g_{BX}) \tag{2.10.5}$$

Donc,

$$F_{AX} = -kT \ln Z_{AX} \tag{2.10.6}$$

Reiss, Katz et Kleppa ont utilisé une expansion en série de puissance pour obtenir :

$$F_{AX} = -kT\left[\ln Z + (g_{AX} - 1)\left(\frac{\partial \ln Z}{\partial g_{AX}}\right)_{g_{AX}=1} + \tfrac{1}{2}(g_{AX} - 1)^2\left(\frac{\partial^2 \ln Z}{\partial g_{AX}^2}\right)_{g_{AX}=1} + \ldots\right] \tag{2.10.7}$$

où

$$\left(\frac{\partial \ln Z}{\partial g_{AX}}\right)_{g_{AX}=1} = \frac{1}{Z(1)}\left(\frac{\partial Z}{\partial g_{AX}}\right)_{g_{AX}=1} \tag{2.10.8}$$

et

$$\left(\frac{\partial^2 \ln Z}{\partial g_{AX}^2}\right)_{g_{AX}=1} = \frac{1}{Z(1)}\left(\frac{\partial^2 Z}{\partial g_{AX}^2}\right)_{g_{AX}=1} - \frac{1}{(Z(1))^2}\left(\frac{\partial Z}{\partial g_{AX}}\right)^2_{g_{AX}=1} \tag{2.10.9}$$

Dans l'équation 2.10.3, l'énergie potentielle U à la composition de référence (au λ de référence) vaut :

$$U = \sum_{a}^{N}\sum_{c}^{N} u_{ac} + \sum_{a}^{N}\sum_{\substack{a' \\ a'>a}}^{N} u_{aa'} + \sum_{c}^{N}\sum_{\substack{c' \\ c'>c}}^{N} u_{cc'} \tag{2.10.10}$$

où u_{ac} est le potentiel des paires a-c (anion-cation), $u_{cc'}$ est le potentiel des paires de cations c-c', et $u_{aa'}$ est le potentiel des paires d'anions a-a', définis comme étant :

$$u_{ac} = \frac{1}{\lambda} f\left(\frac{r}{\lambda}\right) \tag{2.10.11}$$

$$u_{cc'} = \frac{q^2}{kr} \tag{2.10.12}$$

$$u_{aa'} = \frac{q^2}{kr} \tag{2.10.13}$$

où q est la charge cationique (2.10.12) ou anionique (2.10.13), k est la valeur effective de la constante diélectrique et r est la distance de centre à centre entre les 2 ions. L'équation 2.10.10 devient pour une composition autre que la composition de référence (disons $X_{AX} = 1$) :

$$U_{AX} = \sum_{a}^{N}\sum_{c}^{N} g_{AX} u_{ac}(g_{AX} r) + \sum_{a}^{N}\sum_{\substack{a' \\ a'>a}}^{N} u_{aa'} + \sum_{c}^{N}\sum_{\substack{c' \\ c'>c}}^{N} u_{cc'} \tag{2.10.14}$$

donc

$$Z_{AX} = Z(g_{AX}) = \iiint_{v} \exp^{-\frac{U_{AX}}{kT}} (d\tau)^{2N} \tag{2.10.15}$$

Les dérivées des équations 2.10.8 et 2.10.9 peuvent être évaluées par la dérivation de l'équation 2.10.15.

Un traitement similaire est fait pour F_{BX}, et $F_{A,B/X}$ est aussi évaluée de la même manière à l'exception que l'énergie potentielle U des équations 2.10.10 et 2.10.14 sont remplacées par :

$$U_{A,B/X} = \sum_{a}^{N} \sum_{c}^{X_{AX}N} g_{AX} u_{ac}(g_{AX} r) + \sum_{a}^{N} \sum_{c'}^{X_{BX}N} g_{BX} u_{ac}(g_{BX} r)$$
$$+ \sum_{a}^{N} \sum_{\substack{a' \\ a'>a}}^{N} u_{aa'} + \sum_{c}^{X_{AX}N} \sum_{\substack{c' \\ c'>c}}^{X_{AX}N} u_{cc'} + \sum_{c''}^{X_{BX}N} \sum_{\substack{c''' \\ c'''>c''}}^{X_{BX}N} u_{c''c'''} + \sum_{c}^{X_{AX}N} \sum_{c''}^{X_{BX}N} u_{cc''} \qquad (2.10.16)$$

Reiss, Katz et Kleppa ont donc obtenu l'énergie libre de Helmholtz de mélange d'une solution *AX-BX* monovalente comme étant (à partir de 2.10.1) :

$$\Delta F^m = X_{AX} X_{BX} \frac{\lambda^2 kT}{2Z(1)} \left[N^3 \varepsilon + N^3 (N-1)\omega - \frac{\alpha^2}{Z(1)} \right] \left(\frac{\lambda_{BX} - \lambda_{AX}}{\lambda_{BX} \lambda_{AX}} \right)^2 \qquad (2.10.17)$$

où

$$\alpha = \iiint_V \varphi_{ac} \exp^{-\frac{U}{kT}} (d\tau)^{2N} \qquad (2.10.18)$$

$$\varphi_{ac} = u_{ac} + r\left(\frac{\partial u_{ac}}{\partial r} \right) \qquad (2.10.19)$$

$$\varepsilon = \iiint_V \varphi_{ac} \varphi_{ac'} \exp^{-\frac{U}{kT}} (d\tau)^{2N} \qquad (2.10.20)$$

$$\omega = \iiint_V \varphi_{ac} \varphi_{a'c'} \exp^{-\frac{U}{kT}} (d\tau)^{2N} \qquad (2.10.21)$$

L'équation 2.10.17 peut être exprimée comme étant :

$$\Delta F^m = X_{AX} X_{BX} \left[\Phi(T,V) \left(\frac{\lambda_{BX} - \lambda_{AX}}{\lambda_{BX} \lambda_{AX}} \right)^2 \right] \tag{2.10.22}$$

où $\Phi(T,V)$ est une fonction de la température et du volume seulement. Sachant que :

$$\Delta G^m(T,P) = \Delta F^m(T,P) + P \Delta V^m \tag{2.10.23}$$

La variation compositionnelle de l'énergie de Gibbs de mélange à température et pression constante devrait être la même que la variation compositionnelle de l'énergie libre d'Helmholtz, car on peut négliger le dernier terme de l'équation 2.10.23 à P = 1 atm. L'équation 2.10.22 peut donc permettre d'obtenir :

$$\Delta G^{m,non-config} = X_{AX} X_{BX} \theta(T,P) \left(\frac{\lambda_{BX} - \lambda_{AX}}{\lambda_{BX} \lambda_{AX}} \right)^2 \tag{2.10.24}$$

où $\theta(T,P)$ est une fonction de la température et de la pression seulement issue de $\Phi(T,V)$. Alors, sachant que :

$$\Delta H^m = \Delta G^m - T \left(\frac{\partial \Delta G^m}{\partial T} \right)_P \tag{2.10.25}$$

on a que l'enthalpie de mélange d'une solution *AX-BX* monovalente est donnée par :

$$\Delta H^m = X_{AX} X_{BX} \Omega(T,P) \left(\frac{\lambda_{BX} - \lambda_{AX}}{\lambda_{BX} \lambda_{AX}} \right)^2 = X_{AX} X_{BX} \Delta \omega_{A,B/X} \tag{2.10.26}$$

Ce qui confirme la validité du modèle des solutions régulières pour les sels fondus monovalents.

Le terme $\frac{\lambda_{BX} - \lambda_{AX}}{\lambda_{BX}\lambda_{AX}}$ est aussi symbolisé par $\delta_{A,B/X}$.

L'entropie de mélange utilisée est un mélange aléatoire des cations sur un sous-réseau cationique hypothétique et un mélange aléatoire des anions sur un sous-réseau anionique hypothétique intercalé au premier (similairement à Temkin (1945)).

Cependant, Blander (1962) a développé les équations de Reiss, Katz et Kleppa (1962) qui ont utilisé une perturbation du second ordre, pour une perturbation de troisième ordre afin d'évaluer la variation compositionnelle du terme "régulier" pour des mélanges de sels de charges symétriques et a obtenu :

$$\Delta H^m = X_{AX} X_{BX} (q_1 + q_2 X_{AX} + q_3 X_{AX} X_{BX}) \qquad (2.10.27)$$

Le terme q_1 de Blander est donné par l'équation 2.10.26 et les termes q_3 et partiellement q_2 sont dépendents des interactions à courte distance du type polarization et énergies de dispersion de London (Østvold, 1971). L'expression 2.10.27 se transforme aisément en:

$$\Delta H^m = X_{AX} X_{BX} \left(q_1 + (q_2 + q_3) X_{AX} - q_3 X_{AX}^2\right) \qquad (2.10.28)$$

Ce qui confirme la validité de l'expansion polynomiale (sous quelque forme que ce soit) du terme régulier pour les sels fondus monovalents.

Sous une forme plus générale et pour des solutions ternaires à ions communs, Saboungi et Blander (1975) ont montré que l'énergie en excès est donnée par :

$$
\begin{aligned}
g^E = {} & X_A X_B \left(\phi_{AB}^{(11)} + \phi_{AB}^{(21)} X_A + \phi_{AB}^{(22)} X_A X_B\right) + X_A X_C \left(\phi_{AC}^{(11)} + \phi_{AC}^{(21)} X_A + \phi_{AC}^{(22)} X_A X_C\right) \\
& + X_B X_B \left(\phi_{BC}^{(11)} + \phi_{BC}^{(21)} X_B + \phi_{BC}^{(22)} X_B X_C\right) \\
& - X_A X_B X_C \left(\left(\phi_{AB}^{(21)}\right)^{\frac{1}{3}} + \left(\phi_{AC}^{(21)}\right)^{\frac{1}{3}}\right)\left(\left(\phi_{BC}^{(21)}\right)^{\frac{1}{3}} + \left(-\phi_{AB}^{(21)}\right)^{\frac{1}{3}}\right)\left(\left(-\phi_{AC}^{(21)}\right)^{\frac{1}{3}} + \left(-\phi_{BC}^{(21)}\right)^{\frac{1}{3}}\right) \\
& + 2X_A^2 X_B X_C \left(\phi_{AB}^{(22)} \phi_{AC}^{(22)}\right)^{\frac{1}{2}} + 2X_B^2 X_A X_C \left(\phi_{AB}^{(22)} \phi_{BC}^{(22)}\right)^{\frac{1}{2}} + 2X_C^2 X_A X_B \left(\phi_{AC}^{(22)} \phi_{BC}^{(22)}\right)^{\frac{1}{2}}
\end{aligned}
\tag{2.10.29}
$$

Blander a suggéré l'utilisation des fractions équivalentes en remplacement des fractions molaires des ions dans l'équation 2.10.29 pour des systèmes ternaires à asymétrie des charges : cette approche a été testée avec succès par Pelton, Bale et Lin (1984).

Donc à partir des évaluations des coefficients binaires q_i de l'expression 2.10.27, l'expression de g^E du système ternaire peut être évaluée sans l'utilisation de méthode d'estimation (*i.e.* Kohler/Toop/Muggianu) car l'équation 2.10.29 demeure valide selon la théorie des solutions conformes. Pelton, Bale et Lin (1984) recommandent l'utilisation de l'équation 2.10.29 au lieu des méthodes d'estimation (*i.e.* Kohler/Toop/Muggianu) pour les solutions de sels fondus pour lesquelles elle a été développée. Cependant, les méthodes d'estimation peuvent donner des résultats très similaires à ceux de l'équation 2.10.29 et ont l'avantage d'être applicables à des systèmes quaternaires et d'ordre supérieur. Ce dernier point est essentiel pour le développement de bases de données sur la thermodynamique des mélanges de sels fondus.

Pour les solutions ternaires réciproques ($A,B/X,Y$) où il y a plus d'un cation et plus d'un anion, Saboungi et Blander (1974) ont développé l'expression de l'énergie de Gibbs de mélange (par équivalent de solution) suivante pour les sels fondus à asymétrie ionique, dérivée de la théorie des solutions conformes.

$$\begin{aligned}\Delta g^{m} = &(q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\ &+ (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\ &+ Y_A Y_B Y_X \Delta\omega_{A,B/X} + Y_A Y_B Y_Y \Delta\omega_{A,B/Y} \\ &+ Y_X Y_Y Y_A \Delta\omega_{A/X,Y} + Y_X Y_Y Y_B \Delta\omega_{B/X,Y} \\ &+ Y_A Y_Y \Delta g^{éch}_{A,B/X,Y} + Y_A Y_B Y_X Y_Y \Lambda\end{aligned} \tag{2.10.30}$$

où les $\Delta\omega$ sont les paramètres de l'équation 2.10.26 (ou paramètres réguliers) et $\Delta g^{éch}_{A,B/X,Y}$ est l'énergie d'échange (par équivalent) de la réaction suivante :

$$(q_A q_Y)^{-1} A_{q_A} Y_{q_Y} + (q_B q_X)^{-1} B_{q_B} X_{q_X} \Leftrightarrow (q_A q_X)^{-1} A_{q_A} X_{q_X} + (q_B q_Y)^{-1} B_{q_B} Y_{q_Y} \tag{2.10.31}$$

Le terme Λ de l'équation 2.10.30 a été estimé par Blander et Braunstein (1960) (voir aussi Førland (1964)) à partir de la théorie quasichimique (la démonstration complète est faite ci-après) :

$$\Lambda = -\frac{\left(\Delta g^{échange}_{A,B//X,Y}\right)^2}{2ZRT} \tag{2.10.32}$$

Les deux derniers termes de l'équation 2.10.30, qui donnent l'énergie de mélange d'une solution ternaire réciproque *A,B/X,Y*, sont donc des fonctions de l'énergie d'échange. Le premier de ces termes provient de l'expression suivante (obtenue du mélange aléatoire des cations et des anions sur les sites respectifs) :

$$Y_A Y_X g^{o}_{AX} + Y_A Y_Y g^{o}_{AY} + Y_B Y_X g^{o}_{BX} + Y_B Y_Y g^{o}_{BY} \tag{2.10.33}$$

où trois des g^o des sels purs (AX, BX et BY) peuvent être fixés arbitrairement à 0 et le troisième vaut donc $-\Delta g^{éch}_{A,B/X,Y}$. Le second terme, contenant l'énergie d'échange, est une approximation de la contribution à l'énergie de Gibbs de mélange de l'ordonnement à courte distance premiers-voisins qui découle de l'énergie de la réaction d'échange. À partir de la théorie quasichimique qui évalue le changement de configuration avec l'énergie des paires premiers-voisins, Blander et Braunstein (1960) ont évalué la contribution au G de l'ordonnement depuis la réaction quasichimique d'échange :

$$[A-Y]_{paire}+[B-X]_{paire} \Leftrightarrow [A-X]_{paire}+[B-Y]_{paire} \qquad \Delta\omega_{A,B/X,Y}Z^{-1} \tag{2.10.34}$$

qui possède la constante d'équilibre suivante :

$$K_{équ}=\frac{X_{A/X}X_{B/Y}}{X_{A/Y}X_{B/X}}=\exp^{\frac{-N_{Av}\Delta\omega_{A,B/X,Y}}{ZRT}} \tag{2.10.35}$$

Sachant que pour un mélange aléatoire des ions sur leurs sous-réseaux respectifs, les fractions molaires des paires premiers-voisins peuvent être calculées selon :

$$X_{c/a}=Y_cY_a \tag{2.10.36}$$

où c est le cation et a est l'anion. La constante d'équilibre devient :

$$K_{équ}=\frac{(Y_AY_X+y)(Y_BY_Y+y)}{(Y_AY_Y-y)(Y_BY_X-y)}=\exp^{\frac{-N_{Av}\Delta\omega_{A,B/X,Y}}{ZRT}} \tag{2.10.37}$$

$$K_{équ} = \frac{Y_A Y_B Y_X Y_Y \left(1+\frac{y}{Y_A Y_X}\right)\left(1+\frac{y}{Y_B Y_Y}\right)}{Y_A Y_B Y_X Y_Y \left(1-\frac{y}{Y_A Y_Y}\right)\left(1-\frac{y}{Y_B Y_X}\right)} = \exp^{\frac{-N_{Av}\Delta\omega_{A,B/X,Y}}{ZRT}} \tag{2.10.38}$$

où y est la déviation au mélange aléatoire des ions dû à l'ordonnement à courte distance et est fonction du bilan de masse des ions. L'estimation de y en fonction de $\Delta\omega_{A,B/X,Y}$ se fait à l'aide des logarithmes et de leur approximation à l'aide de la série de suivante :

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots \qquad -1 < x \leq 1 \tag{2.10.39}$$

Donc, en utilisant le premier terme de cette série de Taylor, on a :

$$\ln\left(1+\frac{y}{Y_A Y_X}\right) + \ln\left(1+\frac{y}{Y_B Y_Y}\right) - \ln\left(1-\frac{y}{Y_A Y_Y}\right) - \ln\left(1-\frac{y}{Y_B Y_X}\right) = -\frac{N_{Av}\Delta\omega_{A,B/X,Y}}{ZRT} \tag{2.10.40}$$

Étant donné que y ne peut être supérieur ou inférieur à la limite des dénominateurs de par le bilan de masse des ions, l'équation 2.10.39 peut être utilisée pour trouver y :

$$y = -Y_A Y_B Y_X Y_Y \frac{N_{Av}\Delta\omega_{A,B/X,Y}}{ZRT} \tag{2.10.41}$$

La contribution à l'énergie de la déviation y au mélange aléatoire est donnée par :

$$\Delta E^E = yZ\left(\frac{N_{Av}\Delta\omega_{A,B/X,Y}}{Z}\right) = -Y_A Y_B Y_X Y_Y \frac{\left(N_{Av}\Delta\omega_{A,B/X,Y}\right)^2}{ZRT} \tag{2.10.42}$$

Ce qui donne pour l'énergie de Gibbs :

$$\Delta g^E = T\int_0^{\frac{1}{T}} \Delta E^E d\left(\frac{1}{T}\right) = -Y_A Y_B Y_X Y_Y \frac{\left(\Delta g^{éch}_{A,B/X,Y}\right)^2}{2ZRT} \qquad (2.10.43)$$

Cette expression se retrouve à l'équation 2.10.30, cependant que la forme $Y_A Y_B Y_X Y_Y \Lambda$ a été obtenue de la théorie des solutions conformes.

Les équations 2.10.29 et 2.10.30 de la théorie de solutions conformes ont été appliquées sur de nombreux systèmes de sels fondus avec succès (voir Saboungi et Blander (1974) et Pelton, Bale et Lin (1984)). Cependant, lorsque la valeur absolue de l'énergie d'échange de la réaction 2.10.31 dépasse les 50 kJ/équivalents, le modèle est inapte à prédire correctement les surfaces des liquidus des systèmes réciproques. Les termes fonctions de l'énergie d'échange de l'équation 2.10.30, qui décrit l'énergie de mélange, donnent une contribution à l'énergie de Gibbs de la solution beaucoup trop négative à la composition $Y_A=Y_B=Y_X=Y_Y=0.5$, ce qui engendre deux lacunes de miscibilité alignées le long de la ligne de composition donnée par la paire de sels stables (côté droit de la réaction 2.10.31 si l'énergie d'échange est négative) de part et d'autre de la composition médiane.

<u>Généralisation aux systèmes multicomposants réciproques à asymétrie des charges</u>

Les équations 2.10.26 et 2.10.28 démontrent que l'expansion polynomiale des termes $\Delta\omega$ issus du modèle des solutions régulières est tout à fait compatible avec la théorie des solutions conformes de Reiss, Katz et Kleppa (1962).

Partant de ce fait, Pelton (1988) a développé les équations de l'énergie de Gibbs pour les systèmes multicomposants réciproques à asymétrie des charges en remplacant

l'estimation de l'énergie de Gibbs en excès dans les sous-systèmes ternaires à ions communs de la théorie des solutions conformes par les méthodes d'estimation de Kohler et de Toop associées à une division des cations et des anions en chacun deux groupes définis par leur tendance acide/base. L'énergie de Gibbs par équivalent de solution est donnée par (en utilisant les fractions équivalentes) :

$$
\begin{aligned}
g = & \sum_c \sum_a Y_c Y_a g^o_{c/a} + \left(\sum_c q_c X_c \right)^{-1} RT \sum_c X_c \ln X_c + \left(\sum_a q_a X_a \right)^{-1} RT \sum_a X_a \ln X_a \\
& + \sum_a \sum_c \sum_{c'} Y_c Y_{c'} Y_a \Delta\omega_{c,c'/a} + \sum_c \sum_a \sum_{a'} Y_a Y_{a'} Y_c \Delta\omega_{c/a,a'} \\
& + \sum_c \sum_{c'} \sum_{c''} \sum_a Y_c Y_{c'} Y_{c''} Y_a \sum_{i,j,k} \Phi^{(ijk)}_{c,c',c''/a} \frac{Y_c^{i-1} Y_{c'}^{j-1} Y_{c''}^{k-1}}{\left(Y_c + Y_{c'} + Y_{c''}\right)^{i+j+k-3}} \\
& + \sum_a \sum_{a'} \sum_{a''} \sum_c Y_a Y_{a'} Y_{a''} Y_c \sum_{i,j,k} \Phi^{(ijk)}_{c/a,a',a''} \frac{Y_a^{i-1} Y_{a'}^{j-1} Y_{a''}^{k-1}}{\left(Y_a + Y_{a'} + Y_{a''}\right)^{i+j+k-3}} \\
& + \sum_c \sum_{c'} \sum_a \sum_{a'} \sum_{i,j,k,l} Y_c^i Y_{c'}^j Y_a^k Y_{a'}^l \Delta\omega^{(ijkl)}_{c,c'/a,a'}
\end{aligned}
\tag{2.10.44}
$$

où les $g^o_{c/a}$ sont les énergies standards des sels purs en équivalent et les énergies $\Delta\omega_{c,c'/a}$ et $\Delta\omega_{c/a,a'}$ des interactions seconds-voisins sont représentées par des polynômes similaires aux fonctions de Kohler et Toop, selon l'appartenance des ions qui se mélangent aux groupes acide/base définis.

<u>Interaction entre deux cations (c et c') du même groupe (avec l'anion commun a)</u>

$$
\Delta\omega_{c,c'/a} = \Delta\omega^o_{c,c'/a} + \sum_i \sum_j \left(\frac{Y_c}{Y_c + Y_{c'}} \right)^{i-1} \left(\frac{Y_{c'}}{Y_c + Y_{c'}} \right)^{j-1} q^{(ij)}_{c,c'/a} \tag{2.10.45}
$$

<u>Interaction entre deux cations (c et c') de groupes différents (avec l'anion commun a)</u>

$$\Delta\omega_{c,c'/a} = \Delta\omega^{o}_{c,c'/a} + \sum_{i}\sum_{j}\xi_{I}^{\,i-1}\xi_{II}^{\,j-1}q^{(ij)}_{c,c'/a} \qquad (2.10.46)$$

où

$$\xi_{I} = \sum_{\substack{c \\ c\in I}} Y_{c} \text{ et } \xi_{II} = \sum_{\substack{c \\ c\in II}} Y_{c} \text{ avec } \xi_{I} + \xi_{II} = 1 \qquad (2.10.47)$$

Les termes q des équations précédentes sont les paramètres non-réguliers similaires à ceux de l'équation 2.10.28. Les interactions anioniques $\Delta\omega_{c/a,a'}$ sont traitées de la même manière.

Le premier des termes réciproques de l'équation 2.10.44 ($\Delta\omega^{(1111)}_{c,c'/a,a'}$) est donné par l'approximation quasichimique de l'équation 2.10.43.

2.11. Modèle des solutions réciproques ioniques (Hillert, Jansson, Sundman et Ågren, 1985)

Le modèle des solutions réciproques ioniques a été développé par Hillert, Jansson, Sundman et Ågren (1985). Ce modèle suppose la présence de 2 sous-réseaux (ou quasi-réseaux) dans le liquide. L'approche est similaire à celle des sous-réseaux dans les solides. Les sous-réseaux sont occupés par des espèces qui leurs sont propres. Ainsi le premier sous-réseau, cationique, contient les cations du système, alors que le deuxième sous-réseau, anionique contient les anions du système. Temkin (1945) a déjà estimé l'entropie configurationnelle pour le mélange de cations (c) et d'anions (a) sur deux sous-réseaux respectifs en assumant un mélange complètement aléatoire sur chacun des sous-réseaux. La nouveauté du modèle est que des espèces neutres (n) peuvent aussi se mélanger sur le deuxième sous-réseaux (anionique), ainsi que des lacunes (dénommée Va). Par nomenclature, les espèces cationique seront indexées avec la lettre c dans les équations de cette section, alors que les anions, les lacunes et les espèces neutres seront indexées par la lettre a.

L'énergie de Gibbs molaire d'une solution liquide telle que donnée par ce modèle est :

$$g = \sum_c \sum_a y_c y_a g^o_{c_{q_a} a_{q_c}} + RT\left(P\sum_c y_c \ln y_c + Q\sum_a y_a \ln y_a \right) + g^E \qquad (2.11.1)$$

En différenciant les espèces anioniques chargées, neutres et les lacunes, on obtient :

$$\begin{aligned} g = & \sum_c \sum_a y_c y_a g^o_{c_{q_a} a_{q_c}} + \sum_c \sum_n y_c y_n g^o_{c_0 n_{q_c}} + \sum_c y_c y_{Va} g^o_{c_{q_i} Va_{q_i}} \left(\frac{q_{Va}}{q_i} \right) \\ & + RT\left(P\sum_c y_c \ln y_c + Q\left(\sum_c y_a \ln y_a + \sum_n y_n \ln y_n + y_{Va} \ln y_{Va} \right) \right) + g^E \end{aligned} \qquad (2.11.2)$$

où

$$Q = \sum_c q_c y_c \tag{2.11.3}$$

$$P = \sum_a q_a y_a + q_{Va} y_{Va} \tag{2.11.4}$$

$$q_{Va} = Q \tag{2.11.5}$$

où les q_i sont les charges ioniques absolues avec $q_n = 0$, et les y_i sont les fractions molaires des espèces sur les sous-réseaux. L'énergie molaire de Gibbs en excès, g^E, peut être exprimée de plusieurs manières, mais Hillert, Jansson, Sundman et Ågren ont proposé l'utilisation de l'expansion polynomiale de Redlich-Kister sous 8 différents types de paramètres :

- Les termes binaires "métalliques" (*c-Va-c'*)
- Les termes (*n-c-n'*)
- Les termes (*c-Va-n*)
- Les termes (*c-n-c'*) qui sont négligés car ils correspondent à l'interaction entre $c_0 n_{q_c}$ et $c'_0 n_{q_{c'}}$.
- Les termes (*c-a-c'*)
- Les termes (*a-c-a'*)
- Les termes (*Va-c-a*)
- Les termes (*a-c-n*)

Hillert a démontré que le modèle ionique est exactement similaire au modèle d'association pour un système binaire *A-B*. Les mêmes commentaires sur le modèle d'association s'appliquent donc à ce cas précis.

Hillert et Wang (1989) ont utilisé le modèle de solutions ioniques réciproques pour le système $MgO\text{-}SiO_2$ où le liquide est traité comme étant :

$$\left(Mg^{2+}\right)_{4y_{SiO_4^{4-}}+2y_{O^{2-}}}\left(O^{2-},SiO_4^{4-},SiO_2^0\right)_2 \qquad (2.11.6)$$

L'espèce neutre SiO_2 permet d'étendre le champ d'application du modèle aux plus hautes teneurs en silice comparé au traitement classique où seules les espèces anioniques O^{2-} et SiO_4^{4-} sont présentes. La présence de l'espèce anionique SiO_4^{4-} permet d'évaluer l'impact de l'ordonnement à courte distance seconds-voisins *Mg-O-Si* sur l'entropie configurationnelle et l'énergie de Gibbs. Cependant, l'extension de cette approche au système $CaO\text{-}MgO\text{-}SiO_2$ (addition de Ca^{2+} aux espèces cationiques de l'équation 2.11.6) ne permet pas de considérer l'ordonnement à courte distance dû à la réaction d'échange suivante :

$$Ca_2O_2 + Mg_4(SiO_4)_2 \Leftrightarrow Mg_2O_2 + Ca_4(SiO_4)_2 \qquad (2.11.7)$$

Cet effet réciproque peut être extrêmement important pour certains mélanges d'oxydes, au point de produire une lacune de miscibilité liquide-liquide le long de la ligne de composition joignant la paire d'oxydes stables (voir les systèmes $FeO\text{-}CaO\text{-}P_2O_5$ et $MnO\text{-}CaO\text{-}P_2O_5$; ici P^{5+} remplace Si^{4+}).

Un autre aspect du modèle, plus théorique celui-là, qui est source de discussion, est la présence de lacunes anioniques dans un liquide. La présence de lacunes dans un cristal se conçoit bien, mais l'héritage des théories des solides appliquées aux liquides apporte certains artéfacts...

2.12. Modèle des solutions réciproques quasichimiques (Dessureault et Pelton, 1991)

Dessureault et Pelton (1991) ont développé un modèle pour solutions ioniques réciproques qui possède une entropie quasichimique associée au modèle d'Ising. Le modèle, lointain dérivé des théories de Temkin (1945), suppose la présence de 2 sous-réseaux (ou quasi-réseaux) dans le liquide, où les cations et les anions se mélangent sur leurs sous-réseaux respectifs. Le modèle permet d'évaluer l'ordonnement à courte distance premiers-voisins (mélange entre les espèces des sous-réseaux) à partir des énergies des paires premiers-voisins et partiellement influencé par l'énergie des paires seconds-voisins (mélange sur un même sous-réseau). L'énergie d'échange de la réaction :

$$[A-Y]_{paire}+[B-X]_{paire} \Leftrightarrow [A-X]_{paire}+[B-Y]_{paire} \qquad \omega_{A,B/X,Y} \qquad (2.12.1)$$

avec

$$\Delta g^{éch}_{A,B/X,Y} = ZN_{Av}\omega_{A,B/X,Y} \qquad (2.12.2)$$

permet de déterminer quelle paire de liaisons forme la paire dite "stable" et quelle paire de liaisons forme la paire dite "instable". Si $\Delta g^{éch}_{A,B/X,Y}$ est négatif, alors la réaction 2.12.1 favorisera la présence de liaisons *A-X* et *B-Y* (paire stable) dans la solution au détriment des liaisons *A-Y* et *B-X* (paire instable) changeant ainsi la configuration des espèces. L'entropie configurationnelle des modèles de solutions réciproques qui assument un mélange aléatoire des ions sur leurs sous-réseaux respectifs (Temkin) ne peut évaluer correctement l'influence de la réaction réciproque d'échange (2.12.1) sur l'énergie de Gibbs. Plus souvent qu'autrement, ces modèles prédisent l'existance d'une

ou deux lacunes de miscibilité lorsque la valeur absolue de $\Delta g^{éch}_{A,B/X,Y}$ est supérieure à environ 50 kJ/équivalent (voir Dessureault et Pelton, 1991).

Le modèle quasichimique réciproque de Dessureault et Pelton a été conçu afin de tenir compte de l'ordonnement à courte distance dû à l'énergie de la réaction d'échange. Dessureault et Pelton ont développé les équations du modèle pour une solution ionique ternaire réciproque *(A,B/X,Y)* avec des ions monovalents :

$$\begin{aligned} G = {} & n_{A/X} g^o_{AX} + n_{A/Y} g^o_{AY} + n_{B/X} g^o_{BX} + n_{B/Y} g^o_{BY} \\ & + RT(n_A \ln X_A + n_B \ln X_B) + RT(n_X \ln X_X + n_Y \ln X_Y) \\ & + RT\left(n_{A/X} \ln \frac{X_{A/X}}{X_A X_X} + n_{A/Y} \ln \frac{X_{A/Y}}{X_A X_Y} + n_{B/X} \ln \frac{X_{B/X}}{X_B X_X} + n_{B/Y} \ln \frac{X_{B/Y}}{X_B X_Y} \right) \\ & + \frac{X_{A/X} X_{A/Y}}{X_A} \omega_{A/X,Y} + \frac{X_{B/X} X_{B/Y}}{X_B} \omega_{B/X,Y} \\ & + \frac{X_{A/X} X_{B/X}}{X_X} \omega_{A,B/X} + \frac{X_{A/Y} X_{B/Y}}{X_Y} \omega_{A,B/Y} \end{aligned} \tag{2.12.3}$$

où les $n_{c/a}$ sont les nombres de moles de liaisons [*c-a*] de la réaction quasichimique 2.12.1, obtenus par minimisation de la fonction 2.12.13 en respectant le bilan de masse donné par les équations qui suivent. Les fractions molaires des liaisons $X_{c/a}$,, les nombres de moles de cations n_c et d'anions n_a et les fractions molaires ioniques X_c et X_a sont données par :

$$X_{A/X} = \frac{n_{A/X}}{n_{A/X} + n_{A/Y} + n_{B/X} + n_{B/Y}} \tag{2.12.4}$$

$$Zn_A = n_{A/X} + n_{A/Y} \tag{2.12.5}$$

$$Zn_X = n_{A/X} + n_{B/X} \tag{2.12.6}$$

$$X_A = \frac{n_A}{n_A + n_B} = 1 - X_B \tag{2.12.7}$$

$$X_X = \frac{n_X}{n_X + n_Y} = 1 - X_Y \tag{2.12.8}$$

où Z est le nombre de coordination premiers-voisins de la solution. Les termes $\omega_{A/X,Y}$, $\omega_{B/X,Y}$, $\omega_{A,B/X}$ et $\omega_{A,B/Y}$ de l'équation 2.12.3 sont les fonctions régulières (ou polynomiales) des interactions seconds-voisins (même sous-réseau) des sous-systèmes binaires *AX-AY*, *BX-BY*, *AX-BX* et *AY-BY* respectivement. Il est à noter que contrairement au modèle des solutions ioniques conformes, où ces termes binaires sont multipliés par la probabilité de trouver deux ions donnés entourant un ion commun assumant un mélange aléatoire d'ions sur leurs réseaux respectids ($X_A X_B (X_X)$ pour $\omega_{A,B/X}$, etc...), ces termes sont multipliés, dans le modèle quasichimique, par la probabilité de trouver deux paires voisines (assumant un mélange aléatoire de paires) étant donné que ces deux paires partagent un ion commun ($X_{AX} X_{BX} X_X^{-1} \omega_{A,B/X}$). Cette importante différence permet de mieux estimer l'influence des termes de mélange seconds-voisins sur l'énergie de Gibbs du mélange réciproque, car si $\left|\Delta g^{échange}_{A,B//X,Y}\right|$ est grande, alors toutes les contributions au G de mélange des interactions seconds-voisins s'en trouvent diminuées car $X_{AX} X_{BX} X_X^{-1} < X_A X_B X_X$ (car une des paires *A-X* ou *B-X* sera moins présente dans le mélange car elles ne sont pas du même côté de la réaction d'échange 2.12.1). Il ressort de cette analyse que le modèle des solutions ioniques conformes surestime la contribution des interactions seconds-voisins à l'énergie de mélange réciproque si la valeur absolue de l'énergie d'échange est grande.

Dans l'équation de l'énergie de Gibbs, Dessureault et Pelton utilisent directement les fractions molaires ioniques (X_i) dans l'expansions des fonctions ω.

Chartrand (1995) a étendu le modèle quasichimique pour solutions réciproques aux solutions multicomposantes avec des ions de charges asymétriques par l'utilisation des fractions équivalentes (tel que suggéré par Saboungi et Blander, 1975, et utilisé par Pelton, 1988). Un formalisme Kohler/Toop a été introduit pour les sous-systèmes à ions communs afin d'exploiter les différences acide/base des ions. De plus, les fonctions ω ont vu leur expansion transformée par l'utilisation des fractions des liaisons premiers-voisins $X_{c/a}$ au lieu des fractions molaires ioniques X_c et X_a afin de coupler plus fortment l'impact de l'ordonnement à courte distance premiers-voisins avec les énergies des interactions seconds-voisins (ω). L'énergie de Gibbs proposée est :

$$G = \sum_c \sum_a n_{c/a} g^o_{c/a} + RT \sum_c n_c \ln X_c + RT \sum_a n_a \ln X_a + \sum_c \sum_a n_{c/a} \ln \frac{X_{c/a}}{Y_c Y_a} + \left(\tfrac{1}{2} \sum_c q_c n_c + \tfrac{1}{2} \sum_a q_a n_a \right) g^E \tag{2.12.9}$$

Les énergies standards des sels purs, $g^o_{c/a}$ sont définies comme :

$$g^o_{c/a} = g^o_{c_{\frac{1}{q_c}} a_{\frac{1}{q_a}}} \tag{2.12.10}$$

où les q_i sont les valeurs absolues des charges ioniques. On définit aussi :

$$X_{c/a} = \frac{n_{c/a}}{\sum_{cations} \sum_{anions} n_{i/j}} \tag{2.12.11}$$

$$Zn_c = \frac{1}{q_c} \sum_{anions} n_{c/a} \tag{2.12.12}$$

$$Zn_a = \frac{1}{q_a} \sum_{cations} n_{c/a} \tag{2.12.13}$$

$$X_c = \frac{n_c}{\sum_{cations} n_i} \tag{2.12.14}$$

$$X_a = \frac{n_a}{\sum_{anions} n_i} \tag{2.12.15}$$

$$Y_c = \frac{\sum_{anions} n_{c/a}}{\sum_{cations} \sum_{anions} n_{i/j}} \tag{2.12.16}$$

$$Y_a = \frac{\sum_{cations} n_{c/a}}{\sum_{cations} \sum_{anions} n_{i/j}} \tag{2.12.17}$$

où Z est le nombre de coordination premiers-voisins de la solution. L'énergie de Gibbs de la solution est donnée par les valeurs de $n_{c/a}$ qui minimisent G (équ. 2.12.9). L'énergie de Gibbs en excès, g^E, proposée par Chartrand (1995) est :

$$\begin{aligned} g^E = & \sum_c \sum_{c'} \sum_a \frac{X_{c/a} X_{c'/a}}{Y_a} \omega_{cc'/a} + \sum_a \sum_{a'} \sum_c \frac{X_{c/a} X_{c/a'}}{Y_c} \omega_{c/a,a'} \\ & + \sum_c \sum_{c'} \sum_{c''} \sum_a \frac{X_{c/a} X_{c'/a} X_{c''/a}}{Y_a^2} \Phi^{(ijk)}_{cc'c''/a} \frac{X_{c/a}^{i-1} X_{c'/a}^{j-1} X_{c''/a}^{k-1}}{\left(X_{c/a} + X_{c'/a} + X_{c''/a}\right)^{i+j+k-3}} \\ & + \sum_a \sum_{a'} \sum_{a''} \sum_c \frac{X_{c/a} X_{c/a'} X_{c/a''}}{Y_c^2} \Phi^{(ijk)}_{c/aa'a''} \frac{X_{c/a}^{i-1} X_{c/a'}^{j-1} X_{c/a''}^{k-1}}{\left(X_{c/a} + X_{c/a'} + X_{c/a''}\right)^{i+j+k-3}} \\ & + \sum_c \sum_{c'} \sum_a \sum_{a'} \Phi^{(ijkl)}_{cc'/aa'} X_{c/a}^i X_{c'/a}^j X_{c/a'}^k X_{c'/a'}^l \end{aligned} \tag{2.12.18}$$

où les c, c' et c'' sont des cations, les a, a' et a'' sont des anions et les termes Φ sont des paramètres ternaires. L'expansion des termes binaires ω dépend de la nature des ions du sous-système binaire. En effet un formalisme Kohler/Toop avec deux groupes (acides et bases) est utilisé pour chaque sous-réseau (donc 2 groupes pour les cations et 2 groupes pour les anions).

<u>Interaction entre deux cations (c et c') du même groupe (avec l'anion commun a)</u>

$$\omega_{cc'/a} = \omega^{o}_{cc'/a} + \sum_i \sum_j \left(\frac{X_{c/a}}{X_{c/a} + X_{c'/a}} \right)^{i-1} \left(\frac{X_{c'/a}}{X_{c/a} + X_{c'/a}} \right)^{j-1} q^{(ij)}_{cc'/a} \qquad (2.12.19)$$

<u>Interaction entre deux cations (c et c') de groupes différents (avec l'anion commun a)</u>

$$\omega_{cc'/a} = \omega^{o}_{cc'/a} + \sum_i \sum_j \xi^{i-1}_{I(a)} \xi^{j-1}_{II(a)} q^{(ij)}_{cc'/a} \qquad (2.12.20)$$

où

$$\xi_{I(a)} = \frac{\sum\limits_{\substack{\text{cations} \\ \in \text{ groupe I}}} X_{c/a}}{\sum\limits_{\text{cations}} X_{c/a}} \quad \text{et} \quad \xi_{II(a)} = \frac{\sum\limits_{\substack{\text{cations} \\ \in \text{ groupe II}}} X_{c/a}}{\sum\limits_{\text{cations}} X_{c/a}} \qquad (2.12.21)$$

<u>Interaction entre deux anions (a et a') du même groupe (avec le cation commun c)</u>

$$\omega_{c/aa'} = \omega^{o}_{c/aa'} + \sum_i \sum_j \left(\frac{X_{c/a}}{X_{c/a} + X_{c/a'}} \right)^{i-1} \left(\frac{X_{c/a'}}{X_{c/a} + X_{c/a'}} \right)^{j-1} q^{(ij)}_{c/aa'} \qquad (2.12.22)$$

Interaction entre deux anions (a et a') de groupes différents (avec le cation commun c)

$$\omega_{c/aa'} = \omega^{o}_{c/aa'} + \sum_{i}\sum_{j} \xi^{i-1}_{I(c)} \xi^{j-1}_{II(c)} q^{(ij)}_{c/aa'} \tag{2.12.23}$$

où

$$\xi_{I(c)} = \frac{\sum\limits_{\substack{\text{anions} \\ \in \text{ groupe I}}} X_{c/a}}{\sum\limits_{\text{anions}} X_{c/a}} \quad \text{et} \quad \xi_{II(c)} = \frac{\sum\limits_{\substack{\text{anions} \\ \in \text{ groupe II}}} X_{c/a}}{\sum\limits_{\text{anions}} X_{c/a}} \tag{2.12.24}$$

Cas limites du modèle

Si l'énergie d'échange est nulle (2.12.1), alors l'ordonnement à courte distance premiers-voisins n'existe pas et les ions se mélangent de façon aléatoire sur leurs réseaux respectifs. Dans ce cas, la simplification suivante est possible :

$$X_{c/a} = Y_c Y_a \tag{2.12.25}$$

L'énergie de Gibbs par équivalent devient alors :

$$\begin{aligned} g = & \sum_{c}\sum_{a} Y_c Y_a g^{o}_{c/a} + \left(\sum_{c} q_c n_c\right)^{-1} RT \sum_{c} X_c \ln X_c + \left(\sum_{a} q_a n_a\right)^{-1} RT \sum_{a} X_a \ln X_a \\ & + \sum_{c}\sum_{c'}\sum_{a} \frac{(Y_c Y_a)(Y_{c'} Y_a)}{Y_a} \omega_{cc'/a} + \sum_{a}\sum_{a'}\sum_{c} \frac{(Y_c Y_a)(Y_c Y_{a'})}{Y_c} \omega_{c/aa'} \\ & + g^{E}_{ternaire} + g^{E}_{réciproque} \end{aligned} \tag{2.12.26}$$

qui est exactement l'énergie de Gibbs du modèle réciproque proposé par Pelton (1988) et dérivé des équations de Saboungi et Blander (1974) de la théorie des solutions conformes.

Si l'énergie d'échange de l'équation 2.12.1 est légèrement négative (< |-40| kJ/équivalent), alors l'ordonnement à courte distance premiers-voisins est faible et les fractions molaires des paires premiers-voisins sont données par les équations suivantes (à partir du bilan de masse) pour un système réciproque ternaire (*A,B//X,Y*) :

$$X_{A/X} = Y_A Y_X + y \tag{2.12.27}$$

$$X_{A/Y} = Y_A Y_Y - y \tag{2.12.28}$$

$$X_{B/X} = Y_B Y_X - y \tag{2.12.29}$$

$$X_{B/Y} = Y_B Y_Y + y \tag{2.12.30}$$

où y est la déviation par rapport au mélange aléatoire des ions des fractions molaires des paires. L'énergie de Gibbs par équivalent de la solution, en supposant les interactions seconds-voisins nulles (ω), est :

$$\begin{aligned} g = {} & (Y_A Y_X + y) g^o_{A/X} + (Y_A Y_Y - y) g^o_{A/Y} + (Y_B Y_X - y) g^o_{B/X} + (Y_B Y_Y + y) g^o_{B/Y} \\ & + (q_A X_A + q_B X_B)^{-1} RT (X_A \ln X_A + X_B \ln X_B) \\ & + (q_X X_X + q_Y X_Y)^{-1} RT (X_X \ln X_X + X_Y \ln X_Y) \\ & + ZRT\left((Y_A Y_X + y) \ln\left(1 + \frac{y}{Y_A Y_X}\right) + (Y_B Y_Y + y) \ln\left(1 + \frac{y}{Y_B Y_Y}\right)\right) \\ & + ZRT\left((Y_A Y_Y - y) \ln\left(1 - \frac{y}{Y_A Y_Y}\right) + (Y_B Y_X - y) \ln\left(1 - \frac{y}{Y_B Y_X}\right)\right) \end{aligned} \tag{2.12.31}$$

Ce qui vaut :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& + ZRT\left(Y_A Y_X \ln\left(1 + \frac{y}{Y_A Y_X}\right) + Y_B Y_Y \ln\left(1 + \frac{y}{Y_B Y_Y}\right)\right) \\
& + ZRT\left(Y_A Y_Y \ln\left(1 - \frac{y}{Y_A Y_Y}\right) + Y_B Y_X \ln\left(1 - \frac{y}{Y_B Y_X}\right)\right) \\
& + y\Delta g^{éch}_{A,B/X,Y} + yZRT \ln\left(\frac{\left(1 + \frac{y}{Y_A Y_X}\right)\left(1 + \frac{y}{Y_B Y_Y}\right)}{\left(1 - \frac{y}{Y_A Y_Y}\right)\left(1 - \frac{y}{Y_B Y_X}\right)}\right)
\end{aligned}
\tag{2.12.32}
$$

Sachant que $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots$ pour $-1 < x \leq 1$, alors en prenant les deux premiers termes de cette expansion de Taylor appliqués aux lignes 4 et 5 de l'équation 2.12.32, on a :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& + ZRT\left(Y_A Y_X \left[\frac{y}{Y_A Y_X} - \left(\frac{y}{Y_A Y_X}\right)^2\right] + Y_B Y_Y \left[\frac{y}{Y_B Y_Y} - \left(\frac{y}{Y_B Y_Y}\right)^2\right]\right) \\
& + ZRT\left(Y_A Y_Y \left[\frac{-y}{Y_A Y_Y} - \left(\frac{-y}{Y_A Y_Y}\right)^2\right] + Y_B Y_X \left[\frac{-y}{Y_B Y_X} - \left(\frac{-y}{Y_B Y_X}\right)^2\right]\right) \\
& + y\Delta g^{éch}_{A,B/X,Y} + yZRT \ln\left(\frac{\left(1 + \frac{y}{Y_A Y_X}\right)\left(1 + \frac{y}{Y_B Y_Y}\right)}{\left(1 - \frac{y}{Y_A Y_Y}\right)\left(1 - \frac{y}{Y_B Y_X}\right)}\right)
\end{aligned}
\tag{2.12.33}
$$

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& - y^2 \frac{ZRT}{2}\left(\frac{1}{Y_A Y_X} + \frac{1}{Y_B Y_Y} + \frac{1}{Y_A Y_Y} + \frac{1}{Y_B Y_X}\right) \\
& + y\Delta g^{éch}_{A,B/X,Y} + yZRT \ln\left(\frac{\left(1+\frac{y}{Y_A Y_X}\right)\left(1+\frac{y}{Y_B Y_Y}\right)}{\left(1-\frac{y}{Y_A Y_Y}\right)\left(1-\frac{y}{Y_B Y_X}\right)}\right)
\end{aligned}
\tag{2.12.34}
$$

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& + y\Delta g^{éch}_{A,B/X,Y} - y^2 \frac{ZRT}{2Y_A Y_B Y_X Y_Y} + yZRT \ln\left(\frac{\left(1+\frac{y}{Y_A Y_X}\right)\left(1+\frac{y}{Y_B Y_Y}\right)}{\left(1-\frac{y}{Y_A Y_Y}\right)\left(1-\frac{y}{Y_B Y_X}\right)}\right)
\end{aligned}
\tag{2.12.35}
$$

Sachant que $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots$ pour $-1 < x \leq 1$, alors en prenant le premier terme de cette expansion de Taylor appliqués au dernier terme de l'équation 2.12.35, on a :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& + y\Delta g^{éch}_{A,B/X,Y} - y^2 \frac{ZRT}{2Y_A Y_B Y_X Y_Y} + y^2 \frac{ZRT}{Y_A Y_B Y_X Y_Y}
\end{aligned}
\tag{2.12.36}
$$

Ce qui donne :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& + y \Delta g^{éch}_{A,B/X,Y} + \frac{y^2}{2} \frac{ZRT}{Y_A Y_B Y_X Y_Y}
\end{aligned}
\tag{2.12.37}
$$

avec la constante d'équilibre de la réaction 2.12. 1 :

$$
K_{équ} = \frac{(Y_A Y_X + y)(Y_B Y_Y + y)}{(Y_A Y_Y - y)(Y_B Y_X - y)} = \exp\left(\frac{-\Delta g^{éch}_{A,B/X,Y}}{ZRT}\right)
\tag{2.12.38}
$$

on a :

$$
\ln\left(1 + \frac{y}{Y_A Y_X}\right) + \ln\left(1 + \frac{y}{Y_B Y_Y}\right) - \ln\left(1 - \frac{y}{Y_A Y_Y}\right) - \ln\left(1 - \frac{y}{Y_B Y_X}\right) = -\frac{\Delta g^{éch.}_{A,B/X,Y}}{ZRT}
\tag{2.12.39}
$$

Sachant que $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots$ pour $-1 < x \leq 1$, on a que :

$$
y = -Y_A Y_B Y_X Y_Y \frac{\Delta g^{éch.}_{A,B/X,Y}}{ZRT}
\tag{2.12.40}
$$

En remplaçant dans l'équation 2.12.37, on obtient :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& - Y_A Y_B Y_X Y_Y \frac{\left(\Delta g^{éch}_{A,B/X,Y}\right)^2}{ZRT} + \frac{ZRT}{2Y_A Y_B Y_X Y_Y}\left(-Y_A Y_B Y_X Y_Y \frac{\Delta g^{éch}_{A,B/X,Y}}{ZRT}\right)^2
\end{aligned}
\tag{2.12.41}
$$

Ce qui donne :

$$
\begin{aligned}
g = {} & Y_A Y_X g^o_{A/X} + Y_A Y_Y g^o_{A/Y} + Y_B Y_X g^o_{B/X} + Y_B Y_Y g^o_{B/Y} \\
& + (q_A X_A + q_B X_B)^{-1} RT(X_A \ln X_A + X_B \ln X_B) \\
& + (q_X X_X + q_Y X_Y)^{-1} RT(X_X \ln X_X + X_Y \ln X_Y) \\
& - Y_A Y_B Y_X Y_Y \frac{\left(\Delta g^{éch}_{A,B/X,Y}\right)^2}{2ZRT}
\end{aligned}
\tag{2.12.42}
$$

Ce qui est le même terme réciproque obtenu par Blander et Braunstein (1960).

Le modèle quasichimique pour solutions réciproques évalue la configuration dûe à l'ordonnement à courte distance premiers-voisins à partir de l'énergie d'échange des premiers-voisins (entre les réseaux) et de l'énergie d'interaction des seconds-voisins (sur un même réseau). Un écart au mélange aléatoire des ions sur leurs réseaux respectifs (approche de Temkin) est calculé qui permet de calculer l'énergie de Gibbs de la solution.

<u>Les articles suivants ont été produits au cours de cette thèse</u> :

L'article "The Modified Quasichemical Model III : Two Sublattices" en Annexe VIII montre sous une autre approche les équations du modèle quasichimique pour solution réciproque. Dans le même article, une application à la solution de sels fondus réciproque multicomposante à asymétrie de charge Li,Na,K//F,Cl,SO_4 est montrée. Les

projections du liquidus du sous-système ternaire réciproque Li,Na,K//F,Cl ont toutes été reproduites sans aucun terme ternaire et à l'aide d'un changement très mineur aux énergies des sels purs afin de modifier l'énergie d'échange, qui dans le cas du sous-système Li,K//F,Cl dépasse les –61 kJ/mol. Il est pratiquement impossible de reproduire la surface du liquidus du système Li,K//F,Cl avec une approche de Temkin (mélange aléatoire des ions sur leurs sous-réseaux respectifs). Avec le modèle quasichimique réciproque, la projection du liquidus est reproduite avec satisfaction.

L'article "Thermodynamic Phase Diagram Calculations and Cryoscopic Measurements in the $NaCl$-$CaCl_2$-$MgCl_2$-CaF_2 System" en Annexe IX montre un exemple de l'emploi du modèle quasichimique pour solutions réciproques dans le cas d'un système multicomposant à asymétrie des charges (Na,Mg,Ca//F,Cl) où les énergies d'échange des sous-systèmes ternaires sont élevées (jusqu'à -77 kJ/équivalent). Cet article montre la capacité du modèle à reproduire des points expérimentaux du liquidus dans le système multicomposant. Cependant, pour les sous-systèmes ternaires Na,Mg//F,Cl et Na,Ca//F,Cl des termes ternaires réciproques ont du être utilisés et une modification de l'énergie de Gibbs des sels purs a du être effectuée afin d'ajuster les énergies d'échange des sous-systèmes ternaires pour un meilleur lissage des liquidus réciproques. Ces modifications et ajouts dans les sous-systèmes réciproques proviennent de l'incapacité du modèle à traiter correctement l'ordonnement à courte distance seconds-voisins (sur un même réseau), présent dans le cas du système $NaCl$-$MgCl_2$, et son impact sur l'ordonnement premiers-voisins. Il est à noter que les expériences de mesure du liquidus dans le système réciproque quaternaire ont été effectuées par un groupe de l'Université de Trondheim (Norvège) sous la direction du professeur T.Østvold. Les points expérimentaux, dans le tableau 2 de l'article, qui sont notés par un indice "*a)*", ont été mesurés avant que les résultats du modèle ne soient obtenus. Les températures maximales mesurées de ces points (montrées au tableau 2 de cet article) ont été interprétées initialement comme des températures de première cristallisation. Le modèle a ensuite révélé qu'il s'agissait plutôt de températures de seconde cristallisation; ce qui a

été vérifié expérimentalement par la suite à l'aide d'une seconde série de mesures expérimentales par le même groupe. Cette série, notée avec un indice "*b)*" dans le tableau 2 de l'article, montre l'excellent accord avec les prédictions du modèle qui ont été faites avant les mesures. Ceci démontre la capacité prédictive de ce modèle.

2.13 Procédure d'optimisation des paramètres des modèles thermodynamiques

Les modèles précédents comportent des paramètres optimisables dont les valeurs doivent être définies afin de représenter correctement les propriétés thermodynamiques de la solution. Ces paramètres sont obtenus non pas a priori de valeurs théoriques, mais plutôt empiriquement via une procédure d'optimisation qui permet de trouver l'ensemble minimal de paramètres qui reproduisent avec satisfaction toutes les données thermodynamiques expérimentales crédibles portant sur le système chimique étudié.

Les équations de l'énergie de Gibbs d'une solution donnée par les modèles décrits précédemment peuvent être dérivées selon les équations du chapitre 2.0 afin d'obtenir l'enthalpie, l'entropie, la capacité thermique, les potentiels chimiques et les activités. Pour un ensemble de paramètres du modèle de la solution, toutes ces valeurs thermodynamiques peuvent être calculées par dérivation. Il existe donc un ensemble de paramètres du modèle de la solution qui minimise les écarts entre les données expérimentales d'équilibre de phases (égalité des potentiels chimiques entre les phases), les enthalpies, les activités, etc..., et les mêmes valeurs dérivées de cet ensemble de paramètres. Pour obtenir cet ensemble de paramètres du modèle de la solution, qui minimise les erreurs entre les valeurs calculées et les valeurs expérimentales de données thermodynamiques, une routine d'optimisation basée sur les moindres carrés, par example, peut être utilisée. D'autres méthodes sont aussi utilisables.

Le groupe CALPHAD (CALculation of PHAse Diagrams) a développé une méthode, basée sur la description précédente, afin d'obtenir des bases de données complètes de paramètres d'un modèle pour une solution donnée. Ce groupe a principalement utilisé la méthode pour les solutions condensées (solides et liquide) d'alliages métalliques. Au CRCT, la même technique a été appliquée aux liquides et solides des systèmes d'oxydes, de sels fondus, de sulphures, et d'alliages métalliques.

La procédure d'optimisation de CALPHAD consiste en la division du système chimique en sous-systèmes binaires et ternaires afin de simplifier la technique d'optimisation. Ainsi, les paramètres appartenant aux sous-systèmes binaires des solutions du système sont optimisés à partir des données thermodynamiques du binaire concerné (cependant, il est possible d'utiliser des données thermodynamiques ternaires lors de l'optimisation des paramètres binaires des modèles). Une fois les paramètres des phases binaires obtenus pour les 3 binaires d'un sous-système ternaire du système chimique étudié, un modèle d'interpolation, dit modèle « géométrique » (par exemple Kohler/Toop/Muggianu), est utilisé afin de prédire les propriétés thermodynamiques et les équilibres de phases dans le champ de composition ternaire à partir des paramètres binaires. Si les modèles thermodynamiques de toutes les phases présentes ont été bien choisis (s'ils réflètent les aspects chimiques et structurels de la solution), si les optimisations des 3 sous-systèmes binaires du système ternaires ont été bien effectuées, si la méthode d'interpolation choisie est bonne, et si les données thermodynamiques ternaires sont consistantes avec les données binaires, alors les prédictions du modèles dans le champ ternaire de composition devraient être proches des données expérimentales. Dans le cas positif, de petits termes empiriques ternaires (qui n'affectent pas les sous-systèmes binaires) peuvent être optimisés afin de mieux reproduire les données; sinon, il faut réviser le choix du modèle. Lorsque tous les paramètres des modèles des phases des sous-systèmes binaires et ternaires du système chimique étudié ont été optimisés, alors les modèles sont utilisés afin de prédire les données thermodynamiques quaternaires et multicomposantes. À ce point, certains modèles permettent l'utilisation de termes empiriques quaternaires optimisables, afin de corriger les écarts du modèle. Cependant, le modèle devrait être apte à donner une prédiction satisfaisante.

Cette approche empirique d'optimisation des paramètres des modèles thermodynamiques basés sur des théories du mélange des atomes n'obtient pas l'approbation de tous. Les théoriciens préfèrent une approche où tous les paramètres

sont obtenus de calculs provenant des données des espèces. Mais pour une application en recherche industrielle (ingénierie), cette procédure a prouvé maintes fois sa valeur tant pour la reproduction de données thermodynamiques que pour leur prédiction.

3. Contributions aux modèles thermodynamiques pour solutions liquides

Dans les sections qui suivent se trouvent les contributions apportées aux modèles thermodynamiques pour solutions liquides effectuées durant les années de travaux doctoraux. Ces nouvelles contribution ont pour but d'améliorer les prédictions des modèles appliqués à des solutions liquides de plus en plus complexes. La contribution majeure est l'amélioration du modèle quasichimique pour solutions réciproques pour tenir compte simultanément de l'ordonnement des premiers ET seconds voisins et de leurs effets sur l'entropie configurationnelle et l'estimation des propriétés multicomposantes. Ce modèle a été appliqué au liquide du système Li,Na,K,Rb,Cs,Mg,Ca,Sr,Ba//Cl, et au liquide du système réciproque Li,Na,K,Mg,Ca//F,Cl. Une amélioration des méthodes d'estimation géométrique des G^E des systèmes ternaires et multicomposants est discutée, de plus qu'une critique de ces méthodes en général. Un couplage des modèles quasichimiques et d'association est présenté avec un exemple appliqué au système Na_2O-K_2O-Al_2O_3-SiO_2 qui prouve que les avantages des modèles peuvent être parfois combinés afin de résoudre un problème structurel (ici l'effet de compensation de charge dans les systèmes riches en silice). Finalement, plusieurs suggestions de modifications futures sont apportées.

3.1 Critique et amélioration des méthodes d'estimation de l'énergie de Gibbs en excès des systèmes multicomposants à partir des paramètres binaires des modèles.

Les méthodes d'estimation de l'énergie de Gibbs en excès des systèmes multicomposants à partir des paramètres binaires des modèles ont été présentées à la section 3 du chapitre 2 de cette thèse. Ces méthodes sont souvent désignées sous

l'appellation de modèles géométriques, de par l'aspect visuel qui les définit sur le triangle ternaire de Gibbs. Une critique générale de ces "modèles géométriques" sera d'abord présentée, suivie d'une proposition d'améliorations lorsqu'elles sont appliquées aux liquides. La partie finale et générale de cette proposition est présentée dans l'article "On the Choice of "Geometric" Thermodynamic Models" qui est montré en Annexe II de cette thèse.

Défauts des modèles géométriques existants.

La figure 2.2 montre les principaux modèles géométriques utilisés dans les banques de données et programmes thermodynamiques courants. La figure 2.2 est ici reproduite pour mieux situé le lecteur.

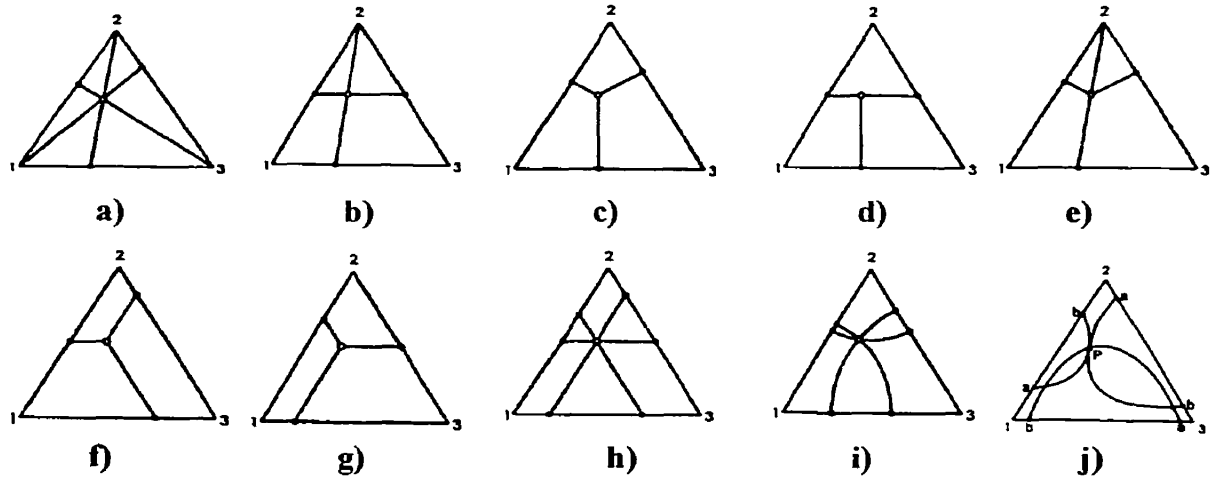


Figure 3.1 : Méthodes d'estimation des propriétés en excès d'une solution ternaire (1-2-3) à partir des paramètres polynomiaux des sous-systèmes binaires (1-2; 1-3; 2-3) : a) Kohler (1960); b) Toop (1965); c) Muggianu (1975); d) Hillert (1980); e) Li (1989); f) Chou (1987) "gauche"; g) Chou (1987) "droite"; h) Colinet (1967); i) Malakhov (1995); j) Ganesan (1997);

Comme décrit à la section 2.3, les méthodes a) à g) sont des méthodes qui n'utilisent qu'une seule composition d'interpolation pour chaque sous-système binaire, alors que

les méthodes h) à j) utilisent deux compositions d'interpolation. Les méthodes a), c) et f) à j) sont dites symétriques du fait que tous les paramètres binaires de la solution ont la même équation qui évalue leur contribution à l'énergie en excès totale de la solution. Les méthodes b), d) et e) sont dites asymétriques car un paramètre des sous-systèmes binaires voit sa contribution à l'énergie en excès de la solution différemment exprimée. Une autre manière, plus classique, de présenter cette dualité "symétrique/asymétrique" est d'associer chacun des constituants de la solution à un groupe (qui peut être défini par la famille chimique, la charge ionique, etc...). Si les 3 constituants de la solution appartiennent au même groupe, une méthode symétrique est utilisée; si un des 3 constituants de la solution appartient à un groupe différent des deux autres, alors une méthode asymétrique est utilisée. Selon cette approche, seulement deux groupes suffisent à englober entièrement tous les constituants de la solution car l'on compare 1 constituant aux deux autres.

Il est proposé dans cette thèse de rejeter les méthodes qui utilisent deux compositions d'interpolation pour chacun des sous-systèmes binaires.

Ces méthodes sont les méthodes de Colinet (1967), de Malakov (1995) et de Ganesan (1997). En effet, ces méthodes proposent une approche assez statistique, basée sur une moyenne des énergies en excès binaires évaluées aux limites des compositions binaires qui engloblent les compositions binaires des autres méthodes. Pour certaines solutions liquides, la variation compositionnelle de l'énergie de formation des paires d'espèces *A-B* est très grande et une approche statistique basée sur une moyenne ne peut donner que de mauvais résultats. Il est toujours possible de rencontrer un cas particulier où une de ces méthodes donne un résultat satisfaisant, voire meilleur que les autres méthodes, mais dans l'optique du développement de bases de données de solutions multicomposantes comportant des sous-systèmes où il y a une forte tendance à l'ordonnement, alors ces méthodes statistiques basées sur une moyenne doivent être rejetées. Ces méthodes apportent une complexité mathématique inutile (ce qui à l'ère de l'informatique n'est

pas un problème en soit) mais cela sans avantages thermodynamiques particuliers. De plus, dans le cas des solutions diluées (soit un solvant unaire *A*, ou pour un solvant binaire *A-B*), les compositions d'interpolation binaires impliquant les solutés sont parfois douteuses car elles vont impliquer des compositions binaires où les solutés deviennent des solvants!

Reste les méthodes de Kohler (1960), Toop (1965), Hillert (1980), Muggianu (1975), Li (1989) et Chou (1987). Ces méthodes, telles que montrées à la figure 3.1, sont géométriquement différentes si elles sont représentées graphiquement pour une solution ternaire.

Il est proposé dans cette thèse de ne pas considérer ces méthodes de par leur aspect géométrique ternaire, mais plutôt de par la fonction qui interpole chacun des paramètres des sous-systèmes binaires dans la solution multicomposante.

Ainsi, les méthodes de Kohler (1960), Toop (1965), Hillert (1980), Muggianu (1975), Li (1989) et Chou (1987) ne se résument qu'à trois fonctions distinctes pour chaque paramètre binaire $\Phi_{AB}^{(ij)}$ qui permet de décrire l'énergie de Gibbs en excès. La contribution d'un paramètre binaire, $\Phi_{AB}^{(ij)}$, au g^E de la solution est une fonction :

$$g^E = X_A X_B f\left(\Phi_{AB}^{(ij)}, X_A, X_B, X_C, \ldots\right) \tag{3.1.1}$$

où l'on définit (voir l'article « On the Choice of "Geometric" Thermodynamic Models » en Annexe II) :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}, X_A, X_B, X_C, \ldots\right) \tag{3.1.2}$$

Les trois fonctions disctinctes mentionnées peuvent dépendre de l'appartenance de A et de B aux deux différents groupes (I et II; acides et bases) de la solution.

Même groupes : A et $B \in$ groupe I ou groupe II :

Première fonction :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{X_A}{X_A + X_B}\right)^{i-1}\left(\frac{X_B}{X_A + X_B}\right)^{j-1}\right) \qquad (i, j \geq 1) \qquad (3.1.3)$$

Si i ou j vaut 1, alors l'équation 3.1.3 donne une interpolation du terme en excès binaire $\Phi_{AB}^{(ij)}$ qui est exactement celle proposée par Kohler (1960), sinon, l'aspect géométrique de Kohler est conservé mais l'équation originale de Kohler est modifiée. L'hypothèse derrière cette fonction est que la contribution du paramètre $\Phi_{AB}^{(ij)}$ à l'énergie de formation de la paire A-B à la composition multicomposante donnée est constante selon le ratio des fractions molaires de A et de B dans cette solution.

Seconde fonction :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(i0)}(X_A - X_B)^i\right) \qquad (i \geq 1) \qquad (3.1.4)$$

Cette deuxième fonction d'interpolation est celle proposée par Muggianu (1975). L'hypothèse derrière cette fonction est que la contribution du paramètre $\Phi_{AB}^{(i0)}$ à l'énergie de formation de la paire A-B à la composition multicomposante donnée est constante selon la différence des fractions molaires de A et de B dans cette solution, ce qui a pour effet de prendre la valeur de l'énergie de formation de la paire A-B à la

composition qui minimise de façon géométrique la "distance" entre le point de composition multicomposant et le binaire *A-B* auquel le paramètre appartient.

Groupes différents : *A* ∈ groupe I et *B* ∈ groupe II :

Troisième fonction :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)} \xi_I^{i-1} \xi_{II}^{j-1}\right) \qquad (3.1.5)$$

où

$$\xi_I = \sum_{\substack{m \\ m \in \text{groupe } I}} X_m \qquad \text{et} \qquad \xi_{II} = \sum_{\substack{n \\ n \in \text{groupe } II}} X_n \qquad (3.1.6)$$

Si i ou j vaut 1, alors l'équation 3.1.5 donne une interpolation du termes en excès binaire $\Phi_{AB}^{(ij)}$ qui est exactement celle proposée par Toop (1965), sinon, l'aspect géométrique de Toop est conservé mais l'équation originale de Toop est modifiée. L'hypothèse derrière cette fonction est que la contribution du paramètre $\Phi_{AB}^{(ij)}$ à l'énergie de formation de la paire *A-B* à la composition multicomposante donnée est constante selon la concentration molaire des groupes I et II dans cette solution, ce qui implique que la solution ne distingue pas les espèces parmi un groupe, mais dinstingue seulement les groupes (pour les interactions *A-B* entre les groupes).

À partir de ces trois fonctions applicables à chaque paramètre binaires $\Phi_{AB}^{(ij)}$, toutes les géométries ternaires de Kohler (1960), Toop (1965), Hillert (1980), Muggianu (1975), Li (1989) et Chou (1987) peuvent être retrouvées. Le tableau 3.1 montre le numéro de la fonction (1 à 3) qui correspond à chaque interaction selon la figure 3.1.

Tableau 3.1 : Relation entre les fonctions #1-3 et les méthodes géométriques.

Méthodes	Sous-système binaire		
	1-2	**2-3**	**3-1**
Kohler (1960)	#1	#1	#1
Toop (1965) 1 et 3 ∈ groupe I 2 ∈ groupe II	#3	#3	#1
Muggianu (1975)	#2	#2	#2
Hillert (1980) 1 et 3 ∈ groupe I 2 ∈ groupe II	#3	#3	#2
Li (1989) 1 et 3 ∈ groupe I 2 ∈ groupe II	#2	#2	#1
Chou gauche (1987)	#3 1 et 3 ∈ groupe I 2 ∈ groupe II	#3 1 et 2 ∈ groupe I 3 ∈ groupe II	#3 2 et 3 ∈ groupe I 1 ∈ groupe II
Chou droite (1987)	#3 2 et 3 ∈ groupe I 1 ∈ groupe II	#3 1 et 3 ∈ groupe I 2 ∈ groupe II	#3 1 et 2 ∈ groupe I 3 ∈ groupe II

Il est à remarquer que la méthode de Li (1989) utilise la fonction #2 de type Muggianu au lieu de la fonction #3 de type Toop lorsque les groupes sont différents pour une interaction binaire donnée. Cette approche est questionnable car l'appartenance à un groupe n'a pas d'impact sur la formulation, c'est à dire que X_C n'entre pas directement dans l'évaluation de l'énergie de formation de la paire *A-B* même si *C* appartient à un même groupe que *A* ou *B*.

Il est donc recommandé dans cette thèse de rejeter la méthode géométrique de Li (1989).

Il est aussi à remarquer que les deux méthodes proposées par Chou (1987) déterminent l'appartenance à un groupe (donc l'utilisation de la fonction #3 de type Toop) selon la paire *A-B* évaluée et selon une rotation de groupe définie ("gauche" et "droite"). La notion de groupe chimique est donc explicitement bafouée car la nature chimique de l'espèce ne détermine plus le groupe.

Dans l'optique du développement d'une base de donnée pour solutions liquides multicomposantes, il est recommandé dans cette thèse de rejeter les méthodes de Chou (1987).

Reste à évaluer la signification physique des trois fonctions proposées (#1 à #3). Comme décrit plus haut, chacune des fonctions est reliée à une certaine hypothèse. Des trois, l'hypothèse de Muggianu (1975) qui supporte la fonction #2 est particulièrement faible pour les solutions diluées binaires (où *A* et *B* sont les solvants et *C* est le soluté). Tel que montré par Pelton, Blander, Clavaguera-Mora, Hoch, Höglund, Lukas, Spencer et Sundman (1997) et à la figure 2b de l'article "On the Choice of "Geometric" Thermodynamic Models" en annexe, les compositions d'évaluation de l'énergie de formation des paires *A-C* et *B-C* contenant le soluté *C* sont à une composition beaucoup trop riche en *C* étant donné que la solution est diluée en *C*. Dans cette même situation, les fonctions #1 (type Kohler) et #3 (type Toop) sont préférables car elles évaluent l'énergie des paires *A-C* et *B-C* à des compositions binaires où *C* est en faible concentration.

Il est recommandé dans cette thèse de faire prévaloir la fonction de type Kohler (#1) à celle de type Muggianu (#2) afin de mieux évaluer l'énergie de formation des paires dans les régions de dilution binaire.

Modification de la fonction de type Toop (fonction #3) et traitement multigroupe

Il ressort de la critique précédente que la méthode de Kohler (1960) et la méthode de Toop (1965), représentées selon la contribution des termes binaires par les fonction de type Kohler (#1) et de type Toop (#3), sont les plus susceptibles de donner une bonne approximation de l'énergie de formation des paires *i-j* dans un système multicomposant.

Les méthodes de Kohler et de Toop s'intègrent parfaitement l'une à l'autre tel que montré pour la géométrie ternaire de Toop (figure 3.1b) où l'interaction 1-3 en est une de type Kohler. Ces deux méthodes s'intègrent aussi très bien lorsque la solution est divisée en deux sous-groupes chimiques. Cependant, dans l'optique de créer une base de données pour une solution multicomposante, le fait de diviser les espèces en seulement deux groupes est insuffisant. Deux exemples sont présentés :

Cas #1 mélange base$_1$-base$_2$-base$_2$-acide : Si Na_2O, CaO, MgO appartiennent au groupe I des bases et que SiO_2 appartient au groupe II des acides, alors les interpolations obtenues avec les fonctions #1 et #3 sont montrées à la figure 3.2 :

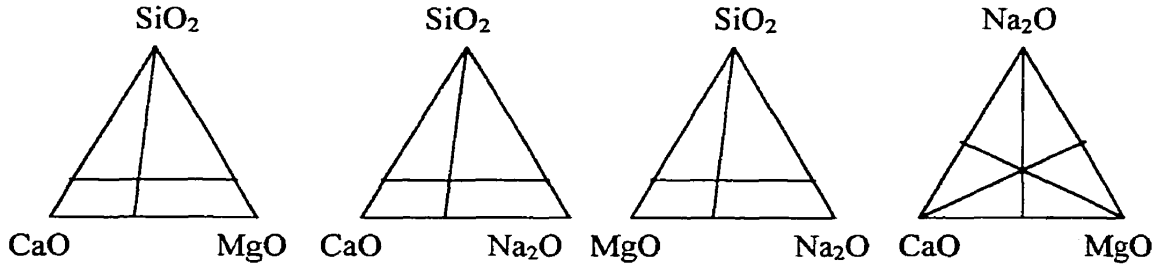


Figure 3.2 : Méthodes d'estimation utilisées pour les 4 sous-systèmes ternaires du système Na_2O-CaO-MgO-SiO_2 lorsque 2 groupes sont utilisés.

Le ternaire Na_2O-CaO-MgO présente un composant qui diffèrent sensiblement des deux autres (Na_2O) même s'il s'agit de trois constituants basiques. Il serait donc préférable dans un formalisme Kohler/Toop de traîter ce ternaire avec la méthode de Toop (avec Na_2O comme espèce asymétrique). Le fait de diviser les espèces en seulement deux groupes crée un problème pour ce système.

Cas #2 mélange base-base-acide-amphotère : Si CaO et MgO sont considérés comme basiques (groupe I) et que SiO_2 est acide (groupe II) alors un mélange CaO-MgO-SiO_2-Al_2O_3 comportant ces deux groupes oblige à déterminer l'appartenance de Al_2O_3 à un des deux groupes acide/base même s'il s'agit d'un constituant amphotère.

Empiriquement, il a été observé que pour le modèle quasichimique, il est préférable de situé Al_2O_3 dans le groupe basique (Eriksson et Pelton, 1993). Le ternaire CaO-MgO-Al_2O_3, comme dans le cas précédent, sera traité par la méthode de Kohler alors que la méthode de Toop est plus logique en première approximation. Ainsi, il existe toute une gamme de composants amphothères, comme l'alumine Al_2O_3, qui sont chimiquement différents des deux groupes précédents. Pour les sels fondus, un formalisme à deux groupes est évidemment insuffisant de par la présence d'ions de charges diverses (2^-, 1^-, 1^+, 2^+, 3^+, ...,6^+).

Il est proposé dans cette thèse, afin d'accomoder un nombre infini de groupes, de modifier la fonction de type Toop (équation 3.1.5) selon :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{\xi_I}{\xi_I+\xi_{II}}\right)^{i-1}\left(\frac{\xi_{II}}{\xi_I+\xi_{II}}\right)^{j-1}\right) \qquad \textbf{(3.1.7)}$$

La fonction modifiée est exactement l'équation 3.1.5 lorsque seulement deux groupes sont utilisés car :

$$\xi_I + \xi_{II} = 1 \quad \text{(pour 2 groupes)} \qquad (3.1.8)$$

L'autre cas limite est celui où il y a N groupes dans un système N composants. Alors chaque espèce délimite sont propre groupe selon :

$$\xi_i = X_i \qquad (i = 1, .., N) \qquad (3.1.9)$$

ce qui fait que la fonction 3.1.7 devient exactement celle de type Kohler (3.1.3); ce qui revient à dire que N groupes dans un système N composants est la même chose que si toutes les espèces étaient traitées avec la même symétrie. Ainsi, si trois espèces

différentes CaO, SiO_2 et Al_2O_3 se mélangent et que les trois appartiennent respectivement aux bases, acides et amphotères, alors pour chaque interaction *Ca-O-Si*, *Ca-O-Al* et *Si-O-Al*, la fonction 3.1.7 est utilisée (car dans chaque cas les groupes cationiques sont différents) et la géométrie de type Kohler (figure 3.1a) est observée même si une équation de type Toop est utilisée.

Cette première modification permet donc de régler le cas #2 où il y a mélange base-acide-amphotère (CaO-SiO_2-Al_2O_3). Dans le cas de ce ternaire, toutes les interactions binaires seront interpolées avec la fonction 3.1.7 comme expliqué au paragraphe précédent.

Cependant, le cas #1, où il y a mélange $base_1$-$base_2$-acide (Na_2O-CaO-SiO_2), demeure problématique. En effet si on utilise 2 groupes (base-acide), la fonction 3.1.7 utilisée pour les interactions *Na-O-Si* et *Ca-O-Si* donnera une géométrie typique de Toop, alors que si 3 groupes sont utilisés ($base_1$-$base_2$-acide) la fonction 3.1.7 utilisée pour les interactions *Na-O-Si*, *Ca-O-Si* et *Na-O-Ca* donnera une géométrie typique de Kohler qui donne de mauvaises prédictions pour la très grande majorité des systèmes SiO_2-$base_1$-$base_2$.

<u>Modification de la fonction de type Toop modifée (fonction 3.1.7) et traitement multigroupe avec sous-groupes</u>

Pour régler ce problème, sachant que la première proposition de cette thèse concernant les fonctions d'interpolation permet d'utiliser plus de deux groupes (fonction 3.1.7), la proposition suivante est faite :

Il est proposé dans cette thèse d'utiliser un nouveau système de groupes qui permet les sous-groupes. Ainsi les groupes I, II, III, etc... et leurs variables

compositionnelles associées ξ_I, ξ_{II}, ξ_{III}, etc... sont divisés en sous groupes I.I, I.II, I.III, ..., II.I, II.II, II.III, ..., etc... avec les variables compositionnelles associées $\xi_{I.I}$, $\xi_{I.II}$, ..., $\xi_{II.III}$, ... etc... La définition des variables compositionnelles est, pour un système à N composants :

$$\xi_{i.j} = \sum_{\substack{k \\ k \in \text{groupe } i \\ k \in \text{sous-groupe } j}}^{N} X_k \tag{3.1.10}$$

$$\xi_i = \sum_{j=1}^{N_{\substack{\text{groupe } i \\ \text{sous-groupes}}}} \xi_{i.j} \tag{3.1.11}$$

$$\sum_{k=1}^{N_{\text{groupes}}} \xi_k = 1 \tag{3.1.12}$$

Avec la fonction 3.1.7 modifiée, on a, si A et B sont du même groupe et du même sous-groupe :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{X_A}{X_A + X_B}\right)^{i-1}\left(\frac{X_B}{X_A + X_B}\right)^{j-1}\right) \tag{3.1.13}$$

On a si A est du groupe I et B est du groupe II :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{\xi_I}{\xi_I + \xi_{II}}\right)^{i-1}\left(\frac{\xi_{II}}{\xi_I + \xi_{II}}\right)^{j-1}\right) \tag{3.1.14}$$

On a si A et B sont du même groupe (I) mais que A est du sous-groupe I.I et que B est du sous-groupe I.II :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{\xi_{I.I}}{\xi_{I.I}+\xi_{I.II}}\right)^{i-1}\left(\frac{\xi_{I.II}}{\xi_{I.I}+\xi_{I.II}}\right)^{j-1}\right) \qquad \textbf{(3.1.15)}$$

Cette nouvelle proposition permet de traiter complètement un système multicomposant en divisant les N espèces parmi M groupes ($M \leq N$) et chacun de ces groupes peut être divisé en sous-groupes de nombre illimités. Ce qui inclue le cas #1 présenté plus haut où il y a mélange acide-base$_1$-base$_2$. Le système Na_2O-CaO-SiO_2 serait divisé en deux groupes, bases et acides, et le groupe des bases serait divisé en deux sous-groupes, cations alcalins et cations alcalins-terres, ce qui permettrait pour les interactions *Ca-O-Si* et *Na-O-Si* l'utilisation de la fonction 3.1.14, et pour l'interaction *Ca-O-Na* l'utilisation de la fonction 3.1.15 avec :

$$\xi_I = X_{SiO_2}$$

$$\xi_{II.I} = X_{Na_2O} \quad \text{et} \quad \xi_{II.II} = X_{CaO}$$

$$\xi_{II} = \xi_{II.I} + \xi_{II.II} = X_{Na_2O} + X_{CaO}$$

Ces groupements des espèces donnerait une géométrie finale d'interpolation du type Toop ce qui est empiriquement la bonne méthode pour les systèmes SiO_2-base$_1$-base$_2$.

Par exemple, la solution liquide Na_2O-K_2O-CaO-MgO-FeO-CrO-Fe_2O_3-Cr_2O_3-Al_2O_3-SiO_2 pourrait être divisée en trois groupes bases, acides et amphotères selon :

<u>Bases</u> : Na_2O-K_2O-CaO-MgO-FeO-CrO

Avec : $\xi_{\text{bases.I}} = X_{Na_2O} + X_{K_2O}$

$\xi_{\text{bases.II}} = X_{MgO} + X_{CaO} + X_{FeO} + X_{CrO}$

Amphotères : Fe_2O_3-Cr_2O_3-Al_2O_3

Avec : $\xi_{\text{amphotères.I}} = X_{Al_2O_3}$

$\xi_{\text{amphotères.II}} = X_{Fe_2O_3} + X_{Cr_2O_3}$

Acides : SiO_2

Avec : $\xi_{\text{acides}} = X_{SiO_2}$

Le choix précédent n'est qu'un exemple et d'autres choix pourraient se révéler meilleurs. Il serait aussi possible d'intégrer un troisième sous-groupe basique pour les cations 2^+ des métaux de transition (Fe^{2+} et Cr^{2+}) alors que le deuxième sous-groupe serait celui des cations 2^+ alcalino-terreux. Le choix des groupes et sous-groupes demeure arbitraire mais peut être basé sur des principes physico-chimiques.

Généralisation des modifications

Il est possible de généraliser toutes les modifications proposées précécemment dans cette thèse concernant les méthodes géométriques avec la proposition suivante :

Il est proposé dans cette thèse d'unir les fonctions 3.1.3 (type Kohler), 3.1.5 (type Toop-classique), 3.1.7 (type Toop-modifié), 3.1.13, 3.1.14 et 3.1.15 sous une seule fonction donnée par l'équation 3.1.16 suivante :

$$\alpha_{AB} = f\left(\Phi_{AB}^{(ij)}\left(\frac{\xi_{AB}}{\xi_{AB}+\xi_{BA}}\right)^{i-1}\left(\frac{\xi_{BA}}{\xi_{AB}+\xi_{BA}}\right)^{j-1}\right) \qquad \textbf{(3.1.16)}$$

où les variables compositionnelles ξ_{ij} sont définies spécifiquement et indépendemment. Il est cependant recommandé d'utiliser la méthodes des

groupes et sous-groupes comme défaut pour la définition des variables compositionnelles ξ_{ij}.

Cette dernière proposition permet de traiter tous les cas précédents (avec groupes et sous-groupes) en plus de déterminer une géométrie de type Kohler/Toop particulière pour un sous-système particulier même s'il fait partie du traitement groupe/sous-groupe. Cette dernière proposition est aussi entièrement explicitée dans l'article "On the Choice of "Geometric" Thermodynamic Models" montré en Annexe II et faisant partie intégrante de cette thèse. L'article reprend et augmente la discussion initiale sur les différents modèles géométriques. Cette dernière proposition clos la contribution de cette thèse aux modèles géométriques.

3.2 Introduction d'espèces associées $NaAlO_2$ et $KAlO_2$ dans les laitiers Na_2O-K_2O-Al_2O_3-SiO_2 pour reproduire l'effet de compensation de charge : un exemple d'intégration des modèles pour traiter un effet structural.

Cette partie de la thèse réfère à l'article "Modeling the Charge Compensation Effect in Silica-Rich Na_2O-K_2O-Al_2O_3-SiO_2 Melts" montré en Annexe I et faisant partie de cette thèse.

Au chapitre 2, les modèles quasichimique modifié et d'association ont été décrits. Chacun de ces modèles traite l'ordonnement à courte distance des liquides d'une manière différente mais qui est mathématiquement proche. D'un point de vu thermodynamique, le modèle d'association est un modèle polynomial avec une entropie de Bragg-Williams où un ou plusieurs sous-systèmes binaires voient leur énergie de Gibbs évaluée à partir d'un mélange d'au moins trois espèces (les espèces principales et non-associées du binaires, A et B, et au moins une espèce associées, A_aB_b). Le modèle polynomial avec entropie de Bragg-Williams est un cas limite du modèle quasichimique lorsque le niveau d'ordonnement de la solution est faible. Il est donc possible d'unir les deux modèles et de traiter une solution binaire A-B comme étant une solution ternaire A, B et A_aB_b quasichimique avec les trois équilibres de paires suivants :

$$[\text{"}A\text{"}-\text{"}A\text{"}]_{paire} + [\text{"}B\text{"}-\text{"}B\text{"}]_{paire} \Leftrightarrow 2[\text{"}A\text{"}-\text{"}B\text{"}]_{paire} \qquad \Delta\omega^{o}_{\text{"}A\text{"},\text{"}B\text{"}} \tag{3.2.1}$$

$$[\text{"}A\text{"}-\text{"}A\text{"}]_{paire} + [\text{"}A_aB_b\text{"}-\text{"}A_aB_b\text{"}]_{paire} \Leftrightarrow 2[\text{"}A\text{"}-\text{"}A_aB_b\text{"}]_{paire} \qquad \Delta\omega^{o}_{\text{"}A\text{"},\text{"}A_aB_b\text{"}} \tag{3.2.2}$$

$$[\text{"}B\text{"}-\text{"}B\text{"}]_{paire} + [\text{"}A_aB_b\text{"}-\text{"}A_aB_b\text{"}]_{paire} \Leftrightarrow 2[\text{"}B\text{"}-\text{"}A_aB_b\text{"}]_{paire} \qquad \Delta\omega^{o}_{\text{"}B\text{"},\text{"}A_aB_b\text{"}} \tag{3.2.3}$$

L'utilité de cette approche est démontrée lorsque qu'appliquée au cas de l'effet de compensantion de charge dans les laitiers Na_2O-K_2O-Al_2O_3-SiO_2 riches en silice. La silice fondue forme un réseau entremêlé de tétraèdes d'oxygène reliés à un atome de silicium central. Le silicium est dans un état d'oxydation 4^+. Lorsqu'un cation alcalin (Na^+ et/ou K^+) est mélangé à la solution avec un cation Al^{3+}, un couplage Al^{3+}-alcalin$^+$ est possible qui compense la charge de Si^{4+} et qui permet à l'aluminium (couplé à l'alcalin) de remplacer le silicium dans le réseau tétraédrique sans détruire ce dernier. Une stabilisation du liquide s'ensuit, grandement majorée lorsque le mélange Al^{3+}/alcalin$^+$ est équimolaire. Les cations Al^{3+} et Na^+ se dissolvent dans la silice fondue comme étant une seule nouvelle particule ajoutée, ce qui a un impact direct sur la pente limite du liquidus de SiO_2 selon l'équation suivante :

$$\left(\frac{\partial X_{SiO_2}^{liquidus}}{\partial T}\right)_{X_{SiO_2}\to 1} - \left(\frac{\partial X_{SiO_2}^{solidus}}{\partial T}\right)_{X_{SiO_2}\to 1} = \frac{\Delta h^o_{fusion}(SiO_2)}{\upsilon R T^2_{fusion}(SiO_2)} \qquad (3.2.4)$$

où ν est le nombre de nouvelles particules introduites par particules de Na_2O-Al_2O_3 ajoutées ($\nu = 2$ pour Na_2O et $\nu = 2$ pour Al_2O_3 car chaque particule de ces espèces introduit 2 cations dans le mélange) . Pour un ratio $X_{Na_2O} / X_{Al_2O_3} = 1$ ($NaAlO_2$), si Na_2O et Al_2O_3 se dissolvaient dans le solution de façon indépendante (mélange aléatoire), alors ν serait 2. Cependant, de par le couplage Al^{3+}/Na^+, les 2 cations entrent dans la silice fondue comme une seule particule "indissociable", donc $\nu = 1$.

Pour cette thèse, l'introduction d'espèces associées $NaAlO_2$ et $KAlO_2$ au modèle quasichimique appliqué aux oxydes fondus (incluant la silice) permet de tenir compte de ce phénomène structurel. Le solution devient un mélange de cations Na^+, K^+, Al^{3+}, Si^{4+}, $NaAl^{4+}$ et KAl^{4+} entourés d'oxygène (O^{2-}, O^- et O^0 selon l'environnement, mais le

modèle n'est valide que lorsque la teneur en silice est élevée, donc la concentration en O^{2-} est minimisée). Les réactions d'équilibres quasichimiques sont donc :

$$[Na-O-Na]_{paire}+[Al-O-Al]_{paire} \Leftrightarrow 2[Na-O-Al]_{paire} \quad (3.2.5a)$$

$$[Na-O-Na]_{paire}+[Si-O-Si]_{paire} \Leftrightarrow 2[Na-O-Si]_{paire} \quad (3.2.5b)$$

$$[K-O-K]_{paire}+[Al-O-Al]_{paire} \Leftrightarrow 2[K-O-Al]_{paire} \quad (3.2.5c)$$

$$[K-O-K]_{paire}+[Si-O-Si]_{paire} \Leftrightarrow 2[K-O-Si]_{paire} \quad (3.2.5d)$$

$$[Na-O-Na]_{paire}+[K-O-K]_{paire} \Leftrightarrow 2[Na-O-K]_{paire} \quad (3.2.5e)$$

$$[Al-O-Al]_{paire}+[Si-O-Si]_{paire} \Leftrightarrow 2[Al-O-Si]_{paire} \quad (3.2.5f)$$

$$[Na-O-Na]_{paire}+[NaAl-O-NaAl]_{paire} \Leftrightarrow 2[Na-O-NaAl]_{paire} \quad (3.2.5g)$$

$$[K-O-K]_{paire}+[NaAl-O-NaAl]_{paire} \Leftrightarrow 2[K-O-NaAl]_{paire} \quad (3.2.5h)$$

$$[Al-O-Al]_{paire}+[NaAl-O-NaAl]_{paire} \Leftrightarrow 2[Al-O-NaAl]_{paire} \quad (3.2.5i)$$

$$[Si-O-Si]_{paire}+[NaAl-O-NaAl]_{paire} \Leftrightarrow 2[Si-O-NaAl]_{paire} \quad (3.2.5j)$$

$$[Na-O-Na]_{paire}+[KAl-O-KAl]_{paire} \Leftrightarrow 2[Na-O-KAl]_{paire} \quad (3.2.5k)$$

$$[K-O-K]_{paire}+[KAl-O-KAl]_{paire} \Leftrightarrow 2[K-O-KAl]_{paire} \quad (3.2.5l)$$

$$[Al-O-Al]_{paire}+[KAl-O-KAl]_{paire} \Leftrightarrow 2[Al-O-KAl]_{paire} \quad (3.2.5m)$$

$$[Si-O-Si]_{paire}+[KAl-O-KAl]_{paire} \Leftrightarrow 2[Si-O-KAl]_{paire} \quad (3.2.5n)$$

$$[NaAl-O-NaAl]_{paire}+[KAl-O-KAl]_{paire} \Leftrightarrow 2[NaAl-O-KAl]_{paire} \quad (3.2.5o)$$

Il serait toutefois possible d'appliquer le modèle à de plus faibles teneurs en SiO_2, voire jusqu'à la région de forte basicité, si l'on pose que l'énergie de formation des espèces associées $NaAlO_2$ et $KAlO_2$ à partir de Na_2O, K_2O et Al_2O_3 (liquides pures) sont des fonctions de la teneur en silice. Ainsi, l'énergie de formation des espèces associées qui doit être fortement négative lorsque la teneur en silice est haute (afin que $AAlO_2$ domine

au lieu de A_2O et Al_2O_3 - A = Na,K) doit aussi être positive lorsque la teneur en silice est faible afin d'obtenir un mélange A^+ et Al^{3+}.

La description complète du couplage des modèles quasichimique et d'association pour représenter l'énergie de Gibbs d'une solution liquide Na_2O-K_2O-Al_2O_3-SiO_2 riche en silice est donnée dans l'article "Modeling the Charge Compensation Effect in Silica-Rich Na_2O-K_2O-Al_2O_3-SiO_2 Melts" en Annexe I.

3.3 Modifications au modèle quasichimique pour solutions liquides

Le modèle quasichimique de Fowler et Guggenheim (1939), présenté à la section 2.7.1, a été modifié par Pelton et Blander (1984), tel que montré à la section 2.7.2. Une autre série de modifications au modèle a été apportée par Pelton, Degterov, Eriksson, Robelin et Dessureault (1999) qui consiste en un changement de la variation compositionnelle de l'énergie de formation des paires *A-B* (Δg_{AB}) et en la variation compositionnelle du nombre de coordination des espèces *A* et *B* d'une solution binaire.

Dans cette thèse, les modifications précédentes sont étendues, dans une première partie, aux solutions multicomposantes (1 réseau) pour traiter l'ordonnement premiers ou seconds voisins et, dans une seconde partie, une nouvelle série de modifications est proposée pour tenir compte des solutions réciproques liquides qui montrent une tendance à l'ordonnement premiers-voisins et seconds-voisins.

L'article « The Modified Quasichemical Model II – Multicomponent Solutions » montré en Annexe III traite des solutions multicomposantes à 1 sous-réseau, et l'article « The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation » montré en Annexe X traite des solutions réciproques.

3.3.1 Systèmes binaires avec mélange sur un sous-réseau seulement

Pelton, Degterov, Eriksson, Robelin et Dessureault (1999) ont présenté une modification à l'expansion compositionnelle de l'énergie de formation des paires *A-B* d'un système binaire *A-B* (ou *A-X-B* où *X* est un ion occupant pleinement un sous-réseau indépendant du sous-réseau où *A* et *B* se mélangent). Selon Pelton et Blander (1984), l'énergie de formation des paires *A-B*, donnée par :

$$[A-A]_{paire}+[B-B]_{paire} \Leftrightarrow 2[A-B]_{paire} \qquad \Delta g_{AB} \qquad (3.3.1.1)$$

peut être exprimée, pour un système binaire *A-B*, comme une fonction de la composition globale selon :

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i,j} Y_A{}^{i-1} Y_B{}^{j-1} q^{(ij)}_{A,B} \qquad (i,j>0) \qquad (3.3.1.2)$$

De plus, pour Pelton et Blander (1984), les fractions équivalentes de coordination sont définies comme étant :

$$Y_A = \frac{Z_A X_A}{Z_A X_A + Z_B X_B} = 1 - Y_B \qquad (3.3.1.3)$$

où Z_A et Z_B sont respectivement les nombres de coordination des espèces *A* et *B* qui se mélangent :

$$Z_A = q_A Z \qquad (3.3.1.4)$$

$$Z_B = q_B Z \qquad (3.3.1.5)$$

où q_A et q_B sont les « charges » absolues (pour les ions) des espèces *A* et *B*, et *Z* est le nombre de coordination de la solution (constante).

La modification de Pelton, Degterov, Eriksson, Robelin et Dessureault (1999) consiste en une expansion compositionnelle qui est fonction des fractions molaires des paires et non des espèces, pour l'énergie de formation des paires (Δg_{AB}) et pour les nombres de coordination des espèces (Z_A et Z_B). Les fonctions 3.3.1.2, 3.3.1.4 et 3.3.1.5 deviennent :

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i,j} X^{i}_{AA} X^{j}_{BB} q^{(ij)}_{A,B} \tag{3.3.1.6}$$

$$Z_A = \left[\frac{1}{2X_{AA} + X_{AB}} \left(\frac{2X_{AA}}{Z^{A}_{AA}} + \frac{X_{AB}}{Z^{A}_{AB}} \right) \right]^{-1} \tag{3.3.1.7}$$

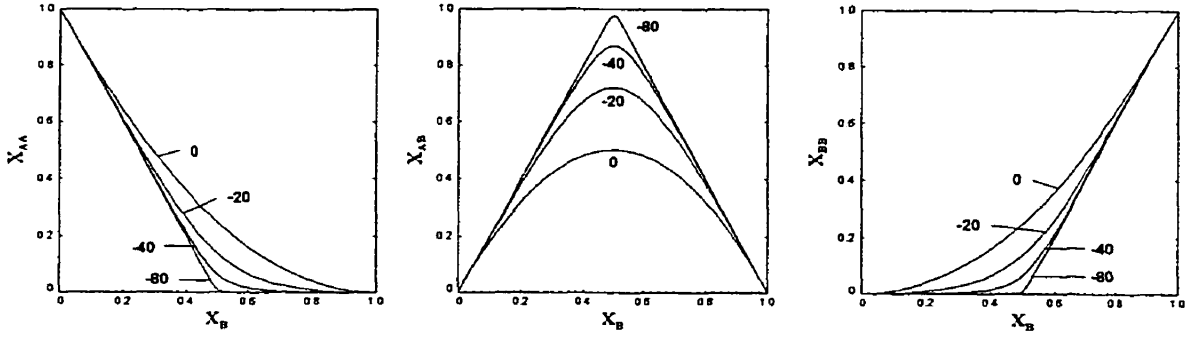
$$Z_B = \left[\frac{1}{2X_{BB} + X_{AB}} \left(\frac{2X_{BB}}{Z^{B}_{BB}} + \frac{X_{AB}}{Z^{B}_{AB}} \right) \right]^{-1} \tag{3.3.1.8}$$

où Z^{A}_{AA} est le nombre de coordination de l'espèce A dans une solution où il n'y a que des paires A-A (donc A pure), Z^{B}_{BB} est le nombre de coordination de l'espèce B dans une solution où il n'y a que des paires B-B (donc B pure), Z^{A}_{AB} est le nombre de coordination de l'espèce A dans une solution hypothétique où il n'y a que des paires A-B, et Z^{B}_{AB} est le nombre de coordination de l'espèce B dans une solution hypothétique où il n'y a que des paires A-B.

La modification de l'équation 3.3.1.6 permet d'exprimer l'énergie de formation des paires A-B selon l'environnement global de paires de cette liaison au lieu de l'environnement global des espèces. De plus, des nombres de coordination variables sont introduits (équations 3.3.1.7 et 3.3.1.8), ce qui permet une grande flexibilité dans le choix de la composition de maximum d'ordonnement configurationnel de la solution binaire (de façon indépendante des nombres de coordination des espèces pures). Les nombres de coordination des espèces étant variables, cela permet de fixer la composition du maximum d'ordonnement de façon indépendante des nombres de coordination des espèces pures (avant cette modification $X_B^{\text{max. ordonnement}} = Z_A/(Z_A + Z_B)$ où Z_i correspond au nombre de coordination de l'espèce i pure). Dans un système ternaire, lorsque les nombres de coordination sont constants, alors il n'existe que deux degrés de libertés sur le choix de la composition du maximum d'ordonnement dans les sous-systèmes binaires : ainsi, si l'on choisi $Z_A = 3$ et $Z_B = 6$ pour fixer le maximum d'ordonnement du

sous-système A-B à X_B = 1/3, et que l'on choisi Z_C=6 pour fixer le maximum d'ordonnement du sous-système B-C à X_B = 1/2, alors le maximum d'ordonnement du sous-système A-C doit se trouver selon le modèle à X_C=1/3, ce qui n'est pas nécessairement le cas. La nouvelle modification permet de changer cela. De plus, il a été montré qu'un nombre de coordination moyen de 2 permet de mieux représenter les données thermodynamiques de solutions très ordonnées (enthalpie de mélange très négative) et qu'un nombre de coordination de 6 permet de mieux représenter les données thermodynamiques de solutions montrant de l'immiscibilité. Des nombres de coordination variables permettent donc de passer d'une valeur donnée pour l'espèce A pure (disons 4) à une valeur proche de 2 lorsque B devient plus concentrée et si la solution est très ordonnée, ou bien à une valeur proche de 6 lorsque B devient plus concentrée et si la solution tend vers l'immiscibilité.

La figure 3.3 montre les fractions molaires X_{AA}, X_{BB} et X_{AB} à l'équilibre pour une solution binaire A-B à 1000°C pour différentes énergies Δg_{AB}. On peut y remarquer que plus Δg_{AB} est négative, plus X_{AA} tend vers 0 pour X_B supérieure à la composition de maximum d'ordonnement et plus X_{BB} tend vers 0 pour X_B inférieure à la composition de maximum d'ordonnement.



(a) (b) (c)

Figure 3.3 : Dépendence compositionnelle des fractions molaires de liaisons X_{AA}, X_{AB} et X_{BB} d'une solution A-B à 1000°C en fonction de l'énergie de formation des paires A-B à partir des paires A-A et B-B (0, -20, -40 et –80 kJ/mol) pour Z_A=Z_B= 2 : a) X_{AA}; b) X_{AB}; c) X_{BB}.

Ces variations des fractions molaires des paires ne sont pas linéaires en fonction de la composition et sont dépendantes de Δg_{AB}. Ce qui fait que la modification de la variation compositionnelle de Δg_{AB} selon X_{ii} au lieu de Y_i est elle-même fonction de Δg_{AB}. Il est donc possible pour un système où Δg^o_{AB} est très négatif et où $q^{(i,0)}_{AB}$ et $q^{(0,j)}_{AB}$ sont très positifs (voir équation 3.3.1.6) d'obtenir une forte déviation négative globale, donc un fort ordonnement, et deux lacunes de miscibilité de part et d'autre de la composition d'ordonnement (4 points d'inflexion de la fonction $G = f(X_B)$). Un exemple de système où un tel comportement est observé est Cu-S. Avec la version de Pelton et Blander (1984) du modèle quasichimique modifié, la variation compositionnelle de Δg_{AB} en fonction de Y_A et Y_B fait en sorte que les termes $q^{(i,0)}_{AB}$ et $q^{(0,j)}_{AB}$ ont un impact de part et d'autre de la composition de maximum d'ordonnement, alors qu'avec la nouvelle approche, $q^{(i,0)}_{AB}$ et $q^{(0,j)}_{AB}$ n'influencent qu'une région précise de composition lorsque l'ordonnement est grand, d'où une meilleure flexibilité lors de l'optimisation des données d'un système binaire (et de meilleurs prédictions).

L'énergie de Gibbs du modèle quasichimique modifié amélioré, pour une solution binaire *A-B*, est donnée par Pelton, Degterov, Eriksson, Robelin et Dessureault (1999) comme étant :

$$\begin{aligned} G &= n_A g^o_A + n_B g^o_B + RT(n_A \ln X_A + n_B \ln X_B) \\ &+ RT\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right) \\ &+ \tfrac{1}{2} n_{AB} \Delta g_{AB} \end{aligned} \tag{3.3.1.9}$$

Avec le bilan de masse suivant :

$$Z_A n_A = 2n_{AA} + n_{AB} \tag{3.3.1.10}$$

$$Z_B n_B = 2n_{BB} + n_{AB} \tag{3.3.1.11}$$

qui se réduit aux équations suivantes à l'aide des équations 3.3.1.7-8.

$$n_A = \frac{2n_{AA}}{Z_{AA}^A} + \frac{n_{AB}}{Z_{AB}^A} \tag{3.3.1.12}$$

$$n_B = \frac{2n_{BB}}{Z_{BB}^B} + \frac{n_{AB}}{Z_{AB}^B} \tag{3.3.1.13}$$

Les nombres de moles de paires (n_{AA}, n_{BB} et n_{AB}) à l'équilibre sont ceux qui minimisent la fonction 3.3.1.9 (énergie de Gibbs).

3.3.2 Extension aux systèmes multicomposants avec mélange sur un sous-réseau seulement.

Les équations multicomposantes sont développées et testées dans cette thèse pour un système non-réciproque. Un formalisme de type Kohler (1960) / Toop (1965) peut être intégré aux équations afin de tenir compte des propriétés acide/base des constituants de la solution. Un formalisme plus général d'estimation des propriétés multicomposantes à partir des paramètres binaires (introduit dans l'article « On the Choice of « Geometric » Thermodynamic Models » en Annexe II) a été intégré aux équations du modèle. Cette partie de la thèse est dans l'article « The Modified Quasichemical Model II – Multicomponent Solutions » montré en Annexe III. Il est aussi montré dans cet article comment l'expression de l'énergie de Gibbs du modèle quasichimique modifié nouvelle version peut servir à calculer l'énergie de Gibbs d'une solution dont les paramètres ont été obtenus pour le modèle quasichimique modifié (type Pelton et Blander – 1984) et pour un modèle polynomial à entropie de Bragg-Williams (voir les équations de conversion en Annexe XII). Il est donc possible de combiner ces modèles, et les bases

de données courantes peuvent être unifiées (du moins partiellement) avec quelques corrections mineures. L'article « The Modified Quasichemical Model II – Multicomponent Solutions » montré en Annexe III, donne les équations générales du modèle en tenant compte de la méthode générale d'estimation des propriétés thermodynamiques multicomposantes à partir des paramètres binaires, cependant que dans cette section de la thèse, seules les équations pour deux groupes (acides et bases) sont données afin que le lecteur puisse apprécier les différences entre les deux approches.

L'énergie de Gibbs d'une solution multicomposante est donnée pour le modèle quasichimique modifié par :

$$G = \sum_i n_i g_i^o + RT\sum_i n_i \ln X_i + RT\sum_i \sum_{j\geq i} n_{ij} \ln \frac{X_{ij}}{(2-\delta_{ij})Y_i Y_j} + \tfrac{1}{2}\sum_i \sum_{j>i} n_{ij}\Delta g_{ij} \tag{3.3.2.1}$$

où δ_{ij} est le delta Kronecker ($\delta_{ij} = 1$ si $i = j$ et $\delta_{ij} = 0$ si $i \neq j$). Les nombres de moles de liaisons i-j, n_{ij}, sont ceux qui minimisent l'énergie de Gibbs en respectant le bilan de masse suivant :

$$Z_i n_i = \sum_j (1+\delta_{ij}) n_{ij} \quad \text{pour tout } i \tag{3.3.2.2}$$

avec

$$Z_i = \left[\frac{1}{\sum_j (1+\delta_{ij}) n_{ij}} \left(\sum_j (1+\delta_{ij}) \frac{n_{ij}}{Z_{ij}^i} \right) \right]^{-1} \quad \text{pour tout } i \tag{3.3.2.3}$$

donc

$$n_i = \sum_j \left(1+\delta_{ij}\right)\frac{n_{ij}}{Z_{ij}^i} \tag{3.3.2.4}$$

L'expansion de l'énergie de formation, Δg_{ij}, en fonction de la composition (fractions molaires des paires X_{ij}) devient pour un formalisme à deux groupes :

<u>Pour A et B même groupe</u> :

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i,j}\left(\frac{X_{AA}}{X_{AA}+X_{AB}+X_{BB}}\right)^i\left(\frac{X_{BB}}{X_{AA}+X_{AB}+X_{BB}}\right)^j \Phi_{AB}^{(ij)} \tag{3.3.2.5}$$

<u>Pour A et B de groupes différents</u> :

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i,j}\left(\sum_{\substack{a,b \\ a,b\in \text{groupe } A}} X_{ab}\right)^i\left(\sum_{\substack{a,b \\ a,b\in \text{groupe } B}} X_{ab}\right)^j \Phi_{AB}^{(ij)} \tag{3.3.2.6}$$

Aux équations précédentes, $\Phi_{AB}^{(ij)}$ est définit comme étant pour A et B du même groupe :

$$\Phi_{AB}^{(ij)} = q_{AB}^{(ij)} + \sum_{\substack{c \\ c\neq A\neq B}}\sum_{\substack{k \\ k\geq 1}} q_{AB(c)}^{(ijk)} Y_c\left(1-Y_A-Y_B\right)^{k-1} \tag{3.3.2.7}$$

et pour A et B de groupes différents :

$$\Phi_{AB}^{(ij)} = q_{AB}^{(ij)} + \sum_{\substack{c \\ c \neq A \neq B \\ c \in \text{groupe de } A \\ c \notin \text{groupe de } B}} \sum_{\substack{k \\ k \geq 1}} q_{AB(c)}^{(ijk)} \frac{Y_c}{\sum_d Y_d} \left(1 - \frac{Y_A}{\sum_d Y_d} \right)^{k-1}$$

$$+ \sum_{\substack{e \\ e \neq A \neq B \\ e \in \text{groupe de } B \\ e \notin \text{groupe de } A}} \sum_{\substack{k \\ k \geq 1}} q_{AB(e)}^{(ijk)} \frac{Y_e}{\sum_f Y_f} \left(1 - \frac{Y_B}{\sum_f Y_f} \right)^{k-1} \qquad (3.3.2.8)$$

où les q_{AB} sont les paramètres optimisables du modèle.

Les équations précédentes ont été développées pour une division des constituants de la solutions en deux groupes chimiques (acides et bases). Les équations multigroupes (générales) sont données dans l'article « The Modified Quasichemical Model II – Multicomponent Solutions » en Annexe II. Dans ce même article, les raisons du choix des différentes fonctions sont données, qui dépendent principalement de restrictions sur les cas limites de mélanges tendant vers l'idéalité, et les mélanges d'espèces de groupes différents.

<u>Cas limites</u>

Si les paramètres Δg_{AB}^{o} et q_i des équations précédentes sont proches de 0, alors le sous-système binaire *A-B* de la solution tend vers l'idéalité et les fractions molaires de liaisons *A-A*, *A-B* et *B-B* peuvent être approximées par leurs valeurs associées à un mélange aléatoire :

$$X_{AA} = Y_A^2 \qquad (3.3.2.9)$$

$$X_{BB} = Y_B^2 \tag{3.3.2.10}$$

$$X_{AB} = 2Y_A Y_B \tag{3.3.2.11}$$

En remplaçant dans l'équation 3.3.2.5 ont obtient :

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i,j} \left(\frac{Y_A}{Y_A + Y_B} \right)^{2i} \left(\frac{Y_B}{Y_A + Y_B} \right)^{2j} \Phi_{AB}^{(ij)} \tag{3.3.2.12}$$

Cette dernière expression est similaire à l'équation 2.6.2.14 du modèle quasichimique modifié de Pelton et Blander (1984) sauf pour les puissances qui sont multipliées par 2. Cependant, il est possible de reproduire l'équation 2.7.2.14 en posant $\Phi_{AB}^{10} = -\Phi_{AB}^{01}$ pour que $\frac{Y_A^2 - Y_B^2}{(Y_A + Y_B)^2} = \frac{Y_A - Y_B}{Y_A + Y_B}$.

L'expression de l'énergie de Gibbs (3.3.2.1) devient :

$$G = \sum_i n_i g_i^o + RT \sum_i n_i \ln X_i + \left(\sum_i n_i \right) \sum_i \sum_{j>i} Y_i Y_j \Delta g_{ij} \tag{3.3.2.13}$$

Ce qui est égal à l'énergie de Gibbs associée à une entropie de Bragg-Williams et une expansion polynomiale de l'énergie en excès.

<u>Intégration des modèles quasichimique modifié et polynomial/Bragg-Williams en un seul modèle</u>

Il est possible de mélanger les différents modèles (quasichimique avec expansion des paires, quasichimique avec expansion des espèces et polynomial/Bragg-Williams) en

une seule expression de l'énergie de Gibbs. Pour ce faire, le dernier terme de l'équation 3.3.2.1 :

$$G = \sum_i n_i g_i^o + RT\sum_i n_i \ln X_i + RT\sum_i \sum_{j\geq i} n_{ij} \ln \frac{X_{ij}}{(2-\delta_{ij})Y_i Y_j} + \tfrac{1}{2}\sum_i \sum_{j>i} n_{ij}\Delta g_{ij} \tag{3.3.2.1}$$

devient :

- Pour le modèle quasichimique modifié avec expansion des paires :
  $\frac{1}{2}\sum_i \sum_{j>i} n_{ij}\left[f\left(X_{ii}, X_{ij}, X_{jj}, T\right)\right]$ (voir équation 3.3.2.5)
- Pour le modèle quasichimique modifié (version de Pelton et Blander, 1984) :
  $\frac{1}{2}\sum_i \sum_{j>i} n_{ij}\left[f\left(Y_i, Y_j, T\right)\right]$ (voir équation 3.3.1.2)
- Pour le modèle polynomial/Bragg-Williams (tel que montré au cas limite précédent) :
  $\sum_i \sum_{j>i}\left(\sum_k Z_{kk}^k n_k\right)\left[f\left(Y_i, Y_j, T\right)\right]$
  et l'on pose que $X_{ij} = 2Y_i Y_j$ à l'équation 3.3.2.1.

Cette « intégration » des modèles est discutée plus en détail aux sections « Reduction to the Random Mixing (Bragg-Williams) Model » et « Combining Models in One Multicomponent Solution Database » de l'article « The Modified Quasichemical Model II – Multicomponent Solutions » en Annexe III. De plus, il est possible de convertir exactement les paramètres optimisés du modèle quasichimique modifié avec expansion en Y_i en paramètres du modèle quasichimique amélioré avec expansion en X_{ii}, tel que montré à l'Annexe XVI. Il est aussi possible de convertir approximativement les

paramètres optimisés du modèle polynomial avec expansion en Y_i en paramètres du modèle quasichimique amélioré avec expansion en X_{ii}, tel que montré à l'Annexe XVI.

Simplification des équations en utilisant des constituants « associés »

Il est possible de simplifier les équations du modèle en utilisant les paires d'espèces comme des constituants de la solution et de traiter ces constituants comme des « associés » (ou « molécules »). Pour ce faire, on peut premièrement définir les énergies standards des paires, g^o_{AA} et g^o_{AB}, à partir des énergies des constituants purs, g^o_A et g^o_B, comme étant :

$$g^o_{AA} = \frac{2g^o_A}{Z^A_{AA}} \qquad \text{(similairement pour } g^o_{BB}\text{)} \tag{3.3.2.14}$$

$$g^o_{AB} = \frac{g^o_A}{Z^A_{AB}} + \frac{g^o_B}{Z^B_{AB}} + \tfrac{1}{2}\Delta g^o_{AB} \tag{3.3.2.15}$$

avec Δg^o_{AB} qui est le paramètre binaire utilisé dans les équations 3.3.2.5-6. L'équation de l'énergie de Gibbs 3.3.2.1 devient alors :

$$\begin{aligned} G = &\sum_i \sum_{j\geq i} n_{ij} g^o_{ij} + RT\sum_i n_i \ln X_i + RT\sum_i \sum_{j\geq i} n_{ij} \ln \frac{(1+\delta_{ij})X_{ij}}{2Y_iY_j} \\ &+ \tfrac{1}{2}\sum_i \sum_{j>i} n_{ij}\left(\Delta g_{ij} - \Delta g^o_{ij}\right) \end{aligned} \tag{3.3.2.16}$$

En remplaçant tous les nombres de moles de liaisons n_{ij} par les nombres de moles « d'associés » selon :

$$n_{i_{\frac{1}{z_{ij}^{i}}} j_{\frac{1}{z_{ij}^{j}}}} = n_{ij} \tag{3.3.2.17}$$

Le bilan de masse reliant les espèces aux liaisons devient un « vrai » bilan de masse chimique (le nombre de moles de i est le même des deux côtés de l'équation) reliant les espèces aux associés :

$$n_i = \left(\frac{2}{Z_{ij}^{i}}\right) n_{i_{\frac{2}{z_{ij}^{i}}}} + \sum_{j \neq i} \left(\frac{1}{Z_{ij}^{i}}\right) n_{i_{\frac{1}{z_{ij}^{i}}} j_{\frac{1}{z_{ij}^{j}}}} \tag{3.3.2.18}$$

Avec cette substitution, l'équation de l'énergie de Gibbs de la solution (3.3.2.16) devient fonction uniquement des fractions molaires des « associées » (exception faite du terme $-T\Delta S^{config}$). La minimisation de l'énergie de Gibbs est grandement facilitée par cette modification, car les constituants « associés » de la solution sont reliés à un « vrai » bilan de masse.

<u>Application du nouveau modèle quasichimique modifié à la solution liquide LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$</u>

Le modèle quasichimique modifié tel que décrit précédemment (éq. 3.3.2.16) à été appliqué dans cette thèse à la solution liquide de chlorures alcalins et alcalino-terreux LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$. Les optimisations des sous-systèmes binaires LiCl-RbCl, LiCl-CsCl, NaCl-RbCl et NaCl-CsCl sont celles de Sangster et Pelton (1987) qui utilisent l'entropie de Bragg-Williams avec expansion polynomiale de g^E. Tous les autres systèmes binaires ont été réoptimisés selon la technique montrée à la section 2.13 avec le modèle quasichimique modifié avec expansion en fonction de fractions molaires des paires pour l'énergie de formation des

paires et pour les nombres de coordination des espèces; exception faite des binaires KCl-RbCl, KCl-CsCl et RbCl-CsCl où les paramètres du g^E du liquide de Sangster et Pelton (1987) sont très proches de 0, ce qui permet de substituer directement l'entropie quasichimique à l'entropie de Bragg-Williams (qui est un cas limite). Les articles suivants, présentés en annexe, décrivent les optimisations de tous les sous-systèmes binaires, ternaires et multicomposants de cette solution :

- Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ System Using the Modified Quasichemical Model. (Annexe IV).

- Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ System Using the Modified Quasichemical Model. (Annexe V).

- Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ System Using the Modified Quasichemical Model. (Annexe VI).

<u>Application du nouveau modèle quasichimique modifié à la solution liquide LiF-NaF-KF-MgF_2-CaF_2</u>

Le modèle quasichimique modifié tel que décrit précédemment (éq. 3.3.2.16) à été appliqué dans cette thèse à la solution liquide de fluorures alcalins et alcalino-terreux LiF-NaF-KF-MgF_2-CaF_2. Tous les sous-systèmes binaires de la solution liquide ont été optimisés avec le nouveau modèle suivant la technique décrite à la section 2.13. L'article suivant, présenté en Annexe VII, décrit les optimisations de tous les sous-systèmes binaires, ternaires et mutlicomposants de cette solution :

- Thermodynamic Evaluation and Optimization of the LiF-NaF-KF-MgF_2-CaF_2 System Using the Modified Quasichemical Model. (Annexe IV).

Application du nouveau modèle quasichimique modifié aux solutions liquides binaires LiCl-LiF, NaCl-NaF, KCl-KF, $MgCl_2$-MgF_2 et $CaCl_2$-CaF_2

Le modèle quasichimique modifié tel que décrit précédemment à été appliqué dans cette thèse aux solutions liquides à cation commun LiCl-LiF, NaCl-NaF, KCl-KF, $MgCl_2$-MgF_2 et $CaCl_2$-CaF_2. Tous ces systèmes binaires et leur solution liquide ont été optimisés avec le nouveau modèle (équ. 3.3.2.16) selon la technique décrite à la section 2.13. L'annexe de l'article suivant, lui-même présenté en Annexe XI, décrit ces optimisations :

- Thermodynamic Evaluation and Optimization of the Li,Na,K,Mg,Ca//F,Cl Reciprocal System Using the Modified Quasichemical Model. (Annexe XI).

Ces trois séries d'optimisations de systèmes (dont deux multicomposants à anion commun) permettent de confronter le modèle et prouver qu'il est apte à donner de bonnes prédictions multicomposantes à partir des sous-systèmes binaires. De plus, plusieurs des sous-systèmes binaires de chlorures et de fluorures présentent des signes importants d'ordonnement à courte distance seconds-voisins (CsCl-$MgCl_2$, RbCl-$MgCl_2$, KCl-$MgCl_2$, KF-MgF_2, etc...). Dans ces cas, le modèle a prouvé être apte à reproduire l'ensemble des données expérimentales thermodynamiques avec une variation des paramètres optimisables consistente dans la suite logique des cations alcalins et alcalins-terre.

Finalement, ces trois séries d'articles permettent d'obtenir une optimisation de la phase liquide de tous les sous-systèmes binaires à ion commun de la solution liquide réciproque Li,Na,K,Mg,Ca//F,Cl faite avec le nouveau modèle quasichimique modifié. Une prochaine étape de cette thèse est le développement des équations de l'énergie de Gibbs et des bilans de masse pour une solution réciproque avec ordonnement entre les sous-réseaux cationique et anionique (premiers-voisins), et ordonnement sur un même réseau (seconds-voisins). L'énergie de Gibbs de ce modèle devra se réduire à l'énergie de Gibbs du modèle quasichimique modifié pour tous les sous-systèmes binaires à ions communs afin que les optimisations précédentes soient directement utilisées. Avant de présenter ce nouveau modèle, voici quelques suggestions de modifications possibles du nouveau modèle applicable à un seul réseau.

3.3.3 Suggestions d'améliorations possibles du modèle quasichimique modifié (pour un seul sous-réseau).

Nouvelles expansions de l'énergie de formation de paires *A-B*.

Les équations 3.3.2.5-6 qui décrivent la variation compositionnelle de l'énergie de formation des liaisons (ou paires) *A-B* dans un système multicomposant dont les espèces sont divisées en deux groupes sont :

Pour A et B même groupe :

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i,j} \left(\frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} \right)^{i} \left(\frac{X_{BB}}{X_{AA} + X_{AB} + X_{BB}} \right)^{j} \Phi^{(ij)}_{AB} \tag{3.3.2.5}$$

avec $\Phi^{(ij)}_{AB}$ décrit à l'équation 3.3.2.7. Pour A et B de groupes différents (pour un formalisme ayant seulement 2 groupes):

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i,j} \left(\sum_{\substack{a,b \\ a,b \in \text{groupe } A}} X_{ab} \right)^{i} \left(\sum_{\substack{a,b \\ a,b \in \text{groupe } B}} X_{ab} \right)^{j} \Phi^{(ij)}_{AB} \tag{3.3.2.6}$$

avec $\Phi^{(ij)}_{AB}$ décrit à l'équation 3.3.2.8. L'expansion 3.3.2.5, dans le cas limite où le mélange devient aléatoire ($\Delta g_{AB} \rightarrow 0$), devient égale à l'expansion 3.3.2.12, remontrée ci-après:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i,j} \left(\frac{Y_A}{Y_A + Y_B} \right)^{2i} \left(\frac{Y_B}{Y_A + Y_B} \right)^{2j} \Phi^{(ij)}_{AB} \tag{3.3.2.12}$$

car

$$\frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} = \frac{Y_A^2}{Y_A^2 + 2Y_A Y_B + Y_B^2} = \frac{Y_A^2}{(Y_A + Y_B)^2} \tag{3.3.3.1}$$

et similairement pour B. Les puissances sont multipliées par un facteur 2.

Il est suggéré dans cette thèse de remplacer l'expression 3.3.2.5 par une nouvelle expansion :

$$\begin{aligned} \Delta g_{AB} = \Delta g^{o}_{AB} &+ \sum_{i,j} \left(\frac{X_{AA}}{X_{AA} + \frac{1}{2} X_{AB}} \right)^{i} \left(\frac{\frac{1}{2} X_{AB}}{X_{AA} + \frac{1}{2} X_{AB}} \right)^{j} \Phi^{(ij)}_{A(B)} \\ &+ \sum_{i,j} \left(\frac{X_{BB}}{X_{BB} + \frac{1}{2} X_{AB}} \right)^{i} \left(\frac{\frac{1}{2} X_{AB}}{X_{BB} + \frac{1}{2} X_{AB}} \right)^{j} \Phi^{(ij)}_{B(A)} \end{aligned} \tag{3.3.3.2}$$

qui dans le cas limite du mélange aléatoire donne exactement une équivalence entre $\Phi^{(i0)}_{A(B)}$ de l'expression 3.3.3.2 et $\Phi^{(i0)}_{AB}$ de l'expression 2.6.2.14, et entre $\Phi^{(i0)}_{B(A)}$ de l'expression 3.3.3.2 et $\Phi^{(0j)}_{AB}$ de l'expression 2.6.2.14, car :

$$\frac{X_{AA}}{X_{AA} + \frac{1}{2} X_{AB}} = \frac{Y_A^2}{Y_A^2 + Y_A Y_B} = \frac{Y_A}{Y_A} \left(\frac{Y_A}{Y_A + Y_B} \right) \tag{3.3.3.3}$$

et similairement pour B. Cependant, il est possible d'utiliser un couplage des paramètres $\Phi^{i0}_{AB} = -\Phi^{0i}_{AB}$ tel que discuté précédemment. La figure 3.3 montre la variation compositionnelle des réactions molaires X_{AA}, X_{AB} et X_{BB} en fonction de X_B et de

l'énergie de formation des paires Δg_{AB}. Si Δg_{AB} est très négative, alors pour $0 \geq X_B \geq X_B^{\text{max. ordonnement}}$, on a que X_{BB} tend vers 0, et que X_{AA} et X_{AB} varient pratiquement linéairement en fonction de X_B.

La figure 3.4 montre la variation compositionnelle des fonctions suivantes en fonction de l'énergie de formation des paires *A-B* à 1000°C (Z_A=Z_B=2) pour une solution binaire *A-B*:

$$f_1(AA) = \frac{X_{AA}}{X_{AA} + \frac{1}{2}X_{AB}} \tag{3.3.3.4}$$

$$f_1(AB) = \frac{\frac{1}{2}X_{AB}}{X_{AA} + \frac{1}{2}X_{AB}} \tag{3.3.3.5}$$

$$f_2(AA) = \frac{X_{AA}}{X_{AA} + X_{AB} + X_{BB}} \tag{3.3.3.6}$$

Les fonctions f_1 sont reliées à l'équation suggérée 3.3.3.2, alors que la fonction f_2 est reliée à l'expansion utilisée dans cette thèse (3.3.2.5). La fonction f_2 est identique à X_{AA} dans le système binaire *A-B* comme on peut le voir en comparant les figures 3.3.1a) et 3.3.2a). Pour $f_1(BB)$ et $f_1(BA)$, les équations sont exactement les fonctions 3.3.3.4-5 en remplaçant X_{AA} par X_{BB}.

Il est très intéressant de noter la TRÈS grande similitude entre la variation compositionnelle de $f_1(AA)$ en fonction de Δg_{AB}, à la figure 3.5 et la variation compositionnelle de l'activité du constituant *A* (a_A) dans la solution en fonction de Δg_{AB}.

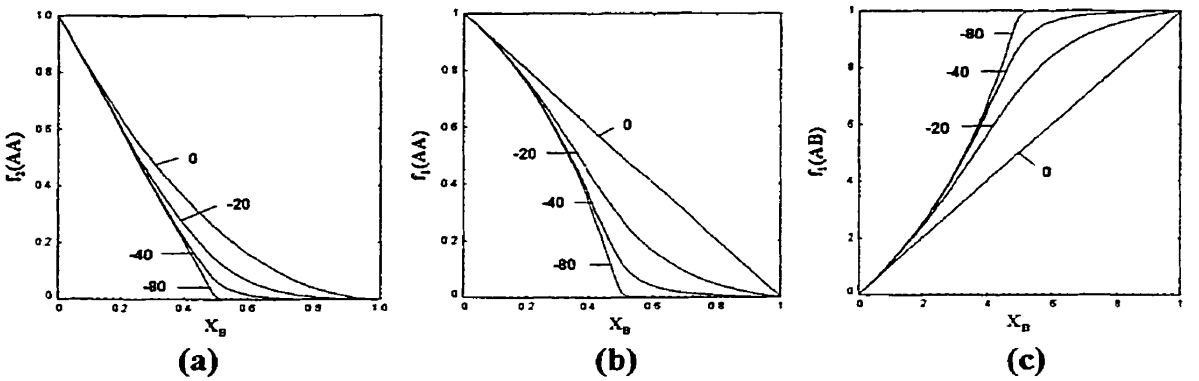


Figure 3.4 : Dépendence compositionnelle des fonctions f_1 et f_2 d'une solution *A-B* à 1000°C en fonction de l'énergie de formation des paires *A-B* à partir des paires *A-A* et *B-B* (0, -20, -40 et –80 kJ/mol) pour Z_A=Z_B = 2 : a) f_2 (*AA*); b) f_1(*AA*); c) f_1(*AB*).

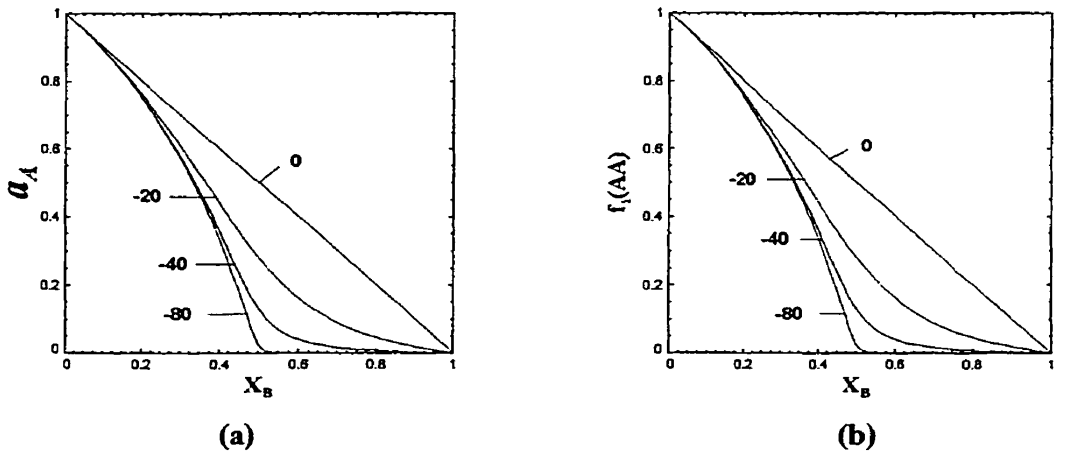


Figure 3.5 : Similitude entre la variation compositionnelle de a_A (a) et de f_1(*AA*) (b) dans la solution *A-B* à 1000°C en fonction de l'énergie de formation des paires *A-B* à partir des paires *A-A* et *B-B* (0, -20, -40 et –80 kJ/mol) pour Z_A=Z_B=2.

Il est possible de prouver l'identité $a_A = f_1(AA)$ si $Z_A = Z_B = 2$ ($Z_{AA}^A = Z_{AB}^A = Z_A = 2$ et $Z_{BB}^B = Z_{AB}^B = Z_B = 2$) et $\Delta g_{AB} = cste$, avec :

$$G = n_A g_A^o + n_B g_B^o + RT(n_A \ln X_A + n_B \ln X_B) + RT\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right)$$

$$+ \frac{n_{AB}}{2} \Delta g_{AB} \tag{3.3.3.7}$$

$$\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{n_B} = \left(\frac{Z_{AA}^A}{2} \right) \left(\frac{\partial G}{\partial n_{AA}} \right)_{n_{BB}, n_{AB}} = g_A^o + RT \ln X_A + \left(\frac{Z_{AA}^A}{2} \right) RT \ln \frac{X_{AA}}{Y_A^2} \tag{3.3.3.8}$$

$$RT \ln a_A = \mu_A - g_A^o = RT \ln \left[\frac{X_A X_{AA}^{\left(\frac{Z_{AA}^A}{2}\right)}}{Y_A^{Z_{AA}^A}} \right] \tag{3.3.3.9}$$

donc, si Z_A=Z_B on a que Y_A=X_A, et alors:

$$a_A = \frac{X_{AA}^{\left(\frac{Z_{AA}^A}{2}\right)}}{Y_A^{Z_{AA}^A - 1}} \tag{3.3.3.10}$$

et

$$f_1(AA) = \frac{X_{AA}}{X_{AA} + \frac{1}{2} X_{AB}} = \frac{X_{AA}}{Y_A} \tag{3.3.3.11}$$

Les équations 3.3.3.10 et 3.3.3.11 ne sont strictement égales que si $Z_A = Z_B = 2$ (implicitement $Z_{AA}^A = Z_A$) et $\Delta g_{AB} = cste$. Afin de pouvoir conserver l'identité entre a_A et $f_1(AA)$ pour différentes conditions, il faudrait transformer $f_1(AA)$ selon :

$$f_1'(AA) = \frac{X_A X_{AA}^{\left(\frac{Z_{AA}^A}{2}\right)}}{\left(X_{AA} + \frac{1}{2} X_{AB}\right)^{Z_{AA}^A}} \tag{3.3.3.12}$$

Cependant cette forme plus « bizarre » de fonction ne semble pas attrayante et pourrait causer des problèmes pour l'estimation des propriétés thermodynamiques dans les systèmes d'ordre supérieur.

Cette similitude de a_A et de $f_I(AA)$ pourrait permettre une meilleure représentation de la variation compositionelle de Δg_{AB} en fonction de X_B. L'utilisation de la fonction 3.3.3.2 au lieu de la fonction 3.3.2.5 est donc suggérée. La séparation des constituants de la solution en groupes acide/base n'a pas été développée pour cette proposition, mais les idées de base sont prêtes.

Complexes multiples

Il est possible de considérer plus d'une composition d'ordonnement par système binaire pour le modèle quasichimique. Pour ce faire, il faut réécrire les équations des nombres de coordination et des bilans de masse en fonction des nombres de moles des « c » complexes binaires dénotés $n_{AB^{(1)}}$, $n_{AB^{(2)}}$, ..., $n_{AB^{(c)}}$. Ainsi, pour un système binaire A-B comportant plusieurs compositions d'ordonnement, les nombres de coordination Z_A et Z_B deviennent :

$$\frac{1}{Z_A} = \frac{1}{2n_{AA} + \sum_c n_{AB^{(c)}}} \left[\frac{2n_{AA}}{Z^A_{AA}} + \sum_c \frac{n_{AB^{(c)}}}{Z^A_{AB^{(c)}}} \right] \tag{3.3.3.13}$$

$$\frac{1}{Z_B} = \frac{1}{2n_{BB} + \sum_c n_{AB^{(c)}}} \left[\frac{2n_{BB}}{Z^B_{BB}} + \sum_c \frac{n_{AB^{(c)}}}{Z^B_{AB^{(c)}}} \right] \tag{3.3.3.14}$$

La restriction suivante s'applique sur les ratios des nombres de coordination :

$$\frac{Z^A_{AB^{(1)}}}{Z^B_{AB^{(1)}}} \neq \frac{Z^A_{AB^{(2)}}}{Z^B_{AB^{(2)}}} \neq \ldots \neq \frac{Z^A_{AB^{(c)}}}{Z^B_{AB^{(c)}}} \tag{3.3.3.15}$$

Le bilan de masse devient :

$$Z_A n_A = 2n_{AA} + \sum_c n_{AB^{(c)}} \tag{3.3.3.16}$$

$$Z_B n_B = 2n_{BB} + \sum_c n_{AB^{(c)}} \tag{3.3.3.17}$$

ou bien :

$$n_A = \frac{2n_{AA}}{Z^A_{AA}} + \sum_c \frac{n_{AB^{(c)}}}{Z^A_{AB^{(c)}}} \tag{3.3.3.18}$$

$$n_B = \frac{2n_{BB}}{Z^B_{BB}} + \sum_c \frac{n_{AB^{(c)}}}{Z^B_{AB^{(c)}}} \tag{3.3.3.19}$$

Les fractions molaires et équivalentes des espèces A et B sont calculées de la manière habituelle et les fractions molaires des paires sont calculées aussi similairement mais en tenant compte des nouvelles paires $AB^{(c)}$:

$$X_{AA} = \frac{n_{AA}}{n_{AA} + n_{BB} + \sum_c n_{AB^{(c)}}} \tag{3.3.3.20}$$

$$X_{AB^{(i)}} = \frac{n_{AB^{(i)}}}{n_{AA} + n_{BB} + \sum_c n_{AB^{(c)}}} \qquad (i = 1, \ldots, c) \tag{3.3.3.21}$$

L'énergie de Gibbs devient :

$$
\begin{aligned}
G = {} & n_A g_A^o + n_B g_B^o \\
& + RT\left(n_A \ln X_A + n_B \ln X_B\right) \\
& + RT\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + \sum_c n_{AB^{(c)}} \ln \frac{X_{AB^{(c)}}}{2Y_A Y_B}\right) \\
& + \sum_c \frac{n_{AB^{(c)}}}{2} \Delta g_{AB^{(c)}}
\end{aligned}
\tag{3.3.3.22}
$$

Les termes $\Delta g_{AB^{(c)}}$ peuvent être exprimés en fonction des Y_i ou des X_{ij}.

Les équations ci-haut, dans le cas limite où tous les $\Delta g_{AB^{(c)}}$ valent 0, ne redonnent cependant pas l'entropie idéale. On pourrait voir ce fait comme un défaut de la proposition, mais l'erreur vient plutôt du fait que par définition, un système idéal ne contient pas plus d'une composition de maximum d'ordonnement! Les équations ci-haut ne doivent s'appliquer que pour des sous-systèmes binaires ayant une tendance à avoir plus d'une composition d'ordonnement et où ces tendances à l'ordonnement sont fortes. Les équations ci-haut redonnent exactement les équations classiques quasichimiques si le nombre de complexes binaires est 1.

Pour une solution très ordonnée, avec plus d'un complexe, où tous les $\Delta g_{AB^{(c)}}$ tendent vers l'infini négatif, le terme $2Y_A Y_B$ de l'entropie configurationnelle vaut 0.5 pour toute composition comprise entre les compositions d'ordonnement. Les nombres de moles de paires *A-A* et *B-B* tendent alors vers 0 pour ces mêmes compositions. On a dans ce cas, pour toute composition comprise entre les compositions d'ordonnement :

$$
\frac{1}{Z_A} = \sum_c \frac{X_{AB^{(c)}}}{Z_{AB^{(c)}}^A}
\tag{3.3.3.23}
$$

$$\frac{1}{Z_B} = \sum_c \frac{X_{AB^{(c)}}}{Z^B_{AB^{(c)}}} \tag{3.3.3.24}$$

et

$$n_A = \sum_c \frac{n_{AB^{(c)}}}{Z^A_{AB^{(c)}}} \tag{3.3.3.25}$$

$$n_B = \sum_c \frac{n_{AB^{(c)}}}{Z^B_{AB^{(c)}}} \tag{3.3.3.26}$$

L'entropie configurationnelle devient :

$$\Delta S^{config} = -R(n_A \ln X_A + n_B \ln X_B) - R\left(\sum_c n_{AB^{(c)}} \ln X_{AB^{(c)}}\right) - R\left(\sum_c n_{AB^{(c)}} \ln 2\right) \tag{3.3.3.27}$$

Le dernier terme de l'équation entropique (3.3.3.27) annule le premier terme pour toute composition comprise entre les compositions d'ordonnement, si les Z des espèces respectent les valeurs données par Pelton et Blander (1984) (mais cela est vrai même s'il n'y a qu'un seul complexe). Ne reste alors que le terme médian qui correspond à un mélange aléatoire de paires binaires complexées.

Cette modification permet de considérer la formation de plusieurs « complexes » dans la solution binaire. La solution liquide NaF-AlF_3 contient, selon les récentes études (Olsen, 1996), les « complexes anioniques » AlF_5^{2-}, AlF^{4-} et AlF_6^{3-} associés aux compositions d'ordonnement Na_2AlF_5, $NaAlF_4$ et Na_3AlF_6 respectivement. Olsen (1996) a déterminé que le complexe anionique AlF_5^{2-} est dominant. En première approximation, seul ce complexe peut être utilisé avec le traitement quasichimique « classique », mais il serait possible d'évaluer l'influence des 3 complexes anioniques

grâce à la nouvelle modification. D'autres systèmes chimiques contiennent plus d'une composition d'ordonnement (mélanges alcalins-*Pb*, alcalins-*Bi*, alcalins-*Te*, etc...).

Polymérisation :

Certains liquides ordonnés présentent une forme de polymérisation. Par exemple, des complexes dimères comme $Al_2Cl_7^-$ sont présents lorsque $AlCl_3$ est mélangé avec un chlorure alcalin (ex : $NaCl$). Le mélange cationique Al^{3+} et Na^+ en est perturbé car pour de fortes teneurs en $AlCl_3$ ($X_{AlCl_3} > 0.5$), les cations Al^{3+} se mélangent avec les cations Na^+ en entrant dans le liquide par paire (1 particule pour 2 atomes d'Al).

Il est proposé pour modéliser cette solution polymérisée avec un modèle quasichimique de s'inspirer de l'approche utilisée dans cette thèse pour l'effet de compensation de charge dans le systtème Na_2O-Al_2O_3-SiO_2 (voir article « Modeling the Charge Compensation Effect in Silica-rich Na_2O-K_2O-Al_2O_3-SiO_2 Melts » en Annexe I). Ainsi, en modélisant la phase liquide binaire $NaCl$-$AlCl_3$ comme étant un mélange cationique Na^+-Al^{3+}-Al_2^{6+} ($NaCl$-$AlCl_3$-Al_2Cl_6), il serait possible de tenir compte simultanément de l'ordonnement $AlCl_4^-$ (complexe binaire entre Na^+ et Al^{3+}) et de l'ordonnement $Al_2Cl_7^-$ (complexe binaire entre Na^+ et Al_2^{6+}). Le liquide pure $AlCl_3$ est en fait fortement dimérisé et Al_2Cl_6 devrait être l'état standard du liquide pure $AlCl_3$. L'énergie de $AlCl_3$ liquide pure (cation Al^{3+}) devrait être plus positive que celle de Al_2Cl_6 (cation Al_2^{6+}). Les réactions quasichimiques deviennent alors :

$$[Na-Cl-Na]_{paire} + [Al-Cl-Al]_{paire} \Leftrightarrow 2[Na-Cl-Al]_{paire} \qquad (3.3.3.28)$$

$$[Na-Cl-Na]_{paire} + [Al_2-Cl-Al_2]_{paire} \Leftrightarrow 2[Na-Cl-Al_2]_{paire} \qquad (3.3.3.29)$$

$$[Al-Cl-Al]_{paire} + [Al_2-Cl-Al_2]_{paire} \Leftrightarrow 2[Al-Cl-Al_2]_{paire} \qquad (3.3.3.30)$$

Seules les énergies des réactions 3.3.3.28 et 3.3.3.29 sont importantes. La région compositionnelle $0.5 < X_{NaCl} < 1$ serait dominée par les paires *Na-Cl-Na* et *Na-Cl-Al*; la région compositionnelle $0.333 < X_{NaCl} < 0.5$ serait dominée par les paires *Na-Cl-Al* et $Na\text{-}Cl\text{-}Al_2$; la région compositionnelle $0 < X_{NaCl} < 0.333$ serait dominée par les paires $Na\text{-}Cl\text{-}Al_2$ et $Al_2\text{-}Cl\text{-}Al_2$ (cependant que le liquide très riche en $AlCl_3$ est principalement moléculaire, formé de dimères Al_2Cl_6).

Aucune modification aux équations de l'énergie de Gibbs n'est nécessaire pour reproduire la dimérisation. Cependant, une méthode d'optimisation de système ternaire est nécessaire pour trouver les paramètres du modèle (au début de cette thèse, aucun logiciel n'était disponible pour optimiser un système ternaire). La même approche pourrait être applicable au mélange chlorures alcalins-$BeCl_2$. Elle peut aussi s'appliquer aux chaînes de silicates (*c.f.* $Si_2O_5^{2-}$) mais avec plus de prudence car la silice pure fondue n'est pas formée de dimères.

<u>Configuration non-aléatoire des paires</u> :

Une bonne partie de travaux de cette thèse porte sur la modification des équations quasichimiques de l'expansion de l'énergie de formation des paires *A-B* (Δg_{AB}) en fonction de l'environnement des paires (X_{ij}) au lieu de l'environnement des espèces (Y_i), dans le but d'obtenir un meilleur lissage des données expérimentales binaires et une meilleure prédiction du modèle dans les systèmes multicomposants.

La théorie quasichimique est basée sur l'évaluation de l'écart au mélange aléatoire des espèces dans une solution à l'aide d'un mélange aléatoire des paires d'espèces. Il est proposé d'appliquer la même approche, mais à un degré supérieur. Ainsi, si l'on pouvait évaluer l'écart au mélange aléatoire des paires (qui évaluerait lui-même un écart au mélange aléatoire des espèces) à l'aide de « paires de paires », il serait possible

d'obtenir une meilleure évaluation de l'entropie configurationnelle de mélange, donc de meilleurs lissages et prédictions.

Ainsi, pour un mélange d'espèces *A* et *B* (à l'état liquide), les paires d'espèces présentes sont les paires *A-A*, *A-B* et *B-B*. Si on introduit les paires de paires *AA-AA*, *AA-AB*, *AA-BB*, *BB-BB*, *BB-AB* et *AB-AB*, il serait possible d'évaluer de subtils effets de mélange sur l'entropie. Ainsi l'énergie de formation des paires *A-B* est exprimée dans cette thèse en fonction de l'environnement global en espèce *A* et *B* (Pelton et Blander, 1984), ou bien en fonction de l'environnement global en paires *A-A* et *B-B* (Pelton, Degterov, Eriksson, Robelin et Dessureault, 1999). La modification proposée permettrait de faire varier l'énergie de formation de paires *A-B* selon l'environnement des paires de paires. Ainsi, le modèle distinguerait les paires *A-A* entourées de paires *A-A* des paires *A-A* entourées de paires *A-B* et des paires *A-A* entourées de paires *B-B*, etc...

Le bilan de masse entre les paires de paires et les paires est :

$$Z_{AA}n_{AA} = 2n_{AA-AA} + n_{AA-AB} + n_{AA-BB} \tag{3.3.3.31}$$

$$Z_{BB}n_{BB} = 2n_{BB-BB} + n_{AA-BB} + n_{BB-AB} \tag{3.3.3.32}$$

$$Z_{AB}n_{AB} = 2n_{AB-AB} + n_{AA-AB} + n_{BB-AB} \tag{3.3.3.33}$$

Les « nombres de coordination » des paires, Z_{ij} sont donnés par :

$$\frac{1}{Z_{AA}} = \frac{1}{2n_{AA-AA} + n_{AA-AB} + n_{AA-BB}}\left[\frac{2n_{AA-AA}}{Z^{AA}_{AA-AA}} + \frac{n_{AA-AB}}{Z^{AA}_{AA-AB}} + \frac{n_{AA-BB}}{Z^{AA}_{AA-BB}}\right] \tag{3.3.3.34}$$

$$\frac{1}{Z_{BB}} = \frac{1}{2n_{BB-BB} + n_{BB-AB} + n_{AA-BB}}\left[\frac{2n_{BB-BB}}{Z^{BB}_{BB-BB}} + \frac{n_{BB-AB}}{Z^{BB}_{BB-AB}} + \frac{n_{AA-BB}}{Z^{BB}_{AA-BB}}\right] \tag{3.3.3.35}$$

$$\frac{1}{Z_{AB}} = \frac{1}{2n_{AB-AB} + n_{AA-AB} + n_{BB-AB}}\left[\frac{2n_{AB-AB}}{Z^{AB}_{AB-AB}} + \frac{n_{AA-AB}}{Z^{AB}_{AA-AB}} + \frac{n_{BB-AB}}{Z^{AB}_{BB-AB}}\right] \tag{3.3.3.36}$$

où Z^{AA}_{AA-AB} est le nombre de paires entourant une paire *A-A* quand cette paire *A-A* est dans un solvant *A-B* (et similairement pour les autres paires). Il est aussi possible de supposer Z_{AA}, Z_{BB} et Z_{AB} constants. Le bilan de masse reliant les paires aux espèces est exactement le même que pour le modèle quasichimique classique :

$$Z_A n_A = 2n_{AA} + n_{AB} \tag{3.3.3.37}$$

$$Z_B n_B = 2n_{BB} + n_{AB} \tag{3.3.3.38}$$

Une variation compositionnelle des nombres de coordination des espèces peut être appliquée. Les fractions molaires des paires de paires sont données par :

$$X_{AA-AA} = \frac{n_{AA-AA}}{n_{AA-AA} + n_{BB-BB} + n_{AB-AB} + n_{AA-AB} + n_{AA-BB} + n_{BB-AB}} \tag{3.3.3.39}$$

et similairement pour les autres paires de paires. Les fractions équivalentes des paires d'espèces sont données par :

$$Y_{AA} = \frac{Z_{AA} n_{AA}}{Z_{AA} n_{AA} + Z_{AB} n_{AB} + Z_{BB} n_{BB}} = X_{AA-AA} + \tfrac{1}{2} X_{AA-AB} + \tfrac{1}{2} X_{AA-BB} \tag{3.3.3.40}$$

$$Y_{AB} = \frac{Z_{AB} n_{AB}}{Z_{AA} n_{AA} + Z_{AB} n_{AB} + Z_{BB} n_{BB}} = X_{AB-AB} + \tfrac{1}{2} X_{AA-AB} + \tfrac{1}{2} X_{BB-AB} \tag{3.3.3.41}$$

$$Y_{BB} = \frac{Z_{BB} n_{BB}}{Z_{AA} n_{AA} + Z_{AB} n_{AB} + Z_{BB} n_{BB}} = X_{BB-BB} + \tfrac{1}{2} X_{AA-BB} + \tfrac{1}{2} X_{BB-AB} \tag{3.3.3.42}$$

Les autres variables compositionnelles (X_i, Y_i, X_{ij}, etc...) sont calculées de la manière habituelle. L'énergie de Gibbs devient :

$$
\begin{aligned}
G = {} & n_A g_A^o + n_B g_B^o \\
& + RT(n_A \ln X_A + n_B \ln X_B) \\
& + RT\left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right) \\
& + RT\left(n_{AA-AA} \ln \frac{X_{AA-AA}}{Y_{AA}^2} + n_{BB-BB} \ln \frac{X_{BB-BB}}{Y_{BB}^2} + n_{AB-AB} \ln \frac{X_{AB-AB}}{Y_{AB}^2} \right) \\
& + RT\left(n_{AA-AB} \ln \frac{X_{AA-AB}}{2Y_{AA} Y_{AB}} + n_{AA-BB} \ln \frac{X_{AA-BB}}{2Y_{AA} Y_{BB}} + n_{BB-AB} \ln \frac{X_{BB-AB}}{2Y_{BB} Y_{AB}} \right) \\
& + \tfrac{1}{2} n_{AB-AB} \Delta g_{AB-AB}^o \\
& + \tfrac{1}{2} n_{AA-AB} \Delta g_{AA-AB} + \tfrac{1}{2} n_{AA-BB} \Delta g_{AA-BB} + \tfrac{1}{2} n_{BB-AB} \Delta g_{BB-AB}
\end{aligned}
\tag{3.3.3.43}
$$

L'énergie de formation des paires de paires *AB-AB* (Δg_{AB-AB}^o) peut être reliée à l'énergie de formation des paires d'espèces *A-B* à partir des paires d'espèces *A-A* et *B-B*. Les énergies de formation des paires de paires « binaires » (Δg_{AA-AB}, Δg_{AA-BB} et Δg_{BB-AB}) peuvent être exprimées comme des fonctions des fractions molaires des paires de paires.

L'utilisation de nombre de coordination des paires qui respectent une valeur de 2 (Pelton et Blander, 1984) permet que le nouveau terme entropique quasichimique pour le mélange des paires de paires soit une valeur exacte (selon le modèle d'Ising linéaire). Ainsi, avec de telles valeurs, l'estimation de l'entropie configurationnelle ne serait pas dégradée.

Si les énergies de formation des paires de paires « binaires » (Δg_{AA-AB}, Δg_{AA-BB} et Δg_{BB-AB}) sont nulles, alors l'équation 3.3.3.43 devrait se réduire à l'énergie de Gibbs d'une solution quasichimique. Il est donc théoriquement possible que toutes les

modifications aux équations quasichimiques de cette thèse puissent être considérées comme un cas limite de l'équation 3.3.3.43 majorées pour les systèmes multicomposant.

Les paires de paires présentent l'avantage d'offrir jusqu'à trois compositions d'ordonnement pour un système binaire, ce qui permettrait de reproduire les complexations multiples dans certains systèmes (K-Pb, Rb-Te, Na-Bi, Au-Cs, etc...). Une formulation quasichimique en quadruplets (A_4, A_3B, A_2B_2, AB_3 et B_4) au lieu des paires de paires pourrait donner des résulats similaires cependant qu'elle ne serait pas une extension aussi simple de la théorie quasichimique des paires, car pour les paires de paires les équations ont été obtenues par le même raisonnement que pour les paires simples. De plus, il n'y a que 5 quadruplets dans un système binaires au lieu de 6 paires de paires car les paires de paires *AB-AB* et *AA-BB* sont « fondues » en un seul quadruplet A_2B_2 (cependant, si la paire *A-B* est très stable, la paire de paire *AA-BB* devrait être pratiquement inexistante dans le mélange).

Il n'est pas dans la portée de cette thèse de développer plus à fond cette proposition (solution multicomposante, groupes acide/base, expansion compositionnelle des variables, complexes multiples, etc...), mais seulement de soulever l'idée que la théorie quasichimique peut être encore grandement améliorée afin de pouvoir reproduire des effets thermodynamiques subtils lors du mélange d'atomes.

3.3.4 Systèmes réciproques (deux sous-réseaux)

Cette partie de la thèse se réfère à l'article "The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation" en Annexe X de cette thèse. L'article décrit un nouveau modèle quasichimique pour solution à deux sous-réseaux qui se réduit au modèle quasichimique modifié (avec toutes les nouveautés apportées telles que décrites dans les sections précédentes) pour un système à ion commun.

L'approche quasichimique consiste à évaluer l'ordonnement d'espèces dans une solution en fonction de l'énergie d'interaction entre ces espèces à l'aide d'un mélange aléatoire de paires d'espèces. Lors d'un mélange d'espèces sur un même quasi-réseau, les paires d'espèces considérées sont des paires d'espèces seconds voisins appartenant au même quasi-réseau :

$$[A-X-A]_{paire}+[B-X-B]_{paire} \Leftrightarrow 2[A-X-B]_{paire} \qquad \Delta g_{A,B/X} \qquad (3.3.4.1)$$

Le modèle quasichimique modifié (sections 2.7 et 3.3) évalue l'ordonnement de ce type d'interaction, c'est-à-dire quelles sont les concentrations des 3 types de paires de l'équation (3.3.4.1) à l'équilibre pour une concentration d'espèces X_{AX} et X_{BX} donnée, à une température donnée. Pour une solution réciproque, qui implique un mélange entre deux quasi-réseaux, alors les paires d'espèces considérées sont des paires d'espèces premiers voisins appartenant à des sous-réseaux différents :

$$[A-Y]_{paire}+[B-X]_{paire} \Leftrightarrow [A-X]_{paire}+[B-Y]_{paire} \qquad \Delta g_{A,B/X,Y} \qquad (3.3.4.2)$$

Le modèle quasichimique pour solution réciproque (section 2.12) évalue l'ordonnement de ce type d'interaction, c'est-à-dire quelles sont les concentrations des 4 types de paires

de l'équation (3.3.4.2) à l'équilibre pour une concentration d'espèces X_A, X_B, X_X et X_Y donnée à une température donnée.

Il existe donc 2 modèles quasichimiques distincts pour évaluer les 2 types d'ordonnement : premiers et seconds voisins. Afin d'évaluer simultanément l'ordonnement du type seconds-voisins de la réaction 3.3.4.1 et l'ordonnement du type premiers-voisins de la réaction 3.3.4.2, un nouveau modèle doit être proposé. S'il peut permettre de se réduire au modèle quasichimique modifié lorsque la solution n'est pas réciproque et au modèle quasichimique pour solution réciproque lorsque tous les binaires à ion commun sont idéaux, alors le nouveaux modèle permettra l'intégration des bases de données actuellement développées pour ces deux modèles.

Le modèle proposé suppose la présence de 2 quasi-réseaux dans le liquide où deux différents types d'espèces se mélangent (cations et anions). Le modèle proposé utilise les quadruplets d'espèces comme unité de mélange de base, tout comme le modèle quasichimique utilise les paires d'espèces. Le quadruplet d'espèces contient 2 espèces de chacun des 2 quasi-réseaux :

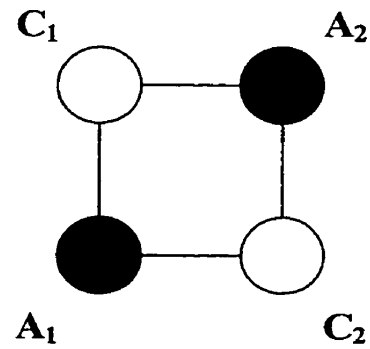


Fig. 3.6 : Quadruplet.

Le quadruplet de base est donc composé des 4 espèces (2 cations C_1 et C_2, et 2 anions A_1 et A_2) qui forment 4 paires premiers-voisins (C_1-A_1, C_1-A_2, C_2-A_1 et C_2-A_2) et 4 paires seconds-voisins (C_1-[A_1]-C_2, C_1-[A_2]-C_2, A_1-[C_1]-A_2 et A_1-[C_2]-A_2). En

attribuant une énergie de Gibbs au quadruplet et en établissant des bilans de masse entre les quadruplets et les espèces et entre les quadruplets et les paires premiers et seconds voisins, l'énergie de Gibbs du mélange aléatoire de quadruplet peut être obtenue si l'entropie configurationnelle peut être calculée. De plus, pour un système à ion commun (A_1=A_2 ou C_1=C_2 pour tous les quadruplets), les quadruplets sont exactement équivalents aux paires seconds-voisins, donc le nouveau modèle devient dans ce cas limite potentiellement exactement équivalent au modèle quasichimique modifié avec expansion de l'énergie de formation des paires fonction des concentrations des paires.

L'article "The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation" en Annexe X donne la totalité des équations de l'énergie de Gibbs d'une solution multicomposante avec ions de charge multiple appartenant à 2 groupes acides/bases. Ces équations sont partiellement reprises dans ce chapitre.

<u>Équations de bases pour système multicomposant</u>

Pour une solution de plus d'un cation ($A,B,C,\ldots$) et de plus d'un anion ($X,Y,Z,\ldots$), les quadruplets sont distribués aléatoirement sur des sites de quadruplets. Chaque quadruplet est présent dans la solution avec un certain nombre de moles ($n_{A_2/XY}$, n_{BC/Y_2}, etc...). Il existe 3 types de quadruplets : les quadruplets unaires (A_2X_2), les quadruplets binaires (A_2XY et ABX_2) et les quadruplets réciproques ($ABXY$). Chaque ion de chaque quadruplet possède un nombre de coordination seconds voisins ($Z^A_{A_2/XY}$, $Z^X_{A_2/XY}$ et $Z^Y_{A_2/XY}$) qui permet de définir le bilan de masse des espèces :

$$Z_A n_A = \Omega_A \tag{3.3.4.1}$$

$$Z_X n_X = \Omega_X \tag{3.3.4.2}$$

avec

$$\Omega_A = 2\sum_{a}\sum_{a'\geq a} n_{A_2/aa'} + \sum_{c\neq A}\sum_{a}\sum_{a'\geq a} n_{Ac/aa'} \tag{3.3.4.3}$$

$$\Omega_X = 2\sum_{c}\sum_{c'\geq c} n_{cc'/X_2} + \sum_{a\neq X}\sum_{c}\sum_{c'\geq c} n_{cc'/Xa} \tag{3.3.4.4}$$

où c et c' sont des cations et a et a' sont des anions. Les fonctions suivantes sont proposées afin de calculer les nombres de coordination globaux des ions (Z_A) :

$$\frac{1}{Z_A} = \frac{1}{\Omega_A}\left[2\sum_{a}\sum_{a'\geq a}\frac{n_{A_2/aa'}}{Z^A_{A_2/aa'}} + \sum_{c\neq A}\sum_{a}\sum_{a'\geq a}\frac{n_{Ac/aa'}}{Z^A_{Ac/aa'}}\right] \tag{3.3.4.5}$$

$$\frac{1}{Z_X} = \frac{1}{\Omega_X}\left[2\sum_{c}\sum_{c'\geq c}\frac{n_{cc'/X_2}}{Z^X_{cc'/X_2}} + \sum_{a\neq X}\sum_{c}\sum_{c'\geq c}\frac{n_{cc'/Xa}}{Z^X_{cc'/Xa}}\right] \tag{3.3.4.6}$$

Ce qui permet de calculer directement les nombres de moles des ions (n_A) en combinant les équations précédentes :

$$n_A = 2\sum_{a}\sum_{a'\geq a}\frac{n_{A_2/aa'}}{Z^A_{A_2/aa'}} + \sum_{c\neq A}\sum_{a}\sum_{a'\geq a}\frac{n_{Ac/aa'}}{Z^A_{Ac/aa'}} \tag{3.3.4.7}$$

$$n_X = 2\sum_{c}\sum_{c'\geq c}\frac{n_{cc'/X_2}}{Z^X_{cc'/X_2}} + \sum_{a\neq X}\sum_{c}\sum_{c'\geq c}\frac{n_{cc'/Xa}}{Z^X_{cc'/Xa}} \tag{3.3.4.8}$$

Les fractions molaires des quadruplets ($X_{AB/XY}$), les fractions molaires ioniques (X_C), et les fractions équivalentes (Y_A) sont définies comme :

$$X_{AB/XY} = \frac{n_{AB/XY}}{\sum_{c}\sum_{c'\geq c}\sum_{a}\sum_{a'\geq a} n_{cc'/aa'}} \tag{3.3.4.9}$$

$$X_A = \frac{n_A}{\sum_c n_c} \tag{3.3.4.10}$$

$$X_X = \frac{n_X}{\sum_a n_a} \tag{3.3.4.11}$$

$$Y_A = \frac{Z_A n_A}{\sum_c Z_c n_c} = \frac{\Omega_A}{\sum_c \Omega_c} = \sum_a \sum_{a' \geq a} X_{A_2/aa'} + \tfrac{1}{2} \sum_{c \neq A} \sum_a \sum_{a' \geq a} X_{Ac/aa'} \tag{3.3.4.12}$$

$$Y_X = \frac{Z_X n_X}{\sum_a Z_a n_a} = \frac{\Omega_X}{\sum_a \Omega_a} = \sum_c \sum_{c' \geq c} X_{cc'/X_2} + \tfrac{1}{2} \sum_{a \neq X} \sum_c \sum_{c' \geq c} X_{cc'/Xa} \tag{3.3.4.13}$$

Pour la solution, un nombre constant de quadruplet émanant de chaque paire ζ est utilisé, ce qui permet de déterminer le bilan de masse des paires premiers-voisins :

$$\zeta n_{A/X} = 4 n_{A_2/X_2} + 2 \sum_{c \neq A} n_{Ac/X_2} + 2 \sum_{a \neq X} n_{A_2/Xa} + \sum_{c \neq A} \sum_{a \neq X} n_{Ac/Xa} \tag{3.3.4.14}$$

Ainsi les fractions molaires des paires premiers-voisins peuvent être calculées :

$$X_{A/X} = \frac{n_{A/X}}{\sum_c \sum_a n_{c/a}} = X_{A_2/X_2} + \tfrac{1}{2} \sum_{c \neq A} X_{Ac/X_2} + \tfrac{1}{2} \sum_{a \neq X} X_{A_2/Xa} + \tfrac{1}{4} \sum_{c \neq A} \sum_{a \neq X} X_{Ac/Xa} \tag{3.3.4.15}$$

Une fois toutes les variables compositionnelles calculées, l'énergie de Gibbs totale de la solution est définie par :

$$G = G^o + G^{config} + G^E_{ion-common} + G^E_{réciproque} \tag{3.3.4.16}$$

avec :

$$G^o = \sum_c \sum_{c' \geq c} \sum_a \sum_{a' \geq a} n_{cc'/aa'} g^o_{cc'/aa'} \tag{3.3.4.17}$$

où les énergies de Gibbs des quadruplets peuvent être calculées avec les équations suivantes selon le type de quadruplet (unaire, binaire ou réciproque) et les énergies de Gibbs molaires des constituants pures A_aX_x (où a et x sont les stoechiométries ioniques) :

$$g^o_{A_2/X_2} = \frac{2g^o_{A_a/X_x}}{aZ^A_{A_2/X_2}} = \frac{2g^o_{A_a/X_x}}{xZ^X_{A_2/X_2}} \tag{3.3.4.18}$$

$$g^o_{A_2/XY} = \tfrac{1}{2}\left[\left(\frac{Z^X_{A_2/X_2}}{Z^X_{A_2/XY}}\right) g^o_{A_2/X_2} + \left(\frac{Z^Y_{A_2/Y_2}}{Z^Y_{A_2/XY}}\right) g^o_{A_2/Y_2} + \Delta g^o_{A_2/XY}\right] \tag{3.3.4.19}$$

où $\Delta g^o_{A_2/XY}$ est l'énergie de Gibbs par mole de quadruplets pour la formation d'une solution hypothétique composée uniquement de quadruplets binaires A_2XY, à partir des quadruplets unaires A_2X_2 et A_2Y_2. Pour les quadruplets réciproques, on a :

$$\begin{aligned} g^o_{AB/XY} = {} & \left(\frac{q_X}{Z^X_{AB/XY}} + \frac{q_Y}{Z^Y_{AB/XY}}\right)^{-1} \Big(\frac{q_X Z^A_{A_2/X_2}}{2Z^A_{AB/XY} Z^X_{AB/XY}} g^o_{A_2/X_2} + \frac{q_X Z^B_{B_2/X_2}}{2Z^B_{AB/XY} Z^X_{AB/XY}} g^o_{B_2/X_2} \\ & + \frac{q_Y Z^A_{A_2/Y_2}}{2Z^A_{AB/XY} Z^Y_{AB/XY}} g^o_{A_2/Y_2} + \frac{q_Y Z^B_{B_2/Y_2}}{2Z^B_{AB/XY} Z^Y_{AB/XY}} g^o_{B_2/Y_2} \Big) \\ & + \tfrac{1}{4}\left(\frac{Z^A_{A_2/XY}}{Z^A_{AB/XY}} \Delta g^o_{A_2/XY} + \frac{Z^B_{B_2/XY}}{Z^B_{AB/XY}} \Delta g^o_{B_2/XY} + \frac{Z^X_{AB/X_2}}{Z^X_{AB/XY}} \Delta g^o_{AB/X_2} + \frac{Z^Y_{AB/Y_2}}{Z^Y_{AB/XY}} \Delta g^o_{AB/Y_2} \right) \\ & + \Delta g^o_{AB/XY} \end{aligned} \tag{3.3.4.20}$$

où Δg^o_{ABXY} est l'énergie de Gibbs de formation (par mole de quadruplets) d'une solution hypothétique composée uniquement de quadruplets $ABXY$ réciproques à partir d'un mélange de quadruplets de quadruplets binaires équimolaires.

L'énergie de Gibbs configurationnelle, G^{config}, est donnée par :

$$G^{config} = -T\Delta S^{config} \tag{3.3.4.21}$$

avec

$$\Delta S^{config} = -R\sum_{c} n_c \ln X_c - R\sum_{a} n_a \ln X_a - R\sum_{c}\sum_{a} n_{c/a} \ln \frac{X_{c/a}}{Y_c Y_a}$$
$$-R\sum_{c}\sum_{c'\geq c}\sum_{a}\sum_{a'\geq a} n_{cc'/aa'} \ln\left[\frac{X_{cc'/aa'}}{\left(\frac{(2-\delta_{cc'})(2-\delta_{aa'})X_{c/a}X_{c'/a}X_{c/a'}X_{c'/a'}}{Y_c Y_{c'} Y_a Y_{a'}}\right)}\right] \tag{3.3.4.22}$$

où $\delta_{cc'}$ et $\delta_{aa'}$ sont des delta Kronecker qui prennent la valeur 0 si c est différent de c' où si a est différent de a', ou la valeur 1 si c est identique à c' et si a est identique à a' respectivement.

Les énergies de Gibbs en excès sont définies comme étant :

$$G^{E}_{ion-commun} = \tfrac{1}{2}\sum_{c}\sum_{a}\sum_{a'>a}\left(n_{c_2/aa'} + \frac{Z^{c}_{c_2/aa'}}{2}\sum_{c'\neq c}\frac{n_{cc'/aa'}}{Z^{c}_{cc'/aa'}}\right)\left(\Delta g_{c_2/aa'} - \Delta g^{o}_{c_2/aa'}\right)$$
$$+\tfrac{1}{2}\sum_{a}\sum_{c}\sum_{c'>c}\left(n_{cc'/a_2} + \frac{Z^{a}_{cc'/a_2}}{2}\sum_{a'\neq a}\frac{n_{cc'/aa'}}{Z^{a}_{cc'/aa'}}\right)\left(\Delta g_{cc'/a_2} - \Delta g^{o}_{cc'/a_2}\right) \tag{3.3.4.23}$$

$$G^{E}_{réciproque} = \tfrac{1}{2}\sum_{c}\sum_{c'>c}\sum_{a}\sum_{a'>a} n_{cc'/aa'}\left(\Delta g_{cc'/aa'} - \Delta g^{o}_{cc'/aa'}\right) \tag{3.3.4.24}$$

Les termes $\Delta g_{c_2/aa'}$ et $\Delta g_{cc'/a_2}$ sont des fonctions compositionnelles exprimant l'énergie de Gibbs de formation (par mole de quadruplet) des quadruplets binaires à partir des

quadruplets unaires. $\Delta g_{cc'/aa'}$ est une fonction compositionnelle exprimant l'énergie de Gibbs de formation (par mole de quadruplet) des quadruplets réciproques à partir des quadruplets binaires. Ces fonctions contiennent les énergies de Gibbs molaires standard $\Delta g^o_{c_2/aa'}$, $\Delta g^o_{cc'/a_2}$ et $\Delta g^o_{cc'/aa'}$ respectivement. Ces fonctions compositionnelles tiennent compte des méthodes d'interpolation multicomposantes avec un formalisme de groupes de type Kohler (1960) et Toop (1965) et elles sont données dans l'article du modèle en Annexe X.

Les nombres de moles des quadruplets à l'équilibre sont ceux qui minimisent l'énergie de Gibbs totale de la solution (équation 3.3.4.16) en respectant le bilan de masse des espèces (ions) donné aux équations 3.3.4.7-8. Pour minimiser l'énergie de Gibbs dans cette thèse, ces équations ont été codées dans la routine générale de minimisation de l'énergie de Gibbs du système FACT, *SOLGASMIX* d'EQUILIB.

Il est montré dans l'article « The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation » en Annexe X que le modèle se réduit au modèle quasichimique modifié avec les améliorations apportées dans cette thèse pour un système à ion commun. Il est aussi montré que le modèle, dans des conditions précises (reliées à la constance des nombres de coordination), se réduit au modèle quasichimique pour solutions réciproques lorsque les interactions seconds-voisins tendent vers 0. Le modèle peut aussi s'appliquer pour des solutions solides (à deux sous-réseaux) si les nombres de coordination des espèces appartenant à un même sous-réseaux sont identiques.

Validation

Les équations du modèle ont été codées dans *SOLGASMIX* (Eriksson et Rosén, 1973), l'algorithme de minimisation de l'énergie de Gibbs, qui permet le calcul d'équilibres de

phases et de propriétés thermodynamiques dans le programme *EQUILIB* du système FACT. Le code des équations a été validé sur des systèmes hypothétiques avec tous les cas de paramètres binaires, ternaires et réciproques possibles. Il a été vérifié que le nouveau modèle reproduise exactement les résultats obtenus avec le modèle quasichimique modifié dans le cas limite d'un système à ion commun. Pour tous les cas, les énergies de Gibbs intégrale et partielles ont été vérifiées.

La généralisation des algorithmes dans *SOLGASMIX* permet de vérifier aisément qu'un système multicomposant est bien calculé avec tous ses paramètres (interactions binaires, ternaires, effet des groupes acide et base, etc...) car l'effet des paramètres est simplement sommatif, de sorte qu'en vérifiant que le sous-système sont bien calculés paramètre par paramètre, le travail est minimisé.

Application

Le modèle a été appliqué à la phase liquide du système LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ dans l'article « Thermodynamic Evaluation and Optimization of the Li,Na,K,Mg,Ca//F,Cl Reciprocal System Using the Modified Quasichemical Model » montré en Annexe XI. Les paramètres du modèle pour les sous-systèmes binaires et ternaires à ion-commun proviennent des articles d'optimisation discutés à la section 3.3.2. L'article traite de l'optimisation des sous-systèmes ternaires réciproques (en annexe de cet article on retrouve les optimisations des sous-systèmes binaires à cation-commun LiF-LiCl, NaF-NaCl, KF-KCl, MgF_2-$MgCl_2$ et CaF_2-$CaCl_2$), et des prédictions du modèles dans les systèmes quaternaires où des données thermodynamiques ont été trouvées (projections du liquidus sur des isopleths).

Le choix du système Li,Na,K,Mg,Ca//F,Cl comme test du modèle est basé sur les fortes tendances d'ordonnement des espèces qu'on y retrouve et sur la grande quantité de

données thermodynamiques expérimentales (mesures du liquidus). Ainsi l'ordonnement premiers voisins de certains sous-systèmes réciproques ternaires est très grand dû à des énergies de Gibbs d'échange des premiers-voisins de l'ordre de 60-100 kJ/équivalent. De plus, l'ordonnement seconds-voisins cationiques est aussi grand, particulièrement pour les systèmes KCl-$MgCl_2$ et $NaCl$-$MgCl_2$. Les énergies de mélange des sous-systèmes de fluorures alkalines avec MgF_2 sont aussi très négatives. Enfin, plusieurs sous-systèmes binaires et reciproques ternaires ont des énergies de mélanges ou d'échange très faibles, faisant en sorte qu'une large plage d'énergie de mélange a été testée à l'aide du modèle sur ce système.

Critiques du modèle

A) Entropie configurationnelle : approximation de la configuration "idéale"

Le modèle d'Ising qui est à la base de l'entropie quasichimique n'est exacte que dans le cas unidimensionnel (chaîne d'atomes, $Z = 2$). Pour un nombre de coordination différent de 2, l'entropie quasichimique n'est qu'approximative. Naturellement cette erreur augmente lorsque Z s'éloigne de 2, mais la tendance à l'ordonnement (diminution de l'entropie configurationnelle lorsque l'interaction entre atomes est de plus en plus négative) est conservée.

Pour le modèle quasichimique réciproque avec ordonnement des premiers et des seconds voisins, une autre approximation est ajoutée. Ainsi, les concentrations théoriques des quadruplets lorsque le mélange des ions est aléatoire sur les deux quasi-réseaux n'est exacte que lorsque l'énergie d'échange est nulle. Les équations suivantes :

$$\frac{X_{A_2X_2}}{\left(\frac{X^4_{A/X}}{Y^2_A Y^2_X}\right)} = 1 \qquad (3.3.4.25)$$

$$\frac{X_{A_2Y_2}}{\left(\frac{X^4_{A/Y}}{Y^2_A Y^2_Y}\right)} = 1 \qquad (3.3.4.26)$$

$$\frac{X_{B_2X_2}}{\left(\frac{X^4_{B/X}}{Y^2_B Y^2_X}\right)} = 1 \qquad (3.3.4.27)$$

$$\frac{X_{B_2Y_2}}{\left(\frac{X^4_{B/Y}}{Y^2_B Y^2_Y}\right)} = 1 \qquad (3.3.4.28)$$

$$\frac{X_{ABX_2}}{\left(\frac{2X^2_{A/X} X^2_{B/X}}{Y_A Y_B Y^2_X}\right)} = 1 \qquad (3.3.4.29)$$

$$\frac{X_{ABY_2}}{\left(\frac{2X^2_{A/Y} X^2_{B/Y}}{Y_A Y_B Y^2_Y}\right)} = 1 \qquad (3.3.4.30)$$

$$\frac{X_{A_2XY}}{\left(\frac{2X^2_{A/X} X^2_{A/Y}}{Y^2_A Y_X Y_Y}\right)} = 1 \qquad (3.3.4.30)$$

$$\frac{X_{B_2XY}}{\left(\frac{2X^2_{B/X} X^2_{B/Y}}{Y^2_B Y_X Y_Y}\right)} = 1 \qquad (3.3.4.31)$$

$$\frac{X_{ABXY}}{\left(\frac{4X_{A/X} X_{B/X} X_{A/Y} X_{B/Y}}{Y_A Y_B Y_X Y_Y}\right)} = 1 \qquad (3.3.4.32)$$

ne sont exactes que si l'énergie d'échange est nulle et les énergies de formation des paires seconds voisins sont nulles. Pour ζ (nombre de quadruplet émanant d'une paire premiers-voisins) valant 1, si les interactions seconds-voisins sont nulles, la valeurs des 9 fonctions précédentes sont celles montrées à la figure 3.7 :

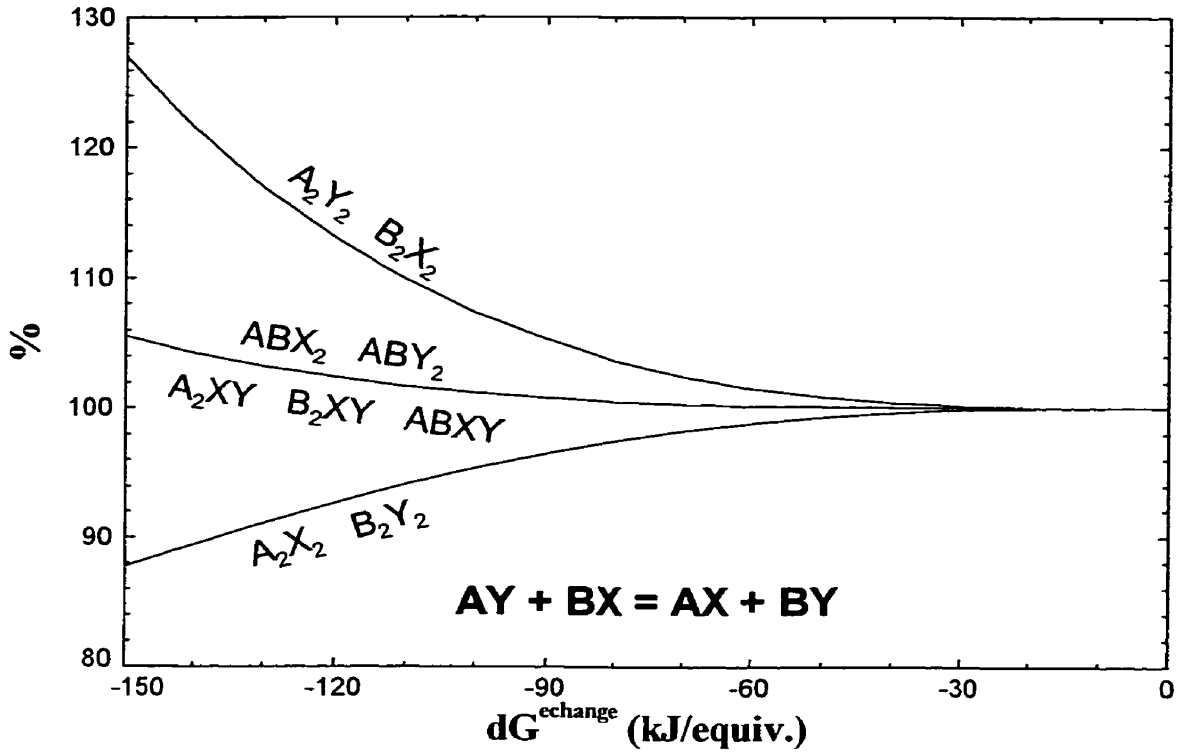


Figure 3.7 : Valeurs des fonctions 3.3.4.25-33 en fonction de l'énergie d'échange pour un système ternaire réciproque *A,B//X,Y* monovalent avec $\zeta = 1$ (tous les binaires sont idéaux).

A la figure précédente, on peut voir que plus l'énergie d'échange est négative, plus les valeurs des fonctions 3.3.4.25 à 3.3.4.33 s'écartent de 1 (100%). Pour les quadruplets « unaires » de la paire stable A_2X_2 et B_2Y_2, la fonction est inférieure à l'unité, ce qui se traduit au logarithme (dans l'entropie) par une stabilisation « artificielle » (contribution partielle négative à l'énergie de Gibbs) de ces deux quadruplets par rapport aux autres, changeant donc la configuration. À –70 kJ/équivalent, l'erreur sur les fonctions 3.3.4.25 et 3.3.4.28 (quadruplets « unaires » de la paire stable) est de 1.8%, l'erreur sur les fonctions 3.3.4.26 et 3.3.4.27 (quadruplets « unaires » de la paire instable) est de 2.4% et l'erreur sur les fonctions 3.3.4.29 à 3.3.4.33 (quadruplets « binaires » et « réciproques ») est de 0.28%. Pour cette valeur de l'énergie d'échange, l'approximation de l'entropie

configurationnelle demeure bonne. À –100 kJ/équivalent, ces valeurs deviennent 4.7%, 7.3% et 1.1%, ce qui est moins bon.

Il existe un cas limite où le long de la diagonale stable *AX-BY* cette approximation de l'entropie configurationnelle peut causer le calcul à l'équilibre d'une mauvaise configuration de quadruplet. Normalement, pour toute valeur de l'énergie d'échange, pour toute valeur de ζ, et pour une composition appartenant à cette diagonale stable, il existe une configuration où tous les quadruplets ont une composition non nulle. Cependant, lors de minimisation de l'énergie de Gibbs dans des systèmes où l'énergie d'échange est grande (< -75 kJ/équiv.), une configuration peut être calculée où seuls les quadruplets « unaires » de la paire stables (A_2X_2 et B_2Y_2) ont une concentration non-nulle (numériquement). Pour expliquer ce fait, un minimum local de la surface d'énergie de Gibbs peut être invoqué, vers lequel converge l'algorithme *SOLGASMIX*. En effet, l'analyse des équations suivantes donne à penser que l'approximation de l'entropie configurationnelle peut mener à une diminution de l'énergie de Gibbs d'une configuration à 2 quadruplets par rapport à une configuration à 9 quadruplets. Donc pour,

$$n_{A_2/X_2} = n_A\left(\frac{Z^A_{A_2/X_2}}{2}\right) = n_X\left(\frac{Z^X_{A_2/X_2}}{2}\right) \tag{3.3.4.33}$$

$$n_{B_2/Y_2} = n_B\left(\frac{Z^B_{B_2/Y_2}}{2}\right) = n_Y\left(\frac{Z^Y_{B_2/Y_2}}{2}\right) \tag{3.3.4.34}$$

$$n_{A_2/XY} = n_{B_2/XY} = n_{AB/X_2} = n_{AB/Y_2} = n_{AB/XY} = 0 \tag{3.3.4.35}$$

on a,

$$X_A = \frac{Z^B_{B_2/Y_2} n_{A_2/X_2}}{Z^B_{B_2/Y_2} n_{A_2/X_2} + Z^A_{A_2/X_2} n_{B_2/Y_2}} = 1 - X_B \tag{3.3.4.36}$$

$$X_X = \frac{Z^Y_{B_2/Y_2} n_{A_2/X_2}}{Z^Y_{B_2/Y_2} n_{A_2/X_2} + Z^X_{A_2/X_2} n_{B_2/Y_2}} = 1 - X_Y \tag{3.3.4.37}$$

$$Y_A = Y_X = X_{A_2/X_2} \tag{3.3.4.38}$$

$$Y_B = Y_Y = X_{B_2/Y_2} \tag{3.3.4.39}$$

$$n_{A/X} = \frac{4}{\zeta} n_{A_2/X_2} \tag{3.3.4.40}$$

$$n_{B/Y} = \frac{4}{\zeta} n_{B_2/Y_2} \tag{3.3.4.41}$$

$$n_{A/Y} = n_{B/X} = 0 \tag{3.3.4.42}$$

L'énergie de Gibbs de mélange devient :

$$\begin{aligned}\frac{\Delta G}{RT} = \frac{2\Delta g^{échange}_{A,B/X,Y}}{Z^A_{A_2/X_2} RT} n_{A_2/X_2} &+ \frac{2n_{A_2/X_2}}{Z^A_{A_2/X_2}} \ln \frac{Z^B_{B_2/Y_2} n_{A_2/X_2}}{Z^B_{B_2/Y_2} n_{A_2/X_2} + Z^A_{A_2/X_2} n_{B_2/Y_2}} \\ &+ \frac{2n_{B_2/Y_2}}{Z^B_{B_2/Y_2}} \ln \frac{Z^A_{A_2/X_2} n_{B_2/Y_2}}{Z^B_{B_2/Y_2} n_{A_2/X_2} + Z^A_{A_2/X_2} n_{B_2/Y_2}} \\ &+ \frac{2n_{A_2/X_2}}{Z^X_{A_2/X_2}} \ln \frac{Z^Y_{B_2/Y_2} n_{A_2/X_2}}{Z^Y_{B_2/Y_2} n_{A_2/X_2} + Z^X_{A_2/X_2} n_{B_2/Y_2}} \\ &+ \frac{2n_{B_2/Y_2}}{Z^Y_{B_2/Y_2}} \ln \frac{Z^X_{A_2/X_2} n_{B_2/Y_2}}{Z^Y_{B_2/Y_2} n_{A_2/X_2} + Z^X_{A_2/X_2} n_{B_2/Y_2}} \\ &+ \frac{4n_{A_2/X_2}}{\zeta} \ln \frac{1}{X_{A_2/X_2}} + \frac{4n_{B_2/Y_2}}{\zeta} \ln \frac{1}{X_{B_2/Y_2}} \\ &+ n_{A_2/X_2} \ln X_{A_2/X_2} + n_{B_2/Y_2} \ln X_{B_2/Y_2}\end{aligned} \tag{3.3.4.43}$$

Si $Z^A_{A_2/X_2} = Z^B_{B_2/Y_2}$ et que $Z^X_{A_2/X_2} = Z^Y_{B_2/Y_2}$ alors :

$$\frac{\Delta G}{RT}=\frac{2\Delta g^{échange}_{A,B/XY}}{Z^{A}_{A_2/X_2}RT}n_{A_2/X_2}+\frac{2n_{A_2/X_2}}{Z^{A}_{A_2/X_2}}\ln X_{A_2/X_2}+\frac{2n_{B_2/Y_2}}{Z^{B}_{B_2/Y_2}}\ln X_{B_2/Y_2}$$
$$+\frac{2n_{A_2/X_2}}{Z^{X}_{A_2/X_2}}\ln X_{A_2/X_2}+\frac{2n_{B_2/Y_2}}{Z^{Y}_{B_2/Y_2}}\ln X_{B_2/Y_2} \qquad (3.3.4.44)$$
$$-\frac{4n_{A_2/X_2}}{\zeta}\ln X_{A_2/X_2}-\frac{4n_{B_2/Y_2}}{\zeta}\ln X_{B_2/Y_2}$$
$$+n_{A_2/X_2}\ln X_{A_2/X_2}+n_{B_2/Y_2}\ln X_{B_2/Y_2}$$

Ce qui donne

$$\frac{\Delta G}{RT}=\frac{2\Delta g^{échange}_{A,B/XY}}{Z^{A}_{A_2/X_2}RT}n_{A_2/X_2}+n_{A_2/X_2}\left(\frac{2}{Z^{A}_{A_2/X_2}}+\frac{2}{Z^{X}_{A_2/X_2}}+1-\frac{4}{\zeta}\right)\ln X_{A_2/X_2}$$
$$+n_{B_2/Y_2}\left(\frac{2}{Z^{B}_{B_2/Y_2}}+\frac{2}{Z^{Y}_{B_2/Y_2}}+1-\frac{4}{\zeta}\right)\ln X_{B_2/Y_2} \qquad (3.3.4.45)$$

Si $Z^{A}_{A_2/X_2}=Z^{X}_{A_2/X_2}$ et que $Z^{B}_{B_2/Y_2}=Z^{Y}_{B_2/Y_2}$ alors il faut que

$$\frac{4}{Z}+1-\frac{4}{\zeta}=0 \qquad (3.3.4.46)$$

pour avoir un mélange mécanique pur de *AX* et de *BX* (car il n'y a aucun quadruplet *ABXY*, ce qui signifie qu'il n'y a pas de mélange de paires non similaires). Pour $Z = 6$, on a $\zeta = 2.4$. Si $\zeta > 2.4$, alors une forte stabilisation des quadruplets de la paire stable peut en découler car une entropie de mélange positive est obtenue de l'équation 3.3.4.45. Cette valeur de $\zeta = 2.4$ est la valeur utilisée pour l'optimisation de la phase liquide du système Li,Na,K,Mg,Ca//F,Cl. Cependant, ce système contient des ions non monovalents et les termes binaires en excès sont fortement négatifs dans certains cas. Il pourrait s'ensuivre certains problèmes de convergence lors de la minimisation de l'énergie de Gibbs, ce qui ferait que l'entropie de l'équation 3.3.4.45 donnerait une contribution négative à l'énergie de Gibbs, ce qui se traduirait par un minimum local de

la surface d'énergie de Gibbs le long de la diagonale *AX-BY* (paire stable) pour la configuration à 2 quadruplets. Des lacunes de miscibilité impliquant un liquide de composition exactement sur la diagonale stable peuvent apparaître.

B) Entropie configurationnelle : seconds-voisins

Une seconde faiblesse de l'entropie configurationnelle est que la nature même du quadruplet utilisé pour évaluer simultanément les concentrations des paires premiers et seconds voisins implique que l'ion formant le 2e voisin d'un ion du quadruplet est le même ion pour les deux paires de paires émanant de l'ion de référence. La figure suivante illustre cet aspect :

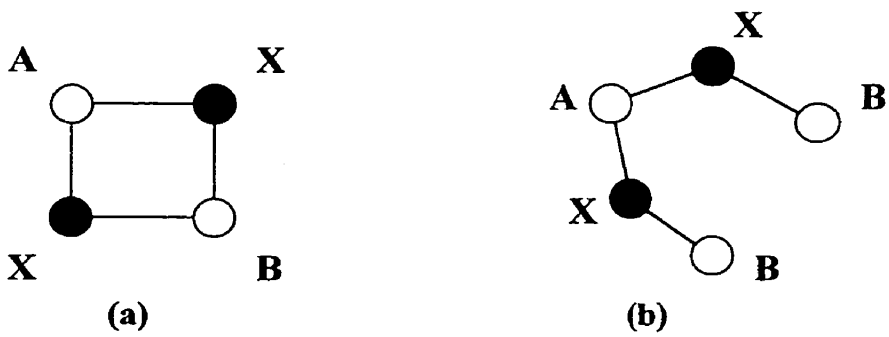


Figure 3.8 : Cation *B* comme second voisin du cation *A*. a) quadruplet. b) autre configuration (plus générale).

Pour certains liquides, la configuration du quadruplet peut très bien convenir, mais ce n'est pas le cas général. Une erreur sur l'entropie configurationnelle peut s'en suivre.

C) Complexation réciproque

Le modèle permet d'évaluer la configuration des quadruplets dans le champ de composition réciproque à l'aide d'un quadruplet de type réciproque (*ABXY*). Cependant si le liquide contient plus d'une composition d'ordonnement réciproque, alors le modèle ne peut reproduire cet effet structurel, mais pourrait, si les ordonnements sont faibles, tout de même reproduire avec satisfaction les propriétés thermodynamiques. Il s'agit d'un problème similaire à celui de l'ordonnement multiple dans un système binaire (*i.e.* Fe-O avec FeO et Fe_2O_3). Un questionnement similaire s'applique s'il y a évidence de polymérisation dans le champ de composition réciproque. Un exemple de système où une complexation réciproque pourrait exister est le système NaF-AlF_3-Al_2O_3-Na_2O où des évidences (spectre Raman) que des « complexes anioniques » $Al_2OF_6^{2-}$, $Al_2O_2F_4^{2-}$ et $Al_3O_4F_4^{3-}$ existent ont été obtenues (Olsen, 1996).

4. Conclusion

La thermodynamique des solutions liquides permet de mieux comprendre le comportement de ce type de solutions dans les systèmes chimiques (industriels ou autres). Une quantification de cette thermodynamique est nécessaire pour l'obtention de prédictions utiles au développement des procédés. Les procédés métallurgiques comportent souvent l'utilisation de hautes températures où les liquides présents sont principalement des liquides ioniques (sels fondus) avec tendances covalentes (oxydes fondus) ou des liquides métalliques. Pour ces liquides, des modèles ont été développés qui permettent une quantification des grandeurs thermodynamiques et des équilibres de phases reliés (une desciption des principaux modèles a été faite dans cette thèse). Cependant ces modèles, qui sont au départ issus de nombreuses simplifications de la théorie, doivent être constamment améliorés afin d'obtenir 1) une meilleure reproduction des données thermodynamiques expérimentales disponibles et 2) de meilleures prédictions des propriétés thermodynamiques des liquides et des équilibres de phases reliés. Le modèle quasichimique largement développé au CRCT depuis des années, a prouvé sa capacité à reproduire et à prédire les quantités thermodynamiques utiles pour les oxydes fondus, les solutions métalliques et les mattes. La version réciproque initiale de ce modèle, qui suppose un ordonnement des ions premiers-voisins et un mélange aléatoire de ions seconds-voisins a aussi prouvé son utilité à prédire les projections du liquidus de systèmes réciproques ternaires et multicomposants de sels. Mais, au début de cette thèse, quelques idées d'améliorations des deux modèles quasichimiques ont été émises, et il devint alors possible de les mettre en application, et de fusionner ces deux modèles en un seul qui puisse évaluer l'ordonnement des atomes en premiers et seconds-voisins.

Cette thèse a démontré que ces améliorations au modèle quasichimique modifié permettent de mieux reproduire et prédire les équilibres de phases et les propriétés thermodynamiques des solutions liquides. Ces améliorations sont 1) l'expansion

compositonnelle de l'énergie de Gibbs de formation des paires d'espèces A-(X-)B à partir des A-(X-)A et B-(X-)B en fonction des fractions molaires des paires d'espèces au lieu des fractions équivalentes des espèces, 2) la variation compositionnelle des nombres de coordination des espèces en fonction des fractions molaires des paires d'espèces, 3) un nouveau modèle qui évalue l'ordonnement premiers et seconds voisins des espèces à partir d'un mélange aléatoire de quadruplets d'espèces contenant 4 paires premiers-voisins et 4 paires seconds-voisins, et qui permet de calculer la thermodynamiques de liquides réciproques multicomposants, et qui se réduit au modèle quasichimique modifié dans le cas de liquides à ion-commun, 4) la combinaison du modèle d'association au modèle quasichimique modifié afin de mieux représenter les propriétés thermodynamiques de liquides montrant un aspect strutural spécial comme l'effet de compensation de charge dans le système Na_2O-K_2O-Al_2O_3-SiO_2, 5) un nouveau modèle « géométrique » multicomposant et souple, qui permet de mieux représenter les différences acides, bases et amphotères des liquides (particulièrement des laitiers à base de SiO_2).

Une grande partie de ces améliorations ont été appliquées, après avoir été codées et validées dans le programme de minimisation de l'énergie de Gibbs EQUILIB du système FACT, à la phase liquide du système de sels LiF-LiCl-NaF-NaCl-KF-KCl-(MgF_2-$MgCl_2$-CaF_2-$CaCl_2$)-(RbCl-CsCl-$SrCl_2$-$BaCl_2$)-[Li_2SO_4-Na_2SO_4-K_2SO_4]. Une nouvelle base de données complète et consistante sur les paramètres des modèles des phases de ce système (liquide, solutions solides et composés pures) a été obtenue durant cette thèse, basée sur des applications au flux de coulée des alliages de magnésium. Il a ainsi été montré que le modèle quasichimique modifié avec les toutes nouvelles améliorations peut être appliqué pour le développement de larges bases de données applicables à l'industrie métallurgique et particulièrement au domaine des sels fondus et des électrolytes ignés.

Certaines limites du modèle quasichimique ont aussi été montrées bien que l' « enveloppe » d'applications potentielles du modèle ait été largement augmentée. Cependant plusieurs suggéstions d'amélioration futures du modèle quasichimique (avec paires et quadruplets) ont été apportées qui permettront éventuellement d'obtenir de meilleures prédictions. Le modèle, bien que développé dans cette thèse pour les solutions liquides, peut s'appliquer à des solutions solides sous certaines contraintes (concernant les nombres de coordination et le nombre de sous-réseaux où des espèces se mélangent).

Un nouveau modèle thermodynamique pour solutions liquides basé sur un mélange de quadruplets a été developpé dans cette thèse et intégré au système FACT de calcul d'équilibres de phases et de propriétés thermodynamiques. Grâce à son interface Windows, FACT permet de facilement calculer, à l'aide du nouveau modèle quasichimique modifié et des nouvelles bases de données développées dans cette thèse, les équilibres de phases d'un mélange complexe de sels LiF-LiCl-(Li_2SO_4)-NaF-NaCl-(Na_2SO_4)-KF-KCl-(K_2SO_4)-(RbCl-CsCl)-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$-($SrCl_2$-$BaCl_2$). Ce système chimique est de grande importance en métallurgie pour la production et l'affinage de métaux réactifs (Mg, Al, Na, Sr, ...), pour le soudage de ces métaux, pour l'électro-déposition de métaux réfractaires (Nb, Ta, ...), pour la corrosion, et pour d'autres procédés métallurgiques.

Il est donc possible, à l'issue de cette thèse, de calculer et de prédire, grâce au logiciel FACT largement distribué dans les compagnies métallurgiques et les universités, les propriétés thermodynamiques et les équilibres de phases qui permettent d'améliorer la compréhension et la simulation des procédés métallurgiques, particulièment ceux impliquant les mélanges de sels fondus.

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ANNEXE I

Article :

Modeling the Charge Compensation Effect in Silica-rich Na_2O-K_2O-Al_2O_3-SiO_2 Melts

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MODELING THE CHARGE COMPENSATION EFFECT IN SILICA-RICH Na_2O-K_2O-Al_2O_3-SiO_2 MELTS

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ABSTRACT At high SiO_2 contents, a model of Na_2O-K_2O-Al_2O_3-SiO_2 melts must take into account the "charge compensation effect" whereby the replacement of a tetravalent Si^{4+} by a trivalent Al^{3+} in the silicate network is facilitated by the formation of $(NaAl)^{4+}$ or $(KAl)^{4+}$ associates. This effect has been taken into account in the quasichemical model by treating the $(NaAl)^{4+}$ and $(KAl)^{4+}$ associates as separate species in the melt, which is then formally treated as consisting of the components $NaO_{1/2}$, $KO_{1/2}$, $AlO_{3/2}$, SiO_2, $(NaAl)O_2$ and $(KAl)O_2$. Optimizations of the Na_2O-Al_2O_3-SiO_2, K_2O-Al_2O_3-SiO_2 and $NaAlSiO_4$-$KAlSiO_4$-SiO_2 systems at high SiO_2 contents are reported.

1. INTRODUCTION

Over the past several years we have used the modified quasichemical model [1-3] for the optimization of a large number of multicomponent molten oxide solutions. This model treats short-range ordering in the pair approximation. For example, for a solution AO_x-BO_y-SiO_2 (such as $NaO_{1/2}$-$AlO_{3/2}$-SiO_2), the parameters of the model are the Gibbs energies of formation of second-nearest-neighbour pairs according to:

$$(A-A)+(Si-Si)=2(A-Si); \qquad \Delta g^o_{ASi}=\omega_{ASi}-\eta_{ASi}T \tag{1}$$

$$(B-B)+(Si-Si)=2(B-Si); \qquad \Delta g^o_{BSi}=\omega_{BSi}-\eta_{BSi}T \tag{2}$$

$$(A-A)+(B-B)=2(A-B); \qquad \Delta g^o_{AB}=\omega_{AB}-\eta_{AB}T \tag{3}$$

where (X-Y) represents a second-nearest-neighbour pair. For example, (Si-Si) represents a pair of network silicons joined by a "bridging" oxygen: (Si-O-Si). The Gibbs energy of the solution is given by:

$$\begin{aligned} G = &\left(n_{AO_x}g^o_{AO_x}+n_{BO_y}g^o_{BO_y}+n_{SiO_2}g^o_{SiO_2}\right)-T\Delta S^{config} \\ &+\left(n_{ASi}\Delta g^o_{ASi}+n_{BSi}g^o_{BSi}+n_{AB}\Delta g^o_{AB}\right) \end{aligned} \tag{4}$$

where n_i and Δg_i^o are the number of moles and standard molar Gibbs energy of component i (i=AO_x, BO_y, SiO_2); n_{xy} is the number of moles of second-nearest-neighbour (X-Y) pairs; and ΔS^{config} is the

configurational entropy which is given by the following (Ising) approximation for the random distribution of the pairs over "pair positions" :

$$\Delta S^{config} = -R\left(n_{AO_x}\ln X_{AO_x} + n_{BO_y}\ln X_{BO_y} + n_{SiO_2}\ln X_{SiO_2}\right)$$
$$-R\left[n_{AA}\ln\frac{X_{AA}}{Y_A^2} + n_{BB}\ln\frac{X_{BB}}{Y_B^2} + n_{SiSi}\ln\frac{X_{SiSi}}{Y_{Si}^2}\right. \tag{5}$$
$$\left. + n_{ASi}\ln\frac{X_{ASi}}{2Y_AY_{Si}} + n_{BSi}\ln\frac{X_{BSi}}{2Y_BY_{Si}} + n_{AB}\ln\frac{X_{AB}}{2Y_AY_B}\right]$$

where X_i is the mole fraction of component i, X_{XY} is the bond fraction of (X-Y) bonds:

$$X_{XY} = n_{XY} / \sum n_{ij} \tag{6}$$

and Y_A, Y_B and Y_{Si} are "equivalent fractions" given by:

$$Y_A = \frac{Z_A X_{AO_x}}{Z_A X_{AO_x} + Z_B X_{BO_y} + Z_{Si} X_{SiO_2}} \tag{7}$$

where Z_i is the second-nearest-neighbour "coordination number" of i.

The equilibrium state is computed by minimizing G subject to the mass balance constraints [1-3].

In a binary system, such as $NaO_{1/2}$-SiO_2, if the parameter Δg^o_{NaSi} (see eq. 1) is very negative then (Na-Si) pairs will predominate, and both the enthalpy and entropy will exhibit minima near the composition $Y_{Na} = Y_{Si} = 0.5$. The corresponding mole fractions are determined by the ratio (Z_{Si}/Z_{Na}). By setting this ratio equal to 4.0, we set the composition of maximum short-range ordering at $X_{NaO_{1/2}}$ =0.8, which is the orthosilicate composition, Na_4SiO_4. Since the expression for ΔS^{config} in Eq. (5) is an approximation, the values of Z_i which yield the best optimizations do not necessarily correspond to the actual coordination numbers (although their ratios correspond to the actual ratios). As discussed previously [1-3], the appropriate values for $NaO_{1/2}$, $AlO_{3/2}$, and SiO_2 are: Z_{Si} = (4 Z_{Na}) = (4/3 Z_{Al}) = 2.7548.

For purposes of optimization of experimental data, the Δg^o_{ij} parameters are expressed as empirical power series in the equivalent fractions [1-3]. For example, the optimization of the $NaO_{1/2}$-SiO_2 binary system [4] gives the following optimized expression for the liquid:

$$\Delta g^o_{NaSi} = -114345 + 43.932\,T - 381598\,Y_{Si} + (123010 + 20.920\,T)\,Y_{Si}^7 \quad J/mol \tag{8}$$

The optimized phase diagram is compared with several experimental data points [5-8] in Fig. 1. Experimental activities in the liquid are also closely reproduced. Details of the optimization, as well as expressions for the standard molar Gibbs energies of all compounds, have been given previously [4].

Note that, as expected, Δg^{o}_{NaSi} is very negative in this binary system, reflecting the strong tendency of the "network modifier", Na_2O, to break the (Si-O-Si) bridges and form stable ordered solutions.

By contrast, the optimization [9] of the $AlO_{3/2}$-SiO_2 system gave the following optimized expression for the liquid:

$$\Delta g^{o}_{AlSi} = 4800 + 100784\, Y^{3}_{Si} - 142068\, Y^{5}_{Si} + 78571\, Y^{7}_{Si} \quad J/mol \qquad (9)$$

In this system, Δg^{o}_{AlSi} is slightly positive. Liquid $AlO_{3/2}$-SiO_2 solutions exhibit slight positive deviations from ideality. The optimized phase diagram is compared with some experimental data points [10, 11] in Fig. 2. Full details of the optimizations and values of standard Gibbs energies of all compounds have been given previously [9].

A similar optimization of the Na_2O-Al_2O_3 system has been performed [12]. Using these three binary optimizations, Wu [12] used Eq. (4) to estimate G of ternary liquid $NaO_{1/2}$-$AlO_{3/2}$-SiO_2 solutions, and then used this estimate to calculate the ternary liquidus surface. In these calculations the asymmetric approximation [2,3] was used; that is, it was assumed that Δg^{o}_{NaSi} and Δg^{o}_{AlSi} in Eq. (4) in the ternary solution are constant along lines of constant Y_{Si}, such that Eqs. (8) and (9) may be substituted directly into Eq. (4), while Δg^{o}_{NaAl} was assumed to be constant along lines of constant ratio (Y_{Na}/Y_{Al}).

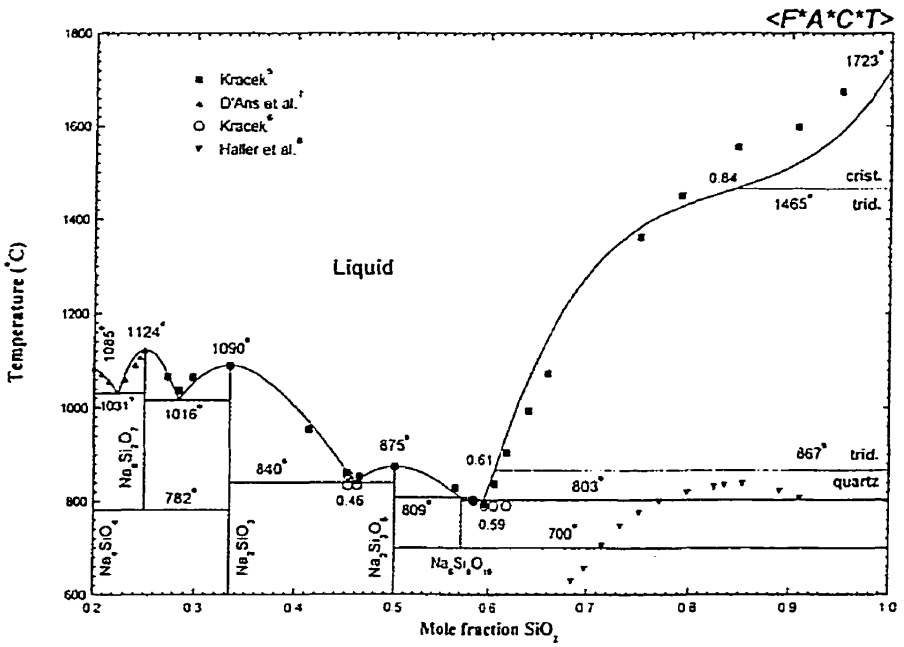


Figure 1: Optimized[4)] $NaO_{0.5}$-SiO_2 phase diagram. Experimental points : □[5)] □[6)] □[7)] □[8)]

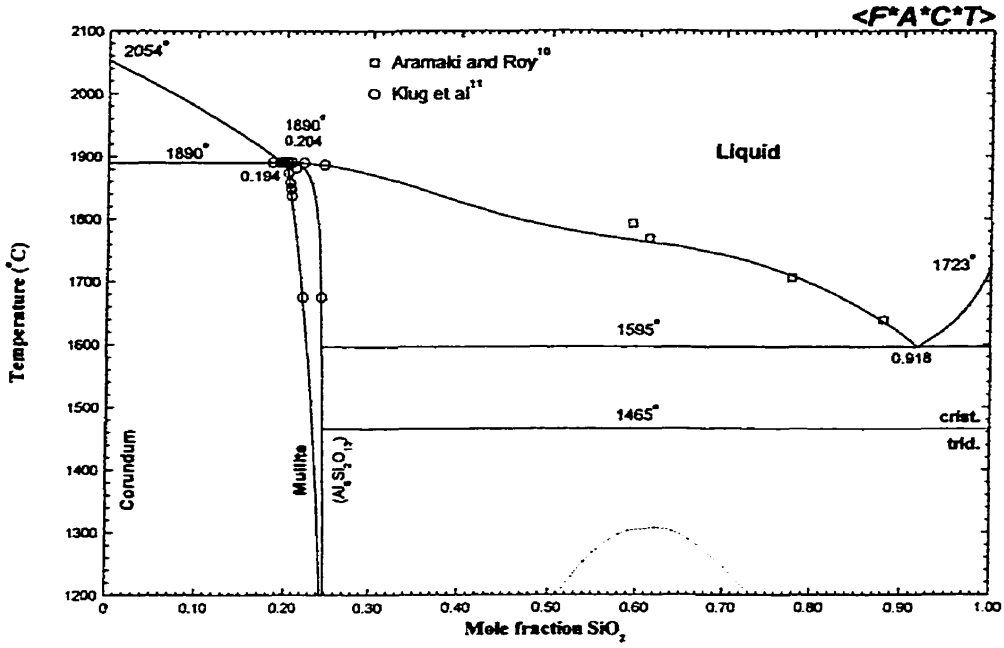


Figure 2: Optimized[9)] $AlO_{1.5}$-SiO_2 phase diagram. Experimental points: □[10)] ○[11)]

The ternary liquidus surface calculated in this way is in very poor agreement with the experimental phase diagram. In order to improve the agreement, Wu [12] included several empirical "ternary parameters". These account for the influence of the third component upon the Gibbs energies of formation Δg^o_{ij} of the binary pairs. For example, the effect of Al upon Δg^o_{NaSi} is modeled by adding terms such as $\omega^{ij}_{NaSi(Al)} Y^i_{Si} (Y_{Al} / (Y_{Al} + Y_{Na}))^j$ to Eq. (8), where $\omega^{ij}_{NaSi(Al)} (j \neq 0)$ is an empirical ternary parameter obtained from the optimization of ternary data.s

Even with 5 large ternary parameters, Wu was unable to obtain a satisfactory representation of the ternary liquidus. This result is in contrast to our finding that, in many other ternary and multicomponent systems involving the components SiO_2-Al_2O_3-CaO-MgO-FeO-Fe_2O_3-PbO-ZnO-CrO-Cr_2O_3-Cu_2O-etc. [2, 3, 9, 12, 13-19], the quasichemical model gives good approximations of the Gibbs energy of the liquid oxide solutions with only a few small, or with no, ternary parameters.

2. MODELING THE CHARGE COMPENSATION EFFECT

Clearly, the assumptions of the model are inadequate in the case of $NaO_{1/2}$-$AlO_{3/2}$-SiO_2 solutions. An indication of how the model might be improved is provided by two features of the experimental liquidus surface. In Fig. 3a it can be seen that the liquidus of mullite descends very steeply from the SiO_2-Al_2O_3 binary system to the SiO_2-$NaAlO_2$ join [20]. This shows that liquid SiO_2-Al_2O_3 solutions are very strongly stabilized by the addition of Na_2O up to a molar Na:Al ratio of 1:1.

The second feature is seen in Fig. 4 which shows the liquidus along SiO_2-$NaAlO_2$ join between SiO_2 and albite, ($NaAlSi_3O_8$). In the limit as $X_{SiO_2} \rightarrow 1$, the limiting slope of the SiO_2-liquidus is given by Raoult's law as:

$$\lim_{X_{SiO_2} \rightarrow 1} \left(dX_{SiO_2} / dT\right) = \Delta h^o_{f(SiO_2)} / \nu R T^2_{fus(SiO_2)} \tag{10}$$

where $\Delta h^o_{f(SiO_2)}$ and $T_{f(SiO_2)}$ are the enthalpy and temperature of fusion of SiO_2 and ν is the number of moles of independent atoms or ions introduced per mole of $NaAlO_2$ (or of $NaAlSi_3O_8$). The experimental [21] points show that the limiting liquidus slope corresponds closely to $\nu = 1$. That is, Na and Al enter into solution as (NaAl) associates. The simple quasichemical model, however, predicts $\nu = 2$ in the limit as $X_{SiO_2} \rightarrow 1$.. (By setting $\Delta g^o_{NaAl} << 0$, the concentration of (Na-Al) nearest-neighbour pairs could, of course, be increased. However, a calculated liquid-liquid miscibility gap would then appear along the $NaAlO_2$-SiO_2 join due to clustering of (Na-Al) and (Si-Si) pairs.)

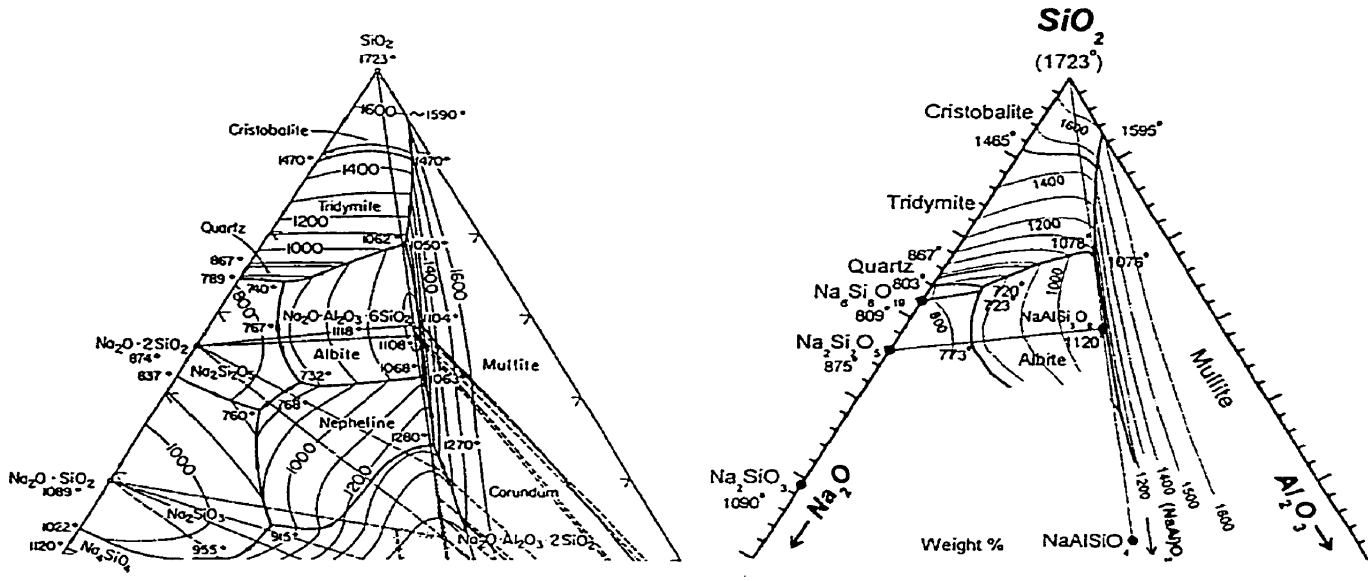
The above observations are usually interpreted as arising from a "charge compensation effect". The dissolution of alumina in silica by the replacement of a tetravalent silicon in the tetrahedral network by a trivalent aluminum is energetically unfavourable because it results in a negative charge centre. However, upon addition of Na_2O this negative charge can be compensated by a Na^+ ion placed next to the aluminum as illustrated in Fig. 5. Hence, the addition of Na_2O, up to a Na:Al ratio of 1:1, decreases the Gibbs energy of the solution markedly.

To model this effect, we consider the $(NaAl)^{4+}$ associates to be a separate species. The ternary solution is then formally treated as a quaternary solution with components $NaO_{1/2}$, $AlO_{3/2}$, SiO_2 and $(NaAl)O_2$ where the mole fraction $X_{(NaAl)O_2}$ gives the concentration of the (NaAl) associates, while $X_{NaO_{1/2}}$ and $X_{AlO_{3/2}}$ are the concentrations of "free" Na and Al. The formation of the (NaAl) associates is formally treated through the Gibbs energy change of the following reaction among the components:

$$NaO_{1/2} + AlO_{3/2} = (NaAl)O_2 \tag{11}$$

$$\Delta G^o_{(NaAl)O_2} = g^o_{(NaAl)O_2} - g^o_{NaO_{1/2}} - g^o_{AlO_{3/2}} \tag{12}$$

where $g^o_{(NaAl)O_2}$ is the standard Gibbs energy of the hypothetical pure component $(NaAl)O_2$. In the modified model, this is a parameter which is determined by optimization.



(a) (b)

Figure 3: Liquidus surface of the Na_2O-Al_2O_3-SiO_2 system in the SiO_2-rich region: (a) as reported by Osborn and Muan[20]; (b) calculated. (composition in weight%; T in °C)

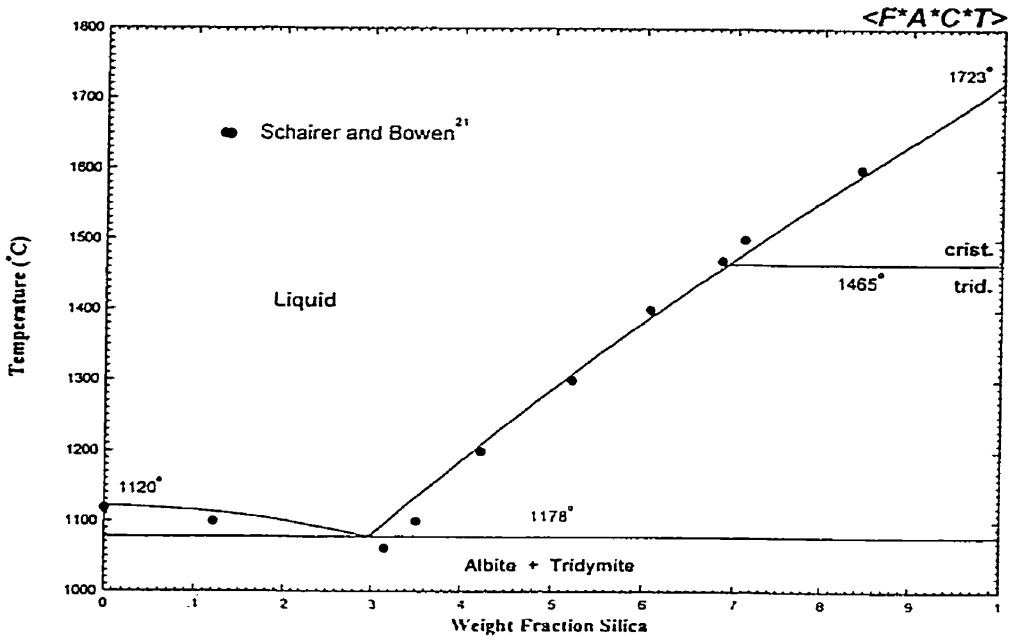


Figure 4: Calculated liquidus surface along the albite ($NaAlSi_3O_8$) – silica (SiO_2) join compared to experimental data[21]

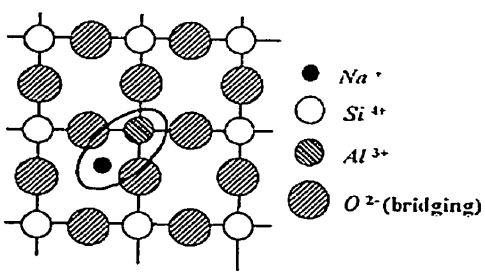


Figure 5: A simplified two-dimensional representation of the charge compensation effect in SiO_2-rich Na_2O-Al_2O_3-SiO_2 melts.

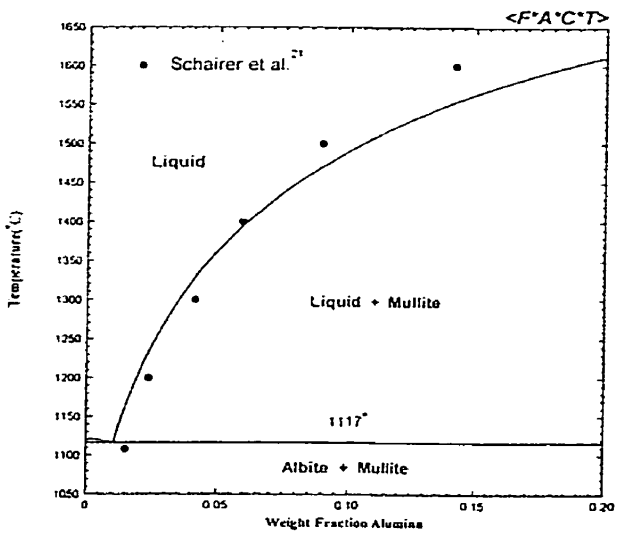


Figure 6: Calculated liquidus surface along the albite ($NaAlSi_3O_8$) – alumina (Al_2O_3) join compared to experimental data[21]

We must now also introduce, as parameters, the Gibbs energies of formation of the following second-nearest-neighbour pairs:

$$(Si-Si)+(NaAl-NaAl)=2(NaAl-Si); \qquad \Delta g^{o}_{(NaAl)Si} \tag{13}$$

$$(Al-Al)+(NaAl-NaAl)=2(NaAl-Al); \qquad \Delta g^{o}_{g(NaAl)Al} \tag{14}$$

$$(Na-Na)+(NaAl-NaAl)=2(NaAl-Na); \qquad \Delta g^{o}_{(NaAl)Na} \tag{15}$$

(One must clearly distinguish an (NaAl) associate from an (Na-Al) pair, the latter being a second-nearest-neighbour pair between a "free" Na and "free" Al.).

The Gibbs energy of the solution is then given by a 4-component quasichemical expression (like Eq. (4) but with a fourth component, CO_2), where ΔS^{config} is given by randomly distributing all types of pairs: (Na-Na), (Al-Al), (Si-Si) (NaAl-NaAl), (Na-Al), (Na-Si), (NaAl-Na), (Al-Si), (NaAl-Al), and (NaAl-Si). Minimizing G subject to the mass balance constraints then gives all the equilibrium bond fractions as well as the equilibrium mole fraction of associates, $X_{(NaAl)O_2}$

2-1. The Na_2O-Al_2O_3-SiO_2 system

The Na_2O-Al_2O_3-SiO_2 system was optimized with the modified model. The coordination number $Z_{(NaAl)}$ was set equal to Z_{Si} = 2.7548. The expressions for Δg^{o}_{NaSi} and Δg^{o}_{AlSi} were taken from the binary optimizations, Eqs. (8,9). The parameters Δg^{o}_{NaAl}, $\Delta g^{o}_{(NaAl)Na}$ and $\Delta g^{o}_{(NaAl)Al}$ were all set to zero. The following optimized expressions were then obtained for $\Delta G^{o}_{(NaAl)O_2}$ and $\Delta g^{o}_{(NaAl)Si}$, both of which have large negative values:

$$\Delta G^{o}_{(NaAl)O_2} = -146440 \quad J/mol \tag{16}$$

$$\Delta g^{o}_{(NaAl)Si} = -44750+16.736\,T-10479\,Y_{Si}-4184\left(Y_{Al}/\left(Y_{Na}+Y_{Al}+Y_{(NaAl)}\right)\right) \quad J/mol \tag{17}$$

The standard Gibbs energies of all components and binary compounds were given previously [4, 9]. For albite ($NaAlSi_3O_8$), the standard Gibbs energy, shown in Table 1, was taken from the literature [22, 23].

The calculated liquidus surface is shown in Fig. 3b, which may be compared to the experimental [20] phase diagram in Fig. 3a. Calculations along the $NaAlSi_3O_8$-SiO_2 join and the $NaAlSi_3O_8$-Al_2O_3 join are compared to measurements [21] in Figs. 4 and 6 respectively. It should be noted that the first three terms of Eq. (17) for $\Delta g^{o}_{(NaAl)Si}$ are "binary" terms for the pseudobinary $(NaAl)O_2$-SiO_2 system, while the final term is a "ternary" term for the $(NaAl)O_2$-$AlO_{3/2}$ – SiO_2 ternary "sub-system". That is, the very good agreement between calculations and measurements was obtained with only one ternary term for this sub-system, and with no ternary terms for the SiO_2-$(NaAl)O_2$-

$NaO_{1/2}$ sub-system. (The final term in Eq. (17) has virtually no effect in the SiO_2-$(NaAl)O_2$-$NaO_{1/2}$ sub-system because the equivalent fraction of "free" Al^{3+} , Y_{Al} , is very small in this sub-system.) In particular, the steep mullite liquidus, and the limiting liquidus slope at $X_{SiO_2} = 1$ in Fig. 4 are very well reproduced.

2-2. The K_2O-Al_2O_3-SiO_2 system

The K_2O-Al_2O_3-SiO_2 system was also optimized with the same model. Experimental [20] and calculated ternary liquidus surfaces are compared in Fig. 7. The optimization of the binary K_2O-SiO_2 system was reported previously [4] along with values of the standard Gibbs energies of K_2O and of the binary compounds. Standard Gibbs energies of the ternary compounds leucite ($KAlSi_2O_6$) and feldspar ($KAlSi_3O_8$), taken from the literature [22, 24], are compiled in Table 1. The value of S^o_{298} of leucite was adjusted by 15.834 J/mol in the present optimization. The parameters Δg^o_{KAl}, $\Delta g^o_{(KAl)K}$ and $\Delta g^o_{(KAl)Al}$ were all set to zero. Optimized expressions were obtained for $\Delta G^o_{(KAl)O_2}$ and $\Delta g^o_{(KAl)Si}$:

$$\Delta G^o_{(KAl)O_2} = -167360 \quad J/mol \tag{18}$$

$$\begin{aligned}\Delta g^o_{(KAl)Si} = & -37681 + 26.397T + 63153\,Y_{Si} \\ & + (21916 - 25.104\,T)\left(Y_{Al} / \left(Y_K + Y_{Al} + Y_{(KAl)}\right)\right) \\ & - 7950\left(Y_K / \left(Y_K + Y_{Al} + Y_{(KAl)}\right)\right) \quad J/mol\end{aligned} \tag{19}$$

The expression for $\Delta g^o_{(KAl)Si}$ contains two ternary parameters for the $(KAl)O_2$-$AlO_{3/2}$-SiO_2 "sub-system" and one ternary parameter for the SiO_2-$(KAl)O_2$-$KO_{1/2}$ "sub-system".

2-3. The Na_2O-K_2O-Al_2O_3-SiO_2 system

The liquidus surface of the SiO_2-$NaAlSiO_4$-$KAlSiO_4$ system, as reported by Schairer [25], is shown in Fig. 8a. This liquidus was calculated using the present model, whereby the liquid is treated as consisting of 6-components, $NaO_{1/2}$-$KO_{1/2}$-$AlO_{3/2}$-$(NaAl)O_2$-$(KAl)O_2$-SiO_2. No additional parameters were used for the liquid. The denominators of the ternary terms in Eqs (17, 19) were set to ($Y_{Al} + Y_{Na} + Y_K + Y_{(NaAl)} + Y_{(KAl)}$) for interpolation into the multicomponent system. The solid solution of $KAlSi_2O_6$ (leucite) and $NaAlSi_2O_6$ (jadeite) was treated as ideal, with the standard Gibbs energy of jadeite, given in Table 1, taken from the literature [22, 23]. The solid solution of $NaAlSi_3O_8$ and $KAlSi_3O_8$ was treated as sub-regular, with the following optimized expression for the excess Gibbs energy :

$$g^E = X_{NaAlSi_3O_8} X_{KAlSi_3O_8}\left(5063 + 4.184T + 6276 X_{NaAlSi_3O_8}\right) \quad J/mol \tag{20}$$

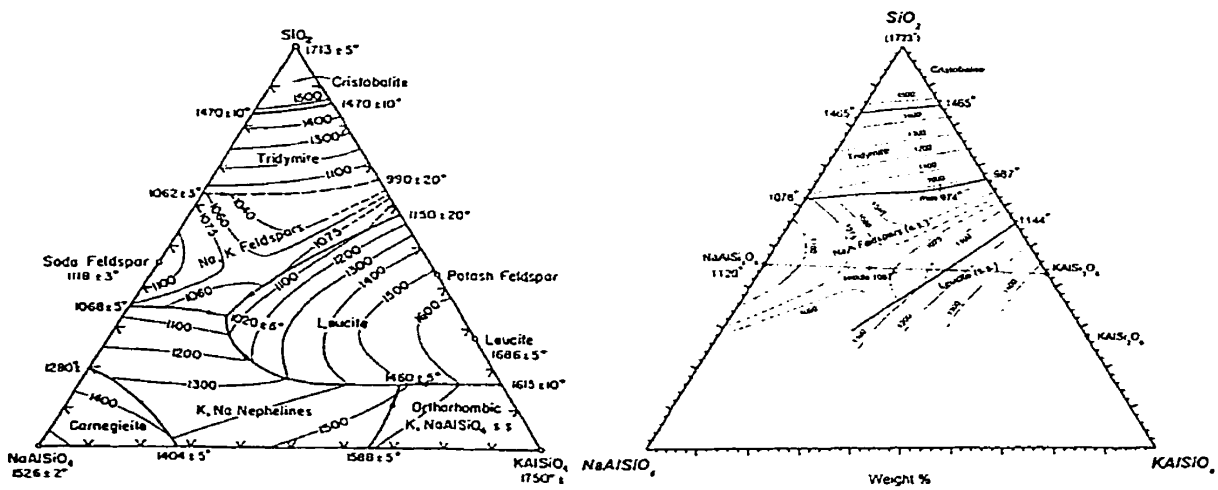
The calculated liquidus surface in Fig. 8b is in good agreement with the measured liquidus.

3. CONCLUSIONS

In SiO_2-rich Na_2O-Al_2O_3-SiO_2 melts, a "charge compensation effect" occurs whereby the substitution of a trivalent Al^{3+} for a tetravalent Si^{4+} in the tetrahedral network is facilitated by association of the Al^{3+} with a Na^+ to form an $(NaAl)^{4+}$ associate. This effect has been successfully modeled by considering the $(NaAl)^{4+}$ associates as separate species in the melt which is then treated formally as a quaternary solution of the components $NaO_{1/2}$-$AlO_{3/2}$-$(NaAl)O_2$-SiO_2 in the quasichemical pair approximation. The liquidus surface at high SiO_2 contents is reproduced very well, with only a few parameters.

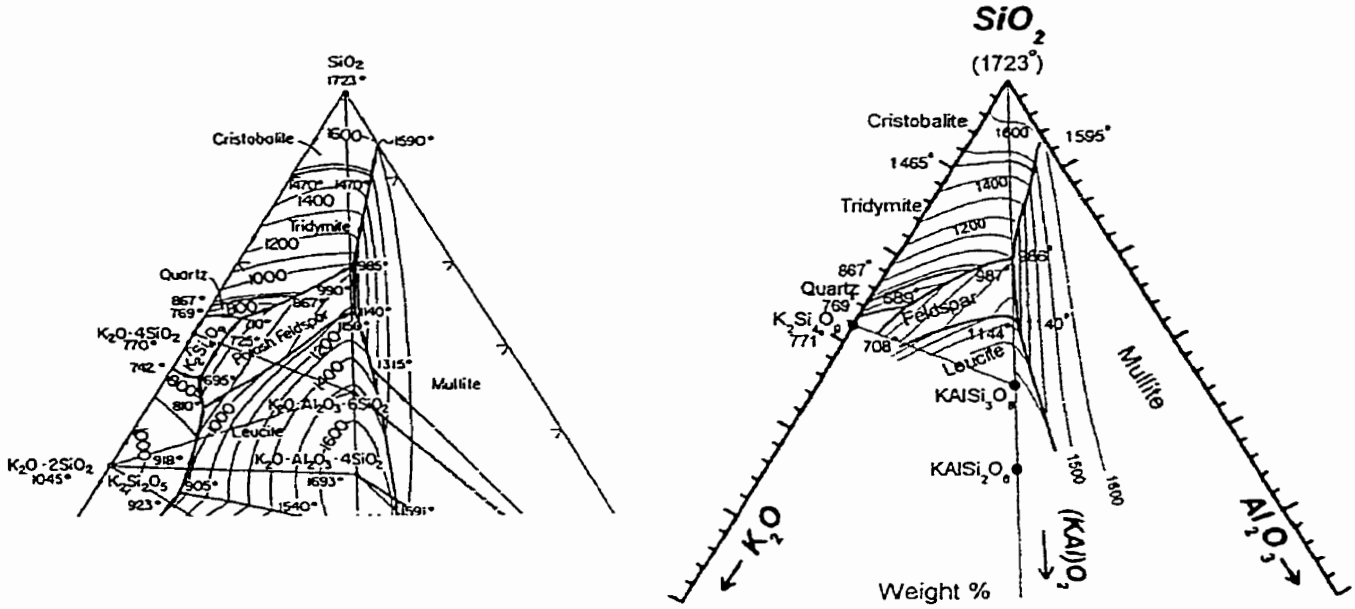
Good agreement has also been obtained for the K_2O-Al_2O_3-SiO_2 and Na_2O-K_2O-Al_2O_3-SiO_2 liquidus surfaces at high SiO_2 contents.

The model is only applicable at molar ratios Si/(Na+K+Al) greater than about 0.6. As the SiO_2 content is decreased below this value, the network structure progressively breaks down, and it becomes easier for alumina to enter the solution even without charge compensation. It may be possible to extend the model to lower SiO_2 contents by permitting the Gibbs energy of formation of $(NaAl)O_2$, $\Delta G^o_{(NaAlO_2)}$, to vary with X_{SiO_2}, becoming less negative as X_{SiO_2} decreases.



(a) (b)

Figure 7: Liquidus surface of the K_2O-Al_2O_3-SiO_2 system in the SiO_2-rich region: (a) as reported by Osborn and Muan[20]; (b) calculated. (composition in weight%; T in °C).



(a) (b)

Figure 8: Liquidus surface of the $NaAlSiO_4$-$KAlSiO_4$-SiO_2 system : (a) as reported by Schairer[25]; (b) calculated. (composition in weight%; T in °C).

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TABLE 1

Thermodynamic Properties Relative to Elements at 298.15 K

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

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

$$C_p\left(J \cdot mol^{-1} \cdot K^{-1}\right) = a + b\left(10^{-3}\right)T + c\left(10^{5}\right)T^{-2} + dT^{-1/2} + e\left(10^{-8}\right)T^{-3} + f\left(10^{-6}\right)T^{2}$$

	T(K)	A	B	a	b	c	d	e	f	Ref
$NaAlSi_3O_8$ (albite)	298-1391	-3919526.2	224.41200	393.63574		-78.92823	-2415.5000	10.706360		22,23
$NaAlSi_2O_6$ (jadeite)	298-1300	-3025118.2	133.57395	311.29297		-53.50264	-2005.1010	6.625669		22,23
$KAlSi_3O_8$ (feldspar)	298-1436	-3970790.8	214.14511	664.35523	-157.33	-84.16546	-6772.4199	18.364255	34.769	22
	1436-1473	-3959703.9	229.15691	381.37231		-120.37252	-1941.0450	18.364255		22
$KAlSi_2O_6$ (leucite)	298-1966	-3029541.9	195.86222*	271.14000		-78.57200	-944.1000	9.592000		22,24 * this work

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ANNEXE II

Article :

On the Choice of « Geometric » Thermodynamic Models

Patrice Chartrand et Arthur D. Pelton,

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2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel ***FIGURE*** développé par l'auteur de cette thèse durant ses études doctorales.

On the Choice of "Geometric" Thermodynamic Models

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A number of "geometric" models have been proposed for estimating the thermodynamic properties of a ternary solution from optimized data for its binary subsystems. Among the most common of these are the Kohler, Muggianu, Kohler/Toop, and Muggianu/Toop models. The latter two are "asymmetric" models in that one component is singled out and treated differently, whereas the first two models are "symmetric". It is shown that the use of a symmetric model when an asymmetric model is more appropriate can often give rise to large errors. Equations are proposed for extending the symmetric/asymmetric dichotomy into N-component systems (N > 3), while still permitting the flexibility to choose either a symmetric or an asymmetric model for any ternary subsystem. An improved general functional form for "ternary terms" in the excess Gibbs energy expression is also proposed. These terms are related to the effect of a third component upon the binary pair interaction energies. All the above considerations also apply when short-range ordering is taken into account by using the modified quasichemical model. Finally, some arguments in favour of the Kohler model over the Muggianu model are presented.

Introduction

The molar excess Gibbs energy of a binary system with components 1 and 2 is often expressed as:

$$g_{12}^{E} = \alpha_{12} X_1 X_2 \qquad (1)$$

where X_1 and X_2 are the mole fractions and α_{12} is a parameter which, under the assumptions of regular solution theory, is equal to the energy of forming two moles of (1-2) nearest-neighbor pairs according to:

$$(1\text{-}1) + (2\text{-}2) = 2\,(1\text{-}2) \qquad (2)$$

where (i – j) represents a first-nearest-neighbor pair.

α_{12} is often expanded as a polynomial in the mole fractions:

$$\alpha_{12} = \sum_{i \geq 0} \sum_{j \geq 0} q_{12}^{ij} X_1^i X_2^j \qquad (3)$$

where the q_{12}^{ij} are empirical coefficients which may be temperature dependent.

Eq (3) is frequently re-arranged into "Redlich-Kister" form:

$$\alpha_{12} = \sum_{i \geq 0} {}^{i}L_{12} (X_1 - X_2)^i \qquad (4)$$

This is done because the coefficients ${}^{i}L_{12}$ tend to be less strongly correlated than the coefficients q_{12}^{ij}. Clearly the set of coefficients q_{12}^{ij} can be calculated from the set of ${}^{i}L_{12}$ and vice versa. Other polynomial expansions, such as Legendre expansions [86 Pel1], are also sometimes used.

For ternary systems, several "geometrical models" have been proposed. Four of these are illustrated in Fig. 1. In each model, g^E in the ternary solution at a composition point p, is estimated from the excess Gibbs energies in the three binary subsystems at points a, b and c by the equation:

$$g^E = X_1 X_2 \alpha_{12(a)} + X_2 X_3 \alpha_{23(b)} + X_3 X_1 \alpha_{31(c)} + (\textit{ternary terms}) \qquad (5)$$

where $\alpha_{12(a)}$, $\alpha_{23(b)}$ and $\alpha_{31(c)}$ are the binary "α-functions" evaluated at points *a*, *b* and *c*. The "ternary terms" are polynomial terms which are identically zero in the three binary subsystems. The empirical coefficients of these ternary terms may be chosen in order to fit ternary experimental data. However, these ternary coefficients should be small. That is, Eq (5) with no ternary terms should provide a reasonable first estimate of g^E in the ternary solution.

If, at a given temperature, all three binary α-functions are constant, independent of composition, then the four models in Fig. 1 are clearly identical.

The Kohler/Toop and Muggianu/Toop models in Figs. 1b and 1d are "asymmetric" models, inasmuch as one component (component "1" in Fig. 1) is singled out, whereas the Kohler and Muggianu models of Figs. 1a and 1c are "symmetric" models. For systems with strong interactions, the four models can give quite different results when the binary α-functions are composition dependent.

In particular, asymmetric models will give better results for some systems, while symmetric models are better for other systems. This will be illustrated in the present article. It will then be shown how this symmetric/asymmetric dichotomy can be extended in a self-consistent way to N-component solutions where N > 3.

Finally, the form of the polynomial "ternary terms" of Eq (5) will be discussed.

Before beginning, however, a few words will be addressed to the choice between using the Kohler of Muggianu symmetric models.

Kohler Versus Muggianu

Suppose that data for the three binary sub-systems of a ternary system have been optimized to give binary coefficients q^{ij}_{mn} of Eq (3) or ${}^{i}L_{mn}$ of Eq (4) and that we wish to estimate g^E in the ternary solution by means of Eq (5) using the Kohler model. Along the line *a*-3 in Fig. 1a, the ratio $X_2/(X_1+X_2)$ is constant. Furthermore, this ratio is equal to X_2 at point *a* where $(X_1+X_2)=1$. Therefore, the function $\alpha_{12(a)}$ in Eq (5) can be simply written:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q^{ij}_{12}\left(\frac{X_1}{X_1+X_2}\right)^i\left(\frac{X_2}{X_1+X_2}\right)^j \qquad (6)$$

where the q^{ij}_{12} are the binary coefficients. Or, if the 1-2 binary system was optimized with a Redlich-Kister expansion, then $\alpha_{12(a)}$ in Eq (5) is written:

$$\alpha_{12(a)} = \sum_{i\geq 0} {}^{i}L_{12}\left(\frac{X_1-X_2}{X_1+X_2}\right)^i \qquad (7)$$

where the ${}^{i}L_{12}$ are the binary coefficients. That is, $\alpha_{12(a)}$, as given in Eq (6) or (7), is constant along the line *a*-3 in Fig. 1a. Similarly, the functions $\alpha_{23(b)}$ and $\alpha_{31(c)}$ may be written in terms of the ratios $X_3/(X_2+X_3)$ and $X_3/(X_3+X_1)$.

To estimate g^E with the Kohler/Toop model, we note that X_1 and $(1-X_1)$ are constant along the line *ac* in Fig. 1b. Hence, $\alpha_{12(a)}$ is set constant along this line by means of the substitution:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q^{ij}_{12} X_1^i (1-X_1)^j \qquad (8)$$

or $$\alpha_{12(a)} = \sum_{i\geq 0} {}^{i}L_{12}(2X_1-1)^i \qquad (9)$$

and similarly for $\alpha_{31(c)}$, while $\alpha_{23(b)}$ is written as in the Kohler model.

In the Muggianu model, we note that (X_1-X_2) is constant along the line *ac* in Fig. 1c. Hence, if α_{12} in the binary system has been expressed by a Redlich-Kister polynomial as in Eq (4) then, as was pointed out by Hillert [80 Hil], Eq (4) can be substituted directly into Eq (5) with no change.

Because of this particularly simple substitution, the Muggianu model is sometimes referred to as the "Muggianu-Redlich-Kister model". However, this is a misnomer. The use of the Muggianu model does not require that the binary α-functions be expressed as Redlich-Kister polynomials. If α_{12} is expressed as a general polynomial as in Eq (3), then we note that the functions $(1+X_1-X_2)/2$ and $(1-X_1+X_2)/2$ are both constant along the line *ac* in Fig. 1c, and that these are equal to X_1 and X_2 respectively in the 1-2 binary system. Hence, in order that $\alpha_{12(a)}$ be constant along the line *ac* we make the substitution:

$$\alpha_{12(a)} = \sum_{i\geq 0}\sum_{j\geq 0} q^{ij}_{12}\left(\frac{1+X_1-X_2}{2}\right)^i\left(\frac{1-X_1+X_2}{2}\right)^j \qquad (10)$$

Conversely, the use of the Kohler or Kohler/Toop models does not preclude expressing the binary α-functions as Redlich-Kister polynomials, as has just been shown in Eqs

(7) and (9). Hence, the choice between using the Kohler of Muggianu symmetric models is not related to the use of Redlich-Kister polynomials.

Brynestad [81 Bry] pointed out that, with the Kohler model, the function $X_3/(X_2 + X_3)$ is not single-valued when $X_1 = 1$ and that this can lead to a singularity in derivatives of the partial excess Gibbs energy of components 2 and 3 at this point. However, Hillert and Sundman [82 Hil] showed that this is of no physical consequence because it only concerns the properties of components at a point where those components are absent.

The Kohler model assumes that the energy change α_{12} of the pair exchange reaction (2) is constant at constant X_1/X_2 ratio, whereas the Muggianu model sets this energy equal to its value at the geometrically closest binary composition. From a physical standpoint, the former assumption seems intuitively more justifiable. Nevertheless, for most concentrated solutions the Kohler and Muggianu models will give quite similar results.

However, in dilute solutions the Kohler model is to be preferred for the reason illustrated in Fig. 2 [97 Pel]. In a ternary solution dilute in component 1, the Kohler model estimates values of $\alpha_{12(a)}$ and $\alpha_{31(c)}$ from values in the binary systems at compositions which are also dilute in component 1, as seems reasonable. On the other hand, the Muggianu model uses values from the binary systems at compositions which are far from dilute.

Hence, the Kohler model presents an advantage and no disadvantages vis-à-vis the Muggianu model. Therefore, we prefer the Kohler model over the Muggianu , and the Kohler/Toop model over the Muggianu /Toop.

The Quasichemical Model

All the consideration and equations in the present article also apply when short-range ordering is taken into account by using the modified quasichemical model in the pair approximation [86 Pel2]. In this model, the excess Gibbs energy in a binary system is given as $g_{12}^{E} = \alpha_{12} X_{12}$, where X_{12} is the fraction of nearest-neighbor pairs which are (1-2) pairs. However, the energy change α_{12} of the pair exchange reaction (2) in a binary system is expressed as a polynomial just as in Eqs (3) or (4). The configurational entropy of mixing is then written as a function of the concentrations of the different nearest neighbor pairs, and the equilibrium pair fractions are calculated by minimizing the Gibbs energy. For estimating ternary properties from the binary coefficients, the values of the α-functions in the ternary solution are assumed to be equal to the values $\alpha_{12(a)}$, $\alpha_{23(b)}$ and $\alpha_{31(c)}$ in the binary solutions according to one of the models in Fig. 1.

The quasichemical model has been applied to many molten oxide, sulfide and salt solutions with large concentration dependent deviations from ideality. It has been found that the choice of a symmetric or an asymmetric model can give very different results.

Symmetric versus Asymmetric Models

In the asymmetric models illustrated in Figs 1b and 1d, the energies of the 1-2 and 1-3 pair interactions are assumed to remain constant at constant X_1. An asymmetric model is thus more physically reasonable than a symmetric model if components 2 and 3 are chemically similar while component 1 is chemically different, as for example in the systems SiO_2-CaO-MgO, S-Fe-Cu, Na-Au-Ag, $AlCl_3$-NaCl-KCl, etc. (where the asymmetric component has been written first in each example).

When g^E is large and α_{12} and α_{31} depend strongly upon composition, a symmetric and an asymmetric model will give very different results. As an example, consider a solution with $\alpha_{12} = \alpha_{31} = -50(1-X_1)$ kJ/mol and $\alpha_{23} = 0$. That is, the binary solutions 1-2 and 1-3 have identical properties and the 2-3 solution is ideal. Clearly, one would expect g^E in the ternary system to be constant at constant X_1 as is predicted by the asymmetric models. However, when the symmetric Kohler model is applied to this solution, an obviously incorrect region of immiscibility is calculated as shown in Fig. 3. Similar incorrect results are obtained with the symmetric Muggianu model.

Hence, we disagree with the current tendency to use the symmetric Muggianu model for nearly all solutions. In many systems, an asymmetric model is more appropriate.

Extension of the Symmetric/Asymmetric Dichotomy to Multicomponent Solutions

In order to extend the Kohler and Kohler/Toop models to N-component systems, where $N > 3$, we originally proposed the following model which has been used until now in all our F*A*C*T [99 Bal] databases. The components 1, 2, 3, 4, . . ., N are separated into group I and group II (sometimes called "acids" and "bases".) If the components of a ternary subsystem are all acids or all bases, then the symmetric Kohler model is used; otherwise the asymmetric Kohler/Toop model is used.

We define :

$$\xi_{I} = \sum_{\text{group I}} X_i \quad \text{and} \quad \xi_{II} = \sum_{\text{group II}} X_i \tag{11}$$

Clearly, $(\xi_{I} + \xi_{II}) = 1$. Then, if components 1 and 2 are in the same group, the expression for g^E in the N-component solution contains a term $X_1 X_2 \alpha_{12}$ where α_{12} is given by replacing X_1 and X_2 of Eq (3) or (4) by $X_1 / (X_1 + X_2)$ and $X_2 / (X_1 + X_2)$ respectively. That is, α_{12} is assumed constant at constant X_1/X_2 ratio. If, on the other hand, component 1 is in group I, while component 2 is a member of group II, then the expression for g^E contains a term $X_1 X_2 \alpha_{12}$, where α_{12} is given by replacing X_1 and X_2 of Eq (3) or (4) by ξ_{I}, and ξ_{II} respectively. That is, α_{12}, the energy of the 1-2 pair interactions, is assumed to be constant at constant "acidity", ξ_{I} (or constant "basicity", ξ_{II}). Were the Muggianu model used instead of the Kohler model, α_{12} would be given by replacing X_1 and X_2 of Eqs (3) or (4) by $(1 + X_1 - X_2)/2$ and $(1 - X_1 + X_2)/2$ respectively when components 1 and 2 are in the same group.

This procedure, however, is not completely satisfactory, since it does not provide sufficient flexibility. For instance, in molten ternary SiO_2-Al_2O_3-CaO slags we have obtained the best optimization with an asymmetric model by choosing SiO_2 to be an acid (group I) and Al_2O_3 and CaO to be bases (group II). Similarly, in SiO_2-Fe_2O_3-CaO slags, we chose SiO_2 to be an acid and Fe_2O_3 and CaO to be bases. Hence, we are now obliged to treat the CaO-Al_2O_3-Fe_2O_3 ternary system with a symmetric model because all three components have already been designated as bases. However, binary CaO-Al_2O_3 and CaO-Fe_2O_3 solutions exhibit similar large negative concentration-dependent α-functions, while binary Al_2O_3-Fe_2O_3 solutions are close to ideal. Hence, an asymmetric model is clearly preferable. In fact, the symmetric Kohler model predicts a spurious and clearly incorrect immiscibility gap at higher CaO concentrations in this ternary system, similar to that shown in Fig. 3.

Consequently, we now propose a new more flexible model which permits any ternary subsystem to be treated either with a symmetric model or an asymmetric model and which gives a reasonable interpolation in the N-component solution. This model reduces to the present procedure as a limiting case.

The model is most clearly and simply presented by an example. Consider the 5-component system in Fig. 4 in which the ternary sub-system 1-2-3 is "asymmetric" (i.e. to be treated by an asymmetric model) with 1 as the asymmetric component, the sub-system 1-2-4 is "symmetric", the system 1-2-5 is "asymmetric" with 5 as asymmetric component, and so on, as illustrated schematically in Fig. 4. We now define

$$\xi_{ij} = X_i + \sum_k X_k \tag{12}$$

where the summation is over all components k in asymmetric i-j-k ternary solutions in which j is the asymmetric component. In the example in Fig. 4:

$$\begin{aligned}
\xi_{12} &= X_1 & \xi_{21} &= X_2 + X_3 \\
\xi_{13} &= X_1 + X_4 & \xi_{31} &= X_3 + X_2 \\
\xi_{14} &= X_1 & \xi_{41} &= X_4 \\
\xi_{15} &= X_1 + X_2 & \xi_{51} &= X_5 \\
\xi_{23} &= X_2 + X_5 & \xi_{32} &= X_3 + X_4 \\
\xi_{24} &= X_2 & \xi_{42} &= X_4 + X_3 \\
\xi_{25} &= X_2 + X_1 + X_4 & \xi_{52} &= X_5 \\
\xi_{34} &= X_3 & \xi_{43} &= X_4 + X_1 \\
\xi_{35} &= X_3 & \xi_{53} &= X_5 + X_2 \\
\xi_{45} &= X_4 + X_2 & \xi_{54} &= X_5
\end{aligned} \tag{13}$$

We then write α_{ij} by replacing X_i and X_j in Eqs (3) and (4) by the functions $\xi_{ij}/(\xi_{ij} + \xi_{ji})$, and $\xi_{ji}/(\xi_{ij} + \xi_{ji})$ respectively in the N-component system. This reduces correctly to the symmetric Kohler or asymmetric Kohler/Toop expression, as in Eqs (6) to (9), in all ternary subsystems, as can be verified by substitution of Eqs (13) into these functions. If the Muggianu or Muggianu/Toop models are used, then α_{ij} is written by replacing X_i and X_j of Eq (3) by the functions $(1 + \xi_{ij} - \xi_{ji})/2$, and $(1 - \xi_{ij} + \xi_{ji})/2$ respectively, or by replacing $(X_i - X_j)$ of Eq. (4) by $(\xi_{ij} - \xi_{ji})$.

As a second example consider a 5-component solution in which components 1, 2 and 3 are chemically similar, forming "group I", while component 4 is in a separate chemical group II, and component 5 is in yet another separate group III. An example would be a liquid solution in which components 1 to 5, are respectively, LiCl, NaCl, KCl, $ZnCl_2$ and $AlCl_3$. In this case, ternary subsystems such as 1-4-5 in which all three components are from different groups might reasonably be treated with a symmetric model, and the choice of symmetric and asymmetric ternary subsystem would then be made as shown in Fig. 5. The ξ_{ij} variables then become:

$$
\begin{aligned}
\xi_{12} &= X_1 & \xi_{21} &= X_2 \\
\xi_{13} &= X_1 & \xi_{31} &= X_3 \\
\xi_{14} &= X_1 + X_2 + X_3 & \xi_{41} &= X_4 \\
\xi_{15} &= X_1 + X_2 + X_3 & \xi_{51} &= X_5 \\
\xi_{23} &= X_2 & \xi_{32} &= X_3 \\
\xi_{24} &= X_2 + X_1 + X_3 & \xi_{42} &= X_4 \\
\xi_{25} &= X_2 + X_1 + X_3 & \xi_{52} &= X_5 \\
\xi_{34} &= X_3 + X_1 + X_2 & \xi_{43} &= X_4 \\
\xi_{35} &= X_3 + X_1 + X_2 & \xi_{53} &= X_5 \\
\xi_{45} &= X_4 & \xi_{54} &= X_5
\end{aligned}
\qquad (14)
$$

Of course, the technique is completely flexible and does not require that the components LiCl, NaCl, KCl, $ZnCl_2$ and $AlCl_3$ be divided *a priori* into three groups. One could take a purely empirical approach, choosing a symmetric or an asymmetric model for each ternary subsystem according to which gives the best empirical representation of the ternary data.

Ternary Terms

If experimental ternary data are available, then these may be included in the optimization to give empirical "ternary terms" in Eq (5). These terms are identically zero in all binary systems. Terms such as

$$q_{123}^{ijk} X_1^i X_2^j X_3^k \qquad (15)$$

where $i \geq 1$, $j \geq 1$ and $k \geq 1$ and q_{123}^{ijk} is an empirical coefficient, are generally used. However, such terms have little theoretical justification. Furthermore, it is not clear how such ternary terms should be extrapolated into systems of four or more components.

Common practice when using the Muggianu model is to include ternary terms of the form:

$$q_{123}^{i} X_1 X_2 X_3 \left((1 - X_1 - X_2 - X_3)/3 + X_i \right) \qquad (16)$$

(i = 1, 2, 3). These are simply a special case of the general form of expression (15). Furthermore, one is limited to three empirical coefficients..

From a physical standpoint, terms such as $q_{123}^{ijk} X_1^i X_2^j X_3^k$ might be related to the energies of triplet interactions. However, the regular solution and quasichemical models are pair approximation models. It thus would seem better to include ternary terms which are designed to represent the effect of a third component, 3, upon the energy α_{12} of the pair exchange reaction (2).

In the Kohler model, Fig. 1a, we propose ternary terms of the form

$$X_1 X_2 \left(q_{12(3)}^{ijk} \left(\frac{X_1}{X_1 + X_2} \right)^i \left(\frac{X_2}{X_1 + X_2} \right)^j X_3^k \right) \qquad (17)$$

where $i \geq 0$, $j \geq 0$ and $k \geq 1$. In the same system, ternary terms of the form

$$X_2 X_3 \left(q_{23(1)}^{ijk} \left(\frac{X_2}{X_2 + X_3} \right)^i \left(\frac{X_3}{X_2 + X_3} \right)^j X_1^k \right) \qquad (18)$$

may also be included, giving the effect of the presence of component 1 upon α_{23}, as well as similar terms giving the effect of component 2 upon α_{31}.

In the Kohler/Toop model, Fig. 1b, expression (18) is used for the effect of component 1 upon α_{23}, while it is proposed to represent the effect of component 3 upon α_{12} by terms of the form:

$$X_1 X_2 \left(q_{12(3)}^{ijk} (X_1)^i (1 - X_1)^j \left(\frac{X_3}{X_2 + X_3} \right)^k \right) \qquad (19)$$

and similarly for the effect of component 2 upon α_{31}.

We have always used ternary terms of this form in the quasichemical model. For multicomponent quasichemical solutions, an extension to N-component solutions based upon the acid/base grouping of components, as in Eq(11), is currently used in the F*A*C*T [99 Ball databases. We propose that such ternary terms also be used generally in the polynomial (regular solution, Bragg Williams) model as well as the quasichemical model. We also now propose to extend these ternary terms to multicomponent systems in a manner consistent with the more general component grouping proposed in the preceding section.

With ξ_{12} and ξ_{21} defined as in Eq(12), the following expressions are proposed for the ternary terms in the N-component (N>3) system.

(i) If the 1-2-3 ternary solution is symmetric, or asymmetric with 3 as the asymmetric component, then the following ternary terms may be included:

$$X_1X_2\left(q^{ijk}_{12(3)}\left(\frac{\xi_{12}}{\xi_{12}+\xi_{21}}\right)^i\left(\frac{\xi_{21}}{\xi_{12}+\xi_{21}}\right)^j X_3\left(1-\xi_{12}-\xi_{21}\right)^{k-1}\right) \tag{20}$$

This reduces to expression (17) in the 1-2-3 ternary system where $(X_1+X_2+X_3)=1$.

(ii) If the 1-2-3 ternary system is asymmetric with 1 as the asymmetric component, then the following ternary terms may be used:

$$X_1X_2\left(q^{ijk}_{12(3)}\left(\frac{\xi_{12}}{\xi_{12}+\xi_{21}}\right)^i\left(\frac{\xi_{21}}{\xi_{12}+\xi_{21}}\right)^j\left(\frac{X_3}{\xi_{21}}\right)\left(1-\frac{X_2}{\xi_{21}}\right)^{k-1}\right) \tag{21}$$

This reduces to expression (19) in the 1-2-3 ternary system.

One might propose a factor X_3^k rather than $X_3\left(1-\xi_{12}-\xi_{21}\right)^{k-1}$ in expression (20). Consider, however, a multicomponent system in which the effects of components 3, 4 and 5 upon α_{12} are identical. That is, $q^{ijk}_{12(3)}=q^{ijk}_{12(4)}=q^{ijk}_{12(5)}$. In the multicomponent system the effects should be additive and so the sum of the three ternary terms should clearly contain the factor $(X_3+X_4+X_5)^k$. This will be the case only if the ternary terms are defined as in expression (20). A similar argument justifies the form of expression (21).

Expressions (20) and (21) reduce to those currently used in the F*A*C*T databases for the quasichemical model when only two groups are defined as in Eq (11).

For the Muggianu and Muggianu/Toop models, it is proposed that these same expressions, (20) and (21) be used for the ternary terms.

Expressions for Partial Properties

The calculation of the partial excess Gibbs energy of component i, g_i^E, from the expression for the integral molar Gibbs energy, g^E, is facilitated by the following particularly simple equation [99 Eri] which does not seem to be widely used:

$$g_i^E = g^E + \left(\partial g^E/\partial X_i\right) - \sum_{j=1}^{N} X_j\left(\partial g^E/\partial X_j\right) \tag{22}$$

where g^E is expressed as a function of $X_1, X_2, \ldots, X_N$, and the partial differentials are calculated as if all N mole fraction were independent variables.

Conclusions

A number of "geometric" models exist for estimating the thermodynamic properties of ternary solutions from optimized data for the binary subsystems. Among these, the Kohler/Toop and Muggianu/Toop models are "asymmetric" in that one component is singled out and treated differently, whereas the Kohler and Muggianu models are "symmetric". When all three binary subsystems are strictly regular, then all four models give identical results. However if the binary thermodynamic properties deviate significantly from regular behaviour, the models can give quite different results. In particular, if two components of a ternary system are chemically similar to each other, but different from the third component, then an asymmetric model is more appropriate. It has been shown that the use of a symmetric model, when an asymmetric model is more appropriate, may give rise to large errors, possibly even resulting in the appearance of spurious immiscibility gaps. Hence, we disagree with the current tendency to use the symmetric Muggianu model almost exclusively.

Equations have been proposed for extending this symmetric/asymmetric dichotomy to N-component solutions (N > 3), while still maintaining the flexibility to choose an asymmetric or a symmetric model for any ternary subsystem.

Arguments have been presented in favor of the Kohler model over the Muggianu model, particularly for solutions dilute in one component. It is a misnomer to refer to the Muggianu model as the "Muggianu-Redlich-Kister" model, since the Muggianu model does not require the use of Redlich-Kister polynomials, nor does the use of Redlich-Kister polynomials preclude the use of other models. The mathematical simplicity afforded by the combined use of the Muggianu model and Redlich-Kister polynomials is only slight.

The "ternary terms" currently in use in the excess Gibbs energy expressions have little physical significance. New ternary terms have been proposed which are related to the effect of a third component upon a binary pair exchange energy.

All the considerations and equations of the present article also apply when short-range ordering is taken into account by using the modified quasichemical model.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. P.C. has received a fellowship from the FCAR (Fonds pour la Formation de Chercheurs et l'Aide à la Recherche) of Quebec

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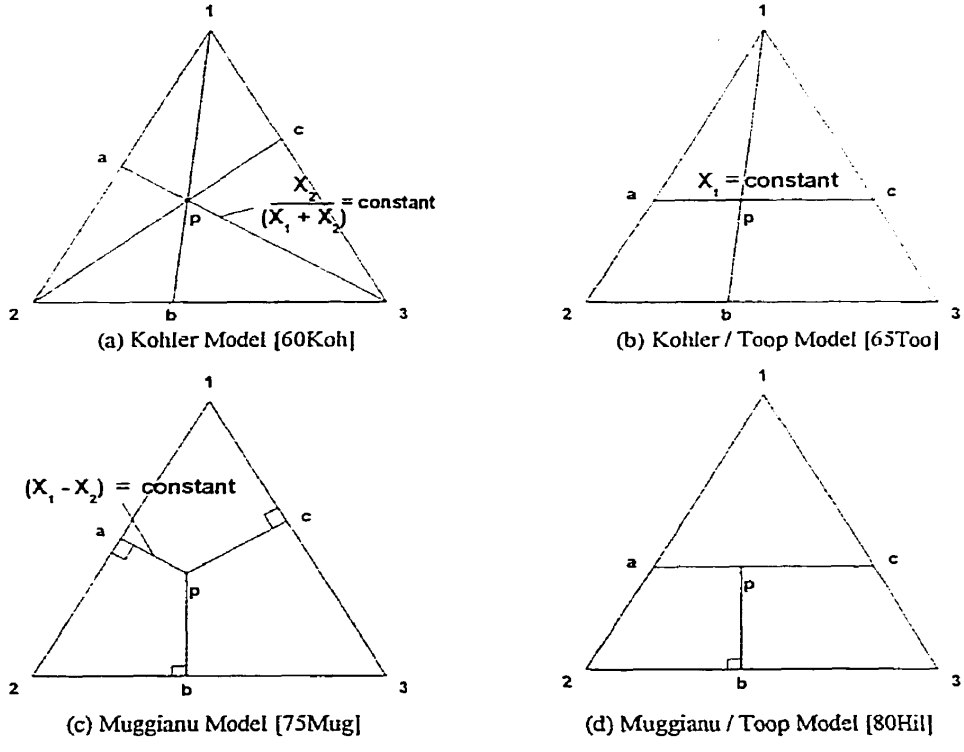

(a) Kohler Model [60Koh]

(b) Kohler / Toop Model [65Too]

(c) Muggianu Model [75Mug]

(d) Muggianu / Toop Model [80Hil]

Fig. 1 : Four "geometric" models for estimating ternary thermodynamic properties from optimized binary data.

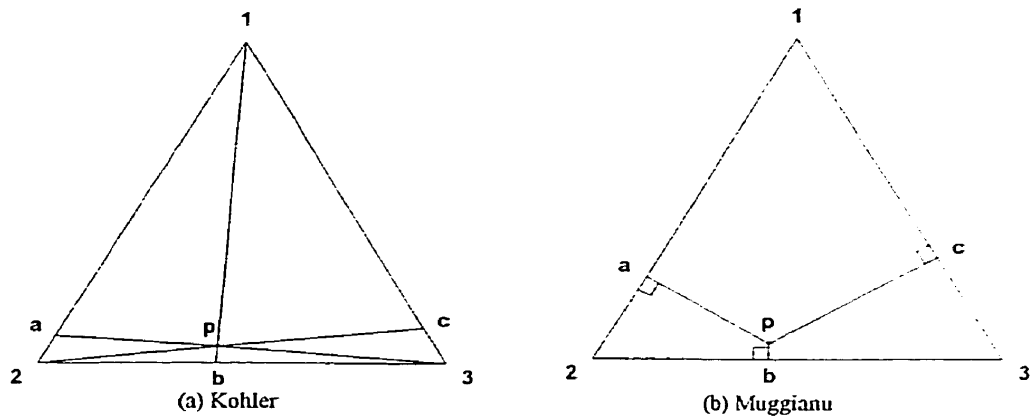

Fig. 2 : The Kohler and Muggianu models applied at a composition dilute in component 1.

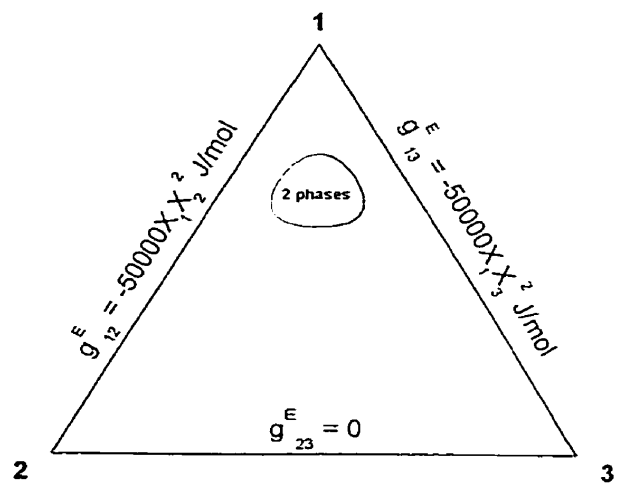

Fig. 3 : Spurious immiscibility gap calculated with the Kohler model at 973K in a solution with $\alpha_{12} = \alpha_{13} = -50(1-X_1)$ kJ/mol and $\alpha_{23} = 0$.

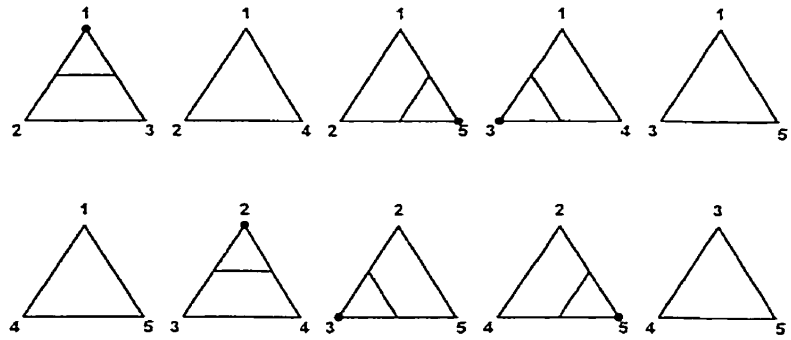

Fig. 4 : A 5-component solution illustrating which ternary subsystems are to be treated by a symmetric model and which are to be treated with an asymmetric model.

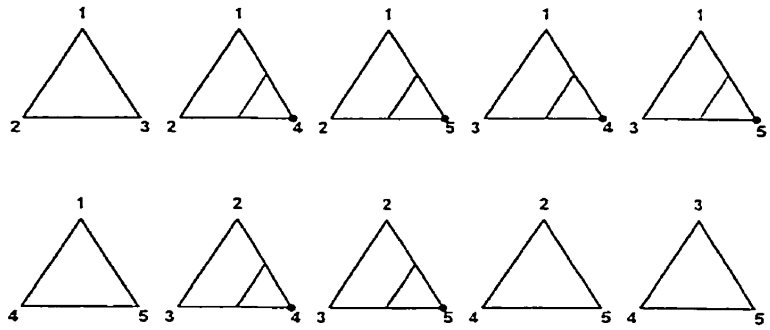

Fig. 5 : Example for the (1) LiCl – (2) NaCl – (3) KCl – (4) $ZnCl_2$ – (5) $AlCl_3$ system when LiCl, NaCl and KCl are in group I, $ZnCl_2$ in group II and $AlCl_3$ in group III.

ANNEXE III

Article :

The Modified Quasichemical Model II – Multicomponent Solutions

Arthur D. Pelton et Patrice Chartrand,

Soumis à *Metallurgical and Materials Transactions B*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel *FIGURE* développé par l'auteur de cette thèse durant ses études doctorales.

The Modified Quasichemical Model II – Multicomponent Solutions

A.D. PELTON and P. CHARTRAND

Further improvements to the modified quasichemical model in the pair approximation for short-range ordering in liquids are extended to multicomponent solutions. The energy of pair formation may be expanded in terms of the pair fractions or in terms of the component fractions, and coordination numbers are permitted to vary with composition. The model permits complete freedom of choice to treat any ternary subsystem with a symmetric or an asymmetric model. An improved general functional form for "ternary terms" in the excess Gibbs energy expression is proposed. These terms are related to the effect of a third component upon the binary pair interaction energies. It is shown how binary subsystems which have been optimized with the quasichemical model can be combined in the same multicomponent Gibbs energy equation with binary subsystems which have been optimized with a random-mixing Bragg-Williams model and a polynomial expression for the excess Gibbs energy. This is of much practical importance in the development of large databases for multicomponent solutions. The model also applies to short-range ordering in solid solutions as a special case when the number of lattice sites and coordination numbers are constant.

I. INTRODUCTION

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

In the current series of articles, further modifications and extensions to the model are described. The first article[6] dealt with binary systems. The present article treats multicomponent solutions. Subsequent articles in this series will treat extensions to liquids with two "sublattices".

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II. MODEL EQUATIONS

Atoms or molecules of the components 1, 2, 3, ... , N of a solution are distributed over the sites of a quasi-lattice. In the pair approximation we consider the pair exchange reactions:

$$(m-m) + (n-n) = 2(m-n) \; ; \quad \Delta g_{mn} \qquad [1]$$

where (m, n = 1, 2, ... ,N) and (m-m), (n-n) and (m-n) represent first-nearest neighbor pairs.

The non-configurational Gibbs energy change for the formation of two moles of (m-n) pairs is Δg_{mn}. Let n_m and Z_m be the number of moles and coordination number of component m, and let n_{mn} be the number of moles of (m-n) pairs (where n_{mn} and n_{nm} represent the same quantity and can be used interchangeably). Then:

$$Z_m n_m = 2 n_{mm} + \sum_{n \neq m} n_{mn} \qquad [2]$$

In the case of a solid solution, clearly, it is required that $Z_1 = Z_2 = \ldots = Z_N$.

Pair fractions X_{mn}, overall mole (or site) fractions X_m, and "coordination-equivalent" fractions Y_m are defined as:

$$X_{mn} = n_{mn} / \sum n_{ij} \qquad [3]$$

$$X_m = n_m / \sum n_i \qquad [4]$$

$$Y_m = Z_m n_m / \sum (Z_i n_i) = Z_m X_m / \sum (Z_i X_i) \qquad [5]$$

(where X_{mn} and X_{nm} represent the same quantity and can be used interchangeably). Substitution of Eq [2] into Eqs [3] and [5]gives:

$$Y_m = X_{mm} + \sum_{n>m} X_{mn}/2 \qquad [6]$$

The Gibbs energy of the solution is given by:

$$G = \sum n_m g_m^o - T\,\Delta S^{config} + \sum_{n>m} n_{mn}\left(\Delta g_{mn}/2\right) \qquad [7]$$

where g_m^o is the molar Gibbs energy of pure component m, and ΔS^{config} is an approximate expression for the configurational entropy of mixing given by randomly mixing the (m-n) pairs:

$$\Delta S^{config} = -R\sum n_m \ln X_m$$
$$-R\left(\sum n_{mm}\ln\left(X_{mm}/Y_m^2\right) + \sum_{m>n} n_{mn}\ln\left(X_{mn}/2Y_mY_n\right)\right) \qquad [8]$$

In the m-n binary system, the energy parameter Δg_{mn} may be expanded as an empirical polynomial in the component fractions Y_m:

$$\Delta g_{mn} = \Delta g_{mn}^o + \sum_{(i+j)\geq 1} q_{mn}^{ij} Y_m^i Y_n^j \qquad [9]$$

where Δg_{mn}^o and q_{mn}^{ij} are empirical binary coefficients which may be functions of temperature and pressure. (These were previously [1-4,6] written as $q_{mn}^{ij} = \left(\omega_{mn}^{ij} - \eta_{mn}^{ij}T\right)$.) Alternatively, Eq [9] can be rearranged into "Redlich-Kister" form:

$$\Delta g_{mn} = \Delta g_{mn}^o + \sum_{i\geq 1} {}^iL_{mn}\left(Y_m - Y_n\right)^i \qquad [10]$$

where the set of empirical coefficients ${}^iL_{mn}$ can clearly be calculated from the set q_{mn}^{ij} and *vice versa* since ($X_m + X_n$) = 1 in the binary system. The empirical binary coefficients Δg_{mn}^o, and q_{mn}^{ij} or ${}^iL_{mn}$, are found by optimization of experimental data in the binary subsystems.

In the preceding article[6] it was proposed to replace the expansion of Eq [9] or [10] by an expansion in terms of the pair fractions X_{mm} and X_{nn}:

$$\Delta g_{mn} = \Delta g_{mn}^o + \sum_{(i+j)\geq 1} g_{mn}^{ij} X_{mm}^i X_{nn}^j \qquad [11]$$

where Eq [11] applies in the m-n binary system and Δg_{mn}^o and g_{mn}^{ij} are empirical coefficients which may be temperature and pressure dependent. This representation has been found[6], in general, to result in improved and easier optimizations. In practice, in most cases, only coefficients g_{mn}^{i0} and g_{mn}^{0j} need be included.

In the preceding article[6] composition-dependent coordination numbers were also introduced. This provides greater flexibility and permits the composition of maximum short-range ordering to be chosen independently in each binary subsystem:

$$\frac{1}{Z_1} = \frac{1}{2n_{11} + \sum_{j\neq 1} n_{1j}}\left(\frac{2n_{11}}{Z_{11}^1} + \sum_{j\neq 1}\frac{n_{1j}}{Z_{1j}^1}\right) \qquad [12]$$

$$\frac{1}{Z_2} = \frac{1}{2n_{22} + \sum_{j\neq 2} n_{2j}}\left(\frac{2n_{22}}{Z_{22}^2} + \sum_{j\neq 2}\frac{n_{2j}}{Z_{2j}^2}\right) \qquad [13]$$

etc.

where Z_{11}^1 and Z_{12}^1 are, respectively, the value of Z_1 when all nearest neighbors of a 1 are 1's and the (hypothetical) value of Z_1 when all nearest neighbors of a 1 are 2's. (Note that Z_{12}^1 and Z_{21}^1 represent the same quantity and can be used interchangeably.)

Z_{mm}^m is a constant for each pure component m, and is the same for all solutions containing m. The composition of maximum short-range ordering in each binary subsystem is determined by the ratio Z_{mn}^m/Z_{mn}^n. The choice of the constants Z_{mm}^m and Z_{mn}^m was discussed previously[6]. Substitution of Eqs [12,13] into Eq [2] gives:

$$n_m = 2n_{mm}/Z_{mm}^m + \sum_{n\neq m} n_{mn}/Z_{mn}^m \qquad [14]$$

Clearly, in the case of a solid solution, all coordination numbers must be equal. That is, $Z_{mm}^m = Z_{nn}^n = Z_{mn}^m = Z_{mn}^n$.

Standard Gibbs energies g_{mm}^o and g_{mn}^o are defined as:

$$g_{mm}^o = 2g_m^o/Z_{mm}^m \qquad [15]$$
$$g_{mn}^o = \Delta g_{mn}^o/2 + g_m^o/Z_{mn}^m + g_n^o/Z_{mn}^n \qquad [16]$$

where Δg_{mn}^o is the binary parameter from Eq [9], [10] or [11]. Substitution into Eq [7] then gives:

$$G = \left(n_{11}g_{11}^o + n_{12}g_{12}^o + n_{22}g_{22}^o + n_{13}g_{13}^o + \ldots\right)$$
$$-T\,\Delta S^{config} + \sum_{n>m}\left(n_{mn}/2\right)\left(\Delta g_{mn} - \Delta g_{mn}^o\right) \qquad [17]$$

with ΔS^{config} given by Eq [8] and Δg_{mn} by Eq [9], [10] or [11]. Dividing though by $\sum n_{ij}$ gives:

$$g\ (\text{per mole of pairs}) = \left(X_{11}g_{11}^{o} + X_{12}g_{12}^{o} + X_{22}g_{22}^{o} + X_{13}g_{13}^{o} + \ldots\right)$$
$$+RT\left(X_{11}\ln X_{11} + X_{12}\ln X_{12} + X_{22}\ln X_{22} + \ldots\right)$$
$$+RT\left(\sum \frac{2X_m}{Z_m}\ln X_m - X_{11}\ln Y_1^2 - X_{22}\ln Y_2^2 - X_{12}\ln(2Y_1Y_2) - \ldots\right)$$
$$+g^E \qquad [18]$$

where:

$$g^E = \left(\frac{X_{12}}{2}\right)\left(\Delta g_{12} - \Delta g_{12}^{o}\right) + \left(\frac{X_{13}}{2}\right)\left(\Delta g_{13} - \Delta g_{13}^{o}\right) + \ldots \qquad [19]$$

The coefficients of Eqs [9], [10] or [11] are obtained by optimization of binary experimental data. Eqs [9] [10] or [11] only apply in the binary subsystems. It is now required to write expressions for Δg_{mn} for compositions within the N-component system for use in Eq [17]

III. INTERPOLATION FORMULAE

A. *When Δg_{mn} in a Binary System is Given by Eq [9] or [10]*

Suppose Δg_{12} in the 1-2 binary subsystem has been expressed as a polynomial in the fractions Y_1 and Y_2 by Eq [9]. We now want an expression for Δg_{12} in a multicomponent solution. We shall consider first a ternary system 1-2-3.

1. *Symmetric Model:*

With the symmetric model illustrated in Fig. 1a, Δg_{12} in the ternary solution is given by:

$$\Delta g_{12} = \left[\Delta g_{12}^{o} + \sum_{(i+j)\geq 1} q_{12}^{ij}\left(\frac{Y_1}{Y_1+Y_2}\right)^i\left(\frac{Y_2}{Y_1+Y_2}\right)^j\right] + \sum_{\substack{k\geq 1\\ i\geq 0\\ j\geq 0}} q_{12(3)}^{ijk}\left(\frac{Y_1}{Y_1+Y_2}\right)^i\left(\frac{Y_2}{Y_1+Y_2}\right)^j Y_3^k \qquad [20]$$

where the first term on the right-hand-side of Eq [20] is constant along the line 3-a in Fig. 1a and equal to Δg_{12} in the 1-2 binary at point a (where $(Y_1 + Y_2) = 1$.). That is, it is assumed that the binary 1-2 pair interaction energy is constant at constant Y_1/Y_2 ratio. The second summation in Eq. [20] consists of "ternary terms" which are all zero in the 1-2 binary, and which give the effect of the presence of component 3 upon the energy Δg_{12} of the 1-2 pair interactions. The empirical ternary coefficients $q_{12(3)}^{ijk}$ are found by optimization of experimental ternary data.

Similar equations give Δg_{23} and Δg_{31}, with the binary terms equal to their values at points b and c respectively in Fig. 1a, and with ternary coefficients $q_{23(1)}^{ijk}$ and $q_{31(2)}^{ijk}$ which give the effect of the presence of component 1 upon the pair energy Δg_{23}, and of component 2 upon Δg_{31}, respectively. It has been proposed[7] that this functional form for the ternary terms is preferable to traditional expressions such as $Y_1^iY_2^jY_3^k$

Alternatively, if Δg_{12} is expressed in the 1-2 binary system by a Redlich Kister expansion as in Eq [10], then the first summation in Eq [20] is replaced by $\sum_{i\geq 1}{}' L_{12}\left(\frac{Y_1 - Y_2}{Y_1 + Y_2}\right)^i$ which is also constant along the line 3-a and equal to Δg_{12} at point a.

This model is "symmetric" in that the three components are treated in the same fashion. For certain systems, however, in which one component is chemically different from the other two (e.q. SiO_2-CaO-MgO, S-Fe-Cu, Na-Au-Ag, etc.) it is more appropriate to use the "asymmetric" model illustrated in Fig. 1b, where component 1 is the "asymmetric component".

2. *Asymmetric Model*

In this case, Δg_{12} in the ternary solution is given by:

$$\Delta g_{12} = \left[\Delta g_{12}^{o} + \sum_{(i+j)\geq 1} q_{12}^{ij} Y_1^i(1-Y_1)^j\right] + \sum_{\substack{k\geq 1\\ i\geq 0\\ j\geq 0}} q_{12(3)}^{ijk} Y_1^i(1-Y_1)^j\left(\frac{Y_3}{Y_2+Y_3}\right)^k \qquad [21]$$

where the binary terms are constant along the line ac and equal to their values at point a in Fig. 1b. A similar expression is written for Δg_{31}, while Δg_{23} is given by an expression similar to Eq [20]. If Δg_{12} is expressed in the binary system by a Redlich-Kister expansion, then the binary terms in Eq [21] are replaced by $\sum_{i\geq 1}{}' L_{12}(2Y_1 - 1)^i$.

It has been shown [7] that for systems with large composition-dependent deviations from ideality, the choice of a symmetric or an asymmetric model can often give very different results. An incorrect choice can even give rise to spurious miscibility gaps.

3. *Multicomponent Solutions*

In order to extend this symmetric/asymmetric dichotomy to N-component solutions, while still

maintaining complete flexibility to treat any ternary subsystem as symmetric or asymmetric, we define:[7]

$$\xi_{ij} = Y_i + \sum_k Y_k \qquad [22]$$

where the summation is over all components k in asymmetric i-j-k ternary subsystems in which j is the asymmetric component. This is best presented by an example[7]. For the 5-component system in Fig. 2, the ternary subsystems 1-2-3 and 1-2-5 are asymmetric with 1 and 5 respectively as asymmetric components, the system 1-2-4 is symmetric, and so on, as illustrated schematically in the figure. In this example then:

$$\begin{aligned}
\xi_{12} &= Y_1 & \xi_{21} &= Y_2 + Y_3 \\
\xi_{13} &= Y_1 + Y_4 & \xi_{31} &= Y_3 + Y_2 \\
\xi_{14} &= Y_1 & \xi_{41} &= Y_4 \\
\xi_{15} &= Y_1 + Y_2 & \xi_{51} &= Y_5 \\
\xi_{23} &= Y_2 + Y_5 & \xi_{32} &= Y_3 + Y_4 \\
\xi_{24} &= Y_2 & \xi_{42} &= Y_4 + Y_3 \\
\xi_{25} &= Y_2 + Y_1 + Y_4 & \xi_{52} &= Y_5 \\
\xi_{34} &= Y_3 & \xi_{43} &= Y_4 + Y_1 \\
\xi_{35} &= Y_3 & \xi_{53} &= Y_5 + Y_2 \\
\xi_{45} &= Y_4 + Y_2 & \xi_{54} &= Y_5
\end{aligned} \qquad [23]$$

Then, in the multicomponent system:

$$\begin{aligned}
\Delta g_{12} = \Delta g_{12}^{o} &+ \sum_{(i+j)\geq 1} \left(\frac{\xi_{12}}{\xi_{12}+\xi_{21}}\right)^{i}\left(\frac{\xi_{21}}{\xi_{12}+\xi_{21}}\right)^{j} q_{12}^{ij} \\
&+ \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \left(\frac{\xi_{12}}{\xi_{12}+\xi_{21}}\right)^{i}\left(\frac{\xi_{21}}{\xi_{12}+\xi_{21}}\right)^{j}\left[\sum_{l} q_{12(l)}^{ijk} Y_l \left(1-\xi_{12}-\xi_{21}\right)^{k-1} + \sum_{m} q_{12(m)}^{ijk}\left(\frac{Y_m}{\xi_{21}}\right)\left(1-\frac{Y_2}{\xi_{21}}\right)^{k-1} + \sum_{n} q_{12(n)}^{ijk}\left(\frac{Y_n}{\xi_{12}}\right)\left(1-\frac{Y_1}{\xi_{12}}\right)^{k-1}\right]
\end{aligned} \qquad [24]$$

where the summations of ternary terms are over (i) all components l in 1-2-l ternary subsystems which are either symmetric or in which l is the asymmetric component; (ii) all components m in 1-2-m subsystems in which 1 is the asymmetric component; and (iii) over all components n in 1-2-n subsystems in which 2 is the asymmetric component.

Eq [24] reduces to Eq [20] in symmetric ternary subsystems (when $(Y_1 + Y_2 + Y_3) = 1$) and to Eq [21] in asymmetric ternary subsystems, as can be verified by substitution of Eqs. [23]. The form of the ternary terms in Eq [24] has been chosen such that if two components, say 3 and 4, have the same effect upon Δg_{12} (that is, if $q_{12(3)}^{ijk} = q_{12(4)}^{ijk}$) then the effect of the presence of both 3 and 4 will be additive. This has been discussed previously[7]. If a Redlich-Kister expansion as in Eq [10] is used in the 1-2 binary system, then the binary terms (the first summation) in Eq [24] are replaced by $\sum_{i\geq 1} {}^{i}L_{12}\left[(\xi_{12}-\xi_{21})/(\xi_{12}+\xi_{21})\right]^{i}$.

Other examples of the application of Eq [22] were given previously[7]. For example, suppose all components are grouped as either "acids" (group I) or "bases" (group II), where a ternary system is symmetric if all three components are in the same group, and asymmetric otherwise. It then follows from the definition of ξ_{ij} that $\xi_{12} = Y_1$ and $\xi_{12}/(\xi_{12}+\xi_{21}) = Y_1/(Y_1+Y_2)$ if 1 and 2 are in the same group, while $\xi_{12} = \sum_{group\ I} Y_i \equiv \xi_I$ and also $\xi_{12}/(\xi_{12}+\xi_{21}) = \xi_I$ if 1 and 2 are in groups I and II respectively.

B. *When Δg_{mn} in a Binary System is Given by Eq [11]*

Suppose that Δg_{12} in the binary system has been expressed as in Eq [11] by a polynomial in terms of the pair fractions. Let us consider first a ternary system 1-2-3.

1. *Symmetric Model:*

In a symmetric ternary system as in Fig. 1a, the following equation for Δg_{12} is proposed:

$$\Delta g_{12} = \Delta g_{12}^{o} + \sum_{(i+j)\geq 1} g_{12}^{ij}\left(\frac{X_{11}}{X_{11}+X_{12}+X_{22}}\right)^{i}\left(\frac{X_{22}}{X_{11}+X_{12}+X_{22}}\right)^{j} + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} g_{12(3)}^{ijk}\left(\frac{X_{11}}{X_{11}+X_{12}+X_{22}}\right)^{i}\left(\frac{X_{22}}{X_{11}+X_{12}+X_{22}}\right)^{j} Y_3^{k} \qquad [25]$$

As with Eq [11], in practice it is usually sufficient to include only terms with $i = 0$ or with $j = 0$. The form of this expression has been chosen for the following reason. As Δg_{12} , Δg_{23} and Δg_{31} become small, the solution approaches ideality and $Y_{11} \to Y_1^2$,, $Y_{22} \to Y_2^2$ and

$Y_{12} \rightarrow 2Y_1Y_2$. In this case, $X_{11}/(X_{11}+X_{12}+X_{22}) \rightarrow [Y_1/(Y_1+Y_2)]^2$ and Eq [25] approaches Eq [20] which, in the limit, becomes the well-known Kohler[8] equation for symmetrical ternary systems.

From Eq [6] it can be seen that the factor Y_3 in the ternary terms in Eq [25] is equal to $(X_{33}+X_{31}/2+X_{23}/2)$. In principle, the effect of these three terms upon Δg_{12} could easily be represented by three independent ternary coefficients. However, this additional complexity is probably not required.

2. *Asymmetric Model*

In an asymmetric ternary system as in Fig. 1b, the following equation is proposed :

$$\Delta g_{12} = \Delta g_{12}^{o} + \sum_{(i+j)\geq 1} g_{12}^{ij} X_{11}^{i} (X_{22}+X_{23}+X_{33})^{j} + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} g_{12(3)}^{ijk} X_{11}^{i} (X_{22}+X_{23}+X_{33})^{j} \left(\frac{Y_3}{Y_2+Y_3}\right)^{k} \qquad [26]$$

In the limit of ideality, this equation reduces to Eq [21] which, in the limit, becomes the well-known Kohler/Toop [9] equation for asymmetrical ternary systems.

3. *Multicomponent Solutions*

To extend this symmetric/asymmetric dichotomy to multicomponent solutions we define:

$$\chi_{12} = \sum_{i=1,k} \sum_{j=1,k} X_{ij} \Big/ \sum_{i=1,2,k,l} \sum_{j=1,2,k,l} X_{ij} \qquad [27]$$

where k represents all values of k in 1-2-k asymmetric ternary subsystems in which 2 is the asymmetric component, and l represents all values of l in asymmetric 1-2-l subsystems in which 1 is the asymmetric component. χ_{ij} is analogous to the ratio $\xi_{ij}/(\xi_{ij}+\xi_{ji})$ defined by Eq. [22] and used in Eq. [24]. Taking the example of Fig. 2, from Eq. [23]:

$$\frac{\xi_{23}}{\xi_{23}+\xi_{32}} = \frac{(Y_2+Y_5)}{(Y_2+Y_5)+(Y_3+Y_4)} \qquad [28]$$

whereas:

$$\chi_{23} = \frac{(X_{22}+X_{55})+X_{25}}{(X_{22}+X_{55})+(X_{33}+X_{44})+X_{25}+X_{23}+X_{24}+X_{53}+X_{54}+X_{34}} \qquad [29]$$

That is, starting from Eq. [28], we can write the expression for χ_{23} in Eq. [29] by replacing the sums $(Y_i + Y_j + Y_k + \ldots)$ in the numerator and denominator of Eq. [28] by the sum of $(X_{ii} + X_{jj} + X_{kk} + \ldots)$ plus all cross terms $(X_{ij} + X_{ik} + X_{jk} + \ldots)$.

In the case where all components are grouped as either "acids" (group I) or "bases" (group II), it follows from the definitions and from Eq. [6] that $\chi_{12} = X_{11}/(X_{11} + X_{12} + X_{22})$ if components 1 and 2 are in the same group and $\chi_{12} = \sum_{group\,I} Y_i \equiv \xi_I$ if components 1 and 2 are in groups I and II respectively.

Then, in the multicomponent system:

$$\Delta g_{12} = \Delta g_{12}^{o} + \sum_{(i+j)\geq 1} \chi_{12}^{i} \chi_{21}^{j} g_{12}^{ij} + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi_{12}^{i} \chi_{21}^{j} \left[\sum_{l} g_{12(l)}^{ijk} Y_l (1-\xi_{12}-\xi_{21})^{k-1} + \sum_{m} g_{12(m)}^{ijk} \left(\frac{Y_m}{\xi_{21}}\right)\left(1-\frac{Y_2}{\xi_{21}}\right)^{k-1} + \sum_{n} g_{12(n)}^{ijk} \left(\frac{Y_n}{\xi_{12}}\right)\left(1-\frac{Y_1}{\xi_{12}}\right)^{k-1} \right] \qquad [30]$$

where the summations over l, m and n are as was described following Eq [24]. Eq. [30] reduces to the correct symmetric or asymmetric ternary equation, [25] or [26], in any ternary subsystem. The analogy to Eq [24] is evident.

IV. DISCUSSION

Substitution of Eq [24] or [30] into Eq [17] gives an equation for G in terms of the pair fractions X_{mn}. For any overall composition given by $(n_1, n_2, \ldots, n_N)$, the equilibrium pair fractions are then calculated by minimizing G subject to the mass balance constraints of Eq [14]. This Gibbs energy minimization is greatly facilitated by the form of Eq [17]. When expressed per mole of pairs as in Eq [18], the Gibbs energy equation is identical, apart from the second configurational entropy term, to commonly used expressions for the Gibbs energy of a randomly mixed solution of "components" (11, 12, 22, . . .); the "excess" terms in Eq [19] are polynomials in the fractions X_{mn} since Δg_{mn} from Eq [24] or [30] is expressed only in terms of X_{mn} (Y_m being given in terms of X_{mn} by Eq [6]). Therefore, the same existing algorithms and computer subroutines which are commonly used for polynomial solution models can be used directly for the quasichemical model by simply including the extra entropy terms.

That is, a significant simplification is achieved by formally considering the mn pairs as the "components" of the solution. A further computational simplification can also be achieved [6] by formally treating these "components" as the "associates" or "molecules" $n_{1/Z^m_{mn}} n_{1/Z^n_{mn}}$. For example, if $Z^m_{mm} = 6$, $Z^n_{nn} = 6$, $Z^m_{mn} = 3$ and $Z^n_{mn} = 6$, then the formal components would be $m_{2/6}$, $n_{2/6}$, and $m_{1/3}n_{1/6}$. Setting

$$n_{n_{1/Z^m_{mn}} n_{1/Z^n_{mn}}} = n_{mn} \qquad [31]$$

and substituting into Eq [14] gives

$$n_m = 2n_{m_{2/Z^m_{mm}}} \Big/ Z^m_{mm} + \sum_{n>m} n_{m_{1/Z^m_{mn}} 1/Z^n_{mn}} \Big/ Z^m_{mn} \qquad [32]$$

which is now a "true" chemical mass balance in that the number of moles of m is the same on both sides of the equation.

The fact that Eq [18] is written solely in terms of the fractions X_{mn} of the "components" mn, permits the chemical potentials to be easily calculated in closed explicit form. As shown previously[6], the chemical potential of m is given by:

$$\mu_m = (\partial G/\partial n_m)_{n_i} = (Z^m_{mm}/2)(\partial G/\partial n_{mm})_{n_{ij}} \qquad [33]$$

Hence:

$$\mu_m = g^o_m + RT \ln X_A + \left(\frac{Z^m_{mm}}{2}\right)\left(RT \ln \frac{X_{mm}}{Y_m^2} + g^E_{mm}\right) \qquad [34]$$

where the partial excess term g^E_{mm} can be calculated in the usual way from the polynomial expansion for g^E in Eq [19]:

$$g^E_{mm} = g^E + (\partial g^E/\partial X_{mm}) - \sum_{(ij \neq mm)} X_{ij}(\partial g^E/\partial X_{ij}) \qquad [35]$$

where Eq [6] is used to express Y_m in terms of X_{mn}.

A. *Reduction to the Random Mixing (Bragg-Williams) Model*

Suppose that it is desired to suppress the formation of short-range ordering and to employ the following commonly-used Bragg-Williams model for a solution with random mixing and a polynomial expression for g^E:

$$G = \sum n_m g^o_m + RT \sum n_m \ln X_m + \sum_{n>m} X_{mn}(\Delta g_{mn}) \qquad [36]$$

with Δg_{mn} given as a polynomial expansion in terms of Y_i by Eq [24]. This can be done by simply replacing all factors X_{mn} (where $m \neq n$) in Eq [18] by $2Y_mY_n$ which is the value of X_{mn} in a randomly mixed (Bragg-Williams) solution or by replacing n_{mn} ($m \neq n$) in Eq [17] by $\left(\sum Z'_{ii} n_i\right) Y_m Y_n$. It is also necessary in this case to set all $Z^m_{mn} = Z^m_{mm}$. Eqs [15] and [16] are still used to give g^o_{mm} and g^o_{mn}. The excess terms then have no effect upon the calculated pair distributions, and so the Gibbs energy minimization will result in a random mixture. That is, the second entropy term in Eq. [18] will automatically become zero, and the result will be the same as if Eq [16] had been used for G.

Hence, the same model subroutine which is used for the quasichemical model can be used, with one minor alteration, for the random mixing Bragg-Williams model.

B. *Combining Models in One Multicomponent Solution Database*

The major importance of this fact is that it is now possible to "mix models" in one multicomponent solution. This is of much practical value. For example, in developing the F*A*C*T[10] database for multicomponent molten salt solutions, we have already performed optimizations on well over 100 binary and ternary common-anion alkali halide, carbonate, sulfate, nitrate and hydroxide systems using the Bragg-Williams polynomial model, which is satisfactory for these systems in which deviations from ideality are relatively small. We are now including alkaline earth salts in this database. Several of the binary liquid solutions (*e.g.* $MgCl_2$-KCl) exhibit large negative deviations from ideality and a large degree of short-range ordering, and require the quasichemical model. Ideally, of course, all previously optimized systems could be re-optimized with the quasichemical model, but the amount of work involved is considerable.

However, it is now easy to combine the models in one multicomponent solution database. If a binary subsystem m-n has been optimized with the quasichemical model with Eq. [9] or [10] for Δg_{mn}, then Eq [24] for Δg_{mn} is substituted into Eq [17]. If another binary subsystem i-j has been optimized with the quasichemical model with Eq [11] for Δg_{ij}, then Eq [30] for Δg_{ij} is substituted into Eq [17]. If yet another binary subsystem k-l has been optimized using the random mixing Bragg-Williams model with Eq [9] or [10] for Δg_{kl}, then Δg_{kl} from Eq [24] is substituted into Eq [17] and, furthermore, n_{kl} is replaced everywhere in Eq [17] by $\left(\sum Z_n^k n_t\right) Y_k Y_l$.

V. CONCLUSIONS

Improvements to the quasichemical model introduced in the first article in the present series[6] have been extended to multicomponent solutions with short-range ordering. The energies Δg_{mn} of pair formation may be expanded as polynomials in the pair fractions, rather than the component fractions. Composition-dependent coordination numbers may also be used. Both these improvements provide better representations by providing greater flexibility.

The properties of a ternary solution may be estimated from optimized data for its binary subsystems by either a symmetric or an asymmetric model. In the former, all components are treated in the same fashion, while in the latter, one component, being chemically different from the other two, is singled out. It has been shown how this symmetric/asymmetric dichotomy can be extended into the N-component solution while still permitting complete flexibility to choose either a symmetric or an asymmetric model for any ternary subsystem.

An improved general functional form for "ternary terms" in the excess Gibbs energy expression has been proposed. These terms are related to the effect of a third component upon the binary pair interaction energies.

By treating the nearest-neighbor pairs as components, a Gibbs energy expression is obtained which is a function of only the pair fractions X_{mn}. This expression is identical, apart from a configurational entropy term, to the equations for a randomly mixed solution of these components with a polynomial expression for the excess Gibbs energy. This permits the quasichemical model to be treated with currently available and relatively simple software. Furthermore, closed explicit equations for the chemical potentials are thereby easily obtained.

By means of a minor alteration, the Gibbs energy expression in the quasichemical model can be made identical to that of a randomly-mixed Bragg Williams solution with a polynomial expansion for g^E. This is of much practical importance because binary subsystems which have previously been optimized with a Bragg-Williams polynomial model can be combined with binary subsystems optimized with the quasichemical model in the same multicomponent solution database.

Although the model has been developed primarily for liquid solutions, it can be applied to treat short-range ordering in solid solutions. In this case, all coordination numbers must be the same.

The model of the present article takes account of mixing on only one lattice. It can, however, be applied to systems with more than one sublattice as long as mixing occurs on only one of the sublattices. For example, it can be applied to common-ion salt systems such as LiCl-NaCl-KCl-$MgCl_2$ where all anion lattice sites are occupied by Cl^- such that mixing occurs only on the cation sublattice.

Subsequent articles in the present series will describe extensions to solutions with mixing on two quasi-sublattices such as reciprocal molten salt solutions with intra- as well as inter-sublattice short-range ordering. It will be shown that the large degree of flexibility in the model also permits the treatment of phenomena such as complexation, polymerization, and multiple compositions of maximum short-range ordering.

An example of the application of the model of the present article to liquid LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ solutions is given in an accompanying publication[11].

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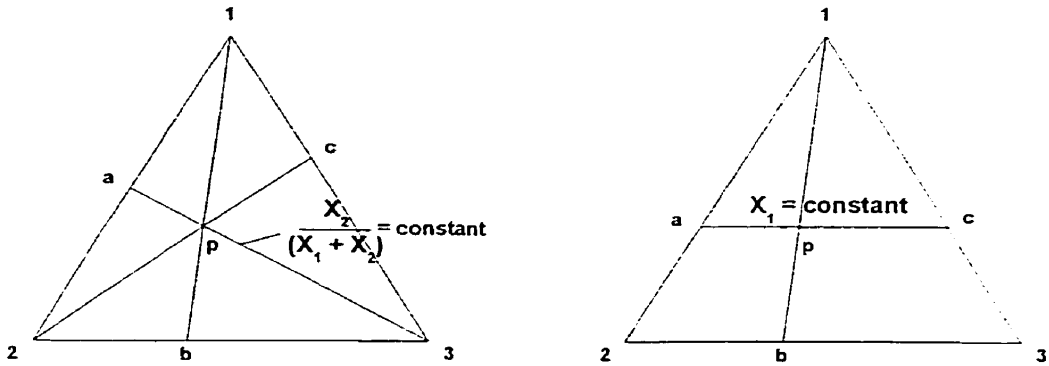

Fig 1. Symmetric (left) and asymmetric (right) schemes for interpolation from binary to ternary solutions.

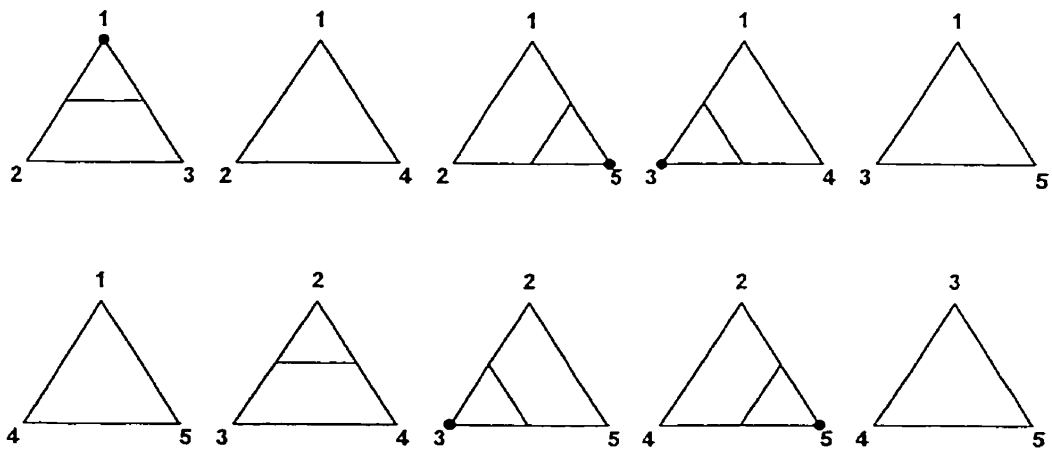

Fig 2. A 5-component example solution illustrating which ternary subsystems are to be treated with a symmetric model and which are to be treated with an asymmetric model.

ANNEXE IV

Article :

Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ System Using the Modified Quasichemical Model

Patrice Chartrand et Arthur D. Pelton,

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Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ System Using the Modified Quasichemical Model

PATRICE CHARTRAND and ARTHUR D. PELTON

A complete critical evaluation and quantitative optimization of all available phase diagram and thermodynamic data has been performed for all condensed phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ system. The model parameters obtained for binary and ternary subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent system. The modified quasichemical model for short-range ordering was used for the molten salt phase.

I. INTRODUCTION

Molten alkali-alkaline earth halide solutions are of much technological importance in, for example, the production of Mg and Na. A large body of experimental thermodynamic and phase equilibrium data exists for these systems. In this article, all available data for binary and ternary subsystems of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ system are critically evaluated and optimized to obtain parameters of models of all solution phases. These parameters form a computer database. The models are then used to predict the thermodynamic properties of the multicomponent system. When used in conjunction with currently available general software for calculating equilibria by Gibbs energy minimization, this database can be used to predict the thermodynamic properties and phase equilibria in uncharted regions of temperature and composition. This article is the first in a series that will be published on alkali-alkaline earth halide systems.

In an accompying article in this journal[1] we have presented a quasichemical model for liquid solutions which takes into account short-range ordering between nearest-neighbors on a lattice or sublattice. Molten alkali chloride-$MgCl_2$ solutions are well known for exhibiting extensive short-range ordering, increasing in importance from LiCl-$MgCl_2$ to CsCl-$MgCl_2$. This ordering gives rise to "V-shaped" enthalpy of mixing and "m-shaped" entropy of mixing curves as in Figures 1 and 2. This has previously been modelled by introducing complex anions such as $MgCl_4^{2-}$ [2,3]. However, until now, no model has been proposed which permits a quantitative optimization of all subsystem data and which can satisfactorily be extrapolated to predict the properties of multicomponent solutions when appreciable short-range ordering is present. The modified quasichemical model[1] achieves this objective. An earlier version of the model has been used very successfully to model molten silicates[4].

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The model does not explicitely introduce complex anions. Instead, short-range ordering is treated by considering the relative numbers of second-nearest-neighbor cation-cation pairs. The parameters of the model are the Gibbs energy changes $\Delta g_{AB/Cl}$ for the pair exchange reactions :

$$(A-Cl-A)_{pair}+(B-Cl-B)_{pair}=2(A-Cl-B)_{pair} \qquad \Delta g_{AB/Cl} \qquad [1]$$

As $\Delta g_{AB/Cl}$ becomes progressively more negative, reaction [1] is shifted progressively to the right, (A-Cl-B) pairs predominate, and the solution becomes progressively more ordered. In the previous article[1] the model was developed in terms of nearest-neighbor pairs (A-B) for species mixing on one lattice. In the present case, since the anion sublattice is occupied only by Cl^- ions, the model can be used directly to treat cation-cation pairs on the cation sublattice. The parameter $\Delta g_{AB/Cl}$ is the parameter Δg_{mn} of the previous article[1].

When $\Delta g_{AB/Cl}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of cations on the cation sublattice. Many subsystems, particularly of alkali halides (such as LiCl-NaCl), have already been evaluated and optimized by assuming a random Bragg-Williams configurational entropy and by expanding the excess Gibbs energy in the usual way as an empirical polynomial in the mole fractions. We have already developed a large evaluated optimized database for alkali halide solutions in this way[5,6]. It would clearly be very useful if this database could be combined with the present quasichemical model database to predict properties of multicomponent solutions, thereby obviating the necessity of re-optimizing all the alkali halide systems. The previous article[1] describes, for the first time, how the models may be combined in this way. This is illustrated in the present article.

The present article demonstrates the application of the new modified quasichemical model to the evaluation, optimization and prediction of thermodynamic properties and phase equilibria.

II. THERMODYNAMIC DATA

All thermodynamic data ($H^{o}_{298.15K}$, $S^{o}_{298.15K}$ and C_p) for the condensed pure phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ system, including optimized values from the present work, are given in Table I.

III. THERMODYNAMIC MODEL FOR THE LIQUID PHASE

The modified quasichemical model[1] is used for the liquid phase. The notation of the previous article[1] is maintained. For example, X_{NaMg} is the mole fraction of second-nearest-neighbor (Na-Cl-Mg) pairs. The model requires the definition of cation-cation coordination numbers Z^{i}_{ij}. The values chosen in the present work are listed in Table II. Note that, for example, the choice of $Z^{Cs}_{CsMg} = \frac{1}{2} Z^{Mg}_{CsMg}$ assures that the composition of maximum short-range ordering will be near the Cs_2MgCl_4 composition. Also, as discussed previously[1], it is necessary to define all ternary sub-systems as either "symmetric" or "asymmetric". In the present case, all ternary systems in which all three components are alkali halides are defined as symmetric. Systems with one alkali and two alkaline-earth chlorides are asymmetric, with the alkali chloride as asymmetric component, and systems with one alkaline-earth and two alkali chlorides are asymmetric, with the alkaline-earth chloride as asymmetric component. To this end, the components are divided into two groups, all alkali halides are in one group, and $MgCl_2$ and $CaCl_2$ form the other group. The composition variables χ_{ij} defined previously[1] then become :

$$\chi_{LiMg} = \chi_{LiCa} = \chi_{NaMg} = \chi_{NaCa} = \chi_{KMg} = \chi_{KCa} = \\ = \chi_{RbMg} = \chi_{RbCa} = \chi_{CsMg} = \chi_{CsCa} = \chi_{Alk} \qquad [2]$$

where $$\chi_{Alk} = \sum_{i=Li}^{Cs} \sum_{j=i}^{Cs} X_{ij} \qquad [3]$$

$$\chi_{MgLi} = \chi_{CaLi} = \chi_{MgNa} = \chi_{CaNa} = \chi_{MgK} = \\ = \chi_{CaK} = \chi_{MgRb} = \chi_{CaRb} = \chi_{MgCs} = \chi_{CaCs} = \chi_{AlkE} \qquad [4]$$

where $$\chi_{AlkE} = \sum_{i=Mg}^{Ca} \sum_{j=i}^{Ca} X_{ij} \qquad [5]$$

and also

$$\chi_{MgCa} = \frac{X_{MgMg}}{X_{MgMg} + X_{MgCa} + X_{CaCa}} \qquad [6]$$

$$\chi_{CaMg} = \frac{X_{CaCa}}{X_{MgMg} + X_{MgCa} + X_{CaCa}} \qquad [7]$$

$$\chi_{LiNa} = \frac{X_{LiLi}}{X_{LiLi} + X_{LiNa} + X_{NaNa}} \qquad [8]$$

$$\chi_{NaLi} = \frac{X_{NaNa}}{X_{LiLi} + X_{LiNa} + X_{NaNa}} \qquad [9]$$

etc.

That is, when i and j are alkalis :

$$\chi_{ij} = \frac{X_{ij}}{X_{ii} + X_{ij} + X_{jj}} \qquad [10]$$

The parameters $\Delta g_{AB/Cl}$ of reaction [1] for each pair are expanded, through optimization of available experimental data, as empirical polynomials in χ_{ij}. For ternary systems, terms may be added giving the effect of the third component upon the pair formation energies $\Delta g_{AB:Cl}$. As described previously[1] this is done by introducing empirical ternary parameters $g^{ijk}_{AB(C)/Cl}$ in the polynomial expansion.

IV. ALKALI CHLORIDE MIXTURES

A. *The LiCl-RbCl, LiCl-CsCl, NaCl-RbCl and NaCl-CsCl Systems*

In previous publications[5,6] a database was developed for alkali halide solutions by evaluation/optimization of all available data. A random (Bragg-Williams) configurational entropy was assumed, and excess Gibbs energies were expressed as polynomials with evaluated binary[5] and ternary[6] parameters. These evaluations are used directly in the present work. It is only necessary to convert the parameters from units of joules per mole of components ACl to joules per mole of second-nearest-neighbor pairs. Since all coordination numbers Z^{i}_{ij} in Table II are equal to 6 when i and j are alkalis, it is sufficient to divide all previous parameters by 3.0. The resultant expressions for $\Delta g_{AB/Cl}$ for the Li-Cl-Rb, Li-Cl-Cs, Na-Cl-Rb and Na-Cl-Cs pairs in the liquid are :

$$\Delta g_{LiRb/Cl} = -5955.3 + 2.4507T - 1602.0\left(\frac{X_{Li}}{X_{Li} + X_{Rb}}\right) \\ + 2.2417T\left(\frac{X_{Rb}}{X_{Li} + X_{Rb}}\right) - 1325.0\left(\frac{X_{Li}}{X_{Li} + X_{Rb}}\right)\left(\frac{X_{Rb}}{X_{Li} + X_{Rb}}\right) \qquad [11]$$

$$\Delta g_{LiCs/Cl} = -6485.3 + 6.8470T + (-2482.7 - 1.0950T)\left(\frac{X_{Li}}{X_{Li} + X_{Cs}}\right) \\ - 3026.7\left(\frac{X_{Li}}{X_{Li} + X_{Cs}}\right)\left(\frac{X_{Cs}}{X_{Li} + X_{Cs}}\right) \qquad [12]$$

$$\Delta g_{NaRb:Cl} = -1074.0 + 0.2257T - 111.7\left(\frac{X_{Na}}{X_{Na} + X_{Cs}}\right) \\ + 1.7483T\left(\frac{X_{Cs}}{X_{Na} + X_{Cs}}\right) \qquad [13]$$

$$\Delta g_{NaCs/Cl} = -1436.7 + 1.9213T + (139.3 - 1.9670T)\left(\frac{X_{Na}}{X_{Na} + X_{Cs}}\right) \quad [14]$$

Expressions for the excess Gibbs energies of the solid solutions were given previously[5,6] and will not be repeated here.

B. *The LiCl-NaCl, KCl-RbCl, KCl-CsCl and RbCl-CsCl Systems*

In a binary ACl-BCl system the quasichemical model converges towards the regular solution model when $\Delta g_{AB/Cl}$ is small. Consequently, if a regular solution model (Bragg-Williams entropy) has been used for a solution and if the parameters of g^E are small, they can be used directly as parameters of the quasichemical model with negligible effect on the thermodynamic properties. This was done for the LiCl-NaCl, KCl-RbCl, KCl-CsCl and RbCl-CsCl binary liquid solutions, where small regular solution parameters were previously obtained[5] by optimization. After dividing by 3.0 (see Section IV-A), the parameters are : $\Delta g_{LiNa/Cl} = -1562$, $\Delta g_{KRb/Cl} = 28$, $\Delta g_{KCs/Cl} = 265$ and $\Delta g_{RbCs/Cl} = 112$ J/mol. Parameters for the solid solutions were given previously[5].

C. *The LiCl-KCl System*

The liquid thermodynamic properties were reoptimized with the quasichemical model[1]. The Gibbs energy of formation of the Li-Cl-K pairs is given by Eq.[15]. The calculated phase diagram is virtually identical to the one published[5] previously.

$$\Delta g_{LiK/Cl} = -4884.6 + 1.1000T + (-1147.3 + 1.5416T)\chi_{KLi} + (-864.7 - 0.3805T)\chi_{LiK} \quad \text{J/mol} \quad [15]$$

D. *The NaCl-KCl System*

Robelin[7] optimized the NaCl-KCl system. The energy parameters for reaction [1] are given by Eq.[16]. The thermodynamic properties of the solid solution[7] were taken from Sangster and Pelton[5].

$$\Delta g_{NaK/Cl} = -695.5 - 67.0\chi_{NaK} \text{ J/mol} \quad [16]$$

V. MIXTURES OF ALKALI CHLORIDES WITH $MgCl_2$

A. *The LiCl-$MgCl_2$ System*

The phase diagram has been measured by zone melting[8], cooling curves[9] and electrical conductivity[10] (Figure 3). All authors reported extensive solid solubility on both sides of the phase diagram (complete miscibility is even reported[9]). There is agreement that the liquidus exhibits a minimum at around 35 mol% $MgCl_2$ and 575°C. Kravchuk[8] shows a maximum in the liquidus at around 1.6 mol% $MgCl_2$. Large uncertainties still remain on subliquidus equilibria but it is clear that extensive solid solutions are present.

Calorimetric measurements are found for the liquid phase[11] (Figure 1), together with activity measurements obtained by an emf technique for LiCl[12,13] and $MgCl_2$[14] (Figure 4). The optimized Gibbs energy of reaction [1] for the Li-Cl-Mg pair is :

$$\Delta g_{LiMg/Cl} = -4147.1 + 0.2356T + (8274.0 - 1.3821T)\chi_{Alk} + (2079.9 - 2.6524T)\chi_{AlkE} \quad \text{J/mol} \quad [17]$$

(where $\chi_{Alk} = X_{LiLi}$ and $\chi_{AlkE} = X_{MgMg}$ in the LiCl-$MgCl_2$ binary system).

$MgCl_2$ dissolves in solid LiCl with formation of cationic vacancies. For very dilute solutions, the Mg^{2+} ions and vacancies are distributed independently on the lattice sites, giving rise to a large entropy term and stabilizing the solid solution relative to the liquid. This could account for the reported[8] maximum in the liquidus near 1.6% $MgCl_2$. However, at slightly higher $MgCl_2$ concentrations there will be a strong electrostatic tendency for the Mg^{2+} ions and vacancies to associate and enter solution as a single species. The entropy then becomes equivalent to a simple Bragg-Williams random mixing entropy. For the LiCl-rich solid solution therefore, the following optimized expression was used :

$$g = X_{LiCl} g^{o,S}_{LiCl} + X_{MgCl_2}\left(g^{o,S}_{MgCl_2} + 5564.7 - 4.1840T\right) + RT\left(X_{LiCl}\ln X_{LiCl} + X_{MgCl_2}\ln X_{MgCl_2}\right) - 1255.2\frac{2X_{LiCl}X_{MgCl_2}}{X_{LiCl} + 2X_{MgCl_2}} \quad \text{J/mol} \quad [18]$$

The thermodynamic properties of the $MgCl_2$-rich solid solution have been represented by a Henrian solution model which, similarly to the model for LiCl-rich solutions, assumes association of the anionic vacancies with the Li^+ cations :

$$g = X_{MgCl_2} g^{o,S}_{MgCl_2} + X_{LiCl}\left(g^{o,S}_{LiCl} + 12552.0 - 4.1840T\right) + RT\left(X_{MgCl_2}\ln X_{MgCl_2} + X_{LiCl}\ln X_{LiCl}\right) \quad \text{J/mol} \quad [19]$$

Both models can be integrated into the compound-energy formalism[15] as described in Section VIII. Figures 1 to 4 show the calculated and experimental phase diagram and thermodynamic properties.

B. *The NaCl-$MgCl_2$ System*

The phase diagram has been measured by thermal analysis, DTA and XRD[16-23] (Figure 5). Reported compounds are NaCl, $MgCl_2$, $NaMgCl_3$, Na_2MgCl_4 and $NaMg_2Cl_5$. The existence of the $NaMg_2Cl_5$ compound is rejected by some authors[21-22], and it is not considered in the present calculation. No solid solubility is reported, and the limiting slopes of the NaCl and $MgCl_2$ liquidus curves respect Eq.[20] which assumes no solid solubility :

$$\lim_{x_m \to 1}\left(\frac{dX_m^{liquidus}}{dT}\right) = \frac{\Delta h^o_{fusion}}{RT^2_{fusion}} \qquad [20]$$

where Δh^o_{fusion} and T_{fusion} are the enthalpy and temperature of melting of the pure salt.

Calorimetric investigations are available for both liquid[11,24,25] and solid phases[25] (Figures 1, 6 and 7). Activities in the liquid have been measured by an emf technique for NaCl[13,26,27] and for $MgCl_2$[28-30] (Figure 8). Seifert and Thiel[23] measured, by solution calorimetry, the enthalpies of reactions [21] and [22] :

$$NaCl_{(s)} + MgCl_{2(s)} = NaMgCl_{3(s)} \qquad [21]$$

$$2\,NaCl_{(s)} + MgCl_{2(s)} = Na_2MgCl_{4(s)} \qquad [22]$$

The value obtained at 298.15K for Eq.[21] is –0.4 (±0.6) kJ/mol and for Eq.[22] it is 0.42 (±0.5) kJ/mol. The optimized values are –0.400 and 0.420 kJ/mol respectively. The heat capacities of $NaMgCl_3$(s) and of Na_2MgCl_4(s) are obtained from fitting data of Denielou *et al.*[25] and the functions are shown in Table I. The optimized Gibbs energy of reaction [1] for the Na-Cl-Mg pair is :

$$\Delta g_{NaMg:Cl} = -10395.8 + 660.5\chi_{Alk} - 4641.5\chi_{AlkE} \quad \text{J/mol} \qquad [23]$$

Figures 1, 2 and 5 to 8 show the calculated phase diagram and thermodynamic properties. Agreement with all the data is good except for the eutectic temperature (Figure 5). The calculated eutectic is at 459°C while experimental results lie between 430°C[16] and 450°C[18,21]. The eutectic temperature can be reproduced by adjusting H^o_{298} and S^o_{298} of the solids, but then the results of Seifert and Thiel[23] cannot be reproduced, and furthermore the solids are then calculated to decompose in eutectoid reactions above 25°C.

C. *The KCl-$MgCl_2$ System*

This system was optimized previously by Pelton *et al.*[31] using the present model[1] for the liquid phase with 3 parameters. In order to fit the data more precisely, a reoptimization is performed in the present work.

The phase diagram has been measured by thermal analysis, DTA and XRD[16,18,22,23,32-35] (Figure 9). Reported intermediate compounds are K_2MgCl_4, $KMgCl_3$, $K_3Mg_2Cl_7$ and K_4MgCl_6. The existence of K_4MgCl_6 has been rejected[33]. No solid solubility is reported, and the limiting slopes of the KCl and $MgCl_2$ liquidus curves agree with Eq.[20].

Calorimetric studies are available[11,36] (Figures 1 and 10). Activities in the liquid have also been measured by emf techniques for KCl[13,27,37] (Figure 11a) and $MgCl_2$ [28,30] (Figures 11a & 11b). Seifert and Thiel[23] measured the enthalpy at 298.15K of reactions [24-26] by solution calorimetry :

$$KCl_{(s)} + MgCl_{2(s)} = KMgCl_{3(s)} \qquad [24]$$

$$2KCl_{(s)} + MgCl_{2(s)} = K_2MgCl_{4(s)} \qquad [25]$$

$$3KCl_{(s)} + 2MgCl_{2(s)} = K_3Mg_2Cl_{7(s)} \qquad [26]$$

$$KMgCl_{3(s)} + K_2MgCl_{4(s)} = K_3Mg_2Cl_{7(s)} \qquad [27]$$

They obtained –5.5 (±0.4) kJ/mol for Eq.[24], –7.75 (±0.4) kJ/mol for Eq.[25] and –15.9 (±0.8) kJ/mol for Eq.[26]. Seifert *et al.*[38] measured the enthalpy of Eq.[24] by calorimetry as –9.9 kJ/mol and by an emf technique as -8.7 kJ/mol. Holm[39] calculated the enthalpy of Eq.[24] as -15.48 kJ/mol and of Eq.[25] as –35.56 kJ/mol from the enthalpy of mixing of the liquid[11] and the enthalpies of fusion[36,40-42]. The optimized value of the enthalpy of reaction [24] at 298K is -9.918 kJ/mol. The optimized value for reaction [25] is –21.39 kJ/mol. Seifert and Thiel[23] used their measurements for Eqs.[24] and [25] to evaluate the enthalpy change of Eq.[27] as –2.65 kJ/mol. The optimized value for Eq.[26] is –9.918 kJ/mol and for Eq.[27] is –2.65 kJ/mol. Hattori *et al.*[43] measured, by endothermic peaks of DSC, the enthalpy of fusion of $KMgCl_3$ at 481°C as 33.05 kJ/mol and of K_2MgCl_4 at 415°C as 37.24 kJ/mol. The respective calculated values at the same temperature are 40.45 kJ/mol and 48.15 kJ/mol. As seen in Figure 10, these agree well with the H_T-H_{298K} data. The optimized Gibbs energy of reaction [1] for the K-Cl-Mg pair is :

$$\Delta g_{KMg:Cl} = -19223.0 - 5.9468T + 0.8491T\ln T + (3324.3 - 1.0130T)\chi_{Alk} - 3158.0\chi_{AlkE} - 9481.7\chi^2_{AlkE} \quad \text{J/mol} \qquad [28]$$

Figures 1, 2 and 9 to 11 show the calculated phase diagram and thermodynamic properties.

D. *The RbCl-$MgCl_2$ System*

The liquidus (Figure 12) has been measured by thermal analysis and DTA[23,32,44]. Reported stable intermediate compounds are Rb_2MgCl_4 and $RbMgCl_3$. No solid solubility is reported, and the limiting slopes of the RbCl and $MgCl_2$ liquidus curves agree with Eq.[20].

Calorimetric measurements were made for the liquid[11,36] and solid phases[36] (Figures 1 and 13). The activity of RbCl has been measured by an emf technique[27] (Figure 14). Enthalpies of formation of Rb_2MgCl_4 and

$RbMgCl_3$ from solid RbCl and $MgCl_2$ at 298.15K have been measured by solution calorimetry [23] and (for $RbMgCl_3$) by an emf technique[45] and have been calculated by Holm[39] from the enthalpies of formation and fusion. The values obtained are -28.0 (±0.4)[23], and -28.45 kJ/mol[39] for Rb_2MgCl_4, and -23.15 (±0.4)[23], -27.1[45] and -51.463[39] kJ/mol for $RbMgCl_3$. The optimized values are -31.15 and -53.00 kJ/mol for Rb_2MgCl_4 and $RbMgCl_3$ respectively. Seifert and Thiel[45] measured the Gibbs energy of formation of $RbMgCl_3$ by an emf technique, obtaining -31.3 and -31.9 kJ/mol at 700K and 800K respectively. The corresponding optimized values are -32.71 and -33.32 kJ/mol. The optimized Gibbs energy of reaction [1] for the Rb-Cl-Mg pair is :

$$\Delta g_{RbMg/Cl} = -22369.8 + 0.4469T + 4863.0\chi_{Alk} - 3120.0\chi^2_{Alk} - 6667.0\chi_{AlkE} - 11781.0\chi^2_{AlkE} \text{ J/mol} \quad [29]$$

Figures 1, 2 and 12 to 14 show the calculated phase diagram and thermodynamic properties.

E. *The CsCl-$MgCl_2$ System*

The liquidus has been measured by DTA[23,44] (Figure 15). Reported intermediate congruent compounds are Cs_3MgCl_5, Cs_2MgCl_4 and $CsMgCl_3$, while $CsMg_3Cl_7$ is reported to melt incongruently. However the stoichiometry of this last compound is uncertain. No solid solubility is reported and the limiting slopes of the CsCl and $MgCl_2$ liquidus curves agree reasonably well with Eq.[20].

Calorimetric measurements are available[11,36] (Figures 1 and 16). Activities in the liquid were measured by emf techniques for CsCl[27] (Figure 17) and for $MgCl_2$[30] (Figure 18). The enthalpy of formation from solid CsCl and $MgCl_2$ of Cs_3MgCl_5, Cs_2MgCl_4 and $CsMgCl_3$ at 298.15K were measured by solution calorimetry[23]. The values obtained are respectively: −19.06 (±0.4) kJ/mol, -21.28 (±0.4) kJ/mol and −29.46 (±0.4) kJ/mol. Holm[39] also calculated the enthalpy of formation of Cs_2MgCl_4 and $CsMgCl_3$ from the enthalpy of mixing of the liquid[11] and the enthalpy of fusion[36,40-42]. His values are -50.208 (±4.184) kJ/mol for Cs_2MgCl_4 and −41.84 (±4.184) kJ/mol for $CsMgCl_3$. The calculated optimized values are 6.05 kJ/mol for Cs_3MgCl_5, -43.4756 kJ/mol for Cs_2MgCl_4 and -41.765 kJ/mol for $CsMgCl_3$. The optimized Gibbs energy of reaction [1] for the Cs-Cl-Mg pair is :

$$\Delta g_{CsMg/Cl} = -24130.0 + 0.5996T + (1404.2 + 0.1129T)\chi_{Alk} - 26822.0\chi_{AlkE} + 43985.0\chi^2_{AlkE} - 42805.0\chi^3_{AlkE} \text{ J/mol} \quad [30]$$

Figures 1, 2 and 15-18 show the calculated phase diagram and thermodynamic properties.

F. *The LiCl-NaCl-$MgCl_2$ System*

There is no reported experimental liquidus projection. The activity of $MgCl_2$ has been measured by an emf technique[46] for two different LiCl / (LiCl + NaCl) molar ratios (Figure 19). No ternary excess parameters were required to fit the activity data[46] (*i.e.* the activities in Figure 19 are calculated solely from the binary parameters). Li^+ may be soluble in both $NaMgCl_3$ and Na_2MgCl_4, but experimental data are not available.

G. *The LiCl-KCl-$MgCl_2$ System*

The liquidus projection has been measured[47] by thermal analysis (Figure 20). The $KMgCl_3$-LiCl join has been measured by conductivity techniques[48] (Figure 22) showing evidence of Li^+ solubility in $KMgCl_3$ and K_2MgCl_4. One ternary (reportedly incongruent) compound $LiKMgCl_4$ was found with a peritectic temperature of 410°C. The activity of $MgCl_2$ in the liquid has been measured by emf techniques[49] (Figures 23 and 24).

In order to reproduce the measured activity of $MgCl_2$[49], the following ternary parameters must be added to the respective binary pair energies of formation :

$$g^{001}_{LiMg(K)/Cl} = -6276.0 \text{ J/mol} \quad [31]$$

$$g^{011}_{LiMg(K)/Cl} = -7113.0 \text{ J/mol} \quad [32]$$

$$g^{001}_{KMg(Li)/Cl} = -6276.0 \text{ J/mol} \quad [33]$$

$$g^{011}_{KMg(Li)/Cl} = -7113.0 \text{ J/mol} \quad [34]$$

Li^+ is soluble in both $KMgCl_3$ and K_2MgCl_4. Hypothetical (metastable) $LiMgCl_3$ and Li_2MgCl_4 are assumed to mix with $KMgCl_3$ and K_2MgCl_4 respectively, with a regular excess Gibbs energy in both cases. The entropies of mixing are given by assuming that Li^+ and K^+ ions mix randomly on one sublattice, while Mg^{2+} and Cl^- occupy other sublattices. Positive Gibbs energies of formation must be assigned to both hypothetical Li compounds because they are unstable in the LiCl-$MgCl_2$ binary system, but since a large solubility is needed to reproduce the ternary data, only small positive enthalpies of formation (Eq.[36] and Eq.[38]) are arbitrarly defined, with large negative regular mixing terms (Eqs.[35] and [37]).

$$g^E = -23430.0 X_{LiMgCl_3} X_{KMgCl_3} \text{ J/mol of (Li,K)MgCl}_3 \quad [35]$$

$$g^{o,hyp}_{LiMgCl_3} = g^{o,S}_{LiCl} + g^{o,S}_{MgCl_2} + 2100 \text{ J/mol} \quad [36]$$

$$g^E = -25104.0 X_{Li_2MgCl_4} X_{K_2MgCl_4} \text{ J/mol of (Li,K)}_2\text{MgCl}_4 \quad [37]$$

$$g^{o,hyp}_{Li_2MgCl_4} = 2g^{o,S}_{LiCl} + g^{o,S}_{MgCl_2} + 4200 \text{ J/mol} \quad [38]$$

The calculated liquidus projection is shown in Figure 21. The optimized thermodynamic properties of the ternary compound $LiKMgCl_4$ are shown in Table I. Calculations

suggest that the compound melts congruently, but is very close to melting incongruently.

H. *The NaCl-KCl-$MgCl_2$ System*

The liquidus projection has been measured by thermal analysis[50] (Figure 25). The $KMgCl_3$-NaCl phase diagram has been measured by conductivity techniques[51] (Figure 27) and evidence of solid solubility between Na_2MgCl_4-K_2MgCl_4 and $NaMgCl_3$-$KMgCl_3$ is reported along with a ternary incongruent compound $NaKMgCl_4$ associated with a peritectic at 398°C. No evidence of solid solution of Na^+ in $K_3Mg_2Cl_7$ is reported. The activity of $MgCl_2$ in the liquid has been measured by emf techniques[28,52] (Figures 28 to 30). In order to reproduce the activity data[28,52], small ternary excess parameters must be added to the respective binary pair energies of formation :

$$g^{001}_{NaMg(K)/Cl} = -1255.2 \text{ J/mol} \quad [39]$$

$$g^{011}_{NaMg(K)/Cl} = -2510.4 \text{ J/mol} \quad [40]$$

$$g^{001}_{KMg(Na)/Cl} = -5857.6 \text{ J/mol} \quad [41]$$

$$g^{011}_{KMg(Na)/Cl} = -4184.0 \text{ J/mol} \quad [42]$$

$NaMgCl_3$ and $KMgCl_3$ are miscible to an unknown extent, as are Na_2MgCl_4 and K_2MgCl_4. Na^+ is assumed to be insoluble in $K_3Mg_2Cl_7$. A regular solution model is used for both the $(Na,K)MgCl_3$ (Eq.[43]) and $(Na,K)_2MgCl_4$ (Eq.[44]) solid solutions as described in Section V-G. No $NaKMgCl_4$ compound[50] was considered in the evaluation. However, note that the $(Na,K)_2MgCl_4$ solid solution appears as a line in Figure 27.

$$g^E = 6903.6 X_{NaMgCl_3} X_{KMgCl_3} \text{ J/mol of } (Na,K)MgCl_3 \quad [43]$$

$$g^E = -5020.8 X_{Na_2MgCl_4} X_{K_2MgCl_4} \text{ J/mol of } (Na,K)_2MgCl_4 \quad [44]$$

Figures 26 to 30 show the calculated phase diagram and thermodynamic properties.

I. *Other Alkali-Chloride $MgCl_2$ Ternary Systems*

No experimental data were found for the LiCl-RbCl-$MgCl_2$, LiCl-CsCl-$MgCl_2$, NaCl-RbCl-$MgCl_2$, NaCl-CsCl-$MgCl_2$, KCl-RbCl-$MgCl_2$, KCl-CsCl-$MgCl_2$ and RbCl-CsCl-$MgCl_2$ systems. For calculational purposes one can assume complete solid solubility among $KMgCl_3$-$RbMgCl_3$-$CsMgCl_3$. An ideal solution is suggested. Very limited solid solubility is expected for $NaMgCl_3$ and $LiMgCl_{3\ hyp.}$ in $(Rb,Cs)MgCl_3$. A similar treatment for K_2MgCl_4-Rb_2MgCl_4-Cs_2MgCl_4 is suggested, with no solubility of Na_2MgCl_4 and $Li_2MgCl_{4\ hyp}$ in $(Rb,Cs)_2MgCl_4$.

VI. MIXTURES OF ALKALI CHLORIDES WITH $CaCl_2$

A. *The LiCl-$CaCl_2$ System*

The liquidus has been measured by DTA and thermal analysis[9,53-58] (Figure 31). An intermediate compound $LiCaCl_3$ is reported[9,54,55] with an upper decomposition temperature of 441±3°C (below the eutectic), and some authors[55] have reported solubility of $CaCl_2$ in LiCl and of LiCl in $CaCl_2$ (up to 16 mol% in both cases). However, the experimental liquidus points agree closely with Eq.[20]. Hence, very limited solid solubility is expected. The enthalpy of mixing of the liquid has been measured calorimetrically[27] (Figure 32). The activity of LiCl in the liquid has been measured by an emf technique[13] (Figure 33). The optimized Gibbs energy of reaction [1] for the Li-Cl-Ca pair is :

$$\Delta g_{LiCa/Cl} = -682.4 - 24.2\chi_{Alk} - 299.6\chi_{AlkE} \text{ J/mol} \quad [45]$$

Figures 31 to 33 show the calculated phase diagram and thermodynamic properties.

B. *The NaCl-$CaCl_2$ System*

The phase diagram has been measured by DTA, thermal analysis and XRD[16,19,59-68] (Figure 34). An intermediate incongruent compound Na_4CaCl_6 was reported by some authors[16,63], while the other authors reported a large solubility of $CaCl_2$ in solid NaCl (up to 20 mol%) which is in agreement with the limiting slope of the liquidus (Eq.[20]). The enthalpy of mixing of the liquid has been measured by calorimetry[27,69] (Figure 32). The activity of NaCl in the liquid has been measured by emf techniques[13,27] (Figure 35). The optimized Gibbs energy of reaction [1] for the Na-Cl-Ca pair is :

$$\Delta g_{NaCa/Cl} = -4710.2 + 0.7805T + (-1347.8 + 0.5726T)\chi_{Alk} + (-1580.0 + 0.1473T)\chi_{AlkE} \text{ J/mol} \quad [46]$$

The NaCl solid solution is modelled as a mixture of Na^+ and associated Ca^{2+}-vacancy pairs. This is the same as the model used for solutions of $MgCl_2$ in solid LiCl in Section V-A.

$$g = X_{NaCl} g^{o,S}_{NaCl} + X_{CaCl_2}\left(g^{o,S}_{CaCl_2} + 33676.0 - 30.0982T\right) + RT\left(X_{NaCl}\ln X_{NaCl} + X_{CaCl_2}\ln X_{CaCl_2}\right) \text{ J/mol} \quad [47]$$

Figures 32, 34 and 35 show the calculated phase diagram and thermodynamic properties.

C. *The KCl-$CaCl_2$ System*

The phase diagram has been measured by DTA[16,68,70-73] (Figure 36). All authors reported the $KCaCl_3$ congruent compound. Possible solid solubility is reported[73] but the liquidus points agree well with Eq.[20], so only very limited solid solubility is expected.

The enthalpy of mixing of the liquid has been measured by calorimetry[27,69] (Figure 32). The activity of KCl in the liquid has been measured by emf techniques[13,27,37,74,75] (Figure 37). Seifert *et al.*[38] used an emf technique to measure the Gibbs energy of formation of $KCaCl_3$ from solid KCl and $CaCl_2$ between 700K and 800K, obtaining −19.19 kJ/mol at 700K and −20.16 kJ/mol at 800K. Corresponding optimized values are −19.00 and -20.34 kJ/mol. Seifert *et al.*[38] also measured the enthalpy of formation of $KCaCl_3$ from KCl(s) and $CaCl_2$(s) by solution calorimetry as −15.2±0.6 kJ/mol. The optimized value is −15.2 kJ/mol. Hattori *et al.*[43] measured the enthalpy of fusion of $KCaCl_3$ at 748°C as 69.45 kJ/mol; the calculated value is 45.71 kJ/mol. The optimized value of C_p for the $KCaCl_3$ compound is 144.604 J/mol-K which is very close to the sum of the heat capacities of KCl(s) and $CaCl_2$(s) The optimized Gibbs energy of reaction [1] for the K-Cl-Ca pair is :

$$\Delta g_{KCa:Cl} = -12281.0 + 3.9706T - 852.6\chi_{Alk} - 5930.6\chi_{AlkE} \quad \text{J/mol} \quad [48]$$

Figures 32, 36 and 37 show the calculated phase diagram and thermodynamic properties.

D. *The RbCl-$CaCl_2$ System*

The phase diagram has been measured by DTA[71,76,77] (Figure 38). All authors reported one congruently melting compound, $RbCaCl_3$, but there is strong disagreement on its temperature of fusion (855°C[76], 840°C[77] and 930°C[71]). No solid solubility is reported and the limiting liquidus slopes agree with Eq.[20].

The enthalpy of mixing of the liquid has been measured by calorimetry[27] (Figure 32). The activity of RbCl in the liquid has been measured by emf techniques[27,74] (Figure 39). Seifert and Thiel[45] measured the Gibbs energy of formation of $RbCaCl_3$ from solid RbCl and $CaCl_2$ by an emf technique at 700K and 800K as −29.68 and −30.62 kJ/mol respectively. Optimized values are −29.37 and −30.29 kJ/mol. Seifert and Thiel[45] also measured, by solution calorimetry, the enthalpy of formation of $RbCaCl_3$ from solid RbCl and $CaCl_2$ as −24.2 kJ/mol. The optimized value is −24.85 kJ/mol. The C_p of $RbCaCl_3$ was optimized as 135 J/mol-K which is close to the sum of the heat capacities of RbCl(s) and $CaCl_2$(s). The liquidus points and temperature of fusion of $RbCaCl_3$ of Shakhno and Plyushchev[76] and Gromakov[77] were favored over those of Dergunov and Bergman[71] because most ternary liquidus projections agree with the former, and because other authors[27,74] report enthalpy and activity measurements in single-phase liquid solutions at compositions and temperatures where Dergunov and Bergman[71] report a 2-phase region. Also, for the CsCl-$CaCl_2$ system, the same authors disagree on the melting point of $CsCaCl_3$, but a third author supports the measurements of Shakhno and Plyushchev[76] over those of Dergunov and Bergman[71] (see next section). The optimized Gibbs energy of reaction [1] for the Rb-Cl-Ca pair is :

$$\Delta g_{RbCa:Cl} = -11668.0 + 0.9375T + (-4179.0 + 4.5342T)\chi_{Alk} + (-12662.0 + 7.2799T)\chi_{AlkE} \quad \text{J/mol} \quad [49]$$

The calculated activities of RbCl (Figure 39) are much lower than the experimental data[74] for mole fractions of $CaCl_2$ higher than 0.4. However, the experimental activity data[74] are closer to those in the NaCl-$CaCl_2$ systems (Figure 35) at the same composition, whereas one would expect that they would be even lower than in the KCl-$CaCl_2$ system (following the same trend as the alkali chloride activities when mixed with $MgCl_2$). That is, the experimental activity data[74] are most likely too high. Figures 32, 38 and 39 show the calculated phase diagram and thermodynamic properties.

E. *The CsCl-$CaCl_2$ System*

The phase diagram has been measured by DTA[71,76,78] (Figure 40). Only one congruently melting compound is reported. No solid solubility was reported. There is a disagreement on the temperature of fusion of $CsCaCl_3$: 910°C[76], 908°C[78] and 930°C[71]. The enthalpy of mixing of the liquid has been measured by calorimetry[27] (Figure 32). No activity data are reported. Liquidus data of Dergunov and Bergman[71] are rejected for reasons similar to those evoked for the RbCl-$CaCl_2$ system. The optimized Gibbs energy of reaction [1] for the Cs-Cl-Ca pair is:

$$\Delta g_{CsCa:Cl} = -15595.0 - 3.6829T + 1610.0\chi_{Alk} - 8744.0\chi_{AlkE} \quad \text{J/mol} \quad [50]$$

Figures 32 and 40 show the calculated phase diagram and thermodynamic properties.

F. *The LiCl-NaCl-$CaCl_2$ System*

The liquidus projection has been reported[79,80] (Figure 41[79]). Since $CaCl_2$ is soluble in NaCl and since LiCl and NaCl form an extended solid solution, $CaCl_2$ must be soluble in the binary LiCl-NaCl solid solution in the NaCl-rich corner; that is, ternary LiCl-NaCl-$CaCl_2$ solid solution must be present. Unfortunately, no experimental data are available. The following expression was used for the Gibbs energy of the solid phase. Parameters in Eq.[51] for the NaCl-$CaCl_2$ binary solution are taken from Eq.[47], while the parameters 9800.0 and −5200.0 are the optimized parameters for the LiCl-NaCl solid solution reported previously[5]. The final term in Eq.[51] assures virtual immiscibility between solid LiCl and $CaCl_2$ while allowing

some limited ternary solubility in NaCl-rich solutions. The dashed line on Figure 42 gives the calculated maximum extent of ternary solid solution in equilibrium with the ternary liquid along the univariant line.

$$
\begin{aligned}
g &= X_{LiCl} g^{o,S}_{LiCl} + X_{NaCl} g^{o,S}_{NaCl} \\
&+ X_{CaCl_2}\left(g^{o,S}_{CaCl_2} + 33676.0 - 30.0982T\right) \\
&+ RT\left(X_{LiCl}\ln X_{LiCl} + X_{NaCl}\ln X_{NaCl} + X_{CaCl_2}\ln X_{CaCl_2}\right) \\
&+ \frac{9800.0 X_{LiCl} X_{NaCl}}{\left(X_{LiCl} + X_{NaCl} + 2X_{CaCl_2}\right)} \\
&- \frac{5200.0 X_{LiCl} X_{NaCl}}{\left(X_{LiCl} + X_{NaCl} + 2X_{CaCl_2}\right)}\left(\frac{X_{NaCl}}{X_{LiCl} + X_{NaCl}}\right) \\
&+ 100000\frac{2X_{LiCl}X_{CaCl_2}\left(1 - X_{NaCl}/\left(X_{LiCl} + X_{NaCl} + 2X_{CaCl_2}\right)\right)}{\left(X_{LiCl} + X_{NaCl} + 2X_{CaCl_2}\right)}
\end{aligned}
$$

J/mol [51]

A small excess ternary term was introduced for the liquid phase :

$$g^{001}_{LiNa(Ca)/Cl} = 4184.0 \text{ J/mol} \qquad [52]$$

G. *The LiCl-KCl-$CaCl_2$ System*

The liquidus projection has been measured[79,81] (Figure 43[79]). Both studies reported two ternary eutectics at 425°C[79] or 412°C[81] and at 340°C[79] or 332°C[81]. The saddle point between LiCl and $KCaCl_3$ was reported at 52 mol% $KCaCl_3$ and 48 mol% Li_3Cl_3 at 442°C[81]. No ternary solid solubility was reported. A small ternary excess parameter was included :

$$g^{001}_{KCa(Li)/Cl} = -4184.0 \text{ J/mol} \qquad [53]$$

The calculated liquidus projection is shown on Figure 44. The saddle point is calculated at 52.7% $KCaCl_3$ and 47.3 Li_3Cl_3 at 445°C. No solubility of Li^+ in $KCaCl_3$ is assumed. From comparison of calculated and experimental liquidus projections, this assumption seems justified.

H. *The NaCl-KCl-$CaCl_2$ System*

The liquidus projection has been measured[19,68,82] (Figure 45[19]). The ternary eutectic was reported at 504°C[19] and at 465°C[82]. The univariant line between $KCaCl_3$ and the (K,Na)Cl solid solution is reported by all authors to have a minimum (532°C[19], 515°C[82] and <540°C[68]) and a maximum (saddle point) (558°C[19] and <560°C[68]). No ternary solid solubility is reported. The enthalpy of mixing of the ternary liquid has been measured by calorimetry[69] (see Table III).

Since $CaCl_2$ is soluble in NaCl and since KCl and NaCl form an extended solid solution, $CaCl_2$ must be soluble in the binary KCl-NaCl solid solution in the NaCl-rich corner. The Gibbs energy expression for the solid phase in Eq.[54] is very similar to Eq.[51]. Binary parameters in Eq.[54] were taken from Eq.[47] for the NaCl-$CaCl_2$ solid solution and from Robelin[7] for the NaCl-KCl solid solution. The dashed line on Figure 46 gives the calculated maximum extent of ternary solid solution in equilibrium with the ternary liquid along the univariant line.

$$
\begin{aligned}
g &= X_{KCl} g^{o,S}_{KCl} + X_{NaCl} g^{o,S}_{NaCl} \\
&+ X_{CaCl_2}\left(g^{o,S}_{CaCl_2} + 33676.0 - 30.0982T\right) \\
&+ RT\left(X_{KCl}\ln X_{KCl} + X_{NaCl}\ln X_{NaCl} + X_{CaCl_2}\ln X_{CaCl_2}\right) \\
&+ \frac{X_{KCl} X_{NaCl}}{\left(X_{KCl} + X_{NaCl} + 2X_{CaCl_2}\right)}\left(14333.0 + 32.7960T - 5.5980T\ln T\right) \\
&+ \frac{3278.0 X_{KCl} X_{NaCl}}{\left(X_{KCl} + X_{NaCl} + 2X_{CaCl_2}\right)}\left(\frac{X_{NaCl}}{X_{KCl} + X_{NaCl}}\right) \\
&+ 100000\frac{2X_{KCl}X_{CaCl_2}\left(1 - X_{NaCl}/\left(X_{KCl} + X_{NaCl} + 2X_{CaCl_2}\right)\right)}{\left(X_{KCl} + X_{NaCl} + 2X_{CaCl_2}\right)}
\end{aligned}
$$

J/mol [54]

The calculated liquidus projection is shown in Figure 46. The calculated enthalpy of mixing of the liquid is given in Table III. No ternary excess parameters for the liquid phase were required. No solid solubility of Na^+ in $KCaCl_3$ was assumed.

I. *The LiCl-RbCl-$CaCl_2$ System*

The liquidus projection has been measured[56] (Figure 47). No solid solubility was reported. A small liquid ternary paremeter was found necessary to reproduce the liquidus surface of this system :

$$g^{001}_{RbCa(Li)/Cl} = -4184.0 \text{ J/mol} \qquad [55]$$

The calculated liquidus surface is shown in Figure 48. No ternary solid solubility of Li^+ in $RbCaCl_3$ was assumed, and the ternary liquidus data are well reproduced with this assumption. Sangster and Pelton[5], from whom the optimization of the LiCl-RbCl subsystem was taken, included the $LiRbCl_2$ incongruent solid phase which is not present on the diagram of Il'yasov *et al.*[56]. For this reason, the calculated eutectic temperature of 305°C is different from the reported value of 270°C[56]. If $LiRbCl_2$ is not included in the equilibrium calculation (this is the same as considering this phase metastable), the calculated eutectic is then at 280°C.

J. *The NaCl-RbCl-$CaCl_2$ System*

Pluyshchev *et al.*[61] measured the liquidus surface (Figure 49). They reported two ternary eutectics at 500°C and 505°C, and a saddle point near 599°C. No solid solubility was reported. A small liquid ternary parameter was required :

$$g^{001}_{RbCa(Na)/Cl} = -2092.0 \quad \text{J/mol} \qquad [56]$$

The calculated liquidus surface is shown in Figure 50. No ternary solid solubility of Na^+ in $RbCaCl_3$ was assumed.

K. *The KCl-RbCl-CaCl₂ System*

The liquidus projection has been measured[79] (Figure 51). Complete solid solution between $KCaCl_3$ and $RbCaCl_3$ was reported. The calculated liquidus projection is shown in Figure 52. No liquid ternary excess parameters were added for calculation. A simple regular solution model was used for the $KCaCl_3$-$RbCaCl_3$ solid solution :

$$g^E = 4184.0 X_{KCaCl_3} X_{RbCaCl_3} \quad \text{J/mol} \qquad [57]$$

L. *The LiCl-CsCl-CaCl₂ System*

No experimental data were found for the LiCl-CsCl-$CaCl_2$ system. No ternary liquid interaction parameter was added to the liquid model. It is suggested for calculational purposes that Li^+ be assumed insoluble in $CsCaCl_3$.

M. *The NaCl-CsCl-CaCl₂ System*

Plyushchev *et al.*[83] measured the liquidus surface (Figure 53). No solid solubility of Na^+ in $CsCaCl_3$ was reported and none was assumed for calculations. No ternary excess parameters for the liquid phase were added. The calculated liquidus surface is shown in Figure 54.

N. *The KCl-CsCl-CaCl₂ System*

Plyushchev *et al.*[79] measured the liquidus surface (Figure 55), reporting a complete solid solution between $KCaCl_3$ and $CsCaCl_3$. No ternary excess parameters for the liquid phase were required. A regular solution model was used for the $KCaCl_3$-$CsCaCl_3$ solid solution :

$$g^E = 5020.8 X_{KCaCl_3} X_{CsCaCl_3} \quad \text{J/mol} \qquad [58]$$

The calculated liquidus projection is shown in Figure 56.

O. *The RbCl-CsCl-CaCl₂ System*

Dergunov and Bergman[71] measured the liquidus surface (Figure 57), reporting a complete solid solution between $RbCaCl_3$ and $CsCaCl_3$. Their reported melting temperatures of both $RbCaCl_3$ and $CsCaCl_3$ are much higher than the melting temperatures found with the present binary optimizations (see Sections VI-D & E). For this reason, the calculated phase diagram (Figure 58) is in disagreement with the reported[71] liquidus projection. Since complete solid solubility between $RbCaCl_3$ and $CsCaCl_3$ is reported by these authors, it was assumed for calculational purposes that the solids mix ideally. No ternary excess parameters for the liquid phase were used.

VII. MIXTURES OF ALKALI CHLORIDES WITH $MgCl_2$ AND $CaCl_2$

A. *The MgCl₂-CaCl₂ System*

The phase diagram was measured by DTA[16,84,85] (Figure 59). The maximum solubility of $MgCl_2$ in solid $CaCl_2$ is reported to be less than 18 mol% $MgCl_2$. Karakaya and Thompson[86] measured, by an emf technique, the activity of $MgCl_2$ in the melt (Figure 60). Figure 61 shows the enthalpy of mixing of the liquid obtained from the smoothed temperature dependence of the emf[87]. The optimized Gibbs energy of reaction [1] for the Mg-Cl-Ca pairs is :

$$\Delta g_{MgCa/Cl} = 437.6 - 0.5171T + (1467.6 - 0.1921T)\chi_{MgMg} + (-730.2 + 1.6255T)\chi_{CaCa} \quad \text{J/mol} \qquad [59]$$

The optimized Gibbs energy of the solid solution of $MgCl_2$ in $CaCl_2$ is given by Eq.[60].

$$g = X_{CaCl_2} g^{o,S}_{CaCl_2} + X_{MgCl_2}\left(g^{o,S}_{MgCl_2} + 29550.2 - 18.4261T\right) + RT\left(X_{CaCl_2} \ln X_{CaCl_2} + X_{MgCl_2} \ln X_{MgCl_2}\right) \quad \text{J/mol} \qquad [60]$$

Figures 59 to 61 show the calculated phase diagram and thermodynamic properties.

B. *The NaCl-MgCl₂-CaCl₂ System*

No experimental liquidus projection is reported for this system. The activity of NaCl in the liquid has been measured by an emf technique[27] for different $MgCl_2$ / ($MgCl_2$ + $CaCl_2$) molar ratios (Figure 62). Karakaya and Thompson[87] measured, by an technique emf, the activity of $MgCl_2$ at 800°C at three different NaCl / (NaCl + $CaCl_2$) ratios (Figure 63). No ternary parameters were required. No solubility of Ca^{2+} was assumed in the $NaMgCl_3$ and Na_2MgCl_4 compounds. The calculated (predicted) liquidus projection is shown in Figure 64.

C. *The KCl-MgCl₂-CaCl₂ System*

A liquidus projection is reported[85] (Figure 65). Zhu *et al.*[88] measured, by an emf technique, the activity of $MgCl_2$ in the liquid for various KCl/$CaCl_2$ molar ratios (Figure 67). No ternary excess parameters were used for the liquid phase. In order to reproduce the measured[85] $KMgCl_3$ and $KCaCl_3$ liquidus curves, a solid solution is required between these compounds. Since a univariant line is reported crossing the $KCaCl_3$-$KMgCl_3$ join (Figure 65), $KCaCl_3$ and $KMgCl_3$ can not be completely miscible. The optimized excess Gibbs energy of the $KMgCl_3$-$KCaCl_3$ solid solution is given by a subregular model (Eq.[61]). No solubility of Ca^{2+} in K_2MgCl_4 or $K_3Mg_2Cl_7$ was assumed. The calculated liquidus projection is shown in Figure 66.

The calculated activities of $MgCl_2$ for $KCl/CaCl_2$ molar ratios of ½ and 2 are shown in Figure 67.

$$g^E = X_{KMgCl_3} X_{KCaCl_3} \left(17573.0 - 9205.0\left(X_{KMgCl_3} - X_{KCaCl_3}\right)\right) \quad \text{J/mol} \qquad [61]$$

D. *Other Ternary Systems with $MgCl_2$ and $CaCl_2$*

No reported data were found for the $LiCl-MgCl_2-CaCl_2$, $RbCl-MgCl_2-CaCl_2$ and $CsCl-MgCl_2-CaCl_2$ systems. One can expect very limited Ca^{2+} solubilities in Mg-perovskites, while larger solubilities of Mg^{2+} in Ca-perovskites should be observed.

E. *The $NaCl-KCl-MgCl_2-CaCl_2$ Quaternary System*

The liquidus projection of the $NaCl-KCl-MgCl_2-CaCl_2$ system at a constant KCl/NaCl weight ratio of 8 was reported[89] (Figure 68). The calculated liquidus projection at the same KCl/NaCl weight ratio is shown in Figure 69. No additional parameters for the liquid phase were used.

Wallevik[90] obtained a cooling curve of a 36.6% $MgCl_2$, 22.7% $CaCl_2$, 39.2% NaCl and 1.5% KCl (by weight) mixture, with thermal arrests at 434°C and 427°C and final solidification at 404°C (with an error of ±4°C). DSC[90] of the same mixture gave peaks at 431 to 436°C, 420 to 424°C and 404°C (with an error of ±4°C). The calculations predict thermal arrests at 433°C and 414°C with final solidification at 406°C.

VIII. GENERAL MODEL FOR SOLID SOLUTIONS

The possible multicomponent solid solutions present in this system are the $(Li,Na,K,Rb,Cs)(Mg,Ca)Cl_3$ perovskite solution, the $(Li,Na,K)_2MgCl_4$ solid solution and the (Li,Na,K,Rb,Cs,[Ca])Cl solid solution. Excess mixing parameters have been given in this article for many subsystems. The compound energy model[15] is suitable for estimating the Gibbs energy of the multicomponent solid solutions, but this model requires that the Gibbs energy of all possible pure mixing components be defined, including metastable (or hypothetical) compounds such as $LiMgCl_3$, $NaCaCl_3$, etc. The hypothetical Gibbs energy of formation of $LiMgCl_3$ and Li_2MgCl_4 from solid pure salts are defined in Eqs.[36] and [38]. Furthermore, we arbitrarily set:

$$g^{o,hyp}_{LiCaCl_3} = g^{o,S}_{LiCl} + g^{o,S}_{CaCl_2} + 20000 \quad \text{J/mol} \qquad [62]$$

$$g^{o,hyp}_{NaCaCl_3} = g^{o,S}_{NaCl} + g^{o,S}_{CaCl_2} + 20000 \quad \text{J/mol} \qquad [63]$$

where the large positive value of +20 kJ/mol assures negligible solubility with other perovskites. The excess Gibbs energy of all binary subsystems must also be defined. For subsystems where immiscibility is observed, a very large positive regular excess Gibbs energy parameter (+100 kJ/mol) is proposed so that virtual immiscibility is calculated : $Li_2MgCl_4-Na_2MgCl_4$, $LiMgCl_3-NaMgCl_3$, $LiMgCl_3-RbMgCl_3$, $LiMgCl_3-CsMgCl_3$, $NaMgCl_3-RbMgCl_3$, $NaMgCl_3-CsMgCl_3$, $LiMgCl_3-LiCaCl_3$, $NaMgCl_3-NaCaCl_3$, $RbMgCl_3-RbCaCl_3$, $CsMgCl_3-CsCaCl_3$, $LiCaCl_3-NaCaCl_3$, $LiCaCl_3-KCaCl_3$, $LiCaCl_3-RbCaCl_3$, $LiCaCl_3-CsCaCl_3$, $NaCaCl_3-KCaCl_3$, $NaCaCl_3-RbCaCl_3$ and $NaCaCl_3-CsCaCl_3$. The Gibbs energy of the perovskite solid solution $(Li,Na,K,Rb,Cs)(Mg,Ca)Cl_3$ is then given by the compound energy model[15] as :

$$\begin{aligned} g = & \sum_{Alk=Li}^{Cs} \sum_{AlkE=Mg}^{Ca} y_{Alk} y_{AlkE} g^{o,S}_{Alk:AlkECl_3} \\ & + RT\left(\sum_{Alk=Li}^{Cs} y_{Alk} \ln y_{Alk} + \sum_{AlkE=Mg}^{Ca} y_{AlkE} \ln y_{AlkE} \right) \\ & + \sum_{Alk=Li}^{Rb} \sum_{Alk'=Alk+1}^{Cs} \sum_{AlkE=Mg}^{Ca} y_{Alk} y_{Alk'} y_{AlkE} \omega_{(Alk:Alk'):AlkECl_3} \\ & + \sum_{Alk=Li}^{Cs} y_{Alk} y_{Mg} y_{Ca} \omega_{Alk:(Mg,Ca)Cl_3} \end{aligned} \qquad [64]$$

where y_i is the sublattice ionic site fraction and all ω terms are binary regular or subregular parameters either optimized or fixed (+100 kJ/mol) for the binary subsystems. The Gibbs energy of the $(Li,Na,K)_2MgCl_4$ solid solution is similarly given by :

$$\begin{aligned} g = & \sum_{Alk=Li}^{K} y_{Alk} g^{o,S}_{Alk_2MgCl_4} + RT\left(2 \sum_{Alk=Li}^{K} y_{Alk} \ln y_{Alk} \right) \\ & + \sum_{Alk=Li}^{Na} \sum_{Alk'=Alk+1}^{K} y_{Alk} y_{Alk'} \omega_{(Alk:Alk')_2MgCl_4} \end{aligned} \qquad [65]$$

IX. CONCLUSIONS

A complete critical evaluation and optimization of all available phase diagram and thermodynamic data for all phases of the $LiCl-NaCl-KCl-RbCl-CsCl-MgCl_2-CaCl_2$ system has been made. All data are reproduced within experimental error limits. The new modified quasichemical model[1] was used for the liquid phase, while the compound energy model[15] was used for the $(Li,Na,K,Rb,Cs)(Mg,Ca)Cl_3$ perovskite phase and the $(Li,Na,K)_2MgCl_4$ and (Li,Na,K,Rb,Cs,[Ca])Cl solid solutions. From the optimized parameters of the binary and ternary subsystems it is possible, from the quasichemical model, to predict the thermodynamic properties of the multicomponent liquid solution. The database of optimized parameters is included in the F*A*C*T[93] database computing system and may be used, along with the other databases and Gibbs energy minimization software, to calculate phase equilibria and all thermodynamic properties in multicomponent systems.

The modified quasichemical model for short-range ordering in the pair approximation has been shown to be very applicable to molten salt systems involving cation-cation ordering. The present calculations also illustrate the feasibility of combining, in the same multicomponent

database, parameters of the quasichemical model for some subsystems with parameters of a simple polynomial (Bragg-Williams) model for other subsystems.

List of Symbols

R	gas constant (8.31451 J/mol-K).
T	absolute temperature (K).
X_i	global mole fraction of cation i.
X_{ACl}	global mole fraction of component ACl.
y_i	sublattice mole fraction of species i in Compound Energy Formalism.
g	molar Gibbs energy (J/mol).
$g^{o,S}_{ACl}$	standard molar Gibbs energy of component ACl (S = solid, L = liquid).
g^E	excess molar Gibbs energy in a random-mixing model.
$g^{ijk}_{AB(C)/Cl}$	a ternary interaction parameter which gives the effect of CCl on $\Delta g_{AB/Cl}$.
H^o_{298}	standard molar enthalpy at 298.15K (J/mol-K)
S^o_{298}	standard molar entropy at 298.15K (J/mol-K)
C_p	molar heat capacity (J/mol-K)
$\Delta g_{ij/Cl}$	Gibbs energy of the pair-exchange reaction $(i-Cl-i)_{pair}+(j-Cl-j)_{pair}=2(i-Cl-j)_{pair}$
X_{ij}	cation-cation pair (i-Cl-j) mole fraction.
Z^i_{ij}	cation-cation pair coordination number of species i.
χ_{Alk}	$\chi_{Alk}=\sum_{i=Li}^{Cs}\sum_{j=i}^{Cs}X_{ij}$
χ_{AlkE}	$\chi_{AlkE}=\sum_{i=Mg}^{Cs}\sum_{j=i}^{Cs}X_{ij}$

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Table I : Thermodynamic Properties of Compounds

		T Range K	$H^{o}_{298.15K}$ ** J/mol	$S^{o}_{298.15}$ J/mol-K	c_p J/mol-K	Ref.
LiCl	S	298.15-2000	-408266.4	59.2998	41.4174+0.0233969T	91
	L	298.15-2000	-395776.3	66.2774	73.3832–0.0094726T	91
NaCl	S	298.15-2000	-411119.8	72.1322	45.9403+0.0163176T	91
	L	298.15-1500	-394956.0	76.0761	77.7638–0.0075312T	91
	L	1500-2000	-390090.1	84.5055	66.9440	91
KCl	S	298.15-2500	-436684.1	82.5503	40.0158+0.0254680T+364845T^{-2}	91
	L	298.15-2500	-421824.9	86.5225	73.5966	91
RbCl	S	298.15-2000	-430533.6	91.6296	48.1160+0.0104182T	91
	L	298.15-2000	-418498.2	98.2792	64.0152	91
CsCl	α	298.15-2000	-442834.6	101.1817	45.8566+0.0220957T	91
	β	298.15-2000	-441267.3	101.2143	59.7308+0.0049371T	91
	L	298.15-2000	-434462.0	101.7186	77.4040	91
$MgCl_2$	S	298.15-2000	-641616.0	89.6290	54.5843+0.0214213T-1112119T^{-2} –0.23567x$10^{-5}T^2$ +399.177$T^{-0.5}$	92
	L	298.15-660	-601680.1	129.2359	193.4089-0.3620139T-3788504T^{-2} +0.0003199871T^2	92
	L	660-2500	-606887.4	117.2971	92.0480	92
$CaCl_2$	S	298.15-1045	-795797.0	104.6020	-338.8218+0.1092566T+7960391T^{-2} -179502.0T^{-1}+15395.460$T^{-0.5}$	92
	S	1045-2000	-793513.8	109.5584	56.3071+0.0293614T+140210T^{-2}	92
	L	298.15-700	-774100.6	123.8678	81.4793+0.0025417T-2789.1T^{-1}	92
	L	700-3000	-784431.8	101.5499	102.5330	92
$LiRbCl_2$	S	298.15-598	-841164.5	143.5742	137.3984-0.0094726T	5
$LiCs_2Cl_3$	S	298.15-656	-1329691.4	199.0689	228.1912-0.0094726T	5
$NaMgCl_3$	S	298.15-1000	-1053135.8	169.9454	90.0000+0.0750000T	*
Na_2MgCl_4	S	298.15-773.15	-1463435.7	243.9958	135.0000+0.1125000T	*
$KMgCl_3$	S	298.15-765	-1088217.8	183.2010	138.9000	*
K_2MgCl_4	S	298.15-715	-1536374.0	253.2299	208.0700	*
$K_3Mg_2Cl_7$	S	298.15-800	-2627241.8	434.5500	$C_p(KMgCl_3) + C_p(K_2MgCl_4)$	*
$KCaCl_3$	S	298.15-1100	-1247681.4	188.0694	144.6037	*
$RbMgCl_3$	S	298.15-873.15	-1103299.6	180.8402	137.5000	*
Rb_2MgCl_4	S	298.15-873.15	-1555683.2	250.6546	60.0000+0.3390000T	*
$RbCaCl_3$	S	298.15-1200	-1251181.0	200.7054	135.0000	*
$CsMgCl_3$	S	298.15-900	-1126215.9	189.2368	144.4600	*
Cs_2MgCl_4	S	298.15-900	-1570760.7	295.3761	230.0000	*
Cs_3MgCl_5	S	298.15-873.15	-1964069.8	479.3527	$3C_p(CsCl\alpha) + C_p(MgCl_2)$	*
$CsMg_3Cl_7$	S	298.15-1000	-2412150.0	$S^{o}_{CsMgCl_3} + 2S^{o}_{MgCl_2}$	$C_p(CsMgCl_3) + 2C_p(MgCl_2)$	*
$CsCaCl_3$	S	298.15-1200	-1288298.9	196.2057	140.0000	*
$LiKMgCl_4$	S	298.15-800	-1530802.7	208.7937	$C_p(LiCl)+C_p(KCl) + C_p(MgCl_2)$	*

* This work.

** Relative to elements at 298.15K.

Table II. Cation-cation "Coordination Numbers" of the Liquid.

i	j	Z^i_{ij}	Z^j_{ij}
Li	Li	6	6
Na	Na	6	6
K	K	6	6
Rb	Rb	6	6
Cs	Cs	6	6
Mg	Mg	6	6
Ca	Ca	6	6
Li	Na	6	6
Li	K	6	6
Li	Rb	6	6
Li	Cs	6	6
Li	Mg	3	5
Li	Ca	3	6
Na	K	6	6
Na	Rb	6	6
Na	Cs	6	6
Na	Mg	3	6
Na	Ca	4	6
K	Rb	6	6
K	Cs	6	6
K	Mg	3	6
K	Ca	3	6
Rb	Cs	6	6
Rb	Mg	3	6
Rb	Ca	3	6
Cs	Mg	3	6
Cs	Ca	3	6
Mg	Ca	6	6

Table III : Experimental[69] and Calculated Enthalpy of Mixing of NaCl-KCl-$CaCl_2$ Melts at 810°C.

Composition (mole fraction)			Enthalpy of mixing (kJ/mol)		Composition (mole fraction)			Enthalpy of mixing (kJ/mol)	
NaCl	KCl	$CaCl_2$	Exp.[69]	Calc.	NaCl	KCl	$CaCl_2$	Exp.[69]	Calc.
0.200	0.200	0.600	-6.00	-5.836	0.144	0.428	0.428	-7.91	-7.922
0.200	0.200	0.600	-5.96	-5.836	0.077	0.692	0.231	-6.56	-6.980
0.428	0.144	0.428	-5.16	-5.189	0.077	0.692	0.231	-6.23	-6.980
0.692	0.077	0.231	-3.57	-3.549	0.431	0.138	0.431	-5.32	-5.147
0.144	0.428	0.428	-8.01	-7.915	0.429	0.142	0.429	-5.52	-5.179
0.154	0.423	0.423	-7.99	-7.827	0.336	0.329	0.336	-6.29	-6.266
0.332	0.334	0.334	-6.49	-6.291	0.336	0.329	0.336	-6.37	-6.266
0.500	0.250	0.250	-4.86	-4.827	0.275	0.450	0.275	-6.32	-6.426
0.502	0.249	0.249	-4.93	-4.809	0.275	0.450	0.275	-6.23	-6.426
0.601	0.200	0.200	-4.06	-3.913	0.273	0.454	0.273	-6.67	-6.423
0.197	0.602	0.201	-6.07	-5.896	0.201	0.599	0.201	-5.77	-5.876
0.199	0.601	0.200	-6.03	-5.878	0.201	0.599	0.201	-5.59	-5.876
0.201	0.599	0.200	-6.00	-5.861	0.131	0.739	0.131	-4.46	-4.500
0.201	0.599	0.200	-6.04	-5.861	0.692	0.077	0.231	-3.54	-3.546
0.427	0.430	0.143	-4.31	-3.999	0.692	0.077	0.231	-3.56	-3.546
0.428	0.429	0.143	-4.31	-3.991	0.599	0.201	0.200	-4.10	-3.924
0.231	0.078	0.691	-4.00	-3.980	0.599	0.201	0.200	-4.11	-3.924
0.200	0.199	0.601	-5.56	-5.822	0.428	0.429	0.143	-4.00	-3.986
0.200	0.199	0.601	-6.23	-5.822	0.428	0.428	0.144	-3.99	-3.988
0.200	0.199	0.601	-6.06	-5.822	0.154	0.692	0.154	-2.75	-2.859
0.200	0.199	0.601	-5.91	-5.822	0.155	0.691	0.155	-2.70	-2.865
0.144	0.428	0.428	-7.36	-7.922	0.154	0.692	0.154	-2.86	-2.859

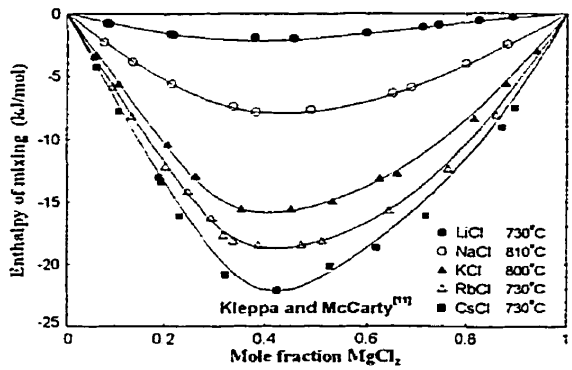

Fig. 1 - Calculated enthalpy of mixing of the liquid for the Alkali-Chlorides with $MgCl_2$ at the same respective temperature as the experimental points of Kleppa and McCarty[11].

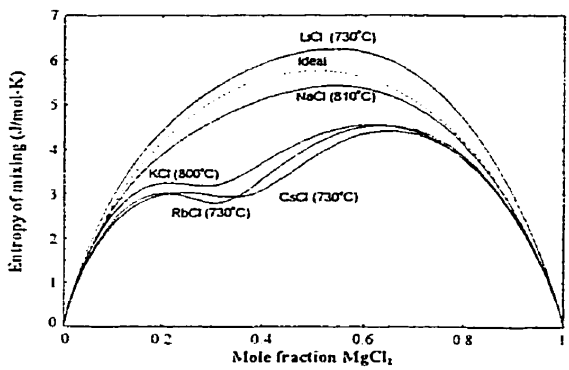

Fig. 2 - Calculated entropy of mixing of the liquid for the Alkali-Chlorides with $MgCl_2$.

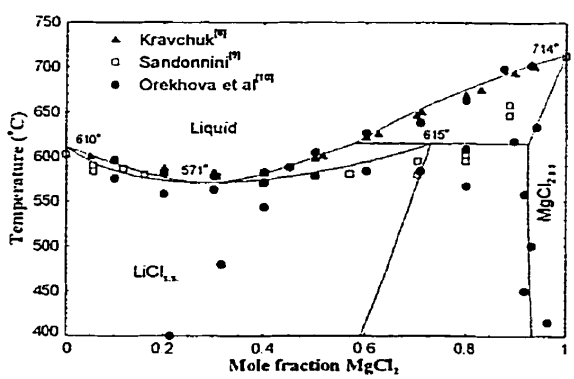

Fig. 3 - LiCl-$MgCl_2$ system : calculated phase diagram.

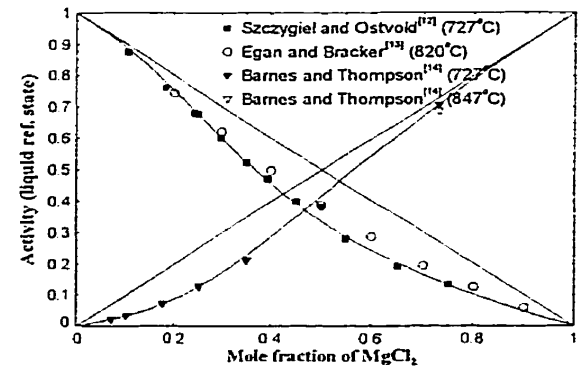

Fig. 4 – LiCl-$MgCl_2$ system : calculated activities in the liquid at 750°C (liquid ref. state).

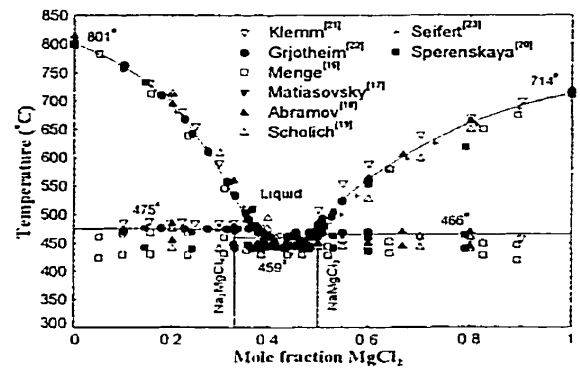

Fig. 5 - NaCl-$MgCl_2$ system: calculated phase diagram.

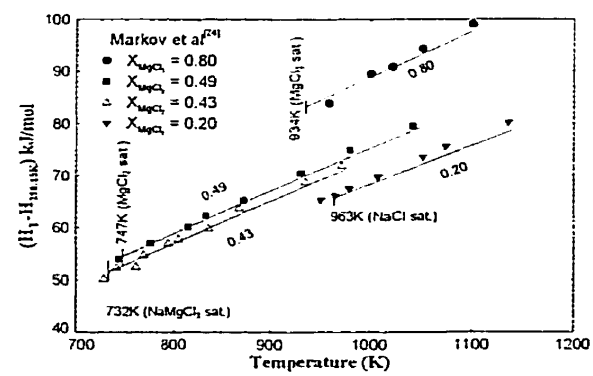

Fig. 6 – NaCl-$MgCl_2$ system : calculated H_T-$H_{298.15K}$ at X_{MgCl_2} = 0.2, 0.43, 0.49, 0.80 (points of Markov *et al.*[24]).

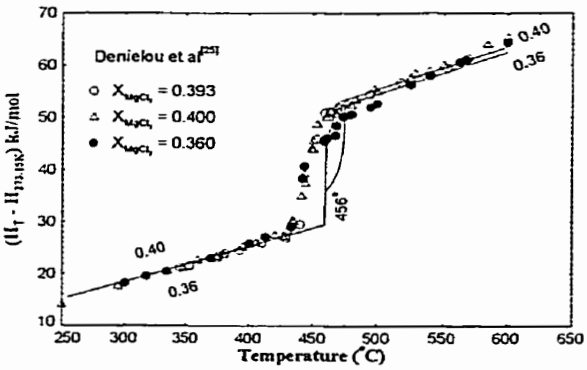

Fig. 7 – $NaCl-MgCl_2$ system : calculated $H_T-H_{273.15K}$ at X_{MgCl_2} = 0.36, 0.393 and 0.40 (points of Denielou *et al.*[25]).

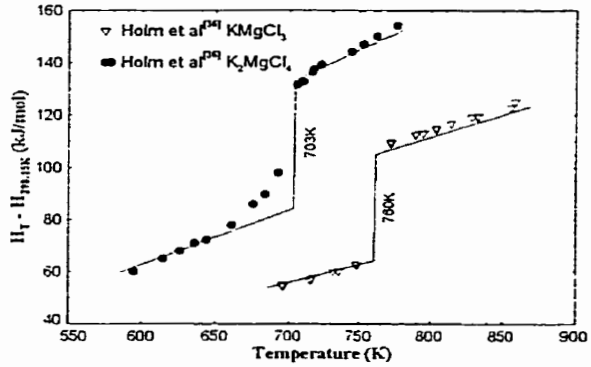

Fig. 10 – $KCl-MgCl_2$ system : calculated $H_T-H_{298.15K}$ at $KMgCl_3$ and K_2MgCl_4 compositions.

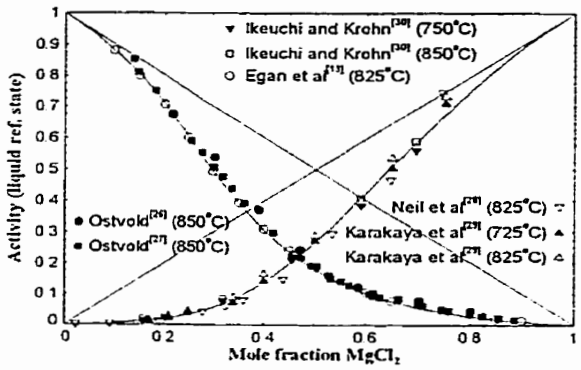

Fig. 8 - $NaCl-MgCl_2$ system : calculated activities in the liquid at 800°C (liquid ref. state).

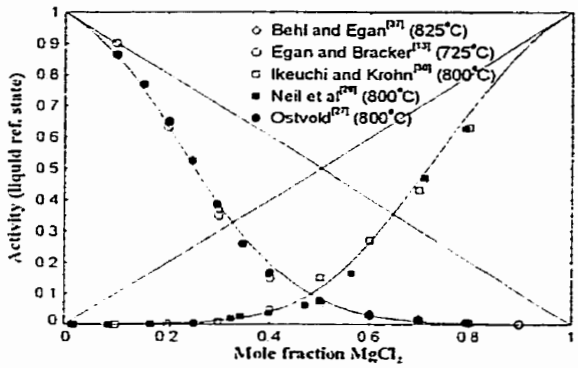

Fig. 11a – $KCl-MgCl_2$ system : calculated activities at 800°C in the liquid (liquid ref. state).

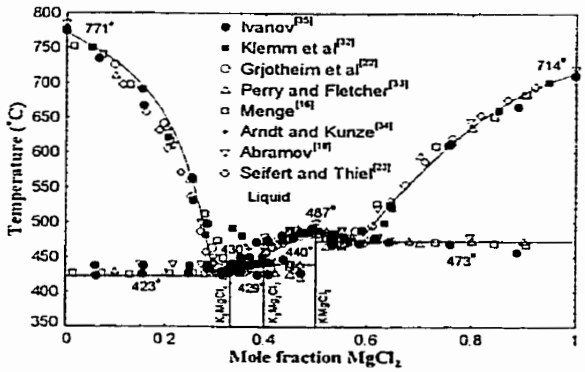

Fig. 9 - $KCl-MgCl_2$ system : calculated phase diagram.

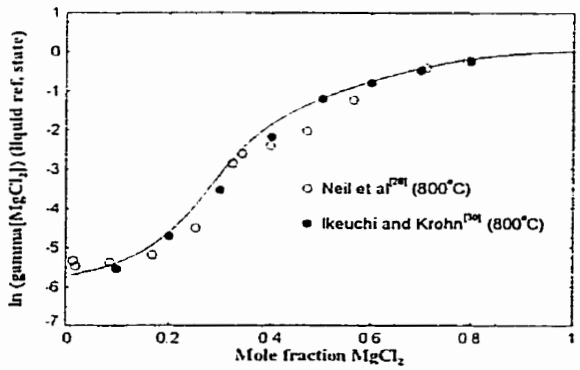

Fig. 11b – $KCl-MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid at 800°C (liquid ref. state).

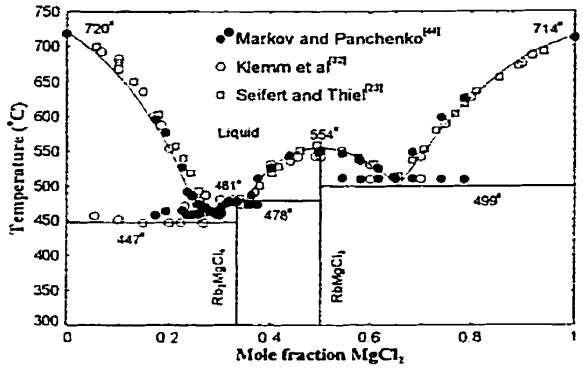

Fig. 12 – RbCl-$MgCl_2$ system : calculated phase diagram.

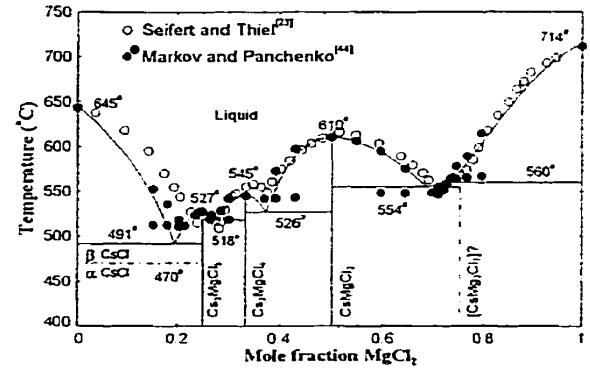

Fig. 15 – CsCl-$MgCl_2$ system : calculated phase diagram.

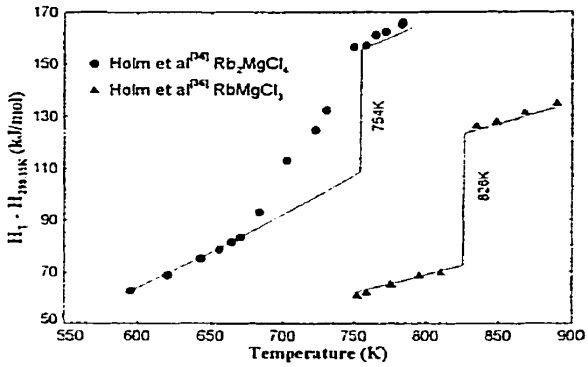

Fig. 13 - RbCl-$MgCl_2$ system : calculated H_T-$H_{298.15K}$ at $RbMgCl_3$ and Rb_2MgCl_4 compositions.

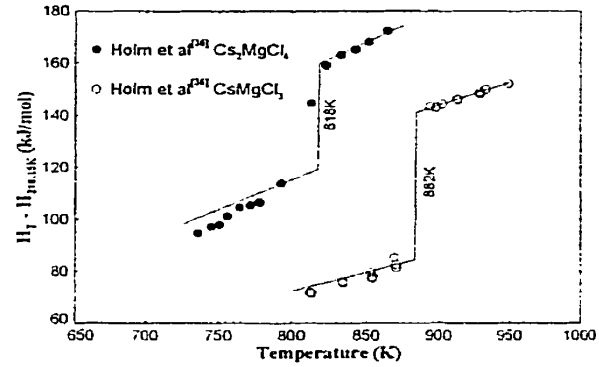

Fig. 16 - CsCl-$MgCl_2$ system : calculated H_T-$H_{298.15K}$ at $CsMgCl_3$ and Cs_2MgCl_4 compositions.

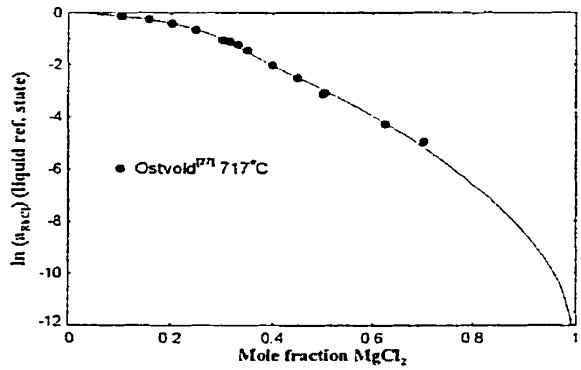

Fig. 14 - RbCl-$MgCl_2$ system : calculated activity of RbCl in the liquid at 717°C (liquid ref. state).

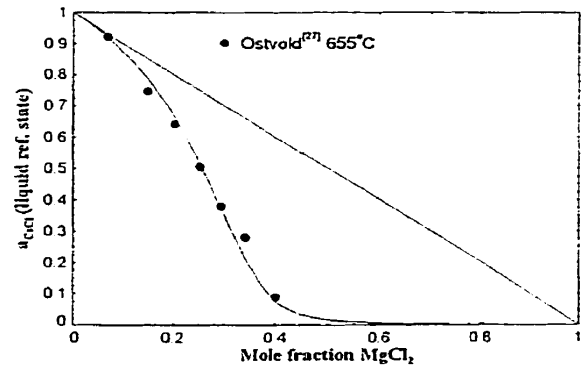

Fig 17 - CsCl-$MgCl_2$ system : calculated activity of CsCl in the liquid at 655°C (liquid ref. state).

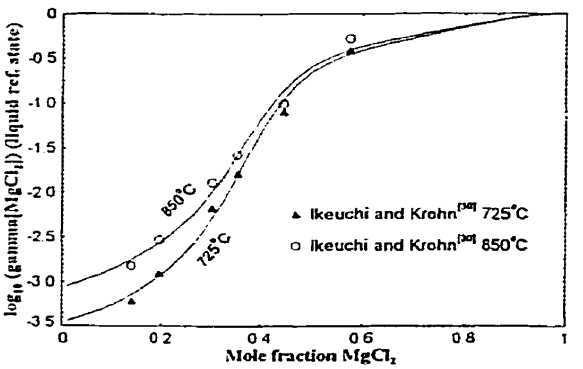

Fig. 18 - CsCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid (liquid ref. state).

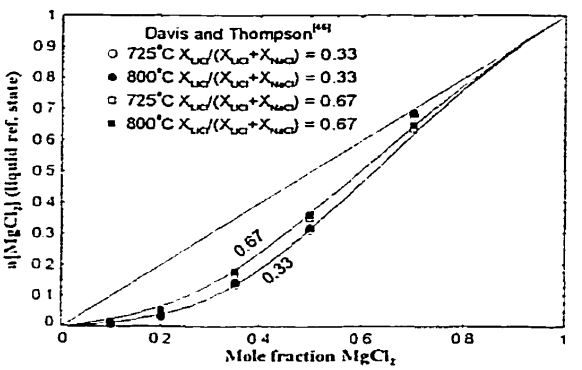

Fig. 19 – LiCl-NaCl-$MgCl_2$ system : calculated activity of $MgCl_2$ in the liquid at 800°C for 2 different LiCl / (LiCl + NaCl) molar ratios with experimental points of Davis and Thompson[46].

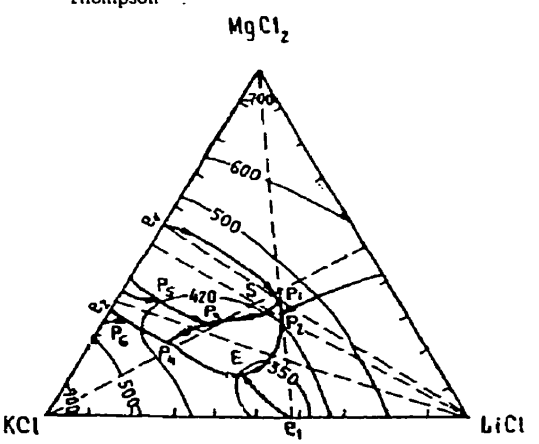

Fig. 20 – LiCl-KCl-$MgCl_2$ system : experimental liquidus projection of Podlesnyak *et al.*[47] (mol.%).

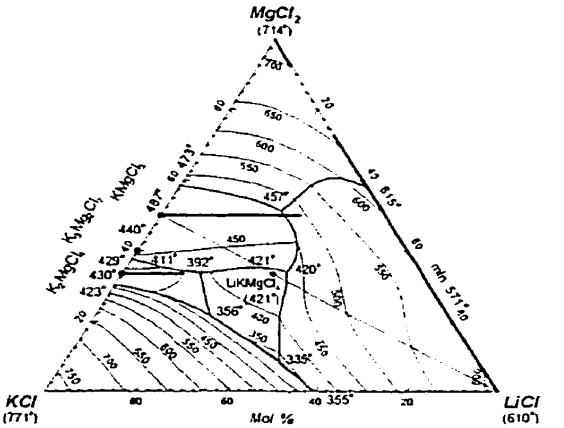

Fig. 21 - LiCl-KCl-$MgCl_2$ system : calculated liquidus projection.

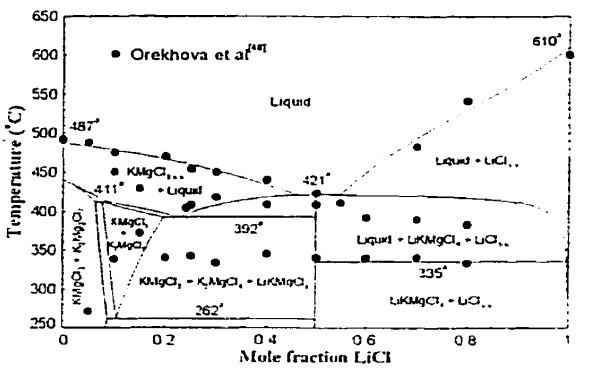

Fig. 22 - LiCl-KCl-$MgCl_2$ system . calculated $KMgCl_3$-LiCl join

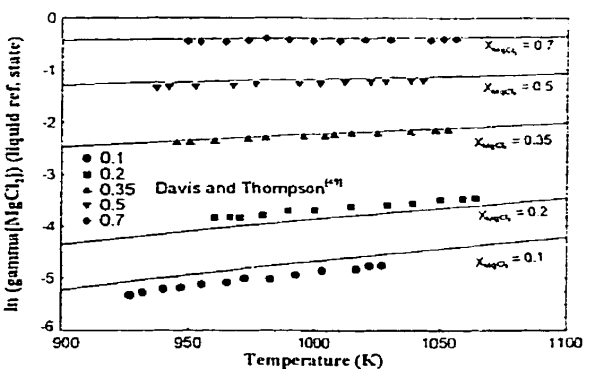

Fig. 23 – LiCl-KCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid for a LiCl / (LiCl + KCl) molar ratio of 1/3 with experimental points of Davis and Thompson[49].

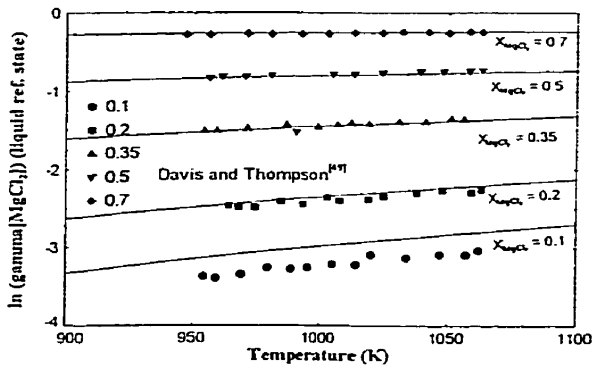

Fig. 24 – LiCl-KCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid for a LiCl / (LiCl + KCl) molar ratio of 2/3 with experimental points of Davis and Thompson[49].

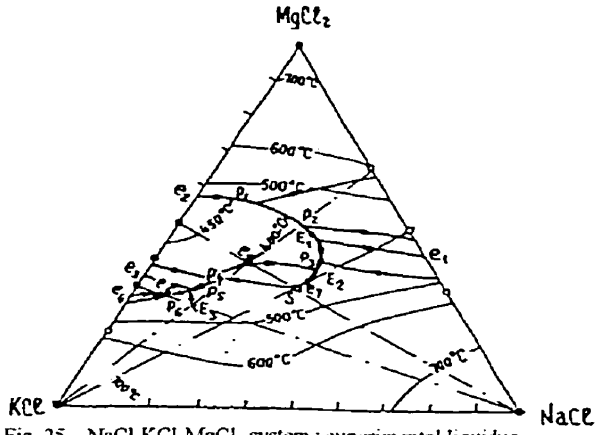

Fig. 25 – NaCl-KCl-$MgCl_2$ system : experimental liquidus projection of Orekhova *et al.*[50] (mol.%)

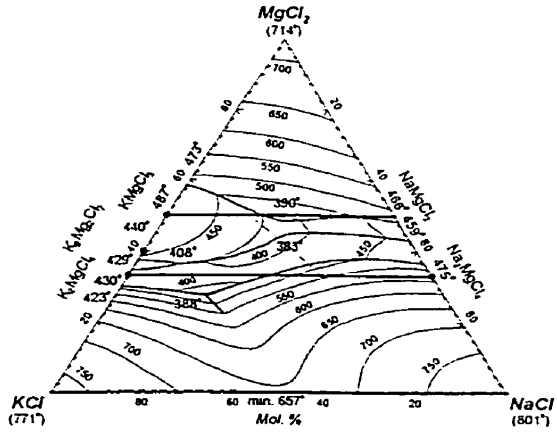

Fig. 26 - NaCl-KCl-$MgCl_2$ system : calculated liquidus projection.

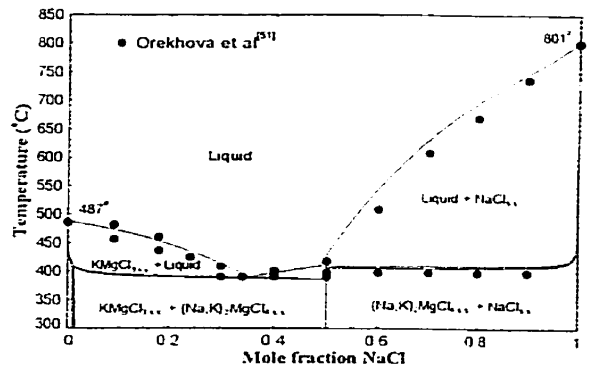

Fig. 27 - NaCl-KCl-$MgCl_2$ system : calculated $KMgCl_3$-NaCl join.

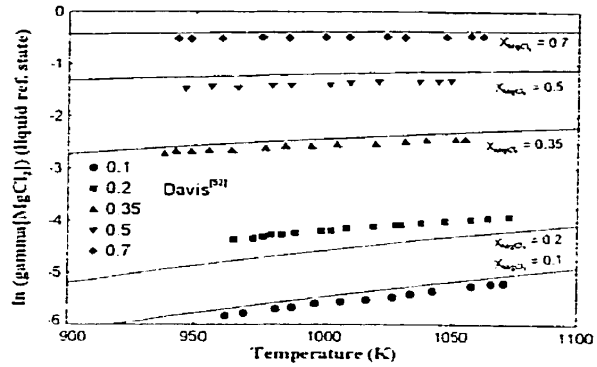

Fig. 28 - NaCl-KCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid for a NaCl / (NaCl + KCl) molar ratio of 1/3 with experimental points of Davis[52].

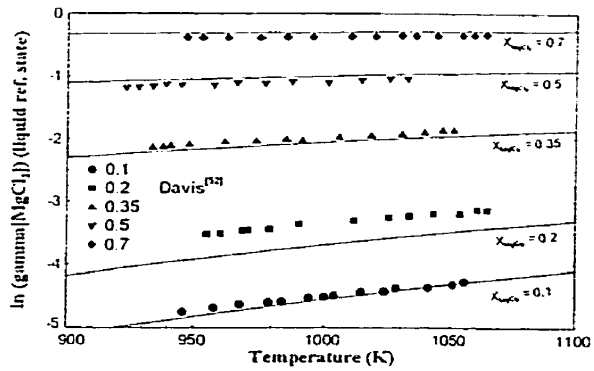

Fig. 29 - NaCl-KCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid for a NaCl / (NaCl + KCl) molar ratio of 2/3 with experimental points of Davis[52].

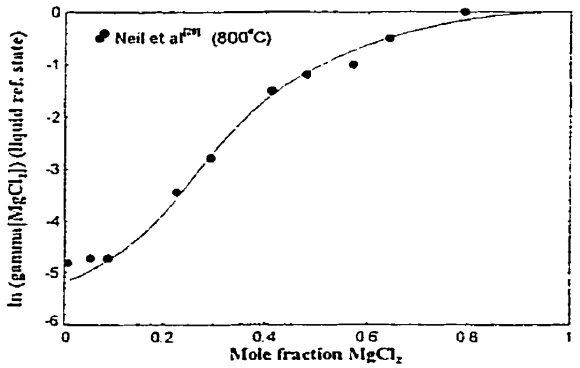

Fig. 30 - NaCl-KCl-$MgCl_2$ system : calculated activity coefficient of $MgCl_2$ in the liquid for a NaCl / (NaCl + KCl) molar ratio of 1/2 with experimental points of Neil *et al.*[28].

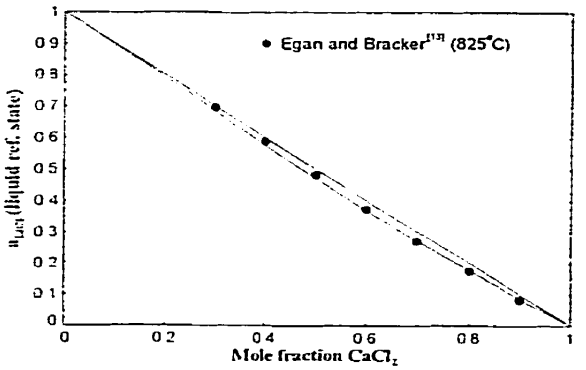

Fig. 33 – LiCl-$CaCl_2$ system : calculated activity of LiCl in the liquid at 825°C (liquid ref. state).

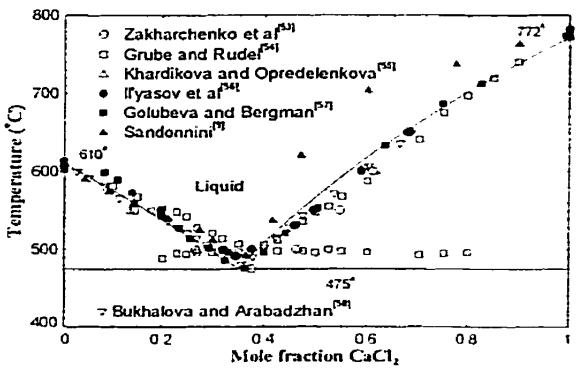

Fig. 31 – LiCl-$CaCl_2$ system : calculated phase diagram.

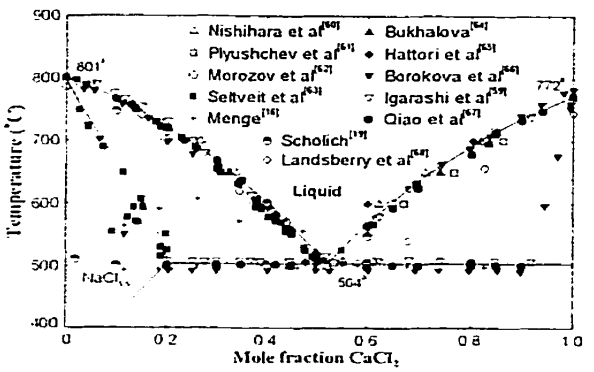

Fig. 34 - NaCl-$CaCl_2$ system : calculated phase diagram.

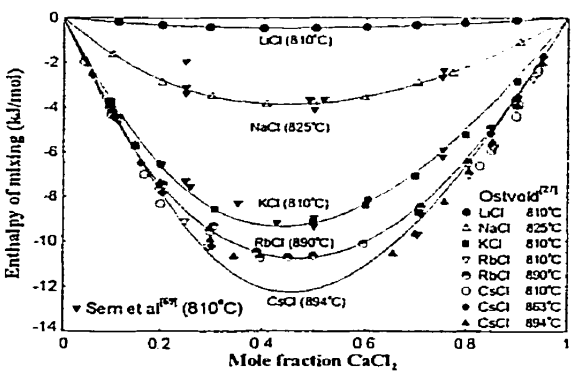

Fig. 32 - Calculated enthalpy of mixing of the liquid for the alkali chlorides with $CaCl_2$.

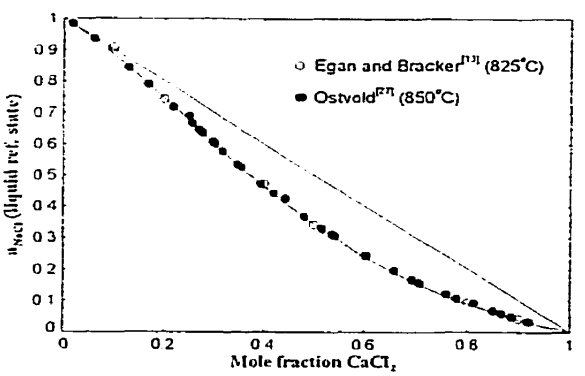

Fig. 35 - NaCl-$CaCl_2$ system : calculated activity of NaCl in the liquid at 825°C (liquid ref. state).

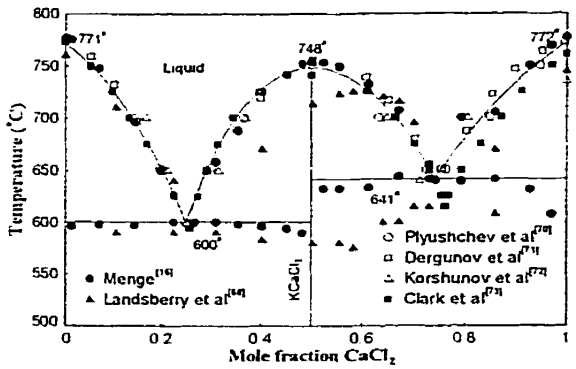

Fig. 36 – KCl-$CaCl_2$ system : calculated phase diagram.

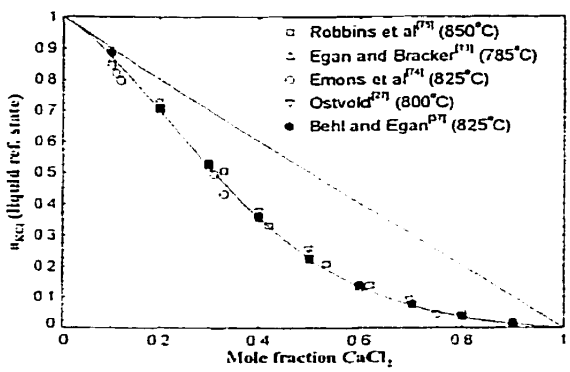

Fig. 37 - KCl-$CaCl_2$ system : calculated activity of KCl in the liquid at 800°C (liquid ref. state).

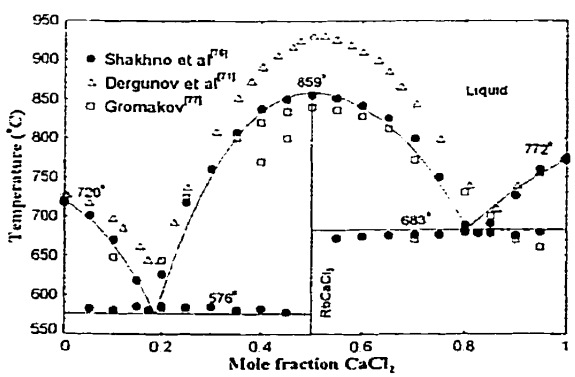

Fig. 38 – RbCl-$CaCl_2$ system : calculated phase diagram.

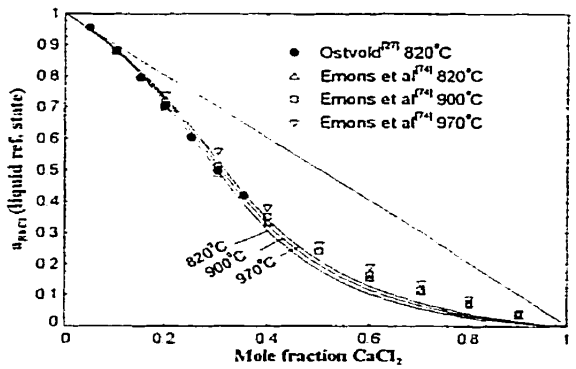

Fig. 39 - RbCl-$CaCl_2$ system : calculated activity of RbCl in the liquid (liquid ref. state).

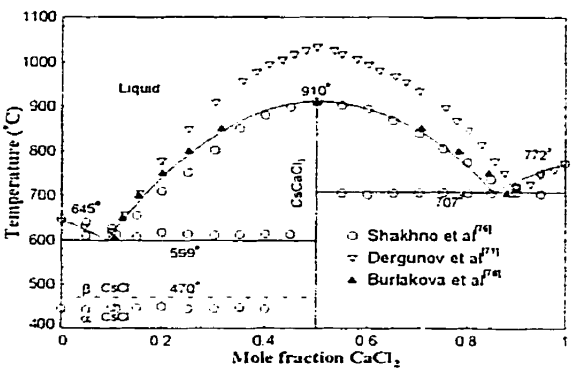

Fig. 40 – CsCl-$CaCl_2$ system : calculated phase diagram.

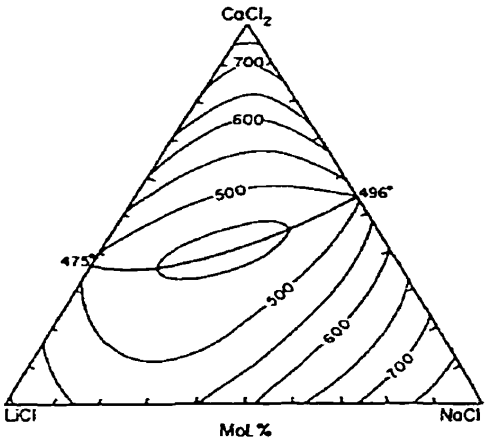

Fig. 41 – LiCl-NaCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[79].

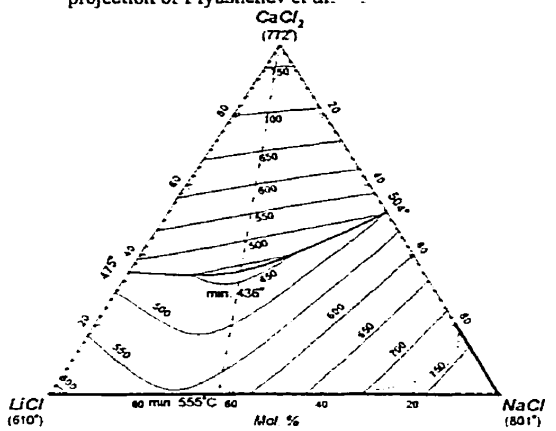

Fig. 42 - LiCl-NaCl-$CaCl_2$ system : calculated liquidus projection.

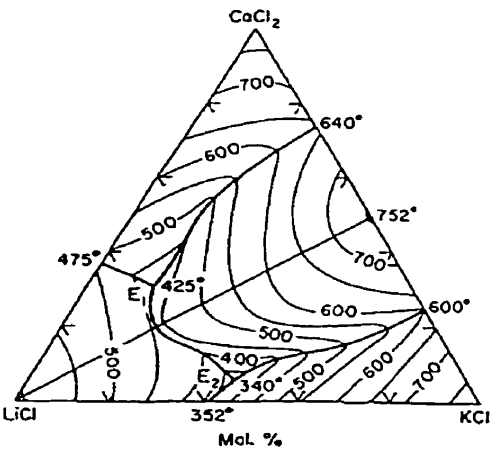

Fig. 43 – LiCl-KCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[79].

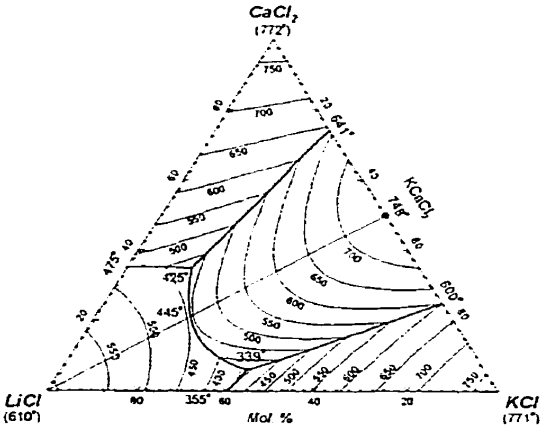

Fig. 44 - LiCl-KCl-$CaCl_2$ system : calculated liquidus projection.

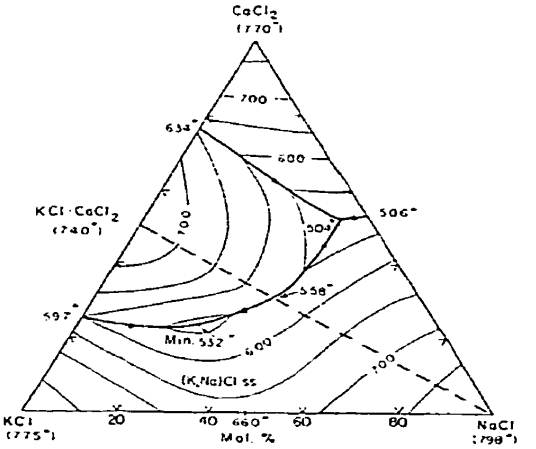

Fig. 45 – NaCl-KCl-$CaCl_2$ system : experimental liquidus projection of Scholich[19].

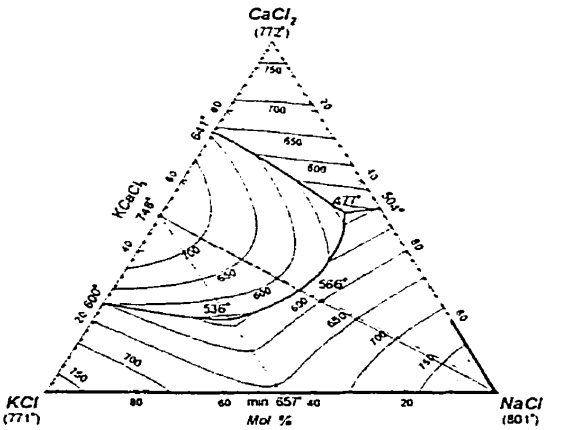

Fig. 46 - NaCl-KCl-$CaCl_2$ system : calculated liquidus projection.

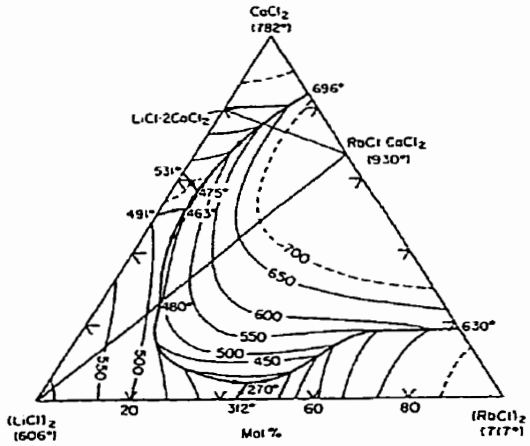

Fig. 47 – $(LiCl)_2$-$(RbCl)_2$-$CaCl_2$ system : experimental liquidus projection of Il'yasov *et al.*[56].

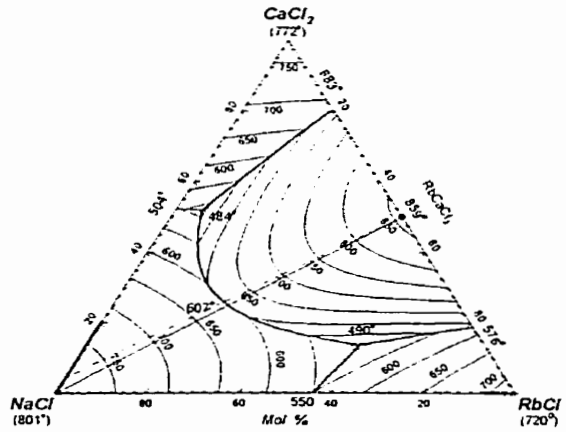

Fig. 50 - NaCl-RbCl-$CaCl_2$ system : calculated liquidus projection.

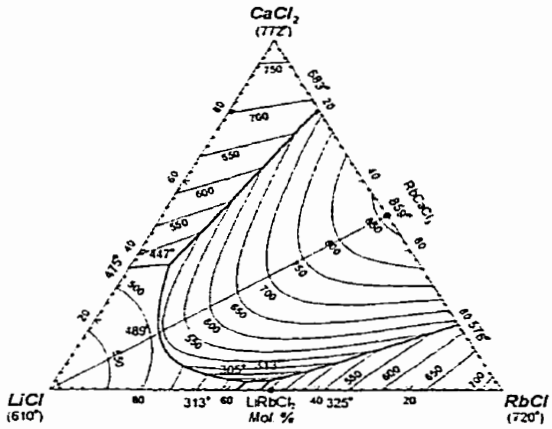

Fig. 48 - LiCl-RbCl-$CaCl_2$ system : calculated liquidus projection.

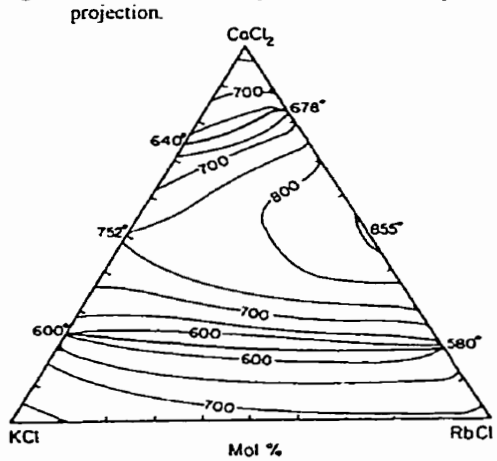

Fig. 51 – KCl-RbCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[79].

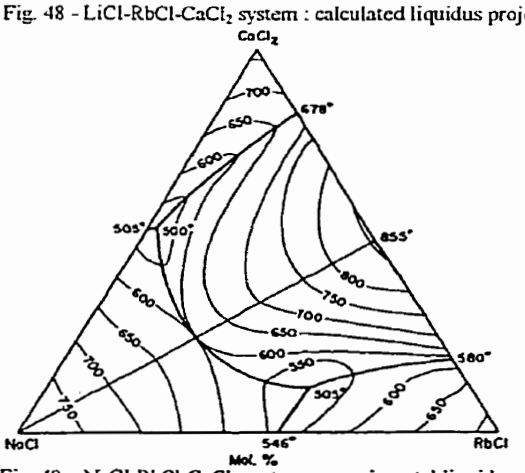

Fig. 49 – NaCl-RbCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[61].

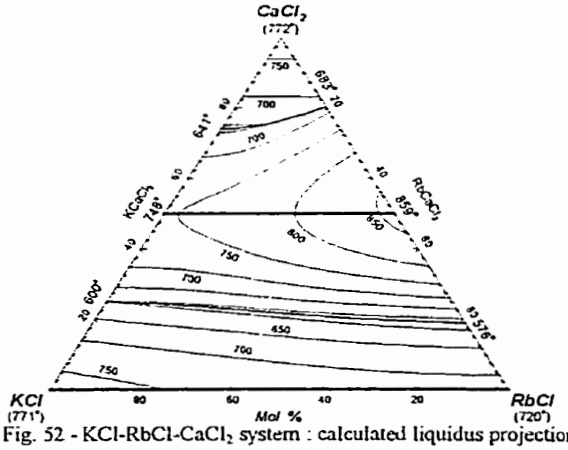

Fig. 52 - KCl-RbCl-$CaCl_2$ system : calculated liquidus projection.

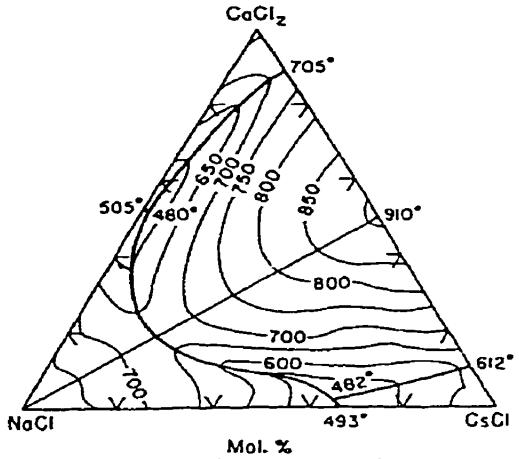

Fig. 53 - NaCl-CsCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[83]

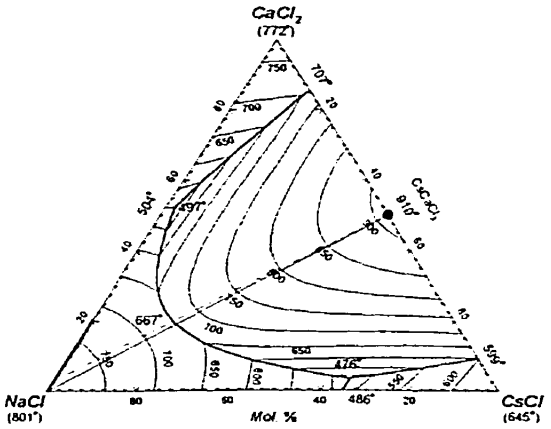

Fig. 54 - NaCl-CsCl-$CaCl_2$ system : calculated liquidus projection.

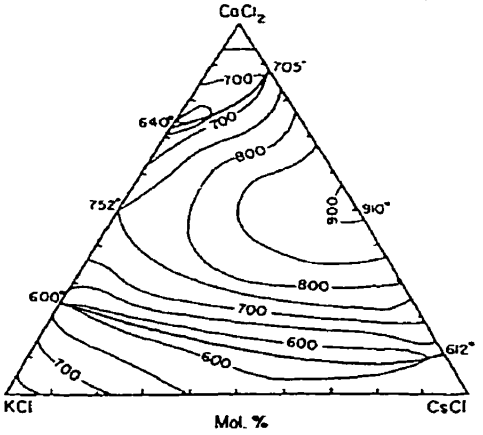

Fig. 55- KCl-CsCl-$CaCl_2$ system : experimental liquidus projection of Plyushchev *et al.*[79].

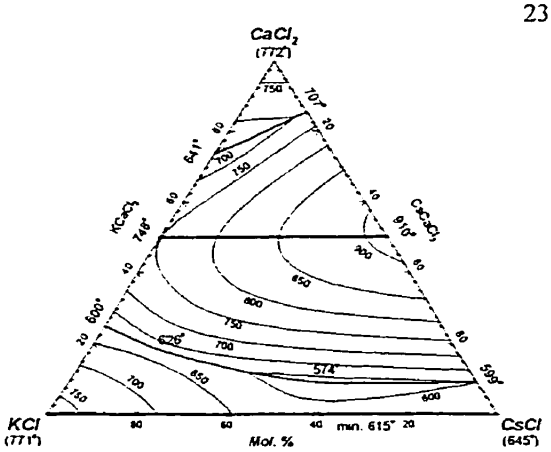

Fig. 56 - KCl-CsCl-$CaCl_2$ system : calculated liquidus projection.

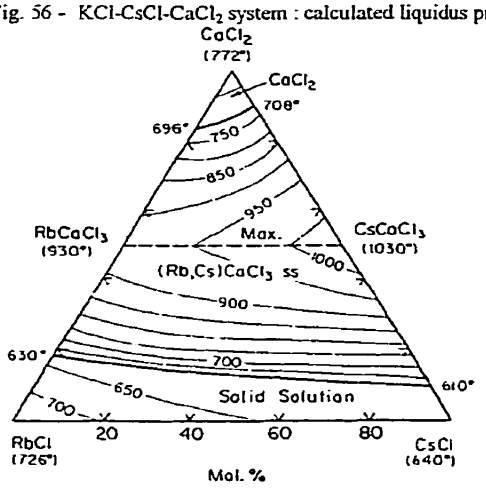

Fig. 57 – RbCl-CsCl-$CaCl_2$ system : experimental liquidus projection of Dergunov and Bergman[71].

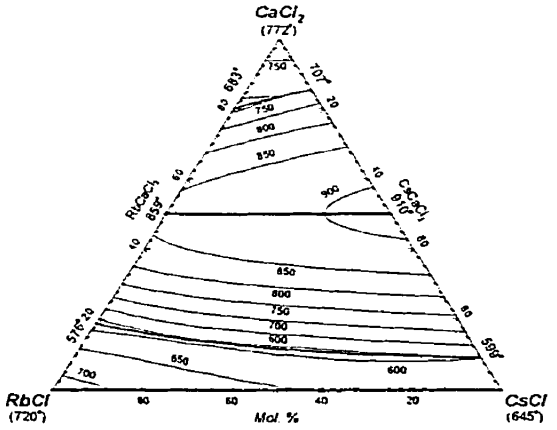

Fig. 58 - RbCl-CsCl-$CaCl_2$ system : calculated liquidus projection.

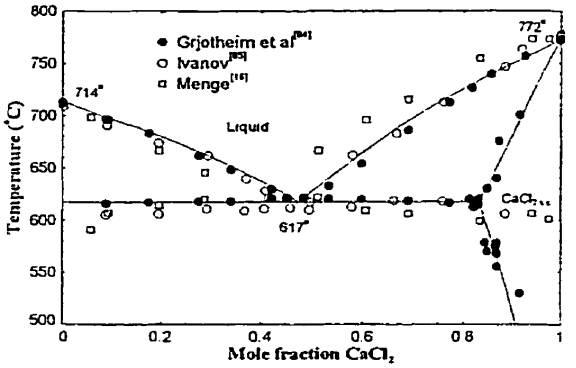

Fig. 59 – $MgCl_2$-$CaCl_2$ system : calculated phase diagram.

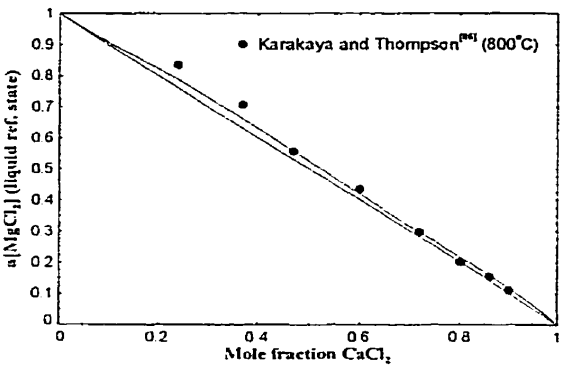

Fig. 60 - $MgCl_2$-$CaCl_2$ system : calculated activity of $MgCl_2$ at 800°C (liquid ref. state).

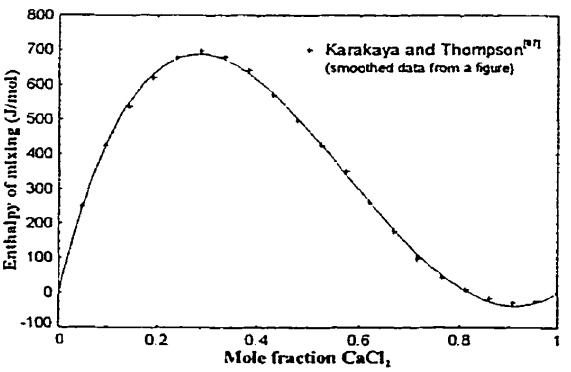

Fig. 61 - $MgCl_2$-$CaCl_2$ system : calculated enthalpy of mixing of the liquid at 800°C.

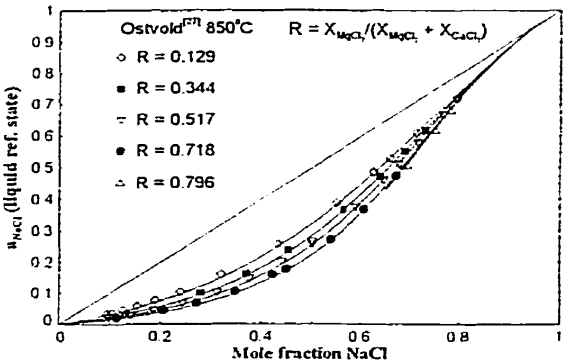

Fig. 62 – NaCl-$MgCl_2$-$CaCl_2$ system : calculated activity of NaCl at 850°C for different $MgCl_2$ / ($MgCl_2$ + $CaCl_2$) molar ratios with experimental points of Østvold[27].

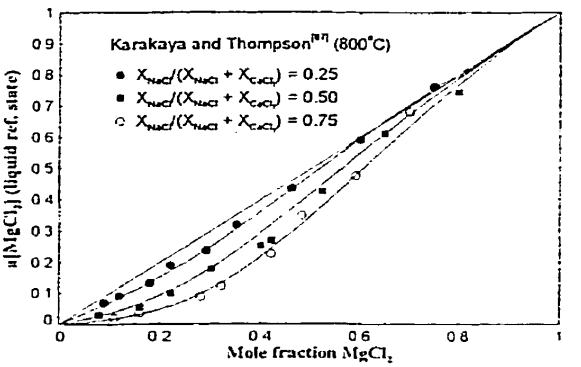

Fig. 63 - NaCl-$MgCl_2$-$CaCl_2$ system : calculated activity of $MgCl_2$ at 800°C for different NaCl / (NaCl + $CaCl_2$) molar ratios with experimental points of Karakaya and Thompson[87].

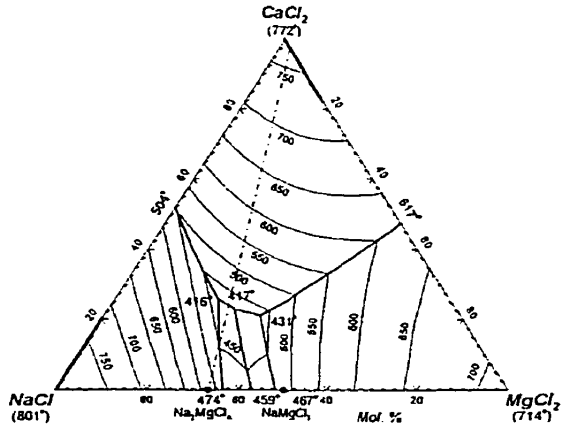

Fig. 64 - NaCl-$MgCl_2$-$CaCl_2$ system : calculated (predicted) liquidus projection.

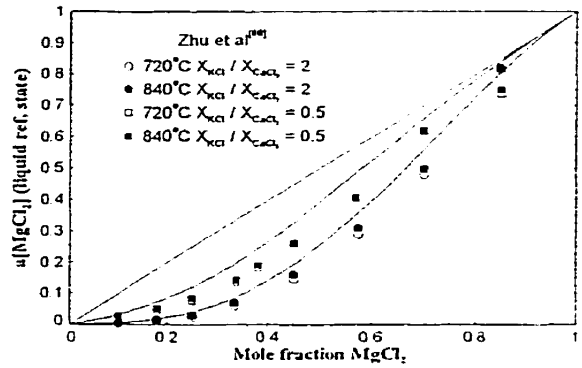

Fig. 67 - KCl-$MgCl_2$-$CaCl_2$ system : calculated activity of $MgCl_2$ at 780°C for different KCl / $CaCl_2$ molar ratios (0.5 and 2) with experimental points of Zhu *et al.*[88].

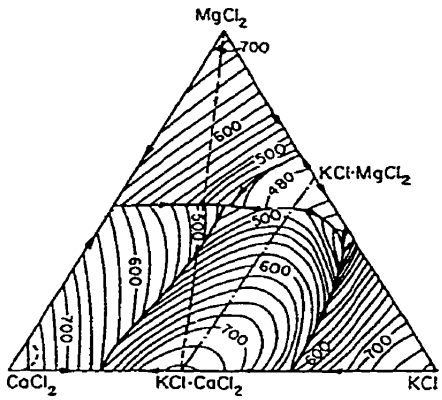

Fig. 65 – KCl-$MgCl_2$-$CaCl_2$ system : experimental liquidus projection of Ivanov[85] (wt.%).

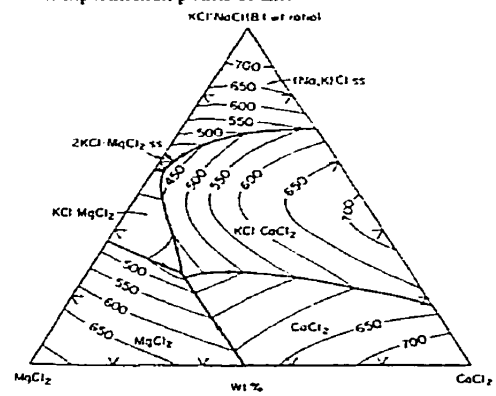

Fig. 68 – NaCl-KCl-$MgCl_2$-$CaCl_2$ system : experimental liquidus projection at KCl / NaCl weight ratio of 8 (Maunts[59]).

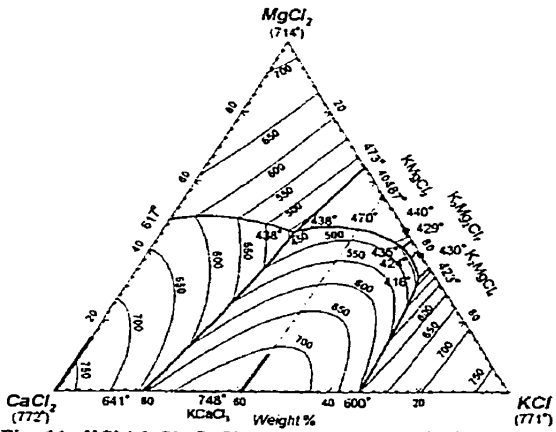

Fig. 66 - KCl-$MgCl_2$-$CaCl_2$ system : calculated liquidus projection (wt. %).

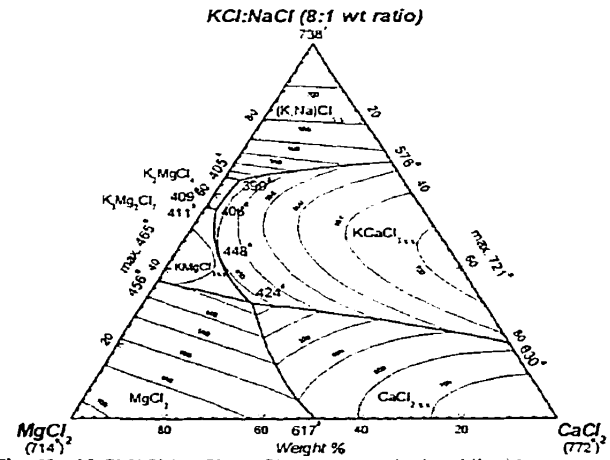

Fig. 69 – NaCl-KCl-$MgCl_2$-$CaCl_2$ system : calculated liquidus projection for a constant KCl / NaCl weight ratio of 8.

ANNEXE V

Article :

Thermodynamic Evaluation and Optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ System Using the Modified Quasichemical Model

Patrice Chartrand et Arthur D. Pelton,

Soumis à *Canadian Metallurgical Quarterly*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel ***FIGURE*** développé par l'auteur de cette thèse durant ses études doctorales.

THERMODYNAMIC EVALUATION AND OPTIMIZATION OF THE LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ SYSTEM USING THE MODIFIED QUASICHEMICAL MODEL

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Abstract - A complete critical evaluation and quantitative optimization of all available phase diagram and thermodynamic data has been performed for all condensed phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ system. The model parameters obtained for binary and ternary subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent system. The modified quasichemical model for short-range ordering was used for the molten salt phase.

Résumé – Une évaluation critique et une optimization quantitative des diagrammes de phase et des données thermodynamiques a été faite pour toutes les phases condensées du système LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$. Les paramètres des modèles obtenus pour les sous-systèmes binaires et ternaires peuvent être utilisés pour prédire les propriétés thermodynamiques et les équilibres de phases pour le système multicomposant. Le modèle quasichimique modifié, qui évalue l'ordonnement à courte distance des cations, a été utilisé pour la phase liquide.

INTRODUCTION

Molten alkali-alkaline earth halide solutions are of much technological importance in, for example, the production of reactive metals. A large body of experimental thermodynamic and phase equilibrium data exists for these systems. In this article, all available data for binary and ternary subsystems of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ system are critically evaluated and optimized to obtain parameters of models of all solution phases. These parameters form a computer database. The models are then used to predict the thermodynamic properties of the multicomponent system. When used with currently available general software for calculating equilibria by Gibbs energy minimization, this database can be used to predict the thermodynamic properties and phase equilibria in uncharted regions of temperature and composition. This article is one in a series on alkali-alkaline earth halide systems.

In a previous article[1] we presented a quasichemical model for liquid solutions which takes into account short-range ordering between nearest-neighbors on a lattice or sublattice. Molten alkali chloride-$MgCl_2$ solutions are well known for exhibiting extensive short-range ordering, increasing in importance from LiCl-$MgCl_2$ to CsCl-$MgCl_2$. This ordering gives rise to "V-shaped" enthalpy of mixing and "m-shaped" entropy of mixing curves. This has previously been modelled by introducing complex anions such as $MgCl_4^{2-}$ [2,3]. Alkali chloride-$SrCl_2$ solutions do not show the same extent of ordering as for $MgCl_2$, but the tendency is present. The modified quasichemical model[1] quantitatively treats the short-range ordering between cations in binary and multicomponent solutions. An earlier version of the model has been used very successfully to model molten silicates[4].

The model does not explicitely introduce complex anions. Instead, short-range ordering is treated by considering the relative numbers of second-nearest-neighbor cation-cation pairs. The parameters of the model are the Gibbs energy changes $\Delta g_{AB/Cl}$ for the pair exchange reactions :

$$(A-Cl-A)_{pair} + (B-Cl-B)_{pair} = 2(A-Cl-B)_{pair} \qquad \Delta g_{AB/Cl} \quad (1)$$

As $\Delta g_{AB/Cl}$ becomes progressively more negative, reaction [1] is shifted progressively to the right, (A-Cl-B) pairs predominate, and the solution becomes progressively more ordered. In the previous article[1] the model was developed in terms of nearest-neighbor pairs (A-B) for species mixing on one lattice. In the present case, since the anion sublattice is occupied only by Cl^- ions, the model can be used directly to treat cation-cation pairs on the cation sublattice. The parameter $\Delta g_{AB/Cl}$ is the parameter Δg_{mn} of the previous article[1]. When $\Delta g_{AB/Cl}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of cations on the cation sublattice.

In a previous article of the present series[5], a complete evaluation and quantitative optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ system with the modified quasichemical model was presented. The present article describes the addition of $SrCl_2$ to that database, and further demonstrates the application of the new modified quasichemical model to the evaluation, optimization and

prediction of thermodynamic properties and phase equilibria.

THERMODYNAMIC DATA

All thermodynamic data ($H^o_{298.15K}$, $S^o_{298.15K}$ and C_p) for the condensed pure phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$ system are given in the previous article[5]. All additional thermodynamic data ($H^o_{298.15K}$, $S^o_{298.15K}$ and C_p) for the condensed pure phases of the $SrCl_2$-containing binary subsystems are given in Table I.

THERMODYNAMIC MODEL FOR THE LIQUID PHASE

The modified quasichemical model[1] is used for the liquid phase. The notation of the previous articles[1,5] is maintained. For example, X_{NaSr} is the mole fraction of second-nearest-neighbor (Na-Cl-Sr) pairs. The model requires the definition of cation-cation coordination numbers Z^i_{ij}. The values chosen in the present work are listed in Table II. Values for pairs not involving Sr were given previously[5]. Note that, for example, the choice of $Z^K_{KSr} = \frac{1}{2} Z^{Sr}_{KSr}$ assures that the composition of maximum short-range ordering will be near the K_2SrCl_4 composition (similar to K_2MgCl_4[5]). Also, as discussed previously[1], it is necessary to define all ternary sub-systems as either "symmetric" or "asymmetric". In the present case, all ternary systems in which all three components are alkali halides are defined as symmetric. Systems with one alkali and two alkaline-earth chlorides are asymmetric, with the alkali chloride as asymmetric component, and systems with one alkaline-earth and two alkali chlorides are asymmetric, with the alkaline-earth chloride as asymmetric component. To this end, the components are divided into two groups, all alkali halides are in one group, and $MgCl_2$, $CaCl_2$ and $SrCl_2$ form the other group. The composition variables χ_{ij} defined previously[1] then become :

$$\chi_{LiMg} = \chi_{LiCa} = \chi_{LiSr} = \chi_{NaMg} = \chi_{NaCa} = \\ = \chi_{NaSra} = \ldots = \chi_{AlkAlkE} = \chi_{Alk} \quad (2)$$

where $$\chi_{Alk} = \sum_{i=Li}^{Cs}\sum_{j=i}^{Cs} X_{ij} \quad (3)$$

$$\chi_{MgLi} = \chi_{CaLi} = \chi_{SrLi} = \chi_{MgNa} = \chi_{CaNa} = \\ = \chi_{SrNa} = \ldots = \chi_{AlkEAlk} = \chi_{AlkE} \quad (4)$$

where $$\chi_{AlkE} = \sum_{i=Mg}^{Sr}\sum_{j=i}^{Sr} X_{ij} \quad (5)$$

and also

$$\chi_{MgSr} = \frac{X_{MgMg}}{X_{MgMg} + X_{MgSr} + X_{SrSr}} \quad (6)$$

$$\chi_{SrMg} = \frac{X_{SrSr}}{X_{MgMg} + X_{MgSr} + X_{SrSr}} \quad (7)$$

etc.

That is, when i and j are both alkaline earths or both alkalis :

$$\chi_{ij} = \frac{X_{ij}}{X_{ii} + X_{ij} + X_{jj}} \quad (8)$$

The parameters $\Delta g_{AB/Cl}$ of reaction [1] for each pair are expanded, through optimization of available experimental data, as empirical polynomials in χ_{ij}. For ternary systems, terms may be added giving the effect of the third component upon the pair formation energies $\Delta g_{AB/Cl}$. As described previously[1] this is done by introducing empirical ternary parameters $g^{ijk}_{AB(C)/Cl}$ in the polynomial expansion.

MIXTURES OF ALKALI CHLORIDES WITH $SrCl_2$

The LiCl-$SrCl_2$ System

The phase diagram (Figure 1) has been measured by cooling curves[6], "the visual-polythermal" method[7-9] and DTA[10]. All authors report a simple eutectic system without solid solubility.

The activity of LiCl in the liquid has been measured by an emf technique[11] (Figure 2). There is no reported measurements of the enthalpy of mixing of the liquid, but it is possible to estimate it by the following method. Figure 3 shows the experimental enthalpy of mixing evaluated at 40 mol% alkaline-earth halide of the LiF-SrF_2[12], LiBr-$SrBr_2$[13], LiCl-$CaCl_2$[13], LiCl-$MgCl_2$[13] and ACl-$SrCl_2$[13] liquid solutions (where A = Na, K, Rb or Cs) as a function of δ_{12} which is defined[13] as :

$$\delta_{12} = \frac{\left[r_1^+ + r_X^-\right] - \left[r_2^{2+} + r_X^-\right]}{\left[r_1^+ + r_X^-\right]\left[r_2^{2+} + r_X^-\right]} \quad (9)$$

where r is the ionic radius and X = F, Cl or Br. The enthalpy of mixing of a family of alkali-alkaline-earth halides varies almost linearly with δ_{12}[13]. It is thus possible to obtain best fit lines for the common Li-X-Sr, common Li-Cl-AlkE (AlkE = alkaline-earth) and common Alk-Cl-Sr (Alk = alkali) groups. The extrapolated (or interpolated) values for the three groups evaluated at δ_{12} of Li-Cl-Sr should be similar, and their mean value is taken as an estimation of the enthalpy of mixing of LiCl-$SrCl_2$ melts at 40 mol.% $SrCl_2$. (This composition was chosen because it corresponds to the approximate composition where the mixing enthalpy of the liquid is most negative in alkali

alkaline-earth halide mixtures). It can be seen that the three extrapolations give similar values at the δ_{12} value (-0.748 nm^{-1}) of Li-Cl-Sr, with the value from the Li-X-Sr and Li-Cl-AlkE lines in excellent agreement and the value from the Alk-Cl-Sr line in less good agreement. Accordingly, this latter value was not included in the average. From the Li-X-Sr line, the interpolated value is −150 J/mol, and from the Li-Cl-AlkE line, the extrapolated value is 120 J/mol. The mean value can be taken to be 0 (±300) J/mol for purposes of calculation.

The optimized Gibbs energy of reaction [1] applied to the *Li-Cl-Sr* pair is :

$$\Delta g_{LiSr/Cl} = 0.2178T - 0.4540T\chi_{Alk} - 2.4901T\chi_{AlkE} \quad \text{J/mol} \qquad (10)$$

(Note that all terms are function of temperature so the enthalpy of mixing is 0). Figures 1, 2, 4 and 5 show the calculated phase diagram and thermodynamic properties.

The NaCl-SrCl₂ System

The phase diagram has been measured by cooling curves[14,15] and the visual-polythermal method[16] (Figure 6). No solid solubility is reported, and the limiting slopes of the NaCl and $SrCl_2$ liquidus curves respect Eq.[11] which assumes no solid solubility.

$$\lim_{X_m \to 1}\left(\frac{dX_m^{liquidus}}{dT}\right) = \frac{\Delta h^o_{fusion}}{RT^2_{fusion}} \qquad (11)$$

where Δh^o_{fusion} and T_{fusion} are respectively the enthalpy and temperature of fusion of the pure salt.

Calorimetric measurements are available for the liquid[13] (Figure 4). The activity of NaCl in the liquid has been measured by emf techniques[11,13,17] (Figure 7). The optimized Gibbs energy of reaction [1] for the *Na-Cl-Sr* pairs is :

$$\Delta g_{NaSr/Cl} = -1119.3 + 0.4175T - 1067.8\chi_{Alk} + (-996.4 - 1.8109T)\chi_{AlkE} \quad \text{J/mol} \qquad (12)$$

Figures 4-7 show the calculated phase diagram and thermodynamic properties.

The KCl-SrCl₂ System

The phase diagram has been measured by DTA[18], the visual-polythermal method[7,19], and cooling curves[14,15] (Figure 8). Reported intermediate compounds are K_2SrCl_4 (congruent) and KSr_2Cl_5 (congruent[15] or incongruent[18,19]). The stoichiometry $K_2Sr_3Cl_8$ was also reported[7] instead of KSr_2Cl_5, but X-ray analysis[18] established that KSr_2Cl_5 is the stable high-$SrCl_2$ compound. No solid solubility is reported, and the limiting slopes of the KCl and $SrCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

Calorimetric measurements are available for the liquid[13] (Figure 4). The activity of KCl in the liquid has been measured by emf techniques[11,13,17,20] (Figure 9). The enthalpy of fusion of K_2SrCl_4 has been measured[21], by endothermic peaks of DSC, as 56.9024 kJ/mol at 865K. The calculated optimized value is 56.76 kJ/mol. The Gibbs energy of formation of KSr_2Cl_5 has been measured[22], by an emf technique, as (−10200 + 0.0T) J/mol. The enthalpy of formation at 298.15K of KSr_2Cl_5 as been measured[22], by solution calorimetry, as -7600 J/mol. The optimized value for the Gibbs energy of formation of KSr_2Cl_5 from $KCl_{(s)}$ and $SrCl_{2(\alpha)}$ is (-7544.0 - 2.884T) J/mol (assuming ΔC_p of formation = 0). The calculated optimized KCl-$SrCl_2$ phase diagram is presented in Figure 8. The optimized Gibbs energy of reaction [1] for the *K-Cl-Sr* pairs is :

$$\Delta g_{KSr/Cl} = -5538.4 + 1.7009T - 1496.2\chi_{Alk} - 2509.0\chi_{AlkE} \quad \text{J/mol} \qquad (13)$$

Figures 4, 5, 8 and 9 show the calculated phase diagram and thermodynamic properties.

The RbCl-SrCl₂ System

The phase diagram has been measured by thermal analysis[19], the visual-polythermal method[23,24] and cooling curves[25] (Figure 10). Reported intermediate compounds are $RbSrCl_3$[19,23-25] and $RbSr_2Cl_5$[23,25]. No solid solubility is reported, and the limiting slopes of the RbCl and $SrCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility. No confirmation of the stoichiometry of $RbSr_2Cl_5$ by X-Ray diffraction has been reported. Hence, this stoichiometry is indicated as tentative on Figure 10.

Calorimetric measurements are available for the liquid[13] (Figure 4). The activity of RbCl in the liquid has been measured by emf techniques[13,17] (Figure 11). The Gibbs energy of reaction [14] has been measured[26], by an emf technique, at 650K as (5.4 - 0.0215T) kJ/mol.

$$RbCl_{(s)} + SrCl_{2(\alpha)} = RbSrCl_{3(s)} \qquad (14)$$

The enthalpy of reaction [14], measured by solution calorimetry at 298.15K, is reported[26] as 3.6 kJ/mol. The optimized value is 3.469 kJ/mol. The optimized Gibbs energy of reaction [14] is (3.954 - 0.02114T) kJ/mol. The heat capacity of $RbSrCl_3$ was estimated as 135 J/mol-K from the values for other perovskite compounds ($NaMgCl_3$[5], $KMgCl_3$[5], $RbCaCl_3$[5], $RbMgCl_3$[5]) and from the sum of the heat capcities of $RbCl_{(s)}$ and $SrCl_{2(\alpha)}$. The Gibbs energy of reaction [15] has been measured[26], by an emf technique, at 298K as (-20.2 + 0.00335T) kJ/mol. The enthalpy change of reaction [15] has been measured[26] at 298K, by calorimetry, as −17.4 kJ/mol.

$$RbCl_{(s)} + 2SrCl_{2(\alpha)} = RbSr_2Cl_{5(s)} \qquad (15)$$

From these results, one would expect a decomposition of $RbSrCl_3$ into 0.5 $RbSr_2Cl_5$ and 0.5 RbCl at low temperature. The optimized Gibbs energy of reaction [15] at 298.15K is (-17.4400 + 0.00208T) kJ/mol. ΔC_p of reaction [15] was assumed to be 0. The optimized Gibbs energy of reaction [1] for the *Rb-Cl-Sr* pairs is :

$$\Delta g_{RbSr/Cl} = -7439.8 + 0.6654T - 2632.9\chi_{AB,E} \text{ J/mol} \quad (16)$$

Figures 4, 5, 10 and 11 show the calculated phase diagram and thermodynamic properties. It can be seen on Figure 5 that the entropies of the KCl-$SrCl_2$ and $RbCl$-$SrCl_2$ solutions do not follow the expected order. However, this discrepancy is within the error limits of the optimizations of the available data.

The CsCl-SrCl₂ System

The phase diagram has been measured by thermal analysis[19], DTA[27] and the visual-polythermal method[27] (Figure 12). A congruent $CsSrCl_3$ compound is reported. No solid solubility is reported, and the limiting slopes of the CsCl and $SrCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

Calorimetric measurements are available for the liquid[13] (Figure 4). No activity measurements were found. No experimental thermodynamic data were found for the $CsSrCl_3$ compound. The optimized thermodynamic properties of the $CsSrCl_3$ compound are given in Table I. A constant C_p value of 140 J/mol-K is assumed, estimated from values for other perovskite compounds : $NaMgCl_3$[5], $KMgCl_3$[5], $KCaCl_3$[5], $CsCaCl_3$[5]. The optimized Gibbs energy of reaction [1] for the *Cs-Cl-Sr* pairs is :

$$\Delta g_{CsSr/Cl} = -9262.2 + 4.6850T - 1919.7\chi_{AB,E} - 1066.2\chi^2_{AB,E} \text{ J/mol} \quad (17)$$

Figures 4, 5 and 12 show the calculated phase diagram and thermodynamic properties.

The LiCl-NaCl-SrCl₂ System

The liquidus projection has been measured[28] by the visual-polythermal method and DTA (Figure 13). A ternary eutectic is reported at 424°C and at 37.5 mol% Li_2Cl_2, 17.5 mol% Na_2Cl_2 and 45 mol% $SrCl_2$. No ternary solid solubility is reported. The binary eutectic temperatures on the reported ternary liquidus projection[28] are approximately 20°C below the optimized binary eutectic temperatures. Therefore, it is assumed that the reported[28] ternary eutectic temperature is also 20°C too low. The calculated liquidus projection is shown in Figure 14. (Note the different composition scales of Figures 13 and 14). No ternary solid solution was assumed. The calculated ternary liquidus minimum is at 444°C at 35.4 mol% Li_2Cl_2, 17.0 mol% Na_2Cl_2 and 47.6 mol% $SrCl_2$. The following small ternary excess parameters were used :

$$g^{001}_{LiSr(Na)/Cl} = -2510.0 \quad \text{J/mol} \quad (18)$$

$$g^{001}_{NaSr(Li)/Cl} = -2510.0 \quad \text{J/mol} \quad (19)$$

The LiCl-KCl-SrCl₂ System

The liquidus projection has been measured[7] by the visual-polythermal method (Figure 15). No ternary solid solution is reported. In order to reproduce the liquidus surface a small ternary excess parameter is necessary (Eq.[20]). The calculated liquidus projection is shown in Figure 16. (Note the different composition scales of Figures 15 and 16). Li^+ is assumed insoluble in K_2SrCl_4 and KSr_2Cl_5. Since the liquidus is well reproduced with a small negative ternary excess paremeter, and since any assumed solubility of Li^+ in these solids would require a larger negative parameter for the liquid, the assumption of negligible solid solubility is supported. The reported[7] invariant temperatures in the binary subsystems are all lower in temperature than the optimized values. Hence, the reported[7] ternary invariant temperatures are also expected to be lower in temperature than the calculated values.

$$g^{001}_{KSr(Li)/Cl} = -4728.0 \quad \text{J/mol} \quad (20)$$

The LiCl-CsCl-SrCl₂ System

The liquidus projection has been measured[27] with the visual-polythermal method and DTA (Figure 17). No solid solubility is reported. The calculated liquidus projection is shown in Figure 18. (Note the different composition scales of Figures 17 and 18). A small ternary parameter (Eq.[21]) was required. No Li^+ solubility in $CsSrCl_3$ is assumed. The optimized invariant temperatures in the LiCl-CsCl binary subsystem[5,29] are approximately 10°C higher than those reported[27] in Figure 17. Therefore, the calculated ternary invariant temperatures at compositions near the LiCl-CsCl binary are also expected to be higher than the reported values[27].

$$g^{001}_{CsSr(Li)/Cl} = -5021.0 \quad \text{J/mol} \quad (21)$$

The NaCl-KCl-SrCl₂ System

The liquidus projection has been measured by cooling curves[14] (Figure 19) and DTA[30]. There is disagreement on the temperatures of the ternary invariant points, the points of Prokhorov *et al.*[30] being appromately 20°C lower than those of Scholich[14]. Prokhorov *et al.*[30] reported a eutectic (K_2SrCl_4-KSr_2Cl_5-NaCl) at 496°C, a eutectic (K_2SrCl_4-KCl-NaCl) at 514°C, a eutectic (KSr_2Cl_5-NaCl-$SrCl_2$) at 504°C and two saddle points, (K_2SrCl_4-NaCl) at 516°C and (KSr_2Cl_5-NaCl) at 528°C. No solid solubility is reported.

With no ternary excess parameters for the liquid, the calculated liquidus projection lies approximately 5°C above that reported by Scholich[14], which is itself higher in temperature than the liquidus of Prokhorov *et al.*[30]. With a

very small ternary term (Eq.[22]) the calculated liquidus projection (Figure 20) is very close to that reported by Scholich[14]. Therefore, it is assumed that the projection of Scholich[14] is the more accurate. No ternary solid solubility was assumed, and the good reproduction of the measured liquidus with only a very small ternary terms tends to support this assumption.

$$g^{001}_{KSr(Na)/Cl} = 1255.2 \quad \text{J/mol} \qquad (22)$$

The NaCl-CsCl-$SrCl_2$ System

The liquidus projection has been measured by the visual-polythermal method[31] (Figure 21). No solid solubility is reported. The liquidus surface is calculated with no ternary excess parameters (Figure 22) and assuming no ternary solid solubility. (Note the different composition scales of Figures 21 and 22). The calculated (NaCl-CsCl-$CsSrCl_3$) eutectic temperature is 456°C whereas the reported value is 400°C[31]. However, from the spacing between the reported[31] isotherms at 600°C, 550°C and 500°C on Figure 21, and from the fact that no 450°C isotherm is shown, it seems likely that the eutectic was reported incorrectly and was actually closer to 450°C.

The KCl-RbCl-$SrCl_2$ System

The liquidus projection has been measured[23] by the visual-polythermal method (Figure 23). Four eutectics and a peritectic are reported : E_1 at 514°C, E_2 at 531°C, E_3 at 614°C, E_4 at 616°C and P at 540°C. The liquidus surface[23] can only be reproduced if solid solubility is assumed : K^+ must be soluble in $RbSrCl_3$, and KSr_2Cl_5 and $RbSr_2Cl_5$ must be mutually soluble to a large extent. (Note that $K_2Sr_3Cl_8$[23] is replaced in this work by KSr_2Cl_5 as described previously). An ideal Henrian solution model is proposed for the $RbSrCl_3$-$KSrCl_{3\,hyp}$ solid solution :

$$g = X_{RbSrCl_3} g^{o,S}_{RbSrCl_3} + X_{KSrCl_3} g^{o,hyp}_{KSrCl_3} + RT\left(X_{RbSrCl_3} \ln X_{RbSrCl_3} + X_{KSrCl_3} \ln X_{KSrCl_3}\right) \quad \text{J/mol} \qquad (23)$$

where the Gibbs energy of hypothetical $KSrCl_3$ is given by :

$$g^{o,hyp}_{KSrCl_3} = g^{o,S}_{KCl} + g^{o,\alpha}_{SrCl_2} - 502.1 \quad \text{J/mol} \qquad (24)$$

A complete solid solution $(Rb,K)Sr_2Cl_5$ is assumed, with its Gibbs energy given by a regular solution model :

$$g = X_{RbSr_2Cl_5} g^{o,S}_{RbSr_2Cl_5} + X_{KSr_2Cl_5} g^{o,S}_{KSr_2Cl_5} + RT\left(X_{RbSr_2Cl_5} \ln X_{RbSr_2Cl_5} + X_{KSr_2Cl_5} \ln X_{KSr_2Cl_5}\right) \quad \text{J/mol} + 6276.0 X_{RbSr_2Cl_5} X_{KSr_2Cl_5} \qquad (25)$$

No solid solubility of Rb^+ in K_2SrCl_4 is assumed. No liquid ternary terms are used. The calculated liquidus projection is shown in Figure 24.

Other alkali-chloride $SrCl_2$ ternary systems

No experimental data were found for the LiCl-RbCl-$SrCl_2$, NaCl-RbCl-$SrCl_2$, KCl-CsCl-$SrCl_2$, and RbCl-CsCl-$SrCl_2$ systems. For purposes of calculation one can assume complete solid solubility between $RbSrCl_3$ and $CsSrCl_3$. An ideal solution of these two compounds is suggested. Very limited solid solubility is expected for Na^+ in $RbSrCl_3$ and limited solid solubility is expected for K^+ in $CsSrCl_3$.

MIXTURES OF ALKALINE-EARTH CHLORIDES WITH $SrCl_2$

The $MgCl_2$-$SrCl_2$ System

The phase diagram has been measured[32] by cooling curves (Figure 25). A simple eutectic system with no solid solubility is reported. The limiting slope of the $MgCl_2$ liquidus curve is in reasonable agreement with Eq.[11], but the limiting slope of the $SrCl_2$ liquidus curve is not, suggesting possible solubility of Mg^{2+} in solid $SrCl_2$.

Calorimetric measurements are available for the liquid[33] (Figure 26). The liquid model parameters were obtained by fitting the enthalpy of mixing data[33] and by then fitting the $MgCl_2$ liquidus points with a single entropic term in Eq.[26] :

$$\Delta g_{MgSr/Cl} = 685.7 - 4.0000T - 3488.4\,\chi_{MgSr} + 6150.3\chi^2_{MgSr} - 3055.5\chi_{SrMg} \quad \text{J/mol} \qquad (26)$$

The reported eutectic temperature[32] was then reproduced by assuming solubility of $MgCl_2$ in solid $SrCl_{2(\alpha)}$. A Henrian model (Eq.[27]) was used, with the same entropic parameter as was used[5] for $MgCl_2$ in solid $CaCl_2$ and with a very similar enthalpic parameter. No solid solubility of Mg^{2+} in $SrCl_{2(\beta)}$ was assumed.

$$g = X_{SrCl_2} g^{o,\alpha}_{SrCl_2} + X_{MgCl_2}\left(g^{o,S}_{MgCl_2} + 27709.2 - 18.4261T\right) + RT\left(X_{SrCl_2} \ln X_{SrCl_2} + X_{MgCl_2} \ln X_{MgCl_2}\right) \quad \text{J/mol} \qquad (27)$$

Figures 25 and 26 show the calculated phase diagram and thermodynamic properties.

The $CaCl_2$-$SrCl_2$ System

The phase diagram has been measured by cooling curves[34,35], the visual-polythermal method[8,36,37] and DTA[36] (Figure 27). All authors reported complete solid solubility with a minimum in the liquidus (at 36 mol.% $SrCl_2$ and 652°C[8]; at 35 mol.% $SrCl_2$ and 646°C[34]; at 34

mol.% $SrCl_2$ and 658°C[35]; and at 35 mol.% $SrCl_2$ and 656°C[36,37];). A solid-solid miscibility gap is reported[34,35] (with a consolute point at 556°C[34] or 543°C[35]).

Calorimetric measurements for the liquid are available[33] (Figure 26). The optimized Gibbs energy of reaction [1] for the Ca-Cl-Sr pairs is :

$$\Delta g_{CaSr/Cl} = -650.5 + 0.6945T \quad \text{J/mol} \qquad (28)$$

A complete solid solution was assumed between $CaCl_2$ and $SrCl_{2(\alpha)}$ and a large solubility of Ca^{2+} in $SrCl_{2(\beta)}$ was also assumed. A subregular substitutional solution model was used to describe the thermodynamic properties of the low-temperature $(Ca,Sr)Cl_2$ α-solid solution (Eq.[29]). The Gibbs energy of the $SrCl_{2(\beta)}$-rich solid solution was described by a Henrian solution model (Eq.[30]).

$$\begin{aligned} g^{\alpha} &= X_{CaCl_2} g^{o,S}_{CaCl_2} + X_{SrCl_2} g^{o,\alpha}_{SrCl_2} \\ &+ RT\left(X_{CaCl_2} \ln X_{CaCl_2} + X_{SrCl_2} \ln X_{SrCl_2}\right) \quad \text{J/mol} \qquad (29) \\ &+ X_{CaCl_2} X_{SrCl_2} \left(4836.2 + 3194.2 X_{CaCl_2}\right) \end{aligned}$$

$$\begin{aligned} g^{\beta} &= X_{SrCl_2} g^{o,\beta}_{SrCl_2} + X_{CaCl_2} \left(g^{o,S}_{CaCl_2} + 8000.0\right) \\ &+ RT\left(X_{CaCl_2} \ln X_{CaCl_2} + X_{SrCl_2} \ln X_{SrCl_2}\right) \quad \text{J/mol} \qquad (30) \end{aligned}$$

Figures 26 and 27 show the calculated phase diagram and thermodynamic properties.

The $MgCl_2$-$CaCl_2$-$SrCl_2$ System

No reported liquidus projection or thermodynamic data were found for the $MgCl_2$-$CaCl_2$-$SrCl_2$ system. Therefore, no additional ternary excess parameters were included in the liquid model.

MIXTURES OF ALKALI CHLORIDES WITH $MgCl_2$ AND $SrCl_2$

No reported liquidus projection or thermodynamic data were found for any AlkCl-$MgCl_2$-$SrCl_2$ systems. Therefore, no ternary excess parameters were included in the liquid model.

MIXTURES OF ALKALI CHLORIDES WITH $CaCl_2$ AND $SrCl_2$

The LiCl-$CaCl_2$-$SrCl_2$ System

The liquidus projection has been measured by the visual-polythermal method[8] (Figure 28). No ternary solid solubility is reported. The calculated liquidus projection is shown in Figure 29. (Note the different composition scales of Figures 17 and 18.) No ternary solid solubility is assumed in the calculations. A small ternary excess parameter was required :

$$g^{001}_{LiCa(Sr)/Cl} = -3138.0 \quad \text{J/mol} \qquad (31)$$

The NaCl-$CaCl_2$-$SrCl_2$ System

The liquidus projection has been measured by DTA[38] (Table III). The reported[38] ternary eutectic is at 744K and at 41.9 mol.% NaCl, 40.0 mol.% $CaCl_2$ and 18.1 mol.% $SrCl_2$. Calculated liquidus points are shown in Table III. No ternary excess parameters for the liquid phase were required. The calculated ternary eutectic is at 737.5K and at 41.5 mol.% NaCl, 41.2 mol.% $CaCl_2$ and 17.3 mol.% $SrCl_2$.

The CsCl-$CaCl_2$-$SrCl_2$ System

The liquidus projection has been measured by the visual-polythermal method and by DTA[36] (Figure 30). A complete solid solution between $CsCaCl_3$ and $CsSrCl_3$ is reported. The calculated liquidus projection is shown in Figure 31. No ternary parameters were used. The optimized Gibbs energy of the $Cs(Ca,Sr)Cl_3$ solid solution is given by a subregular solution model (Eq.[32]). The excess parameters of this solution were optimized from the reported $CsSrCl_3$-$CsCaCl_3$ phase diagram[36].

$$\begin{aligned} g &= X_{CsCaCl_3} g^{o,S}_{CsCaCl_3} + X_{CsSrCl_3} g^{o,S}_{CsSrCl_3} \\ &+ RT\left(X_{CsCaCl_3} \ln X_{CsCaCl_3} + X_{CsSrCl_3} \ln X_{CsSrCl_3}\right) \quad \text{J/mol} \\ &+ X_{CsCaCl_3} X_{CsSrCl_3} 5627.5 \\ &- X_{CsCaCl_3} X_{CsSrCl_3} 4184.0\left(X_{CsCaCl_3} - X_{CsSrCl_3}\right) \end{aligned} \qquad (32)$$

Other alkali-chloride mixtures with $CaCl_2$ and $SrCl_2$

No reported data were found for the KCl-$CaCl_2$-$SrCl_2$ and RbCl-$CaCl_2$-$SrCl_2$ systems. For purposes of calculation one can assume complete solid solubility between $RbSrCl_3$ and $RbCaCl_3$. An ideal solution of these two compounds is suggested. Very limited solid solubility of Sr^{2+} in $KCaCl_3$ is expected.

GENERAL MODEL FOR SOLID SOLUTIONS

The possible Sr-containing multicomponent solid solutions present in this system are the $(Li,Na,K,Rb,Cs)(Mg,Ca,Sr)Cl_3$ perovskite solution, the $(Li,Na,K)_2(Mg,Sr)Cl_4$ solid solution, and the low-temperature $(Ca,Sr,[Mg])Cl_2$ solid solution. Excess mixing parameters have been given in this article for many subsystems. The compound energy model[39] is suitable for estimating the Gibbs energies of the multicomponent solid solutions, but this model requires that the Gibbs energies of all possible pure mixing components be defined, including

metastable (or hypothetical) compounds such as $LiSrCl_3$, Na_2SrCl_4, etc. The hypothetical Gibbs energy of formation of $KSrCl_3$ from solid pure salts is defined in Eq.[24]. Furthermore, we arbitrarily set:

$$g^{o,hyp}_{LiSrCl_3} = g^{o,S}_{LiCl} + g^{o,a}_{SrCl_2} + 20000 \quad \text{J/mol} \tag{33}$$

$$g^{o,hyp}_{NaSrCl_3} = g^{o,S}_{NaCl} + g^{o,a}_{SrCl_2} + 20000 \quad \text{J/mol} \tag{34}$$

$$g^{o,hyp}_{Li_2SrCl_4} = 2g^{o,S}_{LiCl} + g^{o,a}_{SrCl_2} + 20000 \quad \text{J/mol} \tag{35}$$

$$g^{o,hyp}_{Na_2SrCl_4} = 2g^{o,S}_{NaCl} + g^{o,a}_{SrCl_2} + 20000 \quad \text{J/mol} \tag{36}$$

where the large positive value of +20 kJ/mol assures negligible solubility with other perovskites. The excess Gibbs energy of all binary subsystems must also be defined. For subsystems where immiscibility is observed, a very large positive regular excess Gibbs energy parameter (+100 kJ/mol) is proposed so that virtual immiscibility is calculated : Li_2MgCl_4-Li_2SrCl_4, Na_2MgCl_4-Na_2SrCl_4, K_2MgCl_4-K_2SrCl_4, Li_2SrCl_4-Na_2SrCl_4, Li_2SrCl_4-K_2SrCl_4, Na_2SrCl_4-K_2SrCl_4, $LiMgCl_3$-$LiSrCl_3$, $NaMgCl_3$-$NaSrCl_3$, $KMgCl_3$-$KSrCl_3$, $RbMgCl_3$-$RbSrCl_3$, $CsMgCl_3$-$CsSrCl_3$, $LiCaCl_3$-$LiSrCl_3$, $NaCaCl_3$-$NaSrCl_3$, $KCaCl_3$-$KSrCl_3$, $LiSrCl_3$-$NaSrCl_3$, $LiSrCl_3$-$KSrCl_3$, $LiSrCl_3$-$RbSrCl_3$, $LiSrCl_3$-$CsSrCl_3$, $NaSrCl_3$-$KSrCl_3$, $NaSrCl_3$-$RbSrCl_3$, $NaSrCl_3$-$CsSrCl_3$, $KSrCl_3$-$RbSrCl_3$, and $KSrCl_3$-$CsSrCl_3$. The Gibbs energy of the perovskite solid solution $(Li,Na,K,Rb,Cs)(Mg,Ca,Sr)Cl_3$ is then given by the compound energy model[39] as :

$$\begin{aligned} g = & \sum_{Alk=Li}^{Cs} \sum_{AlkE=Mg}^{Sr} y_{Alk} y_{AlkE} g^{o,S}_{Alk:AlkE:Cl_3} \\ & + RT\left(\sum_{Alk=Li}^{Cs} y_{Alk} \ln y_{Alk} + \sum_{AlkE=Mg}^{Sr} y_{AlkE} \ln y_{AlkE} \right) \\ & + \sum_{Alk=Li}^{Rb} \sum_{Alk'=Alk+1}^{Cs} \sum_{AlkE=Mg}^{Sr} y_{Alk} y_{Alk'} y_{AlkE} \omega_{(Alk,Alk'):AlkE:Cl_3} \\ & + \sum_{Alk=Li}^{Cs} \sum_{AlkE=Mg}^{Ca} \sum_{AlkE'=AlkE+1}^{Sr} y_{Alk} y_{AlkE} y_{AlkE'} \omega_{Alk:(AlkE,AlkE'):Cl_3} \end{aligned} \tag{37}$$

where y_i is the sublattice ionic site fraction and all ω terms are binary regular or subregular parameters either optimized or fixed (+100 kJ/mol) for the binary subsystems. The Gibbs energy of the $(Li,Na,K)_2(Mg,Sr)Cl_4$ solid solution is similarly given by :

$$\begin{aligned} g = & \sum_{Alk=Li}^{K} \left(y_{Alk} y_{Mg} g^{o,S}_{Alk_2MgCl_4} + y_{Alk} y_{Sr} g^{o,S}_{Alk_2SrCl_4} \right) \\ & + RT\left(2 \sum_{Alk=Li}^{K} y_{Alk} \ln y_{Alk} + y_{Mg} \ln y_{Mg} + y_{Sr} \ln y_{Sr} \right) \\ & + \sum_{Alk=Li}^{Na} \sum_{Alk'=Alk+1}^{K} \left(y_{Alk} y_{Alk'} y_{Mg} \omega_{(Alk,Alk')_2MgCl_4} + y_{Alk} y_{Alk'} y_{Sr} \omega_{(Alk,Alk')_2SrCl_4} \right) \\ & + \sum_{Alk=Li}^{K} y_{Alk} y_{Mg} y_{Sr} \omega_{Alk_2(Mg,Sr)Cl_4} \end{aligned} \tag{38}$$

CONCLUSIONS

A complete critical evaluation and optimization of all available phase diagram and thermodynamic data for all phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ system has been made. All data are reproduced within experimental error limits. The new modified quasichemical model[1] was used for the liquid phase, while the compound energy model[39] was used for the $(Li,Na,K,Rb,Cs)(Mg,Ca,Sr)Cl_3$ perovskite phase and the $(Li,Na,K)_2MgCl_4$ and $(Li,Na,K,Rb,Cs,[Ca])Cl$ solid solutions. From the optimized parameters of the binary and ternary subsystems it is possible, from the quasichemical model, to predict the thermodynamic properties of the multicomponent liquid solution. The database of optimized parameters is included in the F*A*C*T[40] database computing system and may be used, along with the other databases and Gibbs energy minimization software, to calculate phase equilibria and all thermodynamic properties in multicomponent systems.

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Table I : Thermodynamic properties of pure compounds

		T Range K	$H^{o}_{298.15K}$ ** J/mol	$S^{o}_{298.15}$ J/mol-K	C_p J/mol-K	Ref.
$SrCl_2$	α	298.15-1000	-828850.0	114.8090	$476.3367-0.3814267T+3918734T^{-2}$ $+0.0001973419T^{2}-6019.915T^{-0.5}$	[41]
	α	1000-3000	-841284.6	90.4078	104.6	*
	β	298.15-1000	-822842.2	120.8168	$476.3367-0.3814267T+3918734T^{-2}$ $+0.0001973419T^{2}-6019.915T^{-0.5}$	*
	β	1000-1400	-848198.9	74.1355	123.0100	[41]
	β	1400-3000	-827913.9	102.6090	104.6000	*
	L	298.15-800	-805383.2	135.7316	$-158.9102+0.1056800T-51660.5T^{-1}$ $+6496.385T^{-0.5}$	[41]
	L	800-3000	-805383.2	113.0816	104.6000	[41]
K_2SrCl_4	S	298.15-1000	-1697490.1	295.7851	$2\ C_p(KCl_s) + C_p(SrCl_{2\,\alpha})$	*
KSr_2Cl_5	S	298.15-1000	-2101927.6	315.0519	$C_p(KCl_s) + 2\ C_p(SrCl_{2\,\alpha})$	*
$RbSrCl_3$	S	298.15-1200	-1255915.0	225.8597	135.0000	*
$RbSr_2Cl_5$	S	298.15-1000	-2105672.4	319.1674	$C_p(RbCl_s) + 2\ C_p(SrCl_{2\,\alpha})$	*
$CsSrCl_3$	S	298.15-1200	-1274342.2	235.0465	140.0000	*

* This work.

** Relative to elements at 298.15K.

Table II. Cation-cation "Coordination Numbers" of the Liquid.

i	j	Z^{i}_{ij}	Z^{j}_{ij}
Sr	Sr	6	6
Li	Sr	3	6
Na	Sr	3	6
K	Sr	3	6
Rb	Sr	3	6
Cs	Sr	3	6
Mg	Sr	6	6
Ca	Sr	6	6

Table III : Experimental[38] and calculated liquidus points of the $NaCl$-$CaCl_2$-$SrCl_2$ system.

NaCl mol.%	$SrCl_2$ / ($CaCl_2$ + $SrCl_2$) Molar Ratio											
	0.1		0.2		0.4		0.5		0.6		0.8	
	T_{exp} K	T_{calc} K	T_{exp} K	T_{calc} K	T_{exp} K	T_{calc} K	T_{exp} K	T_{calc} K	T_{exp} K	T_{calc} K	T_{exp} K	T_{calc} K
10	982	981	935	953	902	899	923	922	956	949	1026	1004
20	925	936	895	906	863	861	875	886	908	912	968	961
30	875	879	842	848	823	819	844	845	864	869	911	913
40	806	810	779	778	778	774	803	799	821	821	853	859
55	786	800	795	804	815	814	–	-	828	825	837	837
60	880	876	884	877	887	882	–	-	895	888	894	895
70	943	940	943	940	954	940	–	-	952	942	951	945
80	1004	994	1002	994	1008	993	–	-	1003	992	1004	992
90	1047	1040	1047	1039	1045	1038	–	-	1045	1037	1043	1036

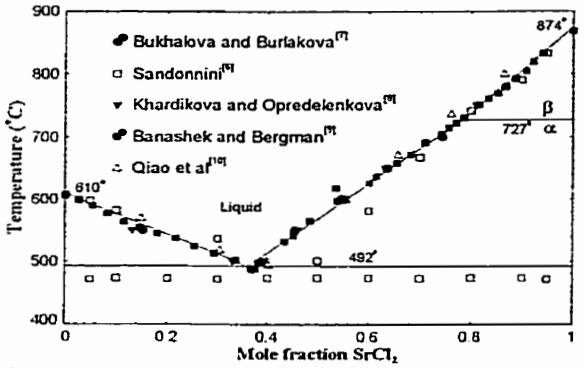

Fig. 1 – $LiCl-SrCl_2$ system : calculated phase diagram.

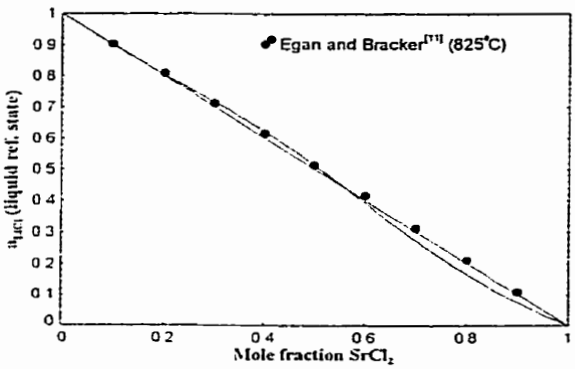

Fig.2 – $LiCl-SrCl_2$ system : calculated activity of LiCl in the liquid at 825°C (liquid ref. state).

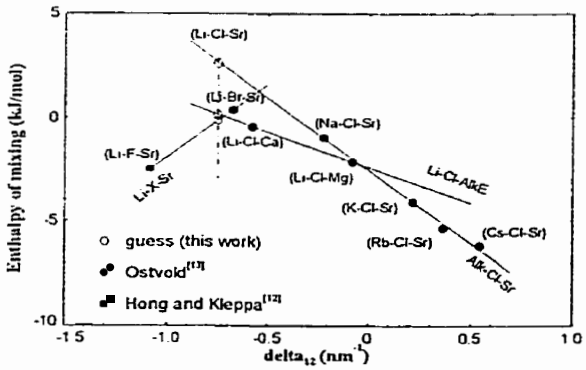

Fig.3 – Experimental enthalpy of mixing of alkali alkaline-earth halide melts evaluated at 40 mol.% alkaline-earth halide and estimations of the enthalpy of $LiCl-SrCl_2$ melts at 40 mol.% $SrCl_2$.

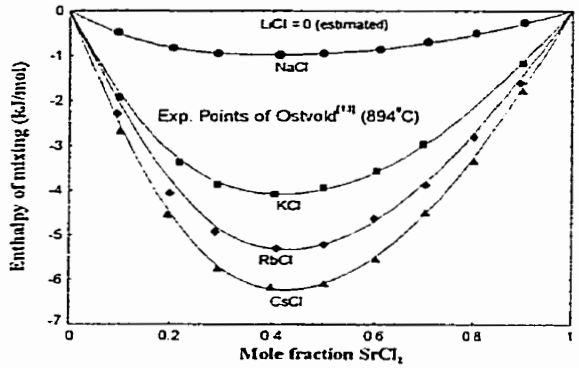

Fig. 4 – Calculated enthalpy of mixing of the liquid for the Alkali-Chlorides with $SrCl_2$ at 894°C with experimental points of Østvold[13].

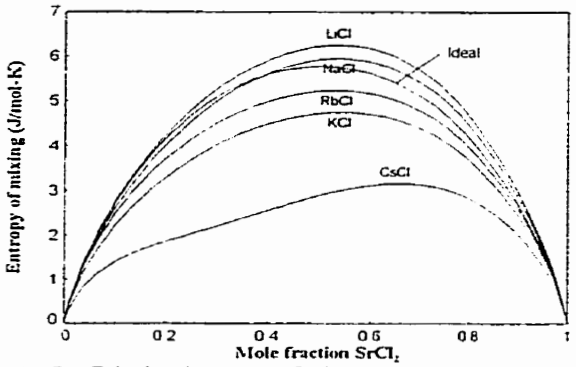

Fig. 5 – Calculated entropy of mixing of the liquid for the Alkali-Chlorides with $SrCl_2$ at 894°C.

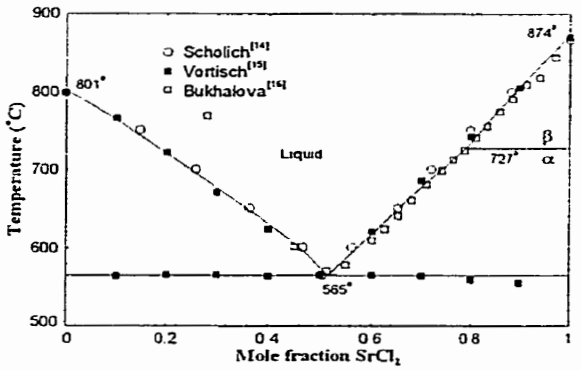

Fig. 6 – $NaCl-SrCl_2$ system : calculated phase diagram.

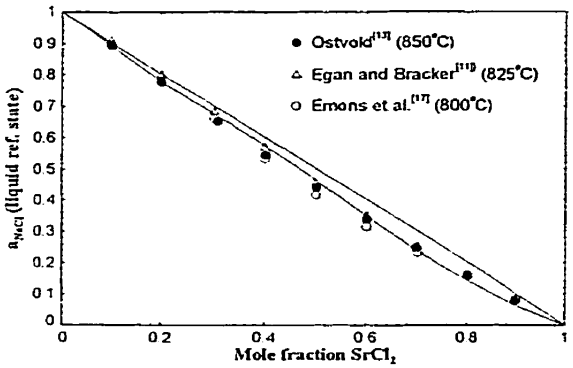

Fig. 7 – NaCl-$SrCl_2$ system : calculated activity of NaCl in the liquid at 825°C (liquid ref. state).

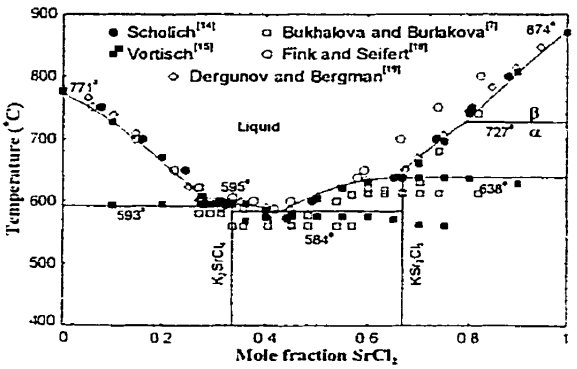

Fig. 8 – KCl-$SrCl_2$ system : calculated phase diagram.

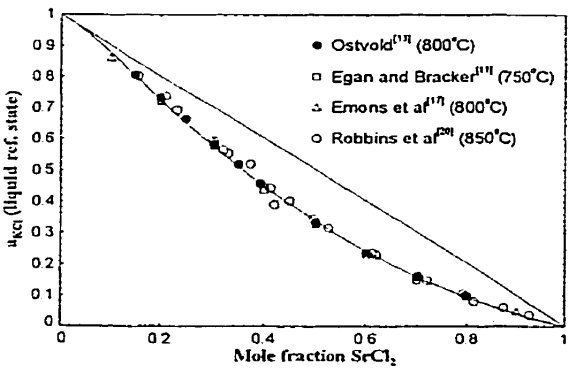

Fig. 9 – KCl-$SrCl_2$ system : calculated activity of KCl in the liquid at 800°C (liquid ref. state).

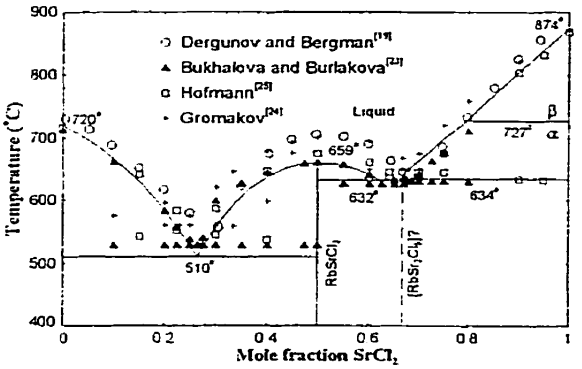

Fig. 10 – RbCl-$SrCl_2$ system : calculated phase diagram.

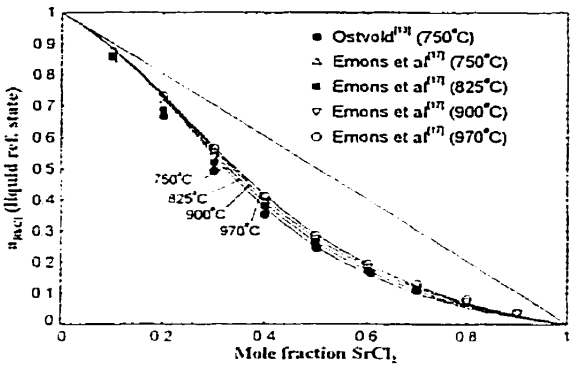

Fig. 11 – RbCl-$SrCl_2$ system : calculated activity of NaCl in the liquid at 750°C, 825°C, 900°C and 970°C (liquid ref. state).

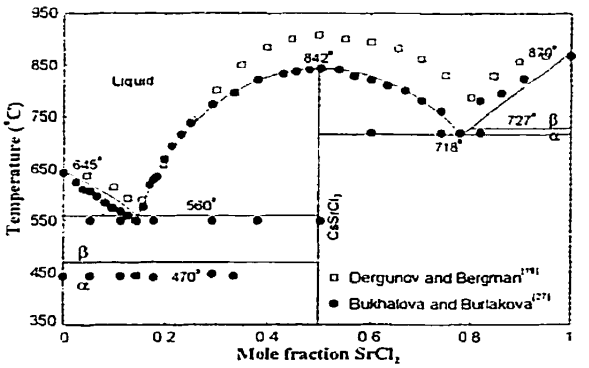

Fig. 12 – CsCl-$SrCl_2$ system : calculated phase diagram.

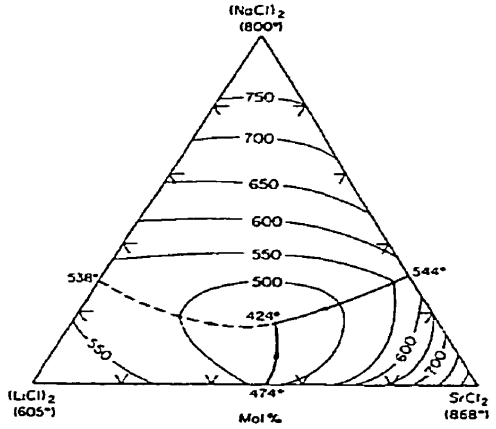

Fig. 13 – Li_2Cl_2-Na_2Cl_2-$SrCl_2$ system : experimental liquidus projection of Bukhalova *et al.*[28].

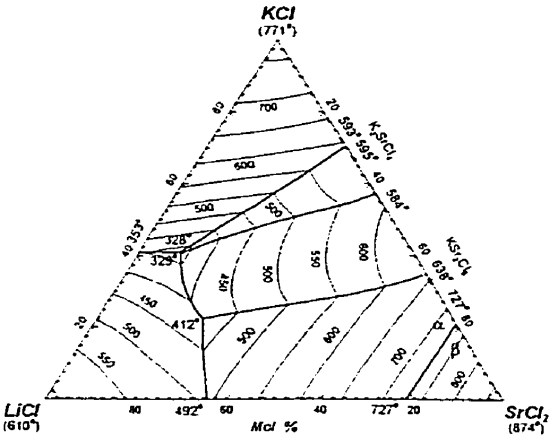

Fig. 16 – LiCl-KCl-$SrCl_2$ system : calculated liquidus projection.

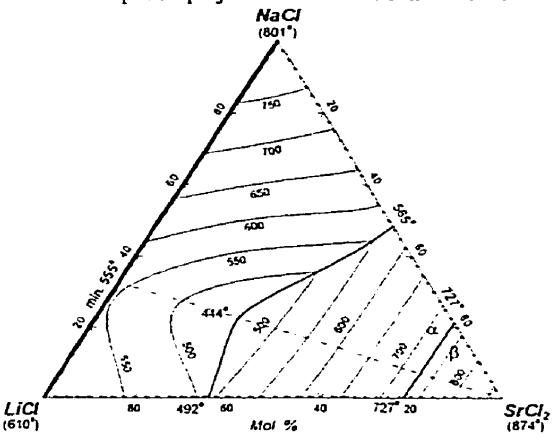

Fig. 14 – LiCl-NaCl-$SrCl_2$ system : calculated liquidus projection.

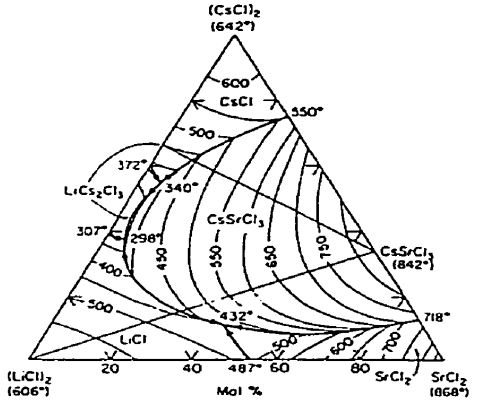

Fig. 17 – Li_2Cl_2-Cs_2Cl_2-$SrCl_2$ system : experimental liquidus projection of Bukhalova and Burlakova[27].

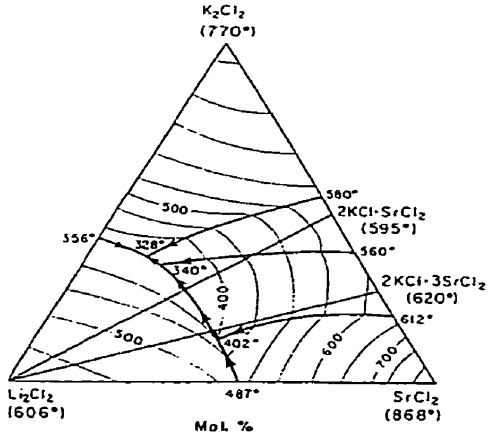

Fig. 15 – Li_2Cl_2-K_2Cl_2-$SrCl_2$ system : experimental liquidus projection of Bukhalova and Burlakova[7].

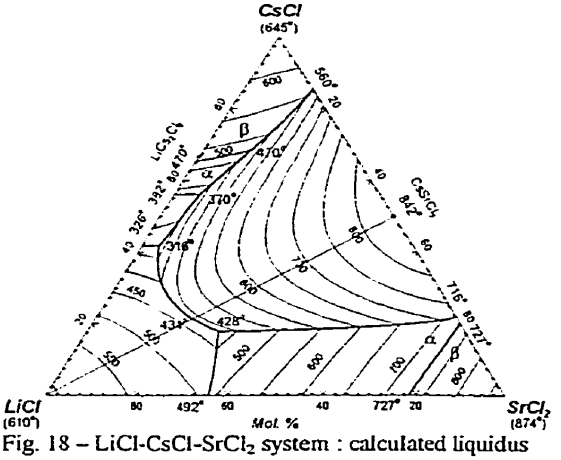

Fig. 18 – LiCl-CsCl-$SrCl_2$ system : calculated liquidus projection.

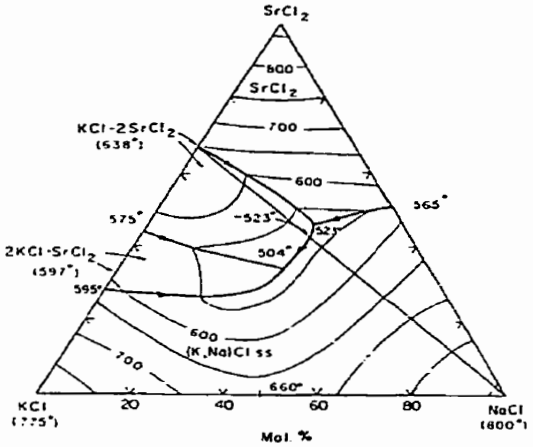

Fig. 19 – NaCl-KCl-$SrCl_2$ system : experimental liquidus projection of Scholich[14].

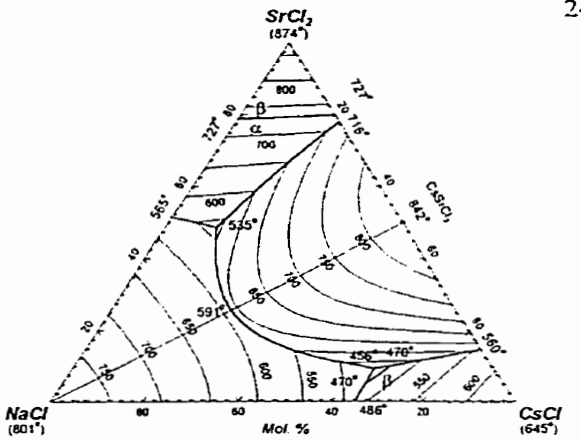

Fig. 22 – NaCl-CsCl-$SrCl_2$ system : calculated liquidus projection.

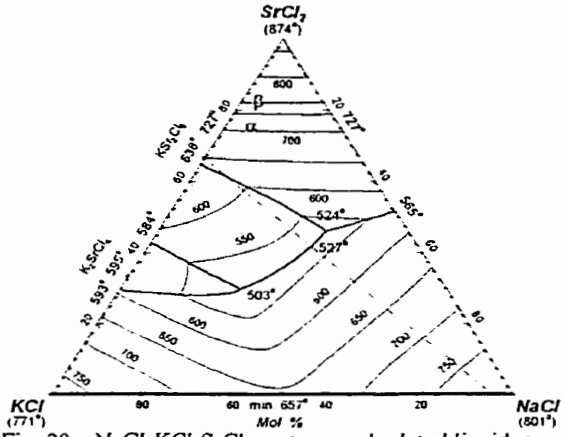

Fig. 20 – NaCl-KCl-$SrCl_2$ system : calculated liquidus projection.

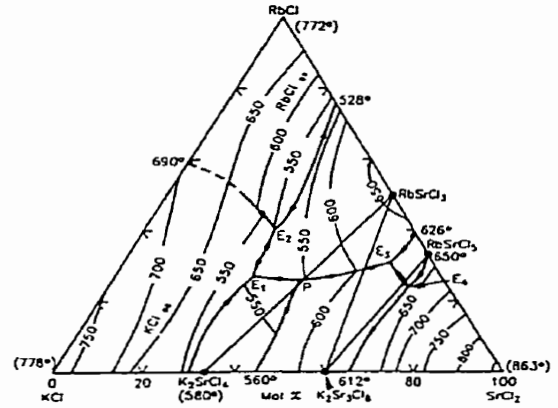

Fig. 23 – KCl-RbCl-$SrCl_2$ system : experimental liquidus projection of Bukhalova and Burlakova[23].

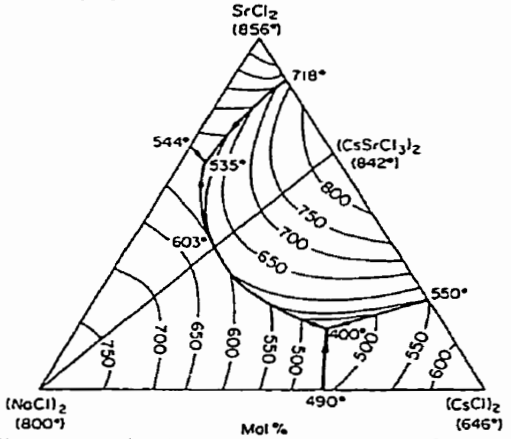

Fig. 21 – Na_2Cl_2-Cs_2Cl_2-$SrCl_2$ system : experimental liquidus projection of Bukhalova *et al.*[31].

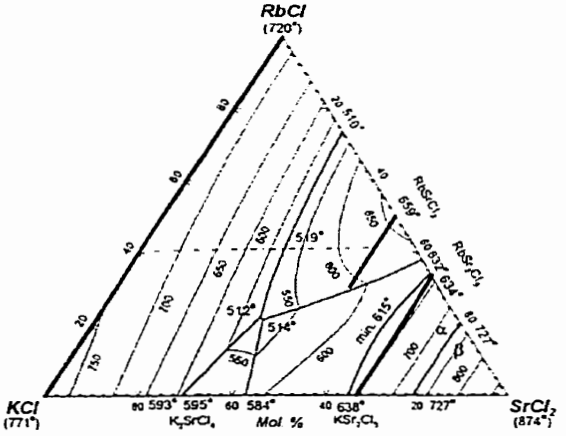

Fig. 24 – KCl-RbCl-$SrCl_2$ system : calculated liquidus projection.

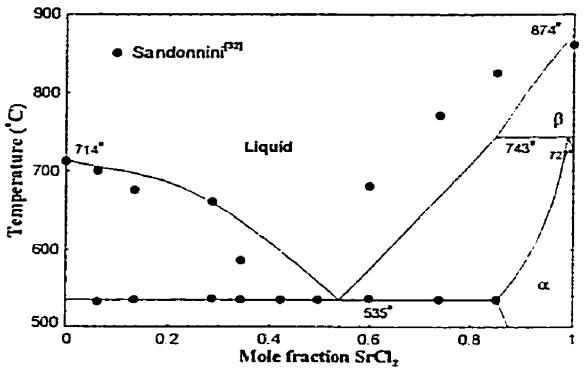

Fig. 25 – $MgCl_2$-$SrCl_2$ system : calculated phase diagram.

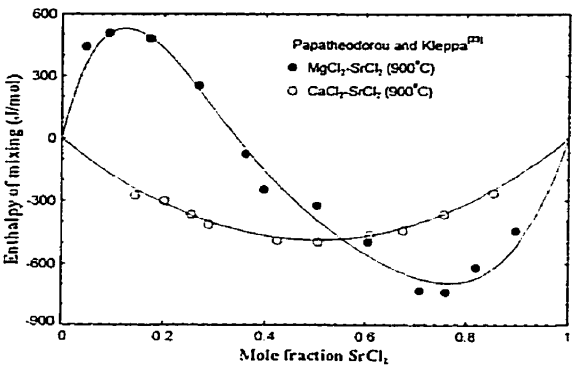

Fig. 26 – $MgCl_2$-$SrCl_2$ and $CaCl_2$-$SrCl_2$ systems : calculated enthalpy of mixing of the liquid at 900°C.

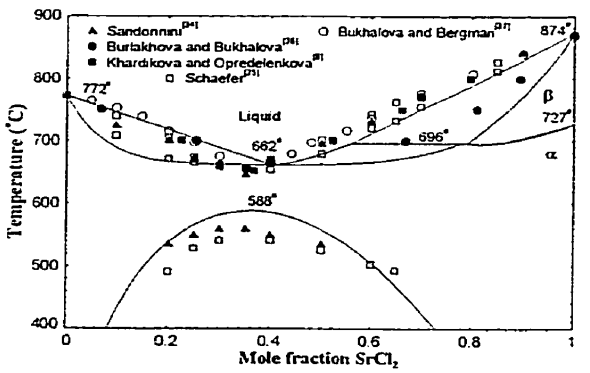

Fig. 27 – $CaCl_2$-$SrCl_2$ system : calculated phase diagram. (The only experimental solidus points are those of Schaefer[35]).

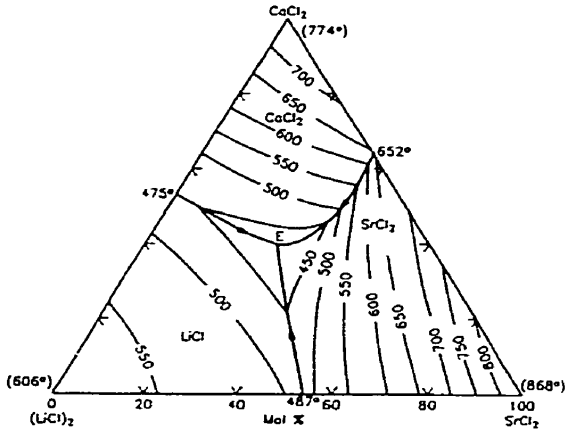

Fig. 28 – Li_2Cl_2-$CaCl_2$-$SrCl_2$ system : experimental liquidus projection of Khardikova and Opredelenkova[8].

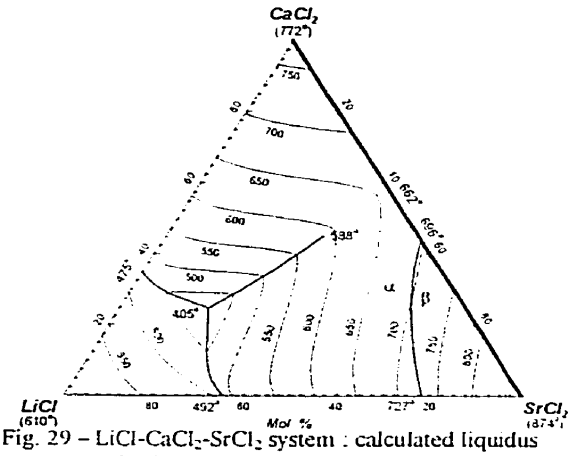

Fig. 29 – LiCl-$CaCl_2$-$SrCl_2$ system : calculated liquidus projection.

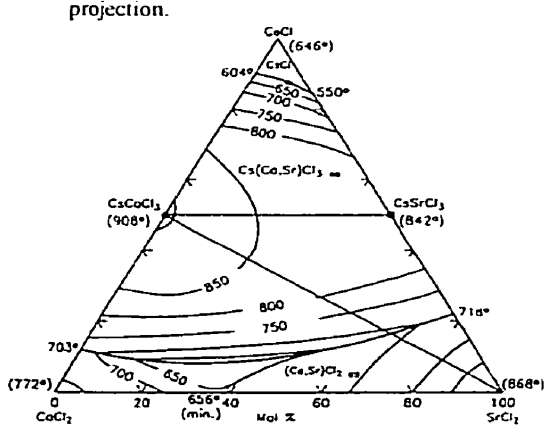

Fig. 30 – CsCl-$CaCl_2$-$SrCl_2$ system : experimental liquidus projection of Burlakova and Bukhalova[36].

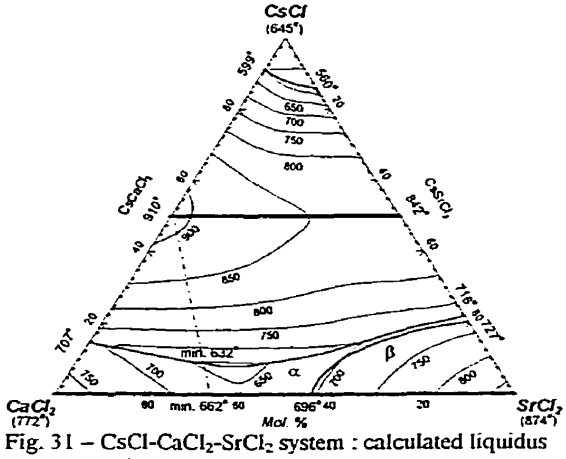

Fig. 31 – $CsCl$-$CaCl_2$-$SrCl_2$ system : calculated liquidus projection.

ANNEXE VI

Article :

Thermodynamic Evaluation and Optimization of the $LiCl$-$NaCl$-KCl-$RbCl$-$CsCl$-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ System Using the Modified Quasichemical Model

Patrice Chartrand et Arthur D. Pelton,

Soumis à *Canadian Metallurgical Quarterly*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel *FIGURE* développé par l'auteur de cette thèse durant ses études doctorales.

THERMODYNAMIC EVALUATION AND OPTIMIZATION OF THE LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ SYSTEM USING THE MODIFIED QUASICHEMICAL MODEL

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Abstract - A complete critical evaluation and quantitative optimization of all available phase diagram and thermodynamic data has been performed for all condensed phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ system. The model parameters obtained for binary and ternary subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent system. The modified quasichemical model for short-range ordering was used for the molten salt phase.

Résumé - Une évaluation critique et une optimization quantitative des diagrammes de phase et des données thermodynamiques a été faite pour toutes les phases condensées du système LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$. Les paramètres des modèles obtenus pour les sous-systèmes binaires et ternaires peuvent être utilisés pour prédire les propriétés thermodynamiques et les équilibres de phases pour le système multicomposant. Le modèle quasichimique modifié, qui évalue l'ordonnement à courte distance des cations, a été utilisé pour la phase liquide.

INTRODUCTION

Molten alkali-alkaline earth halide solutions are of much technological importance in, for example, the production of reactive metals. A large body of experimental thermodynamic and phase equilibrium data exists for these systems. In this article, all available data for binary and ternary subsystems of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ system are critically evaluated and optimized to obtain parameters of models of all solution phases. These parameters form a computer database. The models are then used to predict the thermodynamic properties of the multicomponent system. When used with currently available general software for calculating equilibria by Gibbs energy minimization, this database can be used to predict the thermodynamic properties and phase equilibria in uncharted regions of temperature and composition. This article is one in a series that will be published on alkali-alkaline earth halide systems.

In a previous article[1] we presented a quasichemical model for liquid solutions which takes into account short-range ordering between nearest-neighbors on a lattice or sublattice. Molten alkali chloride-$MgCl_2$ solutions are well known for exhibiting extensive short-range ordering, increasing in importance from LiCl-$MgCl_2$ to CsCl-$MgCl_2$. This ordering gives rise to "V-shaped" enthalpy of mixing and "m-shaped" entropy of mixing curves. This has previously been modelled by introducing complex anions such as $MgCl_4^{2-}$ [2,3]. Alkali chloride-$BaCl_2$ solutions do not show the same extent of ordering as for $MgCl_2$, but the tendency is present. The modified quasichemical model[1] quantitatively treats the short-range ordering between cations in binary and multicomponent solutions. An earlier version of the model has been used very successfully to model molten silicates[4].

The model does not explicitely introduce complex anions. Instead, short-range ordering is treated by considering the relative numbers of second-nearest-neighbor cation-cation pairs. The parameters of the model are the Gibbs energy changes $\Delta g_{AB/Cl}$ for the pair exchange reactions :

$$(A-Cl-A)_{pair}+(B-Cl-B)_{pair}=2(A-Cl-B)_{pair} \qquad \Delta g_{AB/Cl} \quad (1)$$

As $\Delta g_{AB/Cl}$ becomes progressively more negative, reaction [1] is shifted progressively to the right, (A-Cl-B) pairs predominate, and the solution becomes progressively more ordered. In the previous article[1] the model was developed in terms of nearest-neighbor pairs (A-B) for species mixing on one lattice. In the present case, since the anion sublattice is occupied only by Cl^- ions, the model can be used directly to treat cation-cation pairs on the cation sublattice. The parameter $\Delta g_{AB/Cl}$ is the parameter Δg_{mn} of the previous article[1]. When $\Delta g_{AB/Cl}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of cations on the cation sublattice.

In previous articles of the present series[5,6], a complete evaluation and quantitative optimization of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ system with the modified quasichemical model was presented. The present article describes the addition of $BaCl_2$ to that database, and further demonstrates the application of the new modified

quasichemical model to the evaluation, optimization and prediction of thermodynamic properties and phase equilibria.

THERMODYNAMIC DATA

All thermodynamic data ($H^o_{298.15K}$, $S^o_{298.15K}$ and C_p) for the condensed pure phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$ system are given in the previous articles[5,6]. All thermodynamic data ($H^o_{298.15K}$, $S^o_{298.15K}$ and C_p) for the condensed pure phases of the $BaCl_2$ containing binary subsystems are given in Table I.

THERMODYNAMIC MODEL FOR THE LIQUID PHASE

The modified quasichemical model[1] is used for the liquid phase. The notation of the previous articles[1,5,6] is maintained. For example, X_{NaBa} is the mole fraction of second-nearest-neighbor (Na-Cl-Ba) pairs. The model requires the definition of cation-cation coordination numbers Z^i_{ij}. The values chosen in the present work are listed in Table II. Values for pairs not involving Ba were given previously[5,6]. Note that, for example, the choice of $Z^K_{KBa} = \frac{1}{2} Z^{Ba}_{KBa}$ assures that the composition of maximum short-range ordering will be near the K_2BaCl_4 composition (similar to K_2MgCl_4[5]). Also, as discussed previously[1], it is necessary to define all ternary sub-systems as either "symmetric" or "asymmetric". In the present case, all ternary systems in which all three components are alkali halides are defined as symmetric. Systems with one alkali and two alkaline-earth chlorides are asymmetric, with the alkali chloride as asymmetric component, and systems with one alkaline-earth and two alkali chlorides are asymmetric, with the alkaline-earth chloride as asymmetric component. To this end, the components are divided into two groups, all alkali halides are in one group, and alkaline-earth form the other group. The composition variables χ_{ij} defined previously[1] then become :

$$\chi_{LiMg} = \chi_{LiCa} = \chi_{LiSr} = \chi_{LiBa} = \chi_{NaMg} = \chi_{NaCa} = \\ = \chi_{NaSr} = \chi_{NaBa} = \ldots = \chi_{AlkAlkE} = \chi_{Alk} \quad (2)$$

where $$\chi_{Alk} = \sum_{i=Li}^{Cs} \sum_{j=i}^{Cs} X_{ij} \quad (3)$$

$$\chi_{MgLi} = \chi_{CaLi} = \chi_{SrLi} = \chi_{BaLi} = \chi_{MgNa} = \chi_{CaNa} = \\ = \chi_{SrNa} = \chi_{BaNa} = \ldots = \chi_{AlkEAlk} = \chi_{AlkE} \quad (4)$$

where $$\chi_{AlkE} = \sum_{i=Mg}^{Ba} \sum_{j=i}^{Ba} X_{ij} \quad (5)$$

and also

$$\chi_{MgBa} = \frac{X_{MgMg}}{X_{MgMg} + X_{MgBa} + X_{BaBa}} \quad (6)$$

$$\chi_{BaMg} = \frac{X_{BaBa}}{X_{MgMg} + X_{MgBa} + X_{BaBa}} \quad (7)$$

etc.

That is, when i and j are both alkaline-earths or both alkalis:

$$\chi_{ij} = \frac{X_{ij}}{X_{ii} + X_{ij} + X_{jj}} \quad (8)$$

The parameters $\Delta g_{AB/Cl}$ of reaction [1] for each pair are expanded, through optimization of available experimental data, as empirical polynomials in χ_{ij}. For ternary systems, terms may be added giving the effect of the third component upon the pair formation energies $\Delta g_{AB/Cl}$. As described previously[1] this is done by introducing empirical ternary parameters $g^{ijk}_{AB(C)/Cl}$ in the polynomial expansion.

MIXTURES OF ALKALI CHLORIDES WITH $BaCl_2$

Estimation of the Enthalpy of Mixing of the Liquid

No data were found for the enthalpy of mixing of the liquid for the binary alkali chloride-$BaCl_2$ systems. However, many calorimetric measurements of the enthalpy of mixing of the liquid can be found for related systems : alkali chloride-$MgCl_2$[7], alkali chloride-$CaCl_2$[8], alkali chloride-$SrCl_2$[8] (except LiCl-$SrCl_2$), LiF-BaF_2[9], NaF-BaF_2[9], KF-BaF_2[9] and alkali bromide-$BaBr_2$[8]. A technique was used previously[6] to estimate the enthalpy of mixing of liquid LiCl-$SrCl_2$ mixtures at 40 mol.% $SrCl_2$ from experimental measurements[8] and the δ_{12} function[8] of Eq.[9]. (The 40 mol.% alkaline-earth chloride concentration was selected because it corresponds to the approximate concentration of the minimum enthalpy in most alkali alkaline-earth chloride systems.)

$$\delta_{12} = \frac{(r_1^+ + r_X^-) - (r_2^{2+} + r_X^-)}{(r_1^+ + r_X^-)(r_2^{2+} + r_X^-)} \quad (9)$$

In Eq.[9], r is the ionic radius and X is the common halide anion. (The ionic radii were taken from Janz[10]). The enthalpy of mixing of a family of alkali-alkaline-earth halide solutions varies almost linearly with δ_{12}[8]. Best fit lines for various Alk-X-AlkE families (Alk = alkaline, AlkE = alkaline-earth, X = halide) can thus be obtained and plotted (Figures 1-5) at 40 mol.% alkaline-earth chloride. The extrapolated or interpolated value for each line at the δ_{12} value of the Alk-Cl-Ba binary system gives an estimate of the enthalpy of mixing of the Alk-Cl-Ba system. The mean of these estimates is then taken as the final estimate of

the enthalpy of mixing of the AlkCl-$BaCl_2$ system at 40 mol.% $BaCl_2$ at 870°C. This estimated value is then used in the optimizations.

The estimated values at 40 mol.% $BaCl_2$ and at 870°C are : 0.457±0.3 kJ/mol for the LiCl-$BaCl_2$ melts (this value was obtained by including a value for LiBr-$BaBr_2$ melts estimated by extrapolating the Li-Cl-AlkE line as shown in Figure 1), 0.436±0.3 kJ/mol for NaCl-$BaCl_2$ melts, -1.483±0.3 kJ/mol for KCl-$BaCl_2$ melts, -1.875±0.3 kJ/mol for RbCl-$BaCl_2$ melts, and -1.968±0.7 kJ/mol for CsCl-$BaCl_2$ melts.

In the AlkCl-$MgCl_2$, AlkCl-$CaCl_2$ and AlkCl-$SrCl_2$ systems, the curves of the enthalpy of mixing of the liquid versus composition (in equivalent fractions) are quite symmetrical[5,6]. The same symmetry is expected for the AlkCl-$BaCl_2$ solutions. Therefore, in the liquid model, the enthalpic part of the Gibbs energy of reaction [1] was assumed to be given by a constant parameter.

The LiCl-$BaCl_2$ System

The phase diagram was measured by the "visual-polythermal" method[11,12], cooling curves[13] and DTA[14] (Figure 7). No solid solubility is reported, and the limiting slopes of the LiCl and $BaCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

$$\lim_{X_m \to 1}\left(\frac{dX_m^{liquidus}}{dT}\right) = \frac{\Delta h^o_{fusion}}{RT^2_{fusion}} \qquad (11)$$

where Δh^o_{fusion} and T_{fusion} are the enthalpy and temperature of fusion of the pure salt. The optimized Gibbs energy of reaction [1] for the *Li-Cl-Ba* pairs is :

$$\Delta g_{LiBa/Cl} = 739.5 - 2.2322T \quad \text{J/mol} \qquad (18)$$

Figures 6 and 7 show the calculated phase diagram and thermodynamic properties.

The NaCl-$BaCl_2$ System

The phase diagram has been measured by the visual-polythermal method[15-22] and by thermal analysis[23,24] (Figure 8). No solid solubility is reported, and the limiting slopes of the NaCl and $BaCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

The activity of NaCl in the liquid has been measured by emf techniques[8,25,26] (Figure 9). The optimized Gibbs energy of reaction [1] for the *Na-Cl-Ba* pairs is :

$$\Delta g_{NaBa/Cl} = 727.1 - 0.8210T - 0.8151T\chi_{AlkE} \quad \text{J/mol} \qquad (19)$$

Figures 6, 8 and 9 show the calculated phase diagram and thermodynamic properties.

The KCl-$BaCl_2$ System

The phase diagram has been measured by the visual-polythermal method[16,17,27-29] and thermal analysis[30,31] (Figure 10). An intermediate congruently melting compound K_2BaCl_4 is reported by all authors except Elchardus and Laffite[30] who reported an incongruent KBa_3Cl_7 compound. No solid solubility is reported, and the limiting slopes of the KCl and $BaCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

The activity of KCl in the liquid has been measured by emf techniques[25,26,32] (Figure 11). Hattori *et al.*[33] measured the enthalpy of fusion of K_2BaCl_4 by calorimetry as 68.618 kJ/mol at 932K. The calculated optimized value is 68.55 kJ/mol at 932.4K. ΔC_p of formation of K_2BaCl_4 from pure KCl(s) and $BaCl_2(\alpha)$ was assumed to be 0. The optimized Gibbs energy of reaction [1] for the *K-Cl-Ba* pairs is :

$$\Delta g_{KBa/Cl} = -2409.5 + 0.8009T - 1.1399T\chi_{AlkE} \quad \text{J/mol} \qquad (20)$$

Figures 6, 10 and 11 show the calculated phase diagram and thermodynamic properties.

The RbCl-$BaCl_2$ System

The phase diagram has been measured by the visual-polythermal method[34-36] and DTA[37] (Figure 12). An intermediate congruent compound Rb_2BaCl_4 is reported. No solid solubility is reported, and the limiting slopes of the RbCl and $BaCl_2$ liquidus curves satisfy Eq.[11] which assumes no solid solubility.

The activity of RbCl has been measured by an emf technique[26] (Figure 13). At high-RbCl concentrations, the experimental measurements[26] at 820°C and 900°C do not appear to obey Raoult's Law and indicate an extremely large partial entropy of RbCl. That is, this large apparent temperature dependance is very probably in error.

No thermodynamic data were found for the Rb_2BaCl_4 compound. ΔC_p of formation of Rb_2BaCl_4 from solid RbCl and $BaCl_2(\alpha)$ was assumed to be 0. The optimized Gibbs energy of reaction [1] for the *Rb-Cl-Ba* pairs is :

$$\Delta g_{RbBa/Cl} = -2879.6 - 1.9268T + 1.1612T\chi_{AlkE} \quad \text{J/mol} \qquad (21)$$

Figures 6, 12 and 13 show the calculated phase diagram and thermodynamic properties.

The CsCl-$BaCl_2$ System

The phase diagram has been measured by a thermographic method[22] (Figure 14). An incongruent $CsBaCl_3$ compound is reported as well as a congruent Cs_2BaCl_4 compound. No solid solubility is reported and the limiting slope of the CsCl liquidus agrees reasonably well with Eq.[11] which assumes no solid solubility. No verification of the stoichiometry of $CsBaCl_3$ by X-ray

diffraction has been made. Hence, this stoichiometry is shown as tentative on Figure 14.

No activity measurements have been found. No experimental thermodynamic data were found for the $CsBaCl_3$ and Cs_2BaCl_4 compounds. The heat capacity of $CsBaCl_3$ was estimated as 140 J/mol-K from the optimized values for other perovskite[5,6] compounds ($NaMgCl_3$, $KMgCl_3$, $KCaCl_3$, $CsCaCl_3$, etc...). ΔC_p of formation of Cs_2BaCl_4 from solid $CsCl(\alpha)$ and $BaCl_2(\alpha)$ was assumed to be 0. The optimized Gibbs energy of reaction [1] for the *Cs-Cl-Ba* pairs is :

$$\Delta g_{CsBa/Cl} = -3109.8 - 0.2132T - 0.4624T\chi_{AlkE} \quad \text{J/mol} \quad (22)$$

Figures 6 and 14 show the calculated phase diagram and thermodynamic properties.

The LiCl-NaCl-BaCl₂ System

The liquidus projection has been measured by the visual-polythermal method[21,38] and DTA[38] (Figure 15[21]). Zakharchenko and Aslanov[21] reported a "eutectic" at 490°C (minimum of the univariant line $BaCl_2$+(Li,Na)Cl_{ss}) with two compounds, $LiNaCl_2$ and $LiNa_2Cl_3$, that are considered non-existent in the present study. Bukhalova *et al.*[38] reported a minimum of the univariant line $BaCl_2$+(Li,Na)Cl_{ss} at 456°C. No ternary solid solubility is reported. The calculated liquidus projection is shown in Figure 16. No ternary excess parameters were used for the liquid phase. (Note the different composition scales of Figures 15 and 16.) No ternary solid solution was assumed in the calculations.

The LiCl-KCl-BaCl₂ System

The liquidus projection has been measured by the visual-polythermal method[29] (Figure 17). No ternary solid solution is reported. The temperature of the reported ternary eutectic is 320°C. However, extrapolation of the spacing of the 500°C, 450°C and 400°C isotherms of Figure 17 would suggest that this value is too low by about 30°C. The calculated liquidus projection is shown in Figure 18. (Note the different composition scales of Figures 17 and 18.) No ternary excess parameters were included in the liquid model because of the uncertainty of the reported eutectic temperature. No ternary solid solution was assumed in the calculations, and Li^+ was assumed insoluble in K_2BaCl_4.

The NaCl-KCl-BaCl₂ System

The liquidus projection has been measured by the visual-polythermal method[17,20,28] (Figure 19[17]). There is agreement on the temperature of the ternary eutectic reported at 526°C[20] and at 542°C[17,28]. No solid solubility is reported by either author. With a very small ternary term (Eq.[23]) the calculated liquidus projection (Figure 20) is very close to those of both Bukhalova and Yagub'yan[28], and Vortisch[17]. Na^+ is assumed insoluble in K_2BaCl_4.

$$g^{001}_{KBa(Na)/Cl} = -836.8 \quad \text{J/mol} \quad (23)$$

The NaCl-CsCl-BaCl₂ System

The liquidus projection has been measured by the visual-polythermal method[22] (Figure 21). Two ternary peritectics and a ternary eutectic are reported. No solid solubility is reported. The liquidus surface was calculated (Figure 22) with a small ternary term (Eq.[15]) for the liquid model and with no ternary solid solubility. (Note the different composition scales of Figures 21 and 22.)

$$g^{001}_{CsBa(Na)/Cl} = -3138 \quad \text{J/mol} \quad (15)$$

Other Alkali Chloride-BaCl₂ Ternary Systems

No experimental data were found for the LiCl-RbCl-$BaCl_2$, LiCl-CsCl-$BaCl_2$, NaCl-RbCl-$BaCl_2$, KCl-RbCl-$BaCl_2$, KCl-CsCl-$BaCl_2$ and RbCl-CsCl-$BaCl_2$ systems. Solubilities of Li^+, Na^+, K^+ and Rb^+ in $CsBaCl_3$ must be estimated. A large solid solubility of Rb^+ in $CsBaCl_3$ is expected. The following Gibbs energy expression is proposed :

$$g = X_{CsBaCl_3} g^{o,S}_{CsBaCl_3} + X_{RbBaCl_3} g^{o,hyp}_{RbBaCl_3} + RT\left(X_{CsBaCl_3} \ln X_{CsBaCl_3} + X_{RbBaCl_3} \ln X_{RbBaCl_3}\right) \quad (16)$$

with the standard Gibbs energy of hypothetical $RbBaCl_3$ given as :

$$g^{o,hyp}_{RbBaCl_3} = g^{o,S}_{RbCl} + g^{o,\alpha}_{BaCl_2} + 5000 \quad \text{J/mol} \quad (17)$$

where the small positive term in Eq.[17] ensures that hypothetical pure $RbBaCl_3$ is metastable. Only limited solid solubility is expected for K^+ in $CsBaCl_3$ since hypothetical $KBaCl_3$ is expected to be less stable than hypothetical $RbBaCl_3$ and because of the larger ionic radius difference between K^+/Cs^+ versus Rb^+/Cs^+. Li^+, Na^+ and K^+ are assumed insoluble in $CsBaCl_3$.

K_2BaCl_4, Cs_2BaCl_4 and Rb_2BaCl_4 are expected to be mutually soluble, although complete solid solubility of K_2BaCl_4 and Cs_2BaCl_4 may not occur. An ideal solid solution between these three compounds is assumed for purposes of calculation. Na^+ and Li^+ are assumed insoluble in this solution.

MIXTURES OF ALKALINE-EARTH CHLORIDES WITH $BaCl_2$

The MgCl₂-BaCl₂ System

The phase diagram has been measured by the visual-polythermal method[39] and by thermal and X-ray analysis[40] (Figure 23). The reported liquidus curves of

$BaCl_2$[39,40] are in disagreement. The $BaCl_2$-liquidus points of Bondarenko[40] plotted in Figure 23 were read off a NaCl-$MgCl_2$-$BaCl_2$ liquidus projection[40]. Bodarenko[40] reported an incongruent intermediate compound $MgBa_2Cl_6$, while Sandonnini[39] reported no eutectic thermal arrests for $BaCl_2$ concentrations higher than 50 mol.%, and reported a compound of unknown composition. No solid solubility was reported. The limiting slope of the $MgCl_2$ liquidus is in good agreement with Eq.[11].

Calorimetric measurements for the liquid phase are available[41] (Figure 24). For purposes of calculation, no solid solubility is assumed. The optimized Gibbs energy of reaction [1] for the *Mg-Cl-Ba* pairs is :

$$\Delta g_{MgBa/Cl} = -1022.8 - 3.1089T - 2837.6\chi_{MgBa} - 4845.1\chi_{BaMg} \quad \text{J/mol} \qquad (18)$$

The entropy and heat capacity of formation of $MgBa_2Cl_6$ from $MgCl_{2(s)}$ and $BaCl_{2(\alpha)}$ were set to 0. Figures 23 and 24 show the calculated phase diagram and thermodynamic properties.

The $CaCl_2$-$BaCl_2$ System

The $CaCl_2$-$BaCl_2$ phase diagram has been measured by thermal analysis[42-43] and by the visual-polythermal method[27,44-47] (Figure 25). All authors reported an incongruently melting compound $CaBaCl_4$ except Sandonnini[44] who reported no compound. No confirmation of this stoichiometry is available from X-ray diffraction. Hence, this stoichiometry is shown as tentative on Figure 25. No solid solubility is reported. The limiting liquidus slopes are in reasonable agreement with Eq.[11], thereby indicating that terminal solid solubilities are small.

Calorimetric measurements for the liquid phase are available[41] (Figure 24). No thermodynamic properties were found for the $CaBaCl_4$ compound. ΔC_p of formation of $CaBaCl_4$ from pure $CaCl_2$(s) and $BaCl_2(\alpha)$ is set to zero for purposes of calculation. No solid solubility is assumed. The optimized Gibbs energy of reaction [1] for the *Ca-Cl-Ba* pairs is :

$$\Delta g_{CaBa/Cl} = -2627.9 - 451.6\chi_{BaCa} \quad \text{J/mol} \qquad (19)$$

Figures 24 and 25 show the calculated phase diagram and thermodynamic properties.

The $SrCl_2$-$BaCl_2$ System

The phase diagram has been measured by thermal analysis[48], the visual-polythermal method[17,49,50] and DTA[14] (Figure 26). Complete solubility of the α and β solid phases is reported.

Calorimetric measurements for the liquid phase are available[41] (Figure 24). High-temperature $BaCl_{2(\beta)}$ and $SrCl_{2(\beta)}$ have the cubic CaF_2-type structure ($SrCl_{2(\beta)}$ has a distorted structure) and so complete miscibility is possible. The low-temperature allotropes, however, have different structures ($BaCl_{2(\alpha)}$ is orthorombic $PbCl_2$-type and $SrCl_{2(\alpha)}$ is cubic CaF_2-type). Hence, a two-phase region must exist at low temperature. The high-temperature extended solid solution between $SrCl_{2(\beta)}$ and $BaCl_{2(\beta)}$ is represented by a subregular model :

$$\begin{aligned} g &= X_{BaCl_2} g^{o,\beta}_{BaCl_2} + X_{SrCl_2} g^{o,\beta}_{SrCl_2} \\ &+ RT\left(X_{BaCl_2} \ln X_{BaCl_2} + X_{SrCl_2} \ln X_{SrCl_2}\right) \\ &+ 3359.0 X_{BaCl_2} X_{SrCl_2} - 278.6 X_{SrCl_2} X_{BaCl_2}\left(\frac{X_{BaCl_2}}{X_{BaCl_2} + X_{SrCl_2}}\right) \end{aligned} \quad \text{J/mol} \qquad (20)$$

A regular solution model is used to describe the thermodynamic properties of the $(Ba,[Sr])Cl_2$ (α_1) and $(Sr,[Ba])Cl_2$ (α_2) solid solutions (with small positive Henrian parameters) :

$$\begin{aligned} g^{\alpha_1} &= X_{BaCl_2} g^{o,\alpha}_{BaCl_2} + X_{SrCl_2}\left(g^{o,\alpha}_{SrCl_2} + 250.0\right) \\ &+ RT\left(X_{BaCl_2} \ln X_{BaCl_2} + X_{SrCl_2} \ln X_{SrCl_2}\right) \quad \text{J/mol} \qquad (21) \\ &+ 4895.3 X_{BaCl_2} X_{SrCl_2} \end{aligned}$$

$$\begin{aligned} g^{\alpha_2} &= X_{SrCl_2} g^{o,\alpha}_{SrCl_2} + X_{BaCl_2}\left(g^{o,\alpha}_{BaCl_2} + 600.0\right) \\ &+ RT\left(X_{BaCl_2} \ln X_{BaCl_2} + X_{SrCl_2} \ln X_{SrCl_2}\right) \quad \text{J/mol} \qquad (22) \\ &+ 9790.6 X_{BaCl_2} X_{SrCl_2} \end{aligned}$$

The optimized Gibbs energy of reaction [1] for the *Sr-Cl-Ba* pairs is :

$$\Delta g_{SrBa/Cl} = -572.0 + 0.5092T \quad \text{J/mol} \qquad (23)$$

Figures 24 and 26 show the calculated phase diagram and thermodynamic properties.

The $CaCl_2$-$SrCl_2$-$BaCl_2$ System

Schaefer[51] measured the liquidus projection of the $CaCl_2$-$SrCl_2$-$BaCl_2$ system (Figure 27). A ternary eutectic $CaBaCl_4$-$CaCl_{2(s.s.)}$-$SrCl_{2(s.s.)}$ is reported at 590°C. No ternary excess parameters were used for the liquid phase. $CaCl_2$ and $BaCl_2$ are both very soluble in $SrCl_2$ (α and β) but are nearly mutually insoluble. A ternary $SrCl_2$-rich solid solution must then exist. The binary energy parameters for the $SrCl_2$-$CaCl_2$ and $SrCl_2$-$BaCl_2$ solid solutions were given previously (Reference [6] and Eqs [21,22]). The interaction energy parameters of Ca^{2+} and Ba^{2+} in the $SrCl_2$-rich solid solutions must be estimated. A very positive parameter of 65 kJ/mol was assumed for the Ca^{2+}-Ba^{2+} binary interactions, but this parameter was cancelled progressively in the ternary field of composition by a "ternary" parameter (-130 kJ/mol) of opposite sign, to fit the liquidus[51]. The Gibbs energies of the $SrCl_2$-rich solid solutions (α_2 and β) are thus given by a subregular solution model as :

$$g^{\alpha_2} = X_{SrCl_2} g^{o,\alpha}_{SrCl_2} + X_{CaCl_2} g^{o,S}_{CaCl_2} + X_{BaCl_2}\left(g^{o,\alpha}_{BaCl_2} + 600.0\right)$$
$$+RT\left(X_{SrCl_2}\ln X_{SrCl_2} + X_{CaCl_2}\ln X_{CaCl_2} + X_{BaCl_2}\ln X_{BaCl_2}\right)$$
$$+9672.3X_{SrCl_2}X_{CaCl_2} + 9790.6X_{SrCl_2}X_{BaCl_2}$$
$$+6388.4X_{SrCl_2}X_{CaCl_2}\left(\frac{X_{CaCl_2}}{X_{CaCl_2}+X_{SrCl_2}}\right)$$
$$+65000X_{CaCl_2}X_{BaCl_2} - 130000X_{SrCl_2}X_{CaCl_2}X_{BaCl_2}$$
$$\text{J/mol} \quad (24)$$

$$g^{\beta} = X_{SrCl_2} g^{o,\beta}_{SrCl_2} + X_{BaCl_2} g^{o,\beta}_{BaCl_2} + X_{CaCl_2}\left(g^{o,S}_{CaCl_2} + 8000.0\right)$$
$$+RT\left(X_{SrCl_2}\ln X_{SrCl_2} + X_{CaCl_2}\ln X_{CaCl_2} + X_{BaCl_2}\ln X_{BaCl_2}\right)$$
$$+3359.0X_{SrCl_2}X_{BaCl_2} - 278.6X_{SrCl_2}X_{BaCl_2}\left(\frac{X_{BaCl_2}}{X_{BaCl_2}+X_{SrCl_2}}\right)$$
$$+65000X_{CaCl_2}X_{BaCl_2} - 130000X_{SrCl_2}X_{CaCl_2}X_{BaCl_2}$$
$$\text{J/mol} \quad (25)$$

Ca^{2+} was assumed insoluble in the $BaCl_{2(\alpha)}$-rich solid solution. No solid solubility of Sr^{2+} was assumed in $CaBaCl_4$. The calculated liquidus projection is shown in Figure 28.

Other Alkaline-Earth Chloride-$BaCl_2$ Systems

No reported liquidus projection or thermodynamic data were found for the $MgCl_2$-$CaCl_2$-$BaCl_2$ and the $MgCl_2$-$SrCl_2$-$BaCl_2$ systems. Therefore, no ternary excess parameters are included in the liquid model. No solubility of $MgCl_2$ in the $(Sr,Ba)Cl_2(\beta)$ solid solution is assumed for purposes of calculation. In the $MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ system, $BaCl_2$ is soluble in the $SrCl_2$-rich region of the $(Ca,Sr,[Mg,Ba])Cl_2$ solid solution but not in the $CaCl_2$-rich region. The Gibbs energy of this solution is given by :

$$g^{\alpha_2} = X_{CaCl_2} g^{o,S}_{CaCl_2} + X_{SrCl_2} g^{o,\alpha}_{SrCl_2} + X_{BaCl_2}\left(g^{o,\alpha}_{BaCl_2} + 600\right)$$
$$+X_{MgCl_2}\left(g^{o,S}_{MgCl_2} + 29550.2^{[5]} - 18.4261^{[5]}T\right)$$
$$+RT\sum_{AlkE=Mg}^{Ba}\left(X_{AlkECl_2}\ln X_{AlkECl_2}\right)$$
$$+X_{CaCl_2}X_{SrCl_2}\left(9672.3^{[6]} + 6388.4^{[6]}\left(\frac{X_{CaCl_2}}{X_{CaCl_2}+X_{SrCl_2}}\right)\right)$$
$$+9790.6X_{SrCl_2}X_{BaCl_2} - 1841.0X_{MgCl_2}\left(X_{MgCl_2}+X_{SrCl_2}\right)$$
$$+65000X_{CaCl_2}X_{BaCl_2}\left(1-2X_{SrCl_2}\right) + 100000X_{MgCl_2}X_{BaCl_2}$$
$$\text{J/mol} \quad (26)$$

Parameters in Eq.[26] marked with a reference number are taken from that reference. The parameter −1841.0 is the Henrian enthalpy parameter[6] of $MgCl_2$ in the $SrCl_2$-rich solid solution (27709.2 J/mol) minus the Henrian enthalpy parameter[5] of $MgCl_2$ in the $CaCl_2$-rich solid solution (29550.2 J/mol). Because of this slight modification, Eq.[26] does not reduce exactly to the previously optimized[5] Gibbs energy expression in the $(Ca,[Mg])Cl_2$ binary system, but is very close.

MIXTURES OF ALKALI AND ALKALINE-EARTH CHLORIDES WITH $BaCl_2$

The $NaCl$-$MgCl_2$-$BaCl_2$ System

Bondarenko[40] measured the phase diagram by thermal analysis and X-ray analysis (Figure 29). A ternary compound $Na_3Mg_2BaCl_9$ was reported with a very small primary crystallization field. The reported ternary eutectic is at 418°C (at 30.7 wt.% $BaCl_2$, 40.5 wt.% $MgCl_2$ and 28.8 wt.% NaCl). No ternary solid solubility is reported. In order to reproduce the reported liquidus, a small ternary excess parameter was added to the liquid model (Eq.[27]). No solubility of Ba^{2+} in $NaMgCl_3$ and Na_2MgCl_4 is assumed. Na^+ is assumed insoluble in $MgBa_2Cl_6$.

$$g^{001}_{NaMg(Ba)/Cl} = -2719.6 \quad \text{J/mol} \quad (27)$$

The calculated liquidus projection is shown in Figure 30. (Note the compositional scale in weight percent). The reported[40] $Na_3Mg_2BaCl_9$ compound was not considered in the calculations. The calculated ternary eutectic is at 418°C (at 32.8 wt.% $BaCl_2$, 38.1 wt.% $MgCl_2$ and 29.1 wt.% NaCl).

The $LiCl$-$CaCl_2$-$BaCl_2$ System

The liquidus projection has been measured by the visual-polythermal method[52] (Figure 31). No ternary solid solubility is reported. The calculated liquidus projection is shown in Figure 32. (Note the different composition scales of Figures 31 and 32). No ternary solid solubility is assumed. No ternary excess parameter was included.

The $NaCl$-$CaCl_2$-$BaCl_2$ System

The liquidus projection has been reported[20] (Figure 33). No ternary solid solubility is reported. A ternary eutectic at 438°C and a ternary peritectic at 462°C are reported. The calculated liquidus projection is shown in Figure 34. (Note the different composition scales of Figures 33 and 34) No ternary solid solubility was assumed. A small ternary excess terms was required :

$$g^{001}_{NaCa(Ba)/Cl} = -2552.2 \quad \text{J/mol} \quad (28)$$

The KCl-$CaCl_2$-$BaCl_2$ System

The liquidus projection has been measured by the visual-polythermal method[20,27] (Figure 35[27]). No ternary solid solution is reported. Three eutectics and a peritectic are reported as well as two saddle points. The KCl-$KCaCl_3$-K_2BaCl_4 eutectic is reported at 549°C[27] and at 526°C[20], the

K_2BaCl_4-$KCaCl_3$-$BaCl_2$ eutectic is given at 551°C[27] and at 534°C[20], the $CaBaCl_4$-$KCaCl_3$-$CaCl_2$ eutectic is reported at 536°C[27] and at 544°C[20] and the $KCaCl_3$-$CaBaCl_4$-$BaCl_2$ peritectic is given at 564°C[27] and at 572°C[20]. The calculated liquidus projection is shown in Figure 36. (Note the different composition scales of Figures 35 and 36). No ternary excess parameters were used. No solid solubility was assumed. (Ba^{2+} was assumed insoluble in $KCaCl_3$).

The LiCl-$SrCl_2$-$BaCl_2$ System

Qiao *et al.*[14] measured the liquidus surface by DTA. Their results are shown in Table III along with calculated liquidus points. Two small ternary parameters were required :

$$g^{001}_{LiSr(Ba)/Cl} = 4000 \quad \text{J/mol} \qquad (29)$$

$$g^{001}_{LiBa(Sr)/Cl} = 4000 \quad \text{J/mol} \qquad (30)$$

The NaCl-$SrCl_2$-$BaCl_2$ System

The liquidus projection has been measured by the visual-polythermal method[17] (Figure 37). No ternary solid solubility is reported. The calculated liquidus projection is shown in Figure 38. No ternary solid solubility is assumed for calculation purposes. Two ternary excess paremeters were required :

$$g^{011}_{NaSr(Ba)/Cl} = 2426.7 \quad \text{J/mol} \qquad (31)$$

$$g^{011}_{NaBa(Sr)/Cl} = 2426.7 \quad \text{J/mol} \qquad (32)$$

The KCl-$SrCl_2$-$BaCl_2$ System

Vortisch[17] measured the liquidus projection by the visual-polythermal method (Figure 39). Complete miscibility between K_2SrCl_4 and K_2BaCl_4 is reported, as well as an undetermined miscibility of Ba^{2+} in KSr_2Cl_5. To reproduce by calculation the reported univariant lines[17], no ternary excess terms were used for the liquid phase, but ternary solid solution parameters were optimized. The Gibbs energy of the $K_2(Sr,Ba)Cl_4$ solid solution is given by a regular solution model (Eq.[33]), and the Gibbs energy of the $K(Sr,Ba)_2Cl_5$ solid solution is given by a Henrian solution model (Eq.[34]). K^+ is assumed insoluble in $(Sr,Ba)Cl_2$ solid solutions (α_1, α_2 and β). The calculated liquidus projection is shown in Figure 40.

$$g = X_{K_2SrCl_4} g^{o,S}_{K_2SrCl_4} + X_{K_2BaCl_4} g^{o,S}_{K_2BaCl_4} + RT\left(X_{K_2SrCl_4} \ln X_{K_2SrCl_4} + X_{K_2BaCl_4} \ln X_{K_2BaCl_4}\right) + 8368.0 X_{K_2SrCl_4} X_{K_2BaCl_4} \quad \text{J/mol} \qquad (33)$$

$$g = X_{KSr_2Cl_5} g^{o,S}_{KSr_2Cl_5} + X_{KBa_2Cl_5} g^{o,hyp}_{KBa_2Cl_5} + RT\left(X_{KSr_2Cl_5} \ln X_{KSr_2Cl_5} + X_{KBa_2Cl_5} \ln X_{KBa_2Cl_5}\right) \quad \text{J/mol} \qquad (34)$$

where the standard Gibbs energy of hypothetical KBa_2Cl_5 is given by :

$$g^{o,hyp}_{KBa_2Cl_5} = g^{o,S}_{KCl} + 2g^{o,\alpha}_{BaCl_2} + 2092.0 \quad \text{J/mol} \qquad (35)$$

Other Alkali Chloride-Alkaline-Earth Chloride-$BaCl_2$ Mixtures

No reported data were found for the LiCl-$MgCl_2$-$BaCl_2$, KCl-$MgCl_2$-$BaCl_2$, RbCl-$MgCl_2$-$BaCl_2$, CsCl-$MgCl_2$-$BaCl_2$, RbCl-$CaCl_2$-$BaCl_2$, CsCl-$CaCl_2$-$BaCl_2$, RbCl-$SrCl_2$-$BaCl_2$ and CsCl-$SrCl_2$-$BaCl_2$ systems. Ba^{2+} is expected to be immiscible in Mg^{2+}-containing and Ca^{2+}-containing compounds and vice-versa. Ba^{2+} is expected to be miscible in $RbSrCl_3$ but failing any experimental data, immiscibility is assumed for purposes of calculation. Ba^{2+} is also expected to be miscible in $RbSr_2Cl_5$. The Gibbs energy of formation of metastable $RbBa_2Cl_5$ from $RbCl_{(s)}$ and $BaCl_{2(\alpha)}$ is estimated to be the same as the Gibbs energy of formation of metastable KBa_2Cl_5 (Eq.[35]) :

$$g^{o,hyp}_{RbBa_2Cl_5} = g^{o,S}_{RbCl} + 2g^{o,\alpha}_{BaCl_2} + 2092.0 \quad \text{J/mol} \qquad (36)$$

An ideal solution of $RbSr_2Cl_5$ and $RbBa_2Cl_5$ is assumed. $CsBaCl_3$ and $CsSrCl_3$ are expected to be completely miscible, and an ideal solution of these compounds is assumed. Sr^{2+} is expected to be miscible in Rb_2BaCl_4 and in Cs_2BaCl_4. Ideal solutions of metastable Rb_2SrCl_4 in Rb_2BaCl_4 and of Cs_2SrCl_4 in Cs_2BaCl_4 are assumed.

The NaCl-KCl-$CaCl_2$-$BaCl_2$ Quaternary System

Sementsova and Bukhalova[20] measured, by the visual-polythermal method, the liquidus projections of 11 different ternary sections and projected univariant lines on these sections by interpolation and extrapolation of isotherms. Quaternary invariant points were then obtained by extrapolation of the projected univariant lines. The reported quaternary invariant points are the $KCaCl_3$-K_2BaCl_4-NaCl-KCl eutectic at 479°C, the $KCaCl_3$-K_2BaCl_4-NaCl-$BaCl_2$ eutectic at 478°C, the $KCaCl_3$-$CaBaCl_4$-NaCl-$BaCl_2$ peritectic at 446°C and the $KCaCl_3$-$CaBaCl_4$-NaCl-$CaCl_2$ eutectic at 428°C.

From the binary and ternary parameters of the models for all phases, the same invariant points can be calculated. The calculated quaternary invariant points are the $KCaCl_3$-$NaCl_{ss}$-KCl_{ss}-$BaCl_2$ eutectic at 476°C (K_2BaCl_4 is calculated to be on the verge of forming; the metastable $KCaCl_3$-K_2BaCl_4-NaCl-KCl eutectic is at 473°C), the $KCaCl_3$-K_2BaCl_4-KCl_{ss}-$BaCl_2$ eutectic at 476°C, the $KCaCl_3$-$CaBaCl_4$-$NaCl_{ss}$-$BaCl_2$ peritectic at 426°C, and the $KCaCl_3$-$CaBaCl_4$-$NaCl_{ss}$-$CaCl_2$ eutectic at 424°C.

Other Quaternary Systems with $BaCl_2$

No data for other quaternary subsystems with $BaCl_2$ were found. No additional excess parameters are introduced for the liquid and solid solution models.

Unknown quaternary intermediate phases and compounds are not expected to exist. The present models for all solutions, along with the data for the pure compounds, should give satisfactory predictions of phase equilibria in $BaCl_2$-containing quaternary subsystems of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ system (as shown above for the NaCl-KCl-$CaCl_2$-$BaCl_2$ quaternary system).

GENERAL MODEL FOR SOLID SOLUTIONS

The possible Ba-containing multicomponent solid solutions present in this system are the (Li,Na,K,Rb,Cs)(Mg,Ca,Sr,Ba)Cl_3 perovskite solution, the (Li,Na,K,Rb,Cs)$_2$(Mg,Sr,Ba)Cl_4 solid solution, the (K,Rb)(Sr,Ba)$_2Cl_5$ solid solution, and the low-temperature (Ca,Sr,[Mg,Ba])Cl_2 (Eq.[26]) solid solutions. Excess mixing parameters have been given in this paper for many subsystems, and parameters were given previously[5,6] for Mg-, Ca- and Sr-containing solutions. The compound energy model[53] is suitable for estimating the Gibbs energies of the multicomponent solid solutions, but this model requires that the Gibbs energies of all possible pure mixing components be defined, including metastable (or hypothetical) compounds such as $LiBaCl_3$, Na_2BaCl_4, etc. The hypothetical Gibbs energy of formation of $RbBaCl_3$ from solid pure salts is defined in Eq.[17]. Furthermore, we arbitrarily set:

$$g^{o,hyp}_{LiBaCl_3} = g^{o,S}_{LiCl} + g^{o,x}_{BaCl_2} + 20000 \quad \text{J/mol} \tag{37}$$

$$g^{o,hyp}_{NaBaCl_3} = g^{o,S}_{NaCl} + g^{o,x}_{BaCl_2} + 15000 \quad \text{J/mol} \tag{38}$$

$$g^{o,hyp}_{KBaCl_3} = g^{o,S}_{KCl} + g^{o,x}_{BaCl_2} + 10000 \quad \text{J/mol} \tag{39}$$

$$g^{o,hyp}_{Li_2BaCl_4} = 2g^{o,S}_{LiCl} + g^{o,x}_{BaCl_2} + 20000 \quad \text{J/mol} \tag{40}$$

$$g^{o,hyp}_{Na_2BaCl_4} = 2g^{o,S}_{NaCl} + g^{o,x}_{BaCl_2} + 15000 \quad \text{J/mol} \tag{41}$$

where the large positive values assure negligible solubility of these metastable compounds with other stable compounds. The excess Gibbs energy of all binary subsystems must also be defined. For subsystems where immiscibility is observed, a very large positive regular excess Gibbs energy parameter (+100 kJ/mol) is proposed so that virtual immiscibility is calculated : $LiBaCl_3$-$NaBaCl_3$, $LiBaCl_3$-$KBaCl_3$, $LiBaCl_3$-$RbBaCl_3$, $LiBaCl_3$-$CsBaCl_3$, $NaBaCl_3$-$KBaCl_3$, $NaBaCl_3$-$RbBaCl_3$, $NaBaCl_3$-$CsBaCl_3$, $KBaCl_3$-$RbBaCl_3$, $KBaCl_3$-$CsBaCl_3$, $LiMgCl_3$-$LiBaCl_3$, $NaMgCl_3$-$NaBaCl_3$, $KMgCl_3$-$KBaCl_3$, $RbMgCl_3$-$RbBaCl_3$, $CsMgCl_3$-$CsBaCl_3$, $LiCaCl_3$-$LiBaCl_3$, $NaCaCl_3$-$NaBaCl_3$, $KCaCl_3$-$KBaCl_3$, $RbCaCl_3$-$RbBaCl_3$, $CsCaCl_3$-$CsBaCl_3$, $LiSrCl_3$-$LiBaCl_3$, $NaSrCl_3$-$NaBaCl_3$, $KSrCl_3$-$KBaCl_3$, $RbSrCl_3$-$RbBaCl_3$, for the perovskite solution and Li_2BaCl_4-Na_2BaCl_4, Li_2BaCl_4-K_2BaCl_4, Li_2BaCl_4-Na_2BaCl_4, Li_2BaCl_4-K_2BaCl_4, Li_2BaCl_4-Rb_2BaCl_4, Li_2BaCl_4-Cs_2BaCl_4, Na_2BaCl_4-K_2BaCl_4, Na_2BaCl_4-Rb_2BaCl_4, Na_2BaCl_4-Cs_2BaCl_4, Li_2MgCl_4-Li_2BaCl_4, Na_2MgCl_4-Na_2BaCl_4, K_2MgCl_4-K_2BaCl_4, Rb_2MgCl_4-Rb_2BaCl_4, Cs_2MgCl_4-Cs_2BaCl_4, Li_2SrCl_4-Li_2BaCl_4, Na_2SrCl_4-Na_2BaCl_4, Rb_2SrCl_4-Rb_2BaCl_4, Cs_2SrCl_4-Cs_2BaCl_4 for the (Li,Na,K,Rb,Cs)$_2$(Mg,Sr,Ba)Cl_4 solid solution. The Gibbs energy of the perovskite solid solution (Li,Na,K,Rb,Cs)(Mg,Ca,Sr,Ba)Cl_3 is then given by the compound energy model[53] as :

$$\begin{aligned} g = & \sum_{Alk=Li}^{Cs} \sum_{AlkE=Mg}^{Ba} y_{Alk}\, y_{AlkE}\, g^{o,S}_{Alk\,AlkE\,Cl_3} \\ & + RT\left(\sum_{Alk=Li}^{Cs} y_{Alk} \ln y_{Alk} + \sum_{AlkE=Mg}^{Ba} y_{AlkE} \ln y_{AlkE} \right) \\ & + \sum_{Alk=Li}^{Rb} \sum_{Alk'=Alk+1}^{Cs} \sum_{AlkE=Mg}^{Ba} y_{Alk}\, y_{Alk'}\, y_{AlkE}\, \omega_{(Alk\,Alk')\,AlkE\,Cl_3} \\ & + \sum_{Alk=Li}^{Cs} \sum_{AlkE=Mg}^{Sr} \sum_{AlkE'=AlkE+1}^{Ba} y_{Alk}\, y_{AlkE}\, y_{AlkE'}\, \omega_{Alk\,(AlkE\,AlkE')\,Cl_3} \end{aligned} \tag{42}$$

where y_i is the sublattice ionic site fraction and all ω terms are binary regular or subregular parameters either optimized or fixed (+100 kJ/mol) for the binary subsystems. The Gibbs energy of the (Li,Na,K,Rb,Cs)$_2$(Mg,Sr,Ba)Cl_4 solid solution is similarly given by :

$$\begin{aligned} g = & \sum_{Alk=Li}^{Cs} \left(y_{Alk}\, y_{Mg}\, g^{o,S}_{Alk_2MgCl_4} + y_{Alk}\, y_{Sr}\, g^{o,S}_{Alk_2SrCl_4} + y_{Alk}\, y_{Ba}\, g^{o,S}_{Alk_2BaCl_4} \right) \\ & + RT\left(2\sum_{Alk=Li}^{Cs} y_{Alk} \ln y_{Alk} + y_{Mg} \ln y_{Mg} + y_{Sr} \ln y_{Sr} + y_{Ba} \ln y_{Ba} \right) \\ & + \sum_{Alk=Li}^{Rb} \sum_{Alk'=Alk+1}^{Cs} \left(y_{Alk}\, y_{Alk'}\, y_{Mg}\, \omega_{(Alk\,Alk')_2MgCl_4} + y_{Alk}\, y_{Alk'}\, y_{Sr}\, \omega_{(Alk\,Alk')_2SrCl_4} + y_{Alk}\, y_{Alk'}\, y_{Ba}\, \omega_{(Alk\,Alk')_2BaCl_4} \right) \\ & + \sum_{Alk=Li}^{Cs} \left(y_{Alk}\, y_{Mg}\, y_{Sr}\, \omega_{Alk_2(Mg,Sr)Cl_4} + y_{Alk}\, y_{Mg}\, y_{Ba}\, \omega_{Alk_2(Mg,Ba)Cl_4} + y_{Alk}\, y_{Sr}\, y_{Ba}\, \omega_{Alk_2(Sr,Ba)Cl_4} \right) \end{aligned} \tag{43}$$

The Gibbs energy of the $(K,Rb)(Sr,Ba)_2Cl_5$ solid solution is similarly given by :

$$
\begin{aligned}
g &= y_K y_{Sr} g^{o,S}_{KSr_2Cl_5} + y_K y_{Ba} g^{o,hyp}_{Ba_2Cl_5} \\
&+ y_{Rb} y_{Sr} g^{o,S}_{RbSr_2Cl_5} + y_{Rb} y_{Ba} g^{o,hyp}_{RbBa_2Cl_5} \\
&+ RT\left(y_K \ln y_K + y_{Rb} \ln y_{Rb}\right) + 2RT\left(y_{Sr} \ln y_{Sr} + y_{Ba} \ln y_{Ba}\right) \\
&+ y_K y_{Rb} y_{Sr} \omega_{(K,Rb)Sr_2Cl_5} + y_K y_{Rb} y_{Ba} \omega_{(K,Rb)Ba_2Cl_5} \\
&+ y_K y_{Sr} y_{Ba} \omega_{K(Sr,Ba)_2Cl_5} + y_{Rb} y_{Sr} y_{Ba} \omega_{Rb(Sr,Ba)_2Cl_5}
\end{aligned}
\tag{44}
$$

where $g^{o,hyp}_{KBa_2Cl_5}$ and $g^{o,hyp}_{RbBa_2Cl_5}$ are given by Eqs.[35,36].

CONCLUSIONS

A complete critical evaluation and optimization of all available phase diagram and thermodynamic data for all phases of the LiCl-NaCl-KCl-RbCl-CsCl-$MgCl_2$-$CaCl_2$-$SrCl_2$-$BaCl_2$ system has been made. All data are reproduced within experimental error limits. The new modified quasichemical model[1] was used for the liquid phase, while the compound energy model[53] was used for the $(Li,Na,K,Rb,Cs)(Mg,Ca,Sr,Ba)Cl_3$ perovskite phase and the $(Li,Na,K,Rb,Cs)_2(Mg,Sr,Ba)Cl_4$ solid solutions. A substitutional solution model was also used for the $(Ca,Sr,[Mg,Ba])Cl_{2(\alpha)}$, $(Sr,Ba)Cl_{2(\beta)}$ and $(Ba,[Sr])Cl_2$ solid solutions. From the optimized parameters of the binary and ternary subsystems it is possible, from the quasichemical model, to predict the thermodynamic properties of the multicomponent liquid solution. The database of optimized parameters is included in the F*A*C*T[54] database computing system and may be used, along with the other databases and Gibbs energy minimization software, to calculate phase equilibria and all thermodynamic properties in multicomponent systems.

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Table I : Thermodynamic Properties of Pure Compounds

		T Range K	$H^o_{298.15K}$ ** J/mol	$S^o_{298.15}$ J/mol-K	C_p J/mol-K	Ref.
$BaCl_2$	α	298-600	-858557.0	123.6660	$73.2572+0.012675990T-167742T^{-2}$	[55]
	α	600-1198	-867651.5	97.5138	$C_p(\beta)$ (600K-1198K)	[55]
	β	298-600	-841657.0	137.7728	$C_p(\alpha)$ (298K-600K)	*
	β	600-1198	-850751.5	111.6206	$2301.8714-1.270734880T$ $+72386721T^{-2}+0.00037686959T^2$ $-43987.469T^{-0.5}$	[55]
	β	1198-2000	-877165.9	79.7692	123.8460	[55]
	β	2000-3000	-851532.6	108.4368	108.7840	*
	L	298-800	-832478.6	143.4877	$48.3973+0.031543680T$ $-1597267T^{-2}+10525.22T^{-1}$	[55]
	L	800-3000	-847064.1	114.1239	108.7840	[55]
K_2BaCl_4	S	298-600	-1724961.8	301.8555	$2\,C_p(KCl_s) + C_p(BaCl_{2\,\alpha})$	*
	S	600-1198	-1734056.3	275.7033	$2\,C_p(KCl_s) + C_p(BaCl_{2\,\alpha})$	*
Rb_2BaCl_4	S	298-600	-1709449.3	332.2447	$2\,C_p(RbCl_s) + C_p(BaCl_{2\,\alpha})$	*
	S	600-940	-1718543.8	306.0925	$2\,C_p(RbCl_s) + C_p(BaCl_{2\,\alpha})$	*
Cs_2BaCl_4	S	298-600	-1729117.4	355.2090	$2\,C_p(CsCl_s) + C_p(BaCl_{2\,\alpha})$	*
	S	600-950	-1738211.9	329.0569	$2\,C_p(CsCl_s) + C_p(BaCl_{2\,\alpha})$	*
$CsBaCl_3$	S	298-900	-1294274.5	237.1203	140.0000	*
$MgBa_2Cl_6$	S	298-600	-2363130.0	$S^o_{298K}(MgCl_2\,s) + 2\,S^o_{298K}(BaCl_2\alpha)$	$C_p(MgCl_2\,s) + 2\,C_p(BaCl_2\,\alpha)$	*
	S	600-900	-2381318.9	$S^o_{298K}(MgCl_2\,s) + 2\,S^o_{298K}(BaCl_2\alpha)$	$C_p(MgCl_2\,s) + 2\,C_p(BaCl_2\,\alpha)$	*
$CaBaCl_4$	S	298-600	-1645897.8	240.8301	$C_p(CaCl_2\,s) + C_p(BaCl_2\,\alpha)$	*
	S	600-1045	-1654992.3	214.6779	$C_p(CaCl_2\,s) + C_p(BaCl_2\,\alpha)$	*

* This work.

** Relative to elements at 298.15K

Table II. Cation-Cation "Coordination Numbers" of the Liquid.

i	j	Z_{ij}^{i}	Z_{ij}^{j}
Li	Ba	3	6
Na	Ba	3	6
K	Ba	3	6
Rb	Ba	3	6
Cs	Ba	3	6
Mg	Ba	6	6
Ca	Ba	6	6
Sr	Ba	6	6
Ba	Ba	6	6

Table III : Experimental[14] and Calculated Liquidus Points of the $LiCl$-$SrCl_2$-$BaCl_2$ System.

X_{LiCl}	**$SrCl_2$ / ($SrCl_2$ + $BaCl_2$) Molar Ratio**					
	0.3		**0.5**		**0.7**	
	T_{exp}[14] °C	T_{calc} °C	T_{exp}[14] °C	T_{calc} °C	T_{exp}[14] °C	T_{calc} °C
0.20	811	775.6	751	723.5	747	712.2
0.40	698	676.3	663	634.2	636	603.4
0.50	622	622.3	586	588.1	561	565.1
0.55	601	595.1	566	566.0	536	548.6
0.65	506	542.1	502	523.9	492	520.1
0.70	515	521.6	533	529.9	520	529.5
0.80	542	548.8	549	552.5	554	552.1

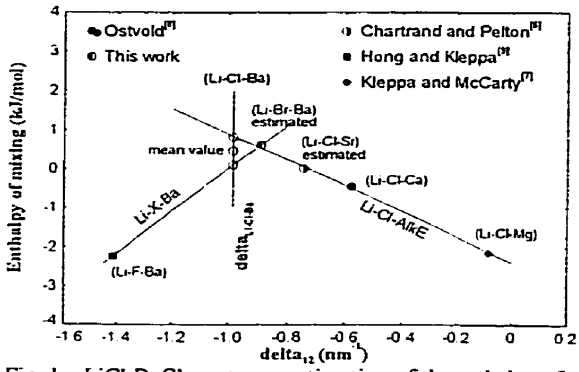

Fig. 1 – $LiCl-BaCl_2$ system : estimation of the enthalpy of mixing of the liquid at 870°C at 40 mol.% $BaCl_2$.

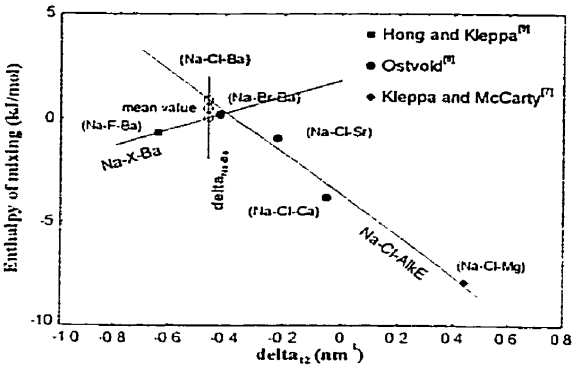

Fig. 2 – $NaCl-BaCl_2$ system : estimation of the enthalpy of mixing of the liquid at 870°C at 40 mol.% $BaCl_2$.

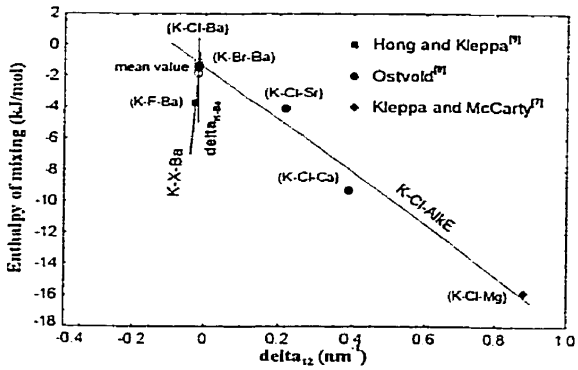

Fig. 3 – $KCl-BaCl_2$ system : estimation of the enthalpy of mixing of the liquid at 870°C at 40 mol.% $BaCl_2$.

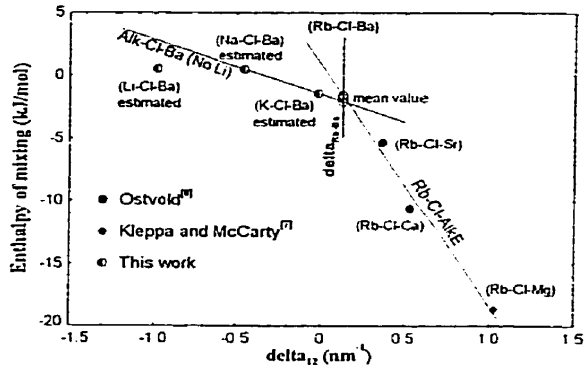

Fig. 4 – $RbCl-BaCl_2$ system : estimation of the enthalpy of mixing of the liquid at 870°C at 40 mol.% $BaCl_2$.

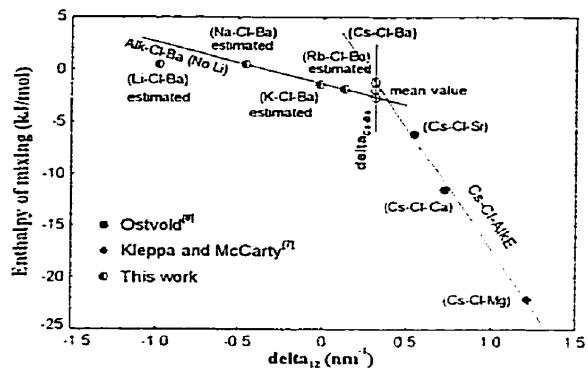

Fig. 5 – $CsCl-BaCl_2$ system : estimation of the enthalpy of mixing of the liquid at 870°C at 40 mol.% $BaCl_2$.

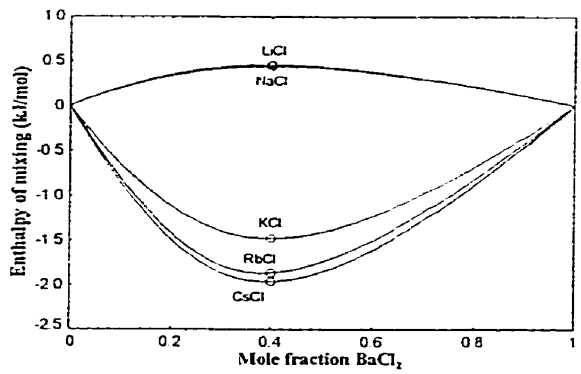

Fig. 6 – Alkali-Chloride-$BaCl_2$ systems : calculated enthalpy of mixing of the liquid at 870°C with estimated values from this work.

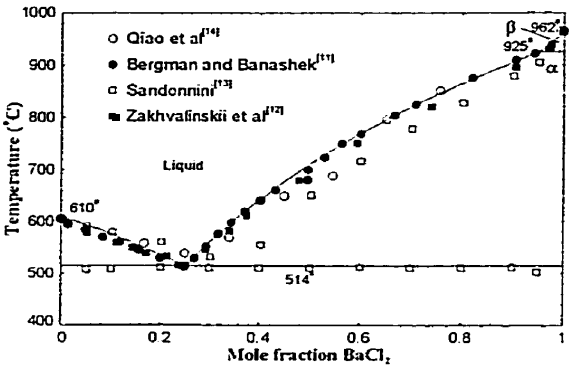

Fig. 7 – $LiCl-BaCl_2$ system : calculated phase diagram.

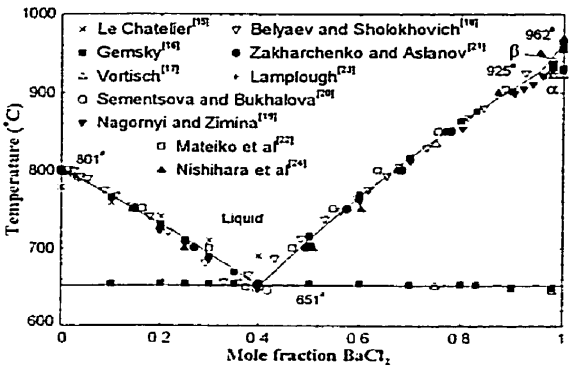

Fig. 8 – $NaCl-BaCl_2$ system : calculated phase diagram.

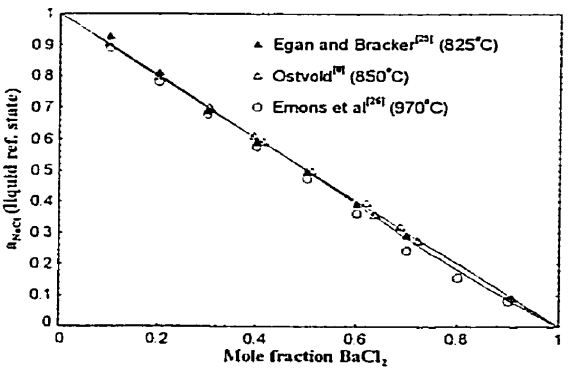

Fig. 9 – $NaCl-BaCl_2$ system : calculated activity of NaCl in the liquid at 850°C (liquid ref. state).

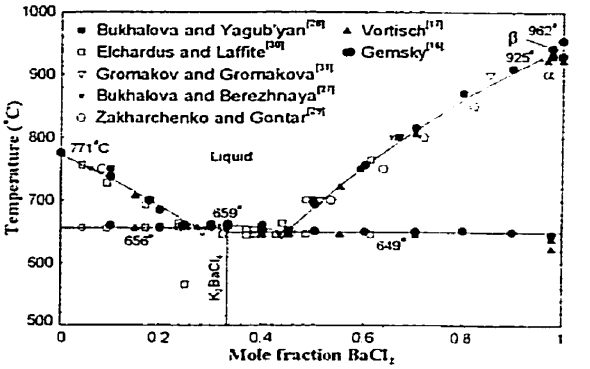

Fig. 10 – $KCl-BaCl_2$ system : calculated phase diagram.

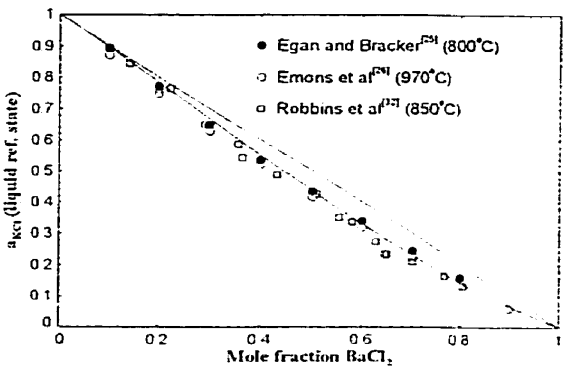

Fig. 11 – $KCl-BaCl_2$ system : calculated activity of KCl in the liquid at 800°C (liquid ref. state).

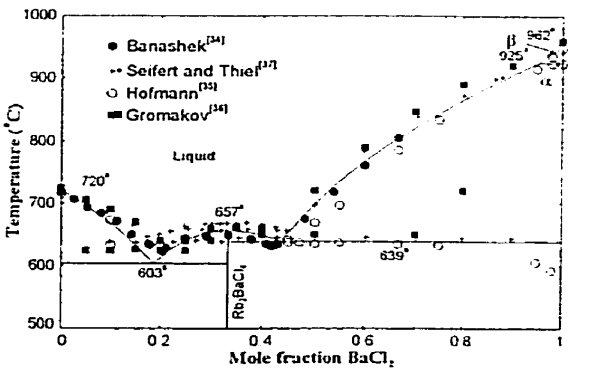

Fig. 12 – $RbCl-BaCl_2$ system : calculated phase diagram.

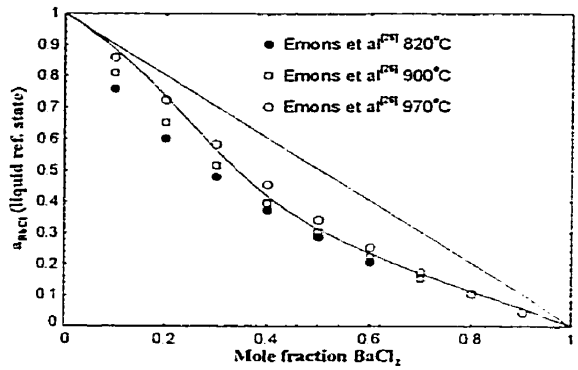

Fig. 13 – $RbCl-BaCl_2$ system : calculated activity of RbCl in the liquid at 900°C (liquid ref. state).

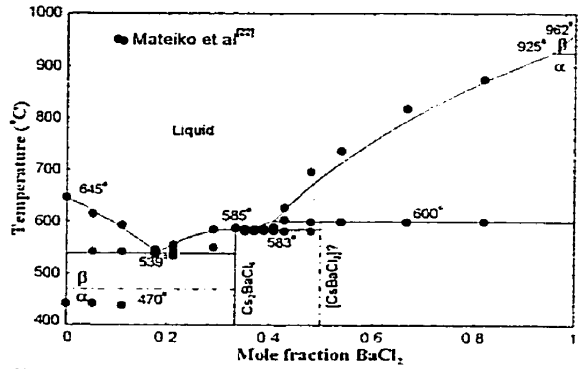

Fig. 14 – $CsCl-BaCl_2$ system : calculated phase diagram.

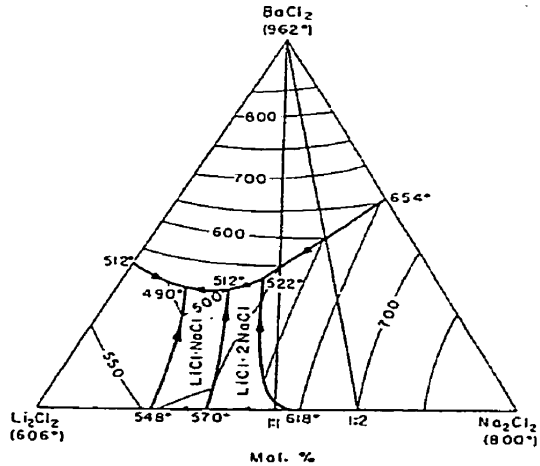

Fig. 15 – $Li_2Cl_2-Na_2Cl_2-BaCl_2$ system : experimental liquidus projection of Zakharchenko and Aslanov[21].

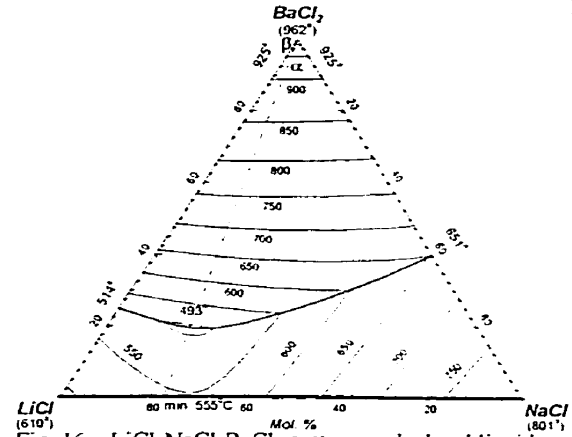

Fig. 16 – $LiCl-NaCl-BaCl_2$ system : calculated liquidus projection.

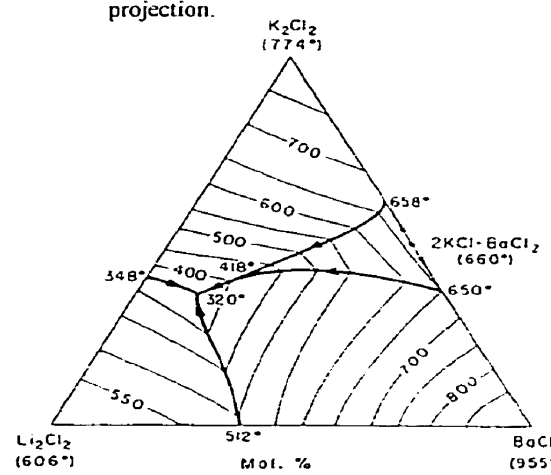

Fig. 17 – $Li_2Cl_2-K_2Cl_2-BaCl_2$ system : experimental liquidus projection of Zakharchenko and Gontar[24].

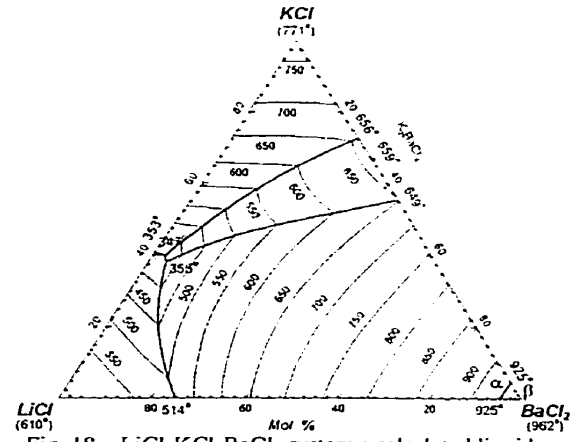

Fig. 18 – $LiCl-KCl-BaCl_2$ system : calculated liquidus projection.

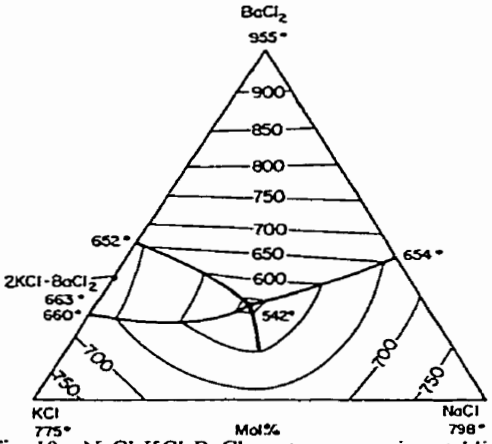

Fig. 19 – NaCl-KCl-$BaCl_2$ system : experimental liquidus projection of Vortisch[17].

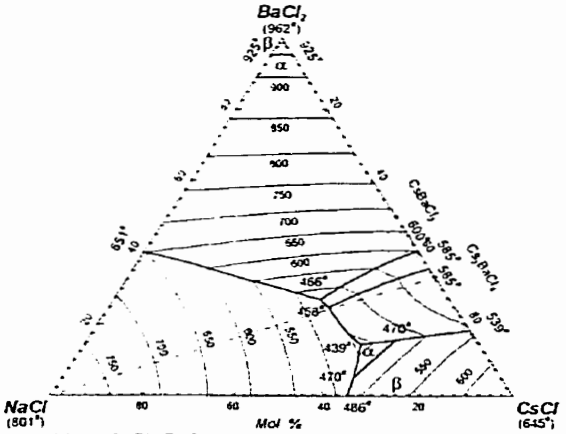

Fig. 22 – NaCl-CsCl-$BaCl_2$ system : calculated liquidus projection.

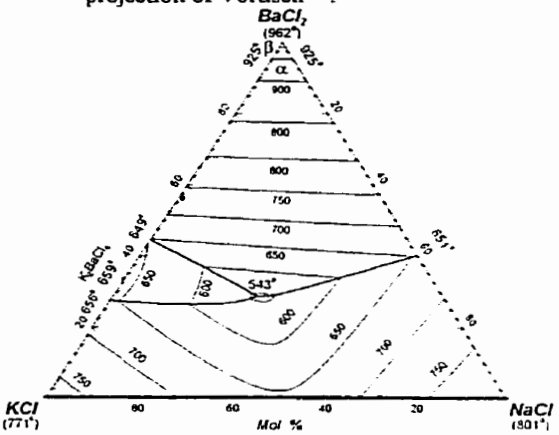

Fig. 20 – NaCl-KCl-$BaCl_2$ system : calculated liquidus projection.

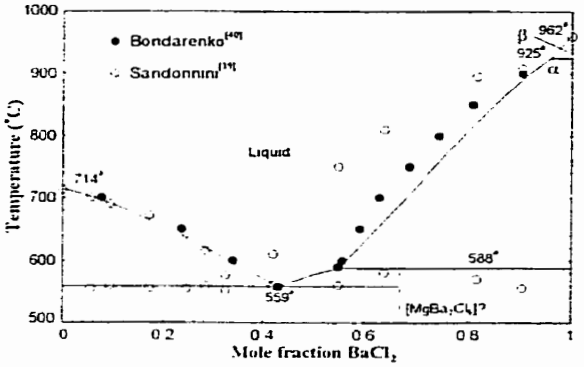

Fig. 23 – $MgCl_2$-$BaCl_2$ system : calculated phase diagram.

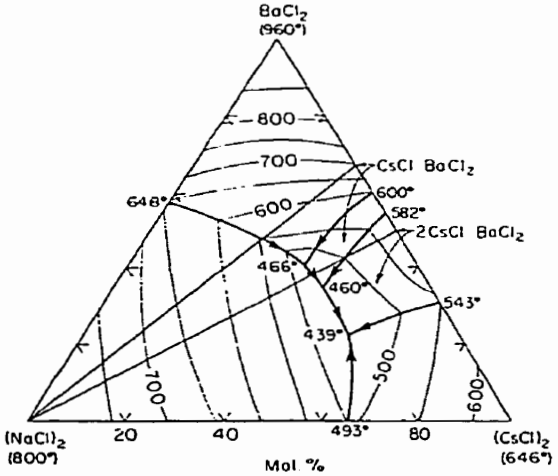

Fig. 21 – Na_2Cl_2-Cs_2Cl_2-$BaCl_2$ system : experimental liquidus projection of Mateiko *et al.*[22].

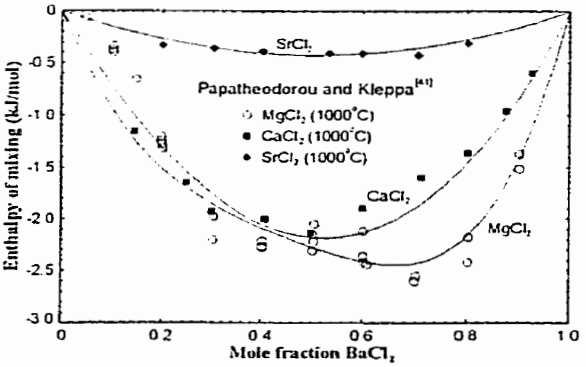

Fig. 24 – Alkaline-earth chloride-$BaCl_2$ binary systems : calculated enthalpy of mixing of the liquid at 1000°C with experimental points of Papatheodorou and Kleppa[41].

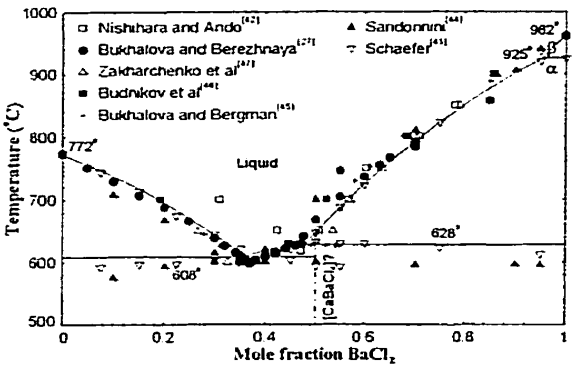

Fig. 25 – $CaCl_2$-$BaCl_2$ system : calculated phase diagram.

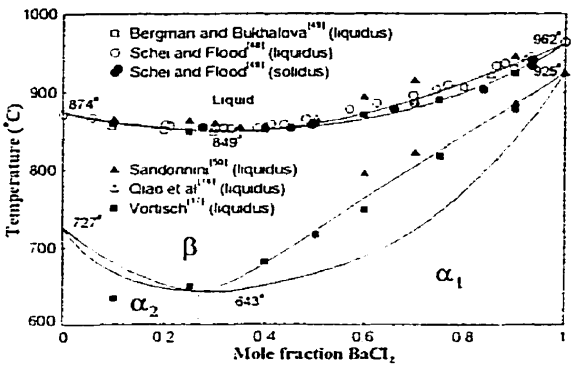

Fig. 26 – $SrCl_2$-$BaCl_2$ system : calculated phase diagram.

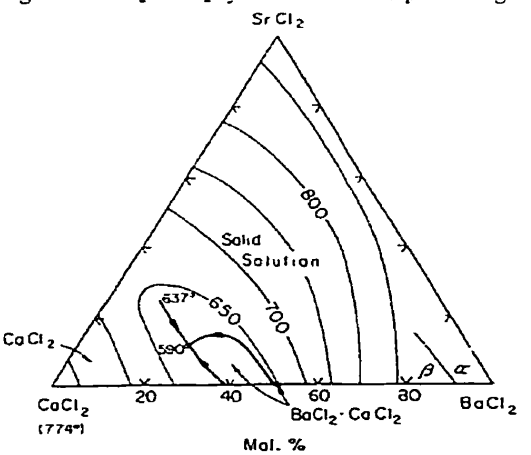

Fig. 27 – $CaCl_2$-$SrCl_2$-$BaCl_2$ system : experimental liquidus projection of Schaefer[51].

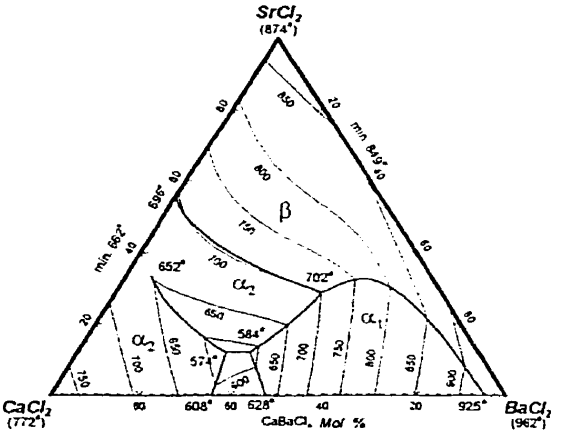

Fig. 28 - $CaCl_2$-$SrCl_2$-$BaCl_2$ system : calculated liquidus projection.

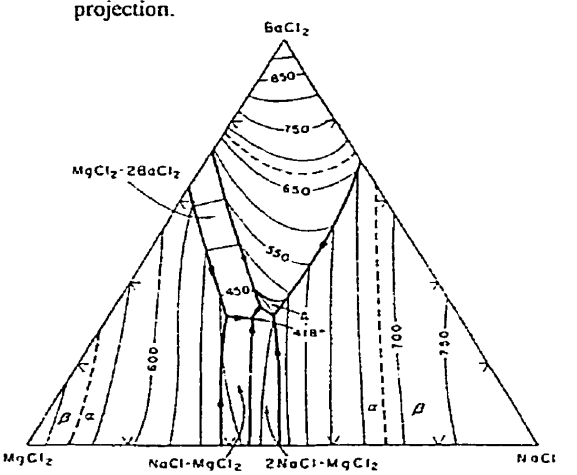

Fig. 29 – $NaCl$-$MgCl_2$-$BaCl_2$ system : experimental liquidus projection of Bodarenko[40] (in wt.%).

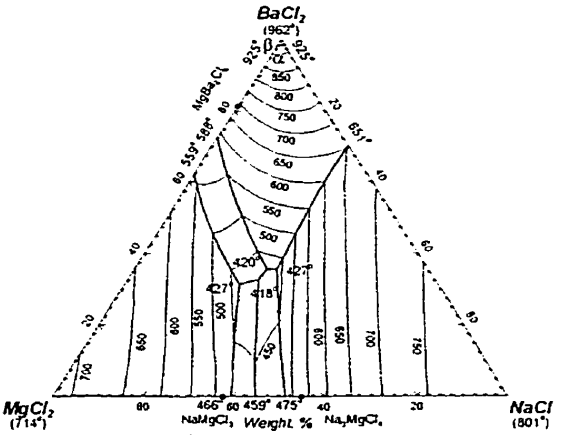

Fig. 30 - $NaCl$-$MgCl_2$-$BaCl_2$ system : calculated liquidus projection.

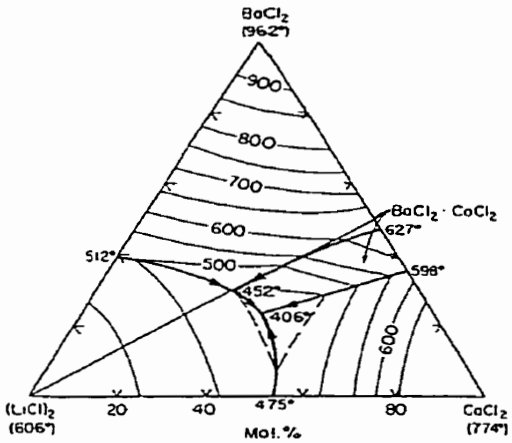

Fig. 31 – Li_2Cl_2-$CaCl_2$-$BaCl_2$ system : experimental liquidus projection of Zakharchenko *et al.*[52].

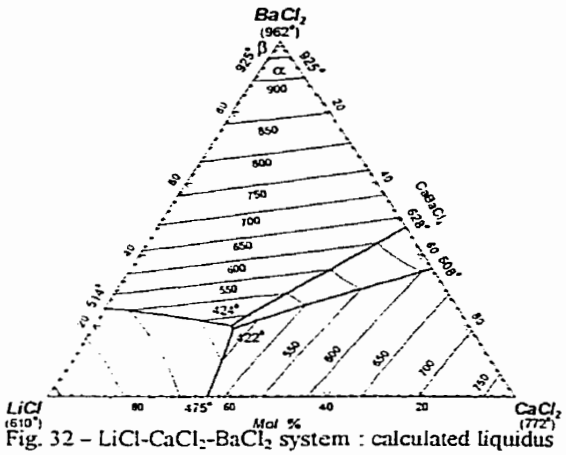

Fig. 32 – LiCl-$CaCl_2$-$BaCl_2$ system : calculated liquidus projection.

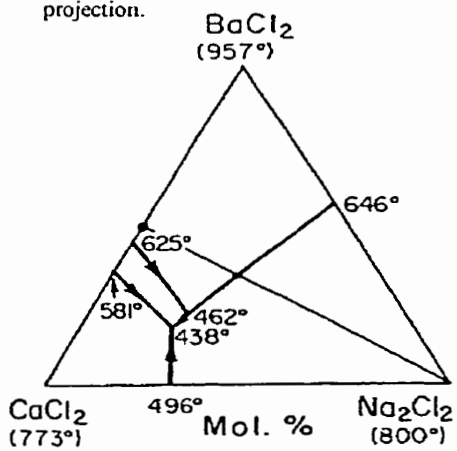

Fig. 33 – Na_2Cl_2-$CaCl_2$-$BaCl_2$ system : experimental liquidus projection of Sementsova and Bukhalova[20].

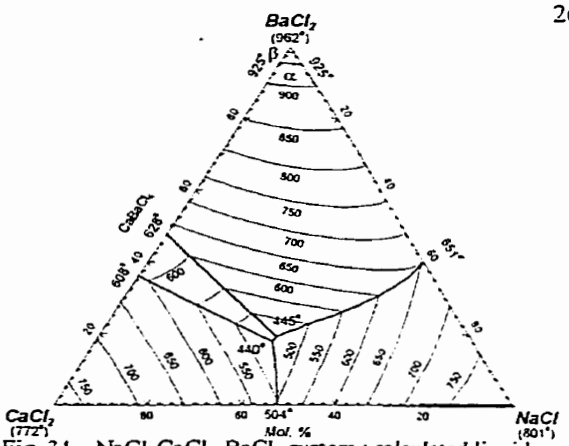

Fig. 34 – NaCl-$CaCl_2$-$BaCl_2$ system : calculated liquidus projection.

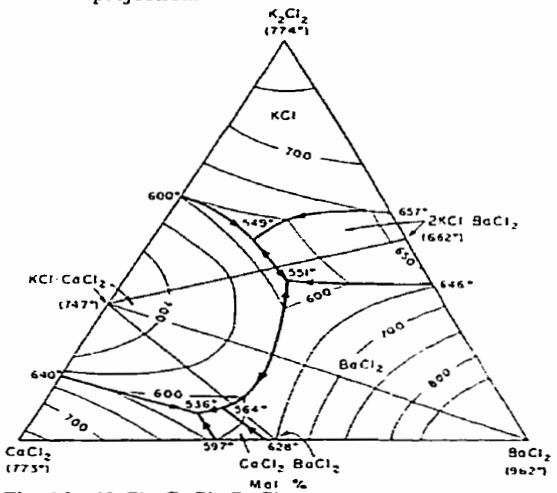

Fig. 35 – K_2Cl_2-$CaCl_2$-$BaCl_2$ system : experimental liquidus projection of Bukhalova and Berezhnaya[27].

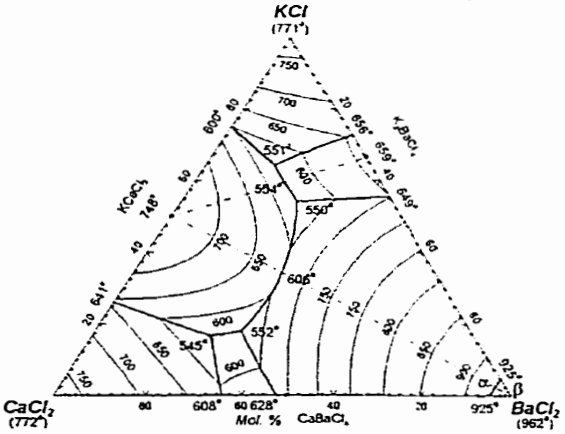

Fig. 36 – KCl-$CaCl_2$-$BaCl_2$ system : calculated liquidus projection.

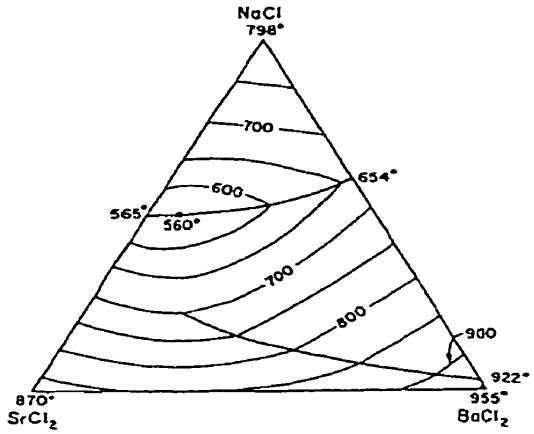

Fig. 37 – $NaCl$-$SrCl_2$-$BaCl_2$ system : experimental liquidus projection of Vortisch[17] (mol.%).

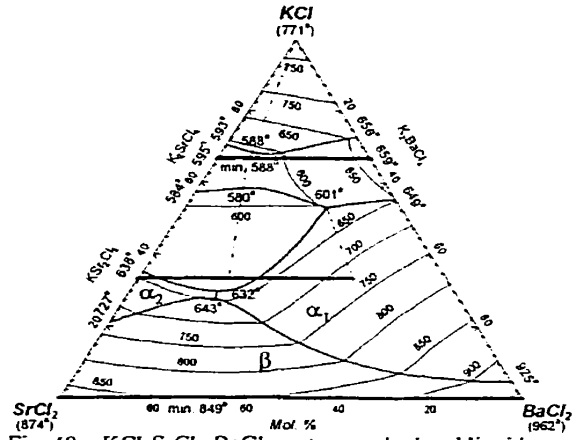

Fig. 40 – KCl-$SrCl_2$-$BaCl_2$ system : calculated liquidus projection.

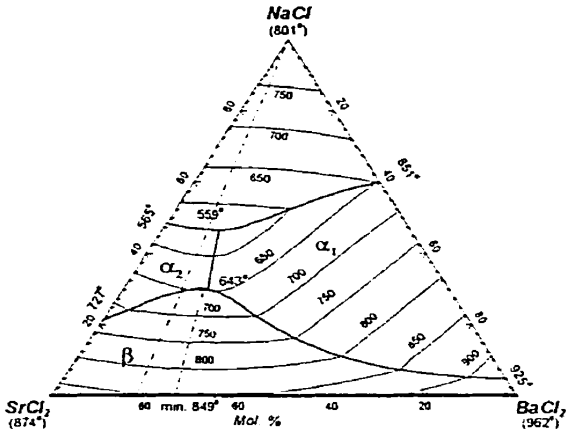

Fig. 38 – $NaCl$-$SrCl_2$-$BaCl_2$ system : calculated liquidus projection.

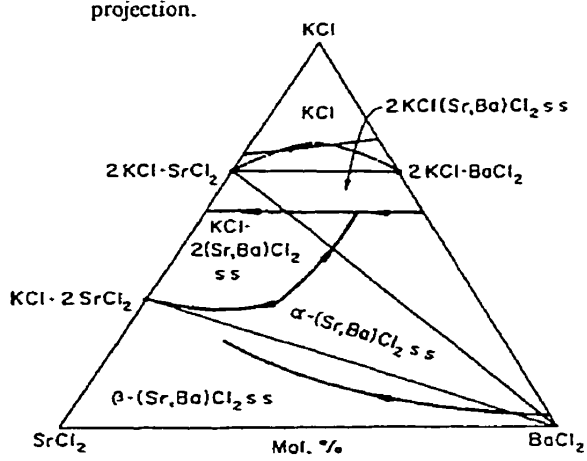

Fig. 39 – KCl-$SrCl_2$-$BaCl_2$ system : reported univariant lines of Vortisch[17].

ANNEXE VII

Article :

Thermodynamic Evaluation and Optimization of the LiF-NaF-KF-MgF_2-CaF_2 System Using the Modified Quasichemical Model

Patrice Chartrand et Arthur D. Pelton,

Soumis à *Metallurgical and Materials Transactions B*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel *FIGURE* développé par l'auteur de cette thèse durant ses études doctorales.

Thermodynamic Evaluation and Optimization of the $LiF-NaF-KF-MgF_2-CaF_2$ System Using the Modified Quasichemical Model

PATRICE CHARTRAND and ARTHUR D. PELTON

A complete critical evaluation and quantitative optimization of all available phase diagram and thermodynamic data has been performed for all condensed phases of the $LiF-NaF-KF-MgF_2-CaF_2$ system. The model parameters obtained for binary and ternary subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent system. The modified quasichemical model for short-range ordering was used for the molten salt phase.

I. INTRODUCTION

Molten alkali-alkaline earth halide solutions are of much technological importance in, for example, the production and fluxing of Al. A large body of experimental thermodynamic and phase equilibrium data exists for these systems. In this article, all available data for binary and ternary subsystems of the $LiF-NaF-KF-MgF_2-CaF_2$ system are critically evaluated and optimized to obtain parameters of models of all solution phases. These parameters form a computer database. The models are then used to predict the thermodynamic properties of the multicomponent system. When used in conjunction with currently available general software for calculating equilibria by Gibbs energy minimization, this database can be used to predict the thermodynamic properties and phase equilibria in uncharted regions of temperature and composition. This article is the second in a series that will be published on alkali-alkaline earth halide systems.

Molten alkali fluorides-MgF_2 solutions are known, from Raman spectroscopy[1], to exhibit extensive short-range ordering, increasing in importance from $LiF-MgF_2$ to $CsF-MgF_2$. Similar behavior in alkali chloride-$MgCl_2$ melts has previously been modelled[2,3] by introducing complex-$MgCl_4^{2-}$ anions. However, until now, no model has been proposed which permits a quantitative optimization of all subsystem data and which can satisfactorily be extrapolated to predict the properties of multicomponent solutions when appreciable short-range ordering is present. The modified quasichemical model[4] achieves this objective. The model has been used for the $LiCl-NaCl-KCl-RbCl-CsCl-MgCl_2-CaCl_2$[5] molten salt phase.

The model does not explicitely introduce complex anions. Instead, short-range ordering is treated by considering the relative numbers of second-nearest-neighbor cation-cation pairs. The parameters of the model are the Gibbs energy changes $\Delta g_{AB/F}$ for the pair exchange reactions :

$$(A-F-A)_{pair}+(B-F-B)_{pair}=2(A-F-B)_{pair} \qquad \Delta g_{AB/F} \qquad [1]$$

As $\Delta g_{AB/F}$ becomes progressively more negative, reaction [1] is shifted progressively to the right, (A-F-B) pairs predominate, and the solution becomes progressively more ordered. In the previous article[4] the model was developed in terms of nearest-neighbor pairs (A-B) for species mixing on one lattice. In the present case, since the anion sublattice is occupied only by F^- ions, the model can be used directly to treat cation-cation pairs on the cation sublattice. The parameter $\Delta g_{AB/F}$ is the parameter Δg_{mn} of the previous article[4]. When $\Delta g_{AB/F}$ is small, the degree of short-range ordering is small, and the solution approximates a random (Bragg-Williams) mixture of cations on the cation sublattice.

Our aim is to develop a database for calculating multicomponent thermodynamic properties and phase equilibria in salt systems related to reactive metals extractive metallurgy. The $LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-MgCl_2-CaF_2-CaCl_2$ multicomponent system is the base system of many processes. The binary and ternary common chloride systems were evaluated and optimized previously[5]. The binary and ternary fluoride systems are treated in the present article, which also demonstrates the application of the new modified quasichemical model[4] to the evaluation, optimization and prediction of thermodynamic properties and phase equilibria.

II. THERMODYNAMIC DATA

All thermodynamic data ($H^o_{298.15K}$, $S^o_{298.15K}$ and C_p) for the condensed pure phases of the $LiF-NaF-KF-MgF_2-CaF_2$ system, including optimized values from the present work, are given in Table I.

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III. THERMODYNAMIC MODEL FOR THE LIQUID PHASE

The modified quasichemical model[4] is used for the liquid phase. The notation of the previous articles[4,5] is maintained. For example, X_{NaMg} is the mole fraction of second-nearest-neighbor (Na-F-Mg) pairs. The model requires the definition of cation-cation coordination numbers Z^{i}_{ij}. The values chosen in the present work are listed in Table II. Note that, for example, the choice of $Z^{K}_{KMg} = \frac{1}{2} Z^{Mg}_{KMg}$ assures that the composition of maximum short-range ordering will be near the K_2MgF_4 composition. Also, as discussed previously[4,5], it is necessary to define all ternary sub-systems as either "symmetric" or "asymmetric". In the present case, all ternary systems in which all three components are alkali halides are defined as symmetric. Systems with one alkali and two alkaline-earth fluorides are asymmetric, with the alkali fluoride as asymmetric component, and systems with one alkaline-earth and two alkali fluorides are asymmetric, with the alkaline-earth fluoride as asymmetric component. To this end, the components are divided into two groups, all alkali halides are in one group, and MgF_2 and CaF_2 form the other group. The composition variables χ_{ij} defined previously[1] then become :

$$\chi_{LiMg} = \chi_{LiCa} = \chi_{NaMg} = \chi_{NaCa} = \chi_{KMg} = \chi_{KCa} = \chi_{Alk} \quad [2]$$

where $\chi_{Alk} = \sum_{i=Li}^{K} \sum_{j=i}^{K} X_{ij}$ [3]

$$\chi_{MgLi} = \chi_{CaLi} = \chi_{MgNa} = \chi_{CaNa} = \chi_{MgK} = \chi_{CaK} = \chi_{AlkE} \quad [4]$$

where $\chi_{AlkE} = \sum_{i=Mg}^{Ca} \sum_{j=i}^{Ca} X_{ij}$ [5]

and also

$$\chi_{MgCa} = \frac{X_{MgMg}}{X_{MgMg} + X_{MgCa} + X_{CaCa}} \quad [6]$$

$$\chi_{CaMg} = \frac{X_{CaCa}}{X_{MgMg} + X_{MgCa} + X_{CaCa}} \quad [7]$$

$$\chi_{LiNa} = \frac{X_{LiLi}}{X_{LiLi} + X_{LiNa} + X_{NaNa}} \quad [8]$$

$$\chi_{NaLi} = \frac{X_{NaNa}}{X_{LiLi} + X_{LiNa} + X_{NaNa}} \quad [9]$$

etc.

That is, when i and j are alkalis :

$$\chi_{ij} = \frac{X_{ij}}{X_{ii} + X_{ij} + X_{jj}} \quad [10]$$

The parameters $\Delta g_{AB/F}$ of reaction [1] for each pair are expanded, through optimization of available experimental data, as empirical polynomials in χ_{ij}. For ternary systems, terms may be added giving the effect of the third component upon the pair formation energies $\Delta g_{AB/F}$. As described previously[4] this is done by introducing empirical ternary parameters $g^{ijk}_{AB(C)/F}$ in the polynomial expansion.

IV. ALKALI FLUORIDE MIXTURES

In previous publications[6,7] a database was developed for alkali halide solutions by evaluation/optimization of all thermodynamic data. A random (Bragg-Williams) configurational entropy was assumed, and excess Gibbs energies were expressed as polynomials. In the present work, the LiF-NaF and LiF-KF binary subsystems were reoptimized with the quasichemical model. For the NaF-KF system, the optimized parameters[6] are very small. Hence, short-range ordering is negligible, and these parameters can be used directly as parameters of the quasichemical model with only negligible differences in the calculated properties and phase diagram.

A. *The LiF-NaF System*

The liquid thermodynamic properties were reoptimized with the quasichemical model. The Gibbs energy of formation of Li-F-Na pairs is given by Eq.[11]. The calculated phase diagram is virtually identical to the one published[6] previously. The thermodynamic properties of the NaF-rich solid solution (Eq.[12]) are taken from Sangster and Pelton[6].

$$\Delta g_{LiNa/F} = -2161.0 + 0.6698T - 574.1\chi_{LiNa} - 332.8\chi_{NaLi} \quad \text{J/mol} \quad [11]$$

$$g = X_{NaF} g^{o,S}_{NaF} + X_{LiF}\left(g^{o,S}_{LiF} + 18895\right) + RT\left(X_{NaF} \ln X_{NaF} + X_{LiF} \ln X_{LiF}\right) \quad \text{J/mol} \quad [12]$$

B. *The LiF-KF System*

The liquid thermodynamic properties were reoptimized with the quasichemical model. The Gibbs energy of formation of Li-F-K pairs is given by Eq.[13]. The calculated phase diagram is virtually identical to the one published[6] previously.

$$\Delta g_{LiK/F} = -5404.6 + 0.6249T + \left(-1100.9 + 1.043\,IT\right)\chi_{LiK} \quad \text{J/mol} \quad [13]$$

C. *The NaF-KF System*

The liquid thermodynamic properties are calculated using the quasichemical model[4] with the optimized polynomial parameters[6] converted from joules per mole of components AF to joules per mole of 2nd nearest-neighbor pairs. Since all coordination number Z^{i}_{ij} in Table II are equal to 6 when i and j are alkalis, it is simply necessary to divide all previous coefficients[6] by 3.0. The resultant

Gibbs energy of formation of Na-F-K pairs is given by Eq.[14]. The Gibbs energy of the KF-rich solid solution is given by Eq.[15] taken from Sangster and Pelton[6]. The calculated phase diagram is almost identical to the one published[6] previously.

$$\Delta g_{NaK/F} = -118.3 + 0.8470T \quad \text{J/mol} \qquad [14]$$

$$g = X_{KF} g^{o,S}_{KF} + X_{NaF}\left(g^{o,S}_{NaF} + 24770.0\right) + RT\left(X_{KF} \ln X_{KF} + X_{NaF} \ln X_{NaF}\right) \quad \text{J/mol} \qquad [15]$$

D. *The LiF-NaF-KF System*

A thermodynamic calculation of the phase diagram was reported previously[7]. The phase diagram was recalculated with the modified quasichemical model[4] for the liquid phase, with the following small ternary excess parameter :

$$q^{001}_{LiK(Na)/F} = -3138 \quad \text{J/mol} \qquad [16]$$

No ternary solid solubility was assumed. The calculated phase diagram, shown in Figure 3, is nearly identical to that calculated previously[7] with the Kohler technique[8], and is also in excellent agreement with experimental measurements as discussed previously[7].

V. MIXTURES OF ALKALI FLUORIDES WITH MgF_2

A. *The LiF-MgF_2 System*

The phase diagram has been measured by equilibration and quenching[9], thermal analysis and the visual-polythermal method[10], and cooling curves[11] (Figure 4). Solid solubility on both sides of the phase diagram is reported[9]. Large uncertainties still remain on subliquidus equilibria but it is clear that extensive solid solutions are present.

Calorimetric measurements are available for the liquid phase[12] (Figure 2). No activity measurements are reported for the liquid phase. The optimized energy of reaction [1] for the Li-F-Mg pair is given by Eq.[17].

$$\Delta g_{LiMg/F} = -7175.0 - 888.8\chi_{AlkE} - 8607.8\chi_{AlkE} \quad \text{J/mol} \qquad [17]$$

MgF_2 dissolves in LiF with formation of cationic vacancies. For very dilute solutions the Mg^{2+} ions and vacancies are distributed independently on the lattice sites, giving rise to a large entropy term and stabilizing the solution relative to the liquid. However, at slightly higher MgF_2 concentrations there will be a strong electrostatic tendency for the Mg^{2+} ions and vacancies to associate and enter solution as a single species. The entropy then becomes equivalent to a simple Bragg-Williams random mixing entropy. For the LiF-rich solid solution therefore, the following optimized expression was used :

$$g = X_{LiF} g^{o,S}_{LiF} + X_{MgF_2}\left(g^{o,S}_{MgF_2} + 11568.8 - 4.1840T\right) + RT\left(X_{LiF} \ln X_{LiF} + X_{MgF_2} \ln X_{MgF_2}\right) \quad \text{J/mol} \qquad [18]$$

The thermodynamic properties of the MgF_2-rich solid solution have been represented by a Henrian solution model which, similarly to the model for LiF-rich solutions, assumes association of anionic vacancies with Li^+ cations :

$$g = X_{MgF_2} g^{o,S}_{MgF_2} + X_{LiF}\left(g^{o,S}_{LiF} + 17154.4\right) + RT\left(X_{MgF_2} \ln X_{MgF_2} + X_{LiF} \ln X_{LiF}\right) \quad \text{J/mol} \qquad [19]$$

Figures 1, 2 and 4 show the calculated and experimental phase diagram and thermodynamic properties. The calculated phase diagram is thermodynamically consistent with the enthalpy of mixing of the liquid and the fusion properties of the pure salts. This is not necessarily the case for the experimental diagrams[9-11] where large discrepencies are observed.

B. *The NaF-MgF_2 System*

The phase diagram has been measured[10,13-18] (Figure 5). The only reported intermediate compound is $NaMgF_3$. No solid solubility is reported, and the limiting slopes of the NaF and MgF_2 liquidus curves respect Eq.[20] which assumes no solid solubility.

$$\lim_{X_m \to 1}\left(\frac{dX_m^{liquidus}}{dT}\right) = \frac{\Delta h^o_{fusion}}{RT^2_{fusion}} \qquad [20]$$

where Δh^o_{fusion} and T_{fusion} are the enthalpy and temperature of melting of the pure salts.

Calorimetric measurements are available for the liquid[12] (Figure 1). Estimated properties of $NaMgF_3$ have also been given. The enthalpy of formation of $NaMgF_3$ from solid NaF and MgF_2 at 298.15K was estimated as -16.74 kJ/mol[12] and -29.29 kJ/mol[19]; the enthalpy of fusion of $NaMgF_3$ was estimated as 84.6±2.0 kJ/mol[20] and 74.15 kJ/mol[12]. The optimized enthalpy of formation of $NaMgF_3$ from pure solids at 298.15K is -16.20 kJ/mol and the optimized enthalpy of fusion is 72.80 kJ/mol. The heat capacity of $NaMgF_3$(s) was estimated in the present work as 135 J/mol-K which is the value obtained for $NaMgCl_3$ in the previous optimization[5]. This value is close to the sum of heat capacities of NaF(s) and MgF_2(s). The optimized Gibbs energy of reaction [1] for the Na-F-Mg pairs is :

$$\Delta g_{NaMg/F} = -14654.0 + 0.7765T + \left(-19886.0 + 5.4000T\right)\chi_{AlkE} \quad \text{J/mol} \qquad [21]$$

Figures 1, 2 and 5 show the calculated phase diagram and thermodynamic properties.

C. *The KF-MgF₂ System*

The phase diagram has been measured[14,21-23] (Figure 6). Reported intermediate compounds are K_2MgF_4 (incongruent) and $KMgF_3$ (congruent). Possible limited solid solubility of KF and MgF_2 in $KMgF_3$ perovskite is reported[21,23]. The limiting slopes of the KF and MgF_2 liquidus curves agree with Eq.[20] which assumes no solid solubility in KF or MgF_2.

Calorimetric measurements are available for the liquid[12] (Figure 2). Volodkovich *et al.*[24] measured the Gibbs energy of reactions [22] and [23] by an emf technique between 735-869.5K and 745-928K respectively, obtaining -10.8(±8.9) - 0.0344(±0.011)T kJ/mol for reaction [22] and -26.0(±5.5) - 0.0097(±0.0065)T kJ/mol for reaction [23].

$$2KF_{(s)} + MgF_{2(s)} = K_2MgF_{4(s)} \qquad [22]$$

$$K_2MgF_{4(s)} + MgF_{2(s)} = 2\,KMgF_{3(s)} \qquad [23]$$

Bouamrane *et al.*[25] measured, by solution calorimetry, the heat of formation of K_2MgF_4 and $KMgF_3$ from the elements at 298.15K as -2317±20 kJ/mol (*cf*: -2274.8±9.0 kJ/mol[24]) and -1727±15 kJ/mol (*cf*: -1712.5±5.3 kJ/mol[24]) respectively. Calculated values are -2285.0 kJ/mol and -1716.7 kJ/mol respectively. The calculated Gibbs energies for reactions [22] and [23] are -46.15 kJ/mol (*cf*: -36.08 kJ/mol[24]) and -34.06 kJ/mol (*cf*: -33.13 kJ/mol[24]) respectively at 735K, and -47.08 kJ/mol (*cf*: -40.73 kJ/mol[24]) and -36.60 kJ/mol (*cf*: -34.44 kJ/mol[24]) at 870K. Errors on the experimental values[24] are large. The optimized heat capacities of K_2MgF_4 and $KMgF_3$ are 150.665 J/mol-K and 115.686 J/mol-K respectively (values close to the sums of the heat capacities of the pure solid salts). No solid solubility of KF of MgF_2 in $KMgF_3$ is assumed for calculation purposes. The optimized Gibbs energy of reaction [1] for *K-F-Mg* pairs is :

$$\Delta g_{KMgF} = -23974.4 + 6.8813T + (1730.7 - 3.2421T)\chi_{Alk} + (-35478.0 + 2.0000T)\chi_{AlkE} + 18875.0\chi_{Alk}^2 \quad \text{J/mol} \qquad [24]$$

Figures 1, 2 and 6 show the calculated and experimental phase diagram and thermodynamic properties. Figure 2 shows the calculated mixing entropy of the liquid at 1000°C, where the "m-shape" related to a high degree of short-range ordering in the melt can clearly be observed.

D. *The LiF-NaF-MgF₂ System*

The liquidus projection has been reported[10] (Figure 7). Two ternary eutectics and a saddle point are reported : the LiF-NaF-$NaMgF_3$ eutectic at 630°C, the LiF-MgF_2-$NaMgF_3$ eutectic between 700°C and 708°C, and the saddle point at 708°C. No ternary solid solubility is reported. The calculated liquidus projection is shown in Figure 8 with no ternary excess terms for the liquid and assuming no solid solubility of Li^+ in $NaMgF_3$.

E. *The LiF-KF-MgF₂ System*

The liquidus projection has been reported[22] (Figure 9). No ternary solid solution is reported. The calculated liquidus projection is shown in Figure 10. No ternary excess parameter is necessary to calculate the liquidus projection. No solid solubility of Li^+ in $KMgF_3$ nor in K_2MgF_4 was necessary to reproduce the liquidus surface.

F. *The NaF-KF-MgF₂ System*

The liquidus projection has been measured[14] (Figure 11). Solid solubility between $NaMgF_3$ and $KMgF_3$ is reported with a quasibinary eutectic at 986°C. No liquid ternary excess parameters are required, but a complete solid solution between these compounds (with a solid-solid miscibility gap only at lower temperatures) is required to reproduce the reported $NaMgF_3$-$KMgF_3$ liquidus. A subregular excess Gibbs energy expression was used for the $(Na,K)MgF_3$ solid solution (Eq.[26]). No assumed solid solubility of Na^+ in K_2MgF_4 was required to reproduce the K_2MgF_4 liquidus and related invariant points, but a limited solid solubility may exists. The calculated liquidus projection is shown in Figure 12.

$$\begin{aligned} g = {} & X_{NaMgF_3} g^{o,S}_{NaMgF_3} + X_{KMgF_3} g^{o,S}_{KMgF_3} \\ & + RT\left(X_{NaMgF_3} \ln X_{NaMgF_3} + X_{KMgF_3} \ln X_{KMgF_3}\right) \\ & + X_{NaMgF_3} X_{KMgF_3}\, 13807.2 \\ & - X_{NaMgF_3} X_{KMgF_3}\, 3138.0\left(X_{KMgF_3} - X_{NaMgF_3}\right) \end{aligned} \quad \text{J/mol} \qquad [25]$$

VI. MIXTURES OF ALKALI FLUORIDES WITH CaF_2

A. *The LiF-CaF₂ System*

The liquidus has been measured[26-32] (Figure 13). A simple eutectic system is reported by all authors and no solid solubility is reported. The limiting slope of the LiF liquidus curve respects Eq.[20] which assumes no solid solubility.

Calorimetric measurements are available for the liquid[33] (Figure 14). The optimized Gibbs energy of reaction [1] for the *Li-F-Ca* pair is :

$$\Delta g_{LiCaF} = -2183.5 + 1.3591T + 595.7\chi_{Alk} - 790.8\chi_{AlkE} \quad \text{J/mol} \qquad [26]$$

Figures 13 to 15 show the calculated phase diagram and thermodynamic properties.

B. *The NaF-CaF_2 System*

The phase diagram has been measured[15,16,34,35] (Figure 16). The system is a simple eutectic with no reported solid solubility which is in agreement with the limiting slope of the NaF liquidus curve given by Eq.[20] which assumes no solid solubility.

Calorimetric measurements are available for the liquid[33] (Figure 14). The optimized Gibbs energy of reaction [1] for the *Na-F-Ca* pair is :

$$\Delta g_{NaCa/F} = -4266.1 + 2.6451T - 2863.4\chi_{Alk} + (-11746.5 + 6.4326T)\chi_{Alk,E} \quad \text{J/mol} \qquad [27]$$

Figures 14 to 16 show the calculated phase diagram and thermodynamic properties.

C. *The KF-CaF_2 System*

The phase diagram has been measured[36,37] (Figure 17). Both authors reported the congruently melting $KCaF_3$ compound. No solid solubility was reported.

Calorimetric measurements are available for the liquid[33] (Figure 14). The heat capacity of $KCaF_3$ is estimated as 145 J/mol-K from the sum of the mean heat capacities of $KF_{(s)}$ and $CaF_{2(\alpha)}$ bewteen 25°C and 1000°C, and also from the optimized heat capacity of $KCaCl_3$[5]. The optimized Gibbs energy of reaction [1] for the *K-F-Ca* pair is :

$$\Delta g_{KCa/F} = -10223.2 + 5.0799T - 907.3\chi_{Alk} + (-9438.7 + 5.5160T)\chi_{Alk,E} \quad \text{J/mol} \qquad [28]$$

Figures 14, 15 and 17 show the calculated phase diagram and thermodynamic properties.

D. *The LiF-NaF-CaF_2 System*

The liquidus projection has been reported[15,38]. A single ternary eutectic (615°C[15] or 607°C[38]) is reported, with no ternary solid solubility (Figure 18). The calculated liquidus projection is shown in Figure 19. No ternary excess parameters were required to fit the liquidus surface. No ternary solid solubility was assumed.

E. *The LiF-KF-CaF_2 System*

The liquidus projection has been measured[38] (Figure 20). A ternary eutectic and peritectic are reported at 490°C and 684°C respectively. No solid solubility is reported. The calculated liquidus projection using a small ternary parameter for the liquid model (Eq.[29]), and assuming a limited solid solubility of Li^+ in $KCaF_3$ is shown in Figure 21. (Note the different composition scales when comparing Figures 20 and 21). The Gibbs energy of the $KCaF_3$-rich solid solution using a regular solution model is given by Eqs.[30,31].

$$g^{001}_{KCa(Li)/F} = 4184.0 \quad \text{J/mol} \qquad [29]$$

$$g = X_{KCaF_3} g^{o,S}_{KCaF_3} + X_{LiCaF_3} g^{o,hyp}_{LiCaF_3} + RT\left(X_{KCaF_3} \ln X_{KCaF_3} + X_{LiCaF_3} \ln X_{LiCaF_3}\right) \quad \text{J/mol} \qquad [30]$$
$$-17573 X_{KCaF_3} X_{LiCaF_3}$$

where the Gibbs energy of hypothetical $LiCaF_3$ is given by:

$$g^{o,hyp}_{LiCaF_3} = g^{o,S}_{LiF} + g^{o,\alpha}_{CaF_2} + 20920 \quad \text{J/mol} \qquad [31]$$

F. *The NaF-KF-CaF_2 System*

The liquidus projection has been measured[35] (Figure 22). The authors reported two ternary eutectics with a saddle point. No solid solubility is reported. The calculated liquidus projection is shown in Figure 23. (Note the different composition scales when comparing Figures 22 and 23). No solid solubility of Na^+ in $KCaF_3$ is assumed but a small excess ternary parameter (Eq.[32]) must be added to the liquid model.

$$g^{001}_{KCa(Na)/F} = 4142.2 \quad \text{J/mol} \qquad [32]$$

G. *The LiF-NaF-KF-CaF_2 Quaternary System*

Temperatures of invariant points of the quaternary LiF-NaF-KF-CaF_2 system are reported[38]. A quaternary eutectic (LiF-NaF-KF-$KCaF_3$) was reported at 444°C and a quaternary peritectic (LiF-NaF-CaF_2-$KCaF_3$) was reported at 566°C. Using the modified quasichemical model[4] for the liquid, with the optimized parameters for the binary and ternary subsystems given above, and with no additional parameters, the LiF-NaF-KF-$KCaF_3$ eutectic is calculated at 456°C and a LiF-NaF-CaF_2-$KCaF_3$ eutectic is calculated at 564°C.

VII. MIXTURES OF ALKALI FLUORIDES WITH MgF_2 AND CaF_2

A. *The MgF_2-CaF_2 System*

The phase diagram has been measured[39-42] (Figure 24). Fedorov and Ol'khovaya[39] reported a solubility of MgF_2 in CaF_2 of less than 3 mol%. A simple eutectic system is reported by both authors. The limiting slopes of the liquidus curves agree well with Eq.[20]. Hence, only limited solid solubility is expected on both sides of the phase diagram.

No thermodynamic data were found for the properties of the liquid. No solid solubility was assumed. The optimized Gibbs energy of reaction [1] for the *Mg-F-Ca* pair is :

$$\Delta g_{MgCa/F} = -2859.0 - 2872.8\chi_{MgCa} - 1417.2\chi_{CaMg} \quad \text{J/mol} \quad [33]$$

The calculated optimized phase diagram is shown in Figure 24.

B. *The LiF-MgF_2-CaF_2 System*

Roake[43] measured the liquidus projection (Figure 25). A single ternary eutectic at 672°C was reported with no ternary solid solubility. Figure 26 shows the calculated liquidus projection. No ternary solid solubility is assumed. A small ternary excess parameter for the liquid model is added in order to reproduce the ternary eutectic :

$$g^{001}_{MgCa(Li)/F} = -3765.5 \quad \text{J/mol} \quad [34]$$

C. *The NaF-MgF_2-CaF_2 System*

The liquidus projection has been reported[15] with two ternary eutectics and a saddle point (Figure 27). No solid solubility is reported. The calculated liquidus projection is given in Figure 28. A small ternary excess parameter for the liquid model is necessary in order to reproduce the saddle point (Eq.[35]). No solid solubility of Ca^{2+} in $NaMgF_3$ was assumed for the calculations. The calculated $NaMgF_3$-CaF_2-MgF_2 eutectic is at 865°C compared to the reported value of 905°C[15] and the calculated $NaMgF_3$-NaF-CaF_2 eutectic is calculated at 766°C compared to the reported value of 745°C[15]. However, the greater part of the reported liquidus surface is reproduced very well with only a very small ternary parameter. The reported ternary eutectic temperatures thus seem inconsistent.

$$g^{001}_{NaMg(Ca)/F} = 3347.2 \quad \text{J/mol} \quad [35]$$

D. *The KF-MgF_2-CaF_2 System*

No reported liquidus projection has been found. Belyaev and Shilov[44] measured the phase diagram along the $KMgF_3$-$KCaF_3$ join by visual and thermographic methods (Figure 29). A solid-solid miscibility gap between solid perovskites was reported with a eutectic at 985°C at 60 mol.% $KCaF_3$ with maximum solubilities of around 10 mol.% $KMgF_3$ in $KCaF_3$ and 20 mol.% $KCaF_3$ in $KMgF_3$. The calculated $KMgF_3$-$KCaF_3$ phase diagram is shown in Figure 29. The Gibbs energy of the liquid is assumed to be solely calculated by the model from the optimized binary parameters. The Gibbs energy of the $KMgF_3$-$KCaF_3$ solid solution was modelled by a subregular equation (Eq.[36]). Complete solid solubility must be assumed in order to even come close to reproducing the reported liquidus[44] but the calculated solidus then differs from the solidus of Belyaev and Shilov[44]. From comparison with other systems, it is very unlikely that large excess ternary parameters are required for the liquid solution. That is, it is not possible, with reasonable parameters for the liquid and solid solutions, to reproduce the reported[44] diagram.

$$\begin{aligned} g = {} & X_{KMgF_3} g^{o,S}_{KMgF_3} + X_{KCaF_3} g^{o,S}_{KCaF_3} \\ & + RT\left(X_{KMgF_3} \ln X_{KMgF_3} + X_{KCaF_3} \ln X_{KCaF_3}\right) \\ & + X_{KMgF_3} X_{KCaF_3} 12552 \\ & - X_{KMgF_3} X_{KCaF_3} 4184\left(X_{KMgF_3} - X_{KCaF_3}\right) \end{aligned} \quad \text{J/mol} \quad [36]$$

For calculating the complete KF-MgF_2-CaF_2 phase diagram it is proposed that no solubility of Ca^{2+} in K_2MgF_4 be assumed. This assumption should give a reasonable calculated liquidus projection.

VIII. GENERAL MODEL FOR SOLID SOLUTIONS

The solid solutions present in this system are the (Li,Na,K)(Mg,Ca)F_3 perovskite solution, and the (Na,[Li])F, the (K,[Na])F, the (Li,[Mg])F and the (Mg,[Li])F_2 solid binary solutions. Excess mixing parameters have been given in this article for many subsystems of the perovskite solution. The compound energy model[45] is suitable for estimating the Gibbs energy of the multicomponent perovskite solution, but this model requires that the Gibbs energies of all possible pure mixing components be defined, including metastable (or hypothetical) compounds such as $LiMgF_3$, $NaCaF_3$, etc. The hypothetical Gibbs energy of formation of $LiCaF_3$ from the pure solid salts is defined in Eq.[31]. Furthermore, we arbitrarily set :

$$NaF_{(S)} + CaF_{2(\alpha)} \rightarrow NaCaF_{3(S)} \qquad \Delta g = 20920.0 \text{ J/mol} \quad [37]$$

$$LiF_{(S)} + MgF_{2(\alpha)} \rightarrow LiMgF_{3(S)} \qquad \Delta g = 418.4 \text{ J/mol} \quad [38]$$

where the positive values assure metastability in the binary systems. The excess Gibbs energies of all binary subsystems must also be defined. For subsystems where immiscibility is observed, a very large positive regular excess Gibbs energy parameter (+100 kJ/mol) is proposed so that virtual immiscibility is calculated : $LiMgF_3$-$LiCaF_3$, $LiMgF_3$-$NaMgF_3$, $LiMgF_3$-$KMgF_3$, $LiCaF_3$-$NaCaF_3$, $NaMgF_3$-$NaCaF_3$, and $NaCaF_3$-$KCaF_3$. The Gibbs energy of the perovskite solid solution (Li,Na,K)(Mg,Ca)F_3 is then given by the compound energy model[45] as :

$$
\begin{aligned}
g = & \sum_{Alk=Li}^{K} \sum_{AlkE=Mg}^{K} y_{Alk} y_{AlkE} g^{o,S}_{AlkAlkEF_3} \\
& + RT\left(\sum_{Alk=Li}^{K} y_{Alk} \ln y_{Alk} + \sum_{AlkE=Mg}^{Ca} y_{AlkE} \ln y_{AlkE} \right) \\
& + \sum_{Alk=Li}^{Na} \sum_{Alk'=Alk+1}^{K} \sum_{AlkE=Mg}^{Ca} y_{Alk} y_{Alk'} y_{AlkE} \omega_{(Alk,Alk')AlkEF_3} \\
& + \sum_{Alk=Li}^{K} y_{Alk} y_{Mg} y_{Ca} \omega_{Alk(Mg,Ca)F_3}
\end{aligned}
\qquad [39]
$$

where y_i is the sublattice ionic site fraction and all ω terms are binary regular or subregular parameters either optimized or fixed (+100 kJ/mol) for the binary subsystems.

IX. CONCLUSIONS

A complete critical evaluation and optimization of all available phase diagram and thermodynamic data for all phases of the LiF-NaF-KF-MgF_2-CaF_2 system has been made. All data are reproduced within experimental error limits. The new modified quasichemical model[4] was used for the liquid phase, while the compound energy model[45] was used for the (Li,Na,K)(Mg,Ca)F_3 perovskite phase and a Henrian solution model for the limited solid solutions in LiF, NaF, KF and MgF_2. From the optimized parameters of the binary and ternary subsystems it is possible, from the quasichemical model, to predict the thermodynamic properties of the multicomponent liquid solution. The database of optimized parameters is included in the F*A*C*T[46] database computing system and may be used, along with the other databases and Gibbs energy minimization software, to calculate phase equilibria and all thermodynamic properties in multicomponent systems.

The modified quasichemical model for short-range ordering in the pair approximation has been shown to be very applicable to molten salt systems involving cation-cation ordering. A coming paper will discuss the integration of the model (and parameters) of the LiF-NaF-KF-MgF_2-CaF_2 molten salt solution with the model (and parameters) of the LiCl-NaCl-KCl-[RbCl-CsCl]-$MgCl_2$-$CaCl_2$ molten salt solution[5] into a single model which account for simultaneous first- and second-nearest-neighbor short-range ordering in reciprocal salt solutions. This model will permit reliable thermodynamic calculations in complex salt systems of importance to reactive metals processing.

List of Symbols

R	gas constant (8.31451 J/mol-K).
T	absolute temperature (K).
X_i	global mole fraction of cation i.
X_{AF}	global mole fraction of component AF.
y_i	sublattice mole fraction of species i in Compound Energy Formalism.
g	molar Gibbs energy (J/mol).
$g^{o,S}_{AF}$	standard molar Gibbs energy of component AF (S = solid, L = liquid).
g^{E}	excess molar Gibbs energy in a random-mixing model.
$g^{ijk}_{AB(C)iF}$	a ternary interaction parameter which gives the effect of CF on $\Delta g_{AB/F}$.
H^{o}_{298}	standard molar enthalpy at 298.15K (J/mol-K)
S^{o}_{298}	standard molar entropy at 298.15K (J/mol-K)
C_p	molar heat capacity (J/mol-K)
$\Delta g_{ij/F}$	Gibbs energy of the pair-exchange reaction: $(i-F-i)+(j-F-j)=2(i-F-j)$
X_{ij}	cation-cation pair (i-F-j) mole fraction.
Z^{i}_{ij}	cation-cation pair coordination number of species i.
χ_{Alk}	$\chi_{Alk} = \sum_{i=Li}^{K} \sum_{j=i}^{K} X_{ij}$
χ_{AlkE}	$\chi_{AlkE} = \sum_{i=Mg}^{Ca} \sum_{j=i}^{Ca} X_{ij}$

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Table I : Thermodynamic Properties of Compounds

		T Range K	$H^{o}_{298.15K}$ ** J/mol	$S^{o}_{298.15}$ J/mol-K	c_P J/mol-K	Ref
LiF	S	298.15-2000	-612956.0	35.6477	$42.6894+0.0174180T-530113T^{-2}$	47
	L	298.15-2000	-594581.6	42.9975	64.18256	47
NaF	S	298.15-2500	-573626.4	51.2958	$46.5888+0.0098993T-212966T^{-2}$	47
	L	298.15-2500	-556784.4	51.1576	70.5673	47
KF	S	298.15-2000	-567350.4	66.6093	$45.9822+0.0144222T$	47
	L	298.15-2000	-547978.6	75.6703	66.9440	47
MgF_2	S	298.15-1536	-1124241.0	57.2550	$94.5209-0.0066217T+217230T^{-2}$ $+2.43554\times10^{-6}T^{2}-10040.6T^{-1}$	48
	S	1536-2000	-1148699.2	-1.7474	$85.4036+28572438T^{-2}-73261.0T^{-1}$ $+1325.984T^{-0.5}$	48
	L	298.15-1000	-1072354.9	89.9722	$90.9259-1925945T^{-2}-276.42742T^{-0.5}$ $+219560782T^{-3}$	48
	L	1000-3000	-1086504.7	63.4194	94.9220	48
CaF_2	α	298.15-1424	-1225912.0	68.5720	$122.8224+0.0284802T-6489901T^{-2}+72535.5T^{-1}$ $-4023.107T^{-0.5}$	48
	α	1424-1425	-1245599.3	34.7482	104.0000	48
	β	298.15-1424	-1221142.0	71.9217	$C_p(\alpha)$ $(298.15 \le T \le 1424)$	*
	β	1424-2000	-1255460.7	20.0842	$107.9890+0.0104600T$	48
	β	2000-2001	-1221263.2	53.2548	$C_p(L)$ $(1000 \le T \le 4000)$	*
	L	298.15-1000	-1186067.9	92.5655	$161.2395+0.0211805T-7683116T^{-2}$ $+93543.1T^{-1}-5633.815T^{-0.5}$	48
	L	1000-4000	-1200017.3	66.2345	99.9140	48
$NaMgF_3$	S	298.15-1350	-1714068.7	110.6889	135.0000	*
$KMgF_3$	S	298.15-1400	-1716700.0	145.8000	115.6861	*
K_2MgF_4	S	298.15-1200	-2285000.0	224.6000	150.6647	*
$KCaF_3$	S	298.15-1350	-1795102.4	137.9561	145.0000	*

* This work.

** Relative to elements at 298.15K

Table II. Cation-cation "Coordination Numbers" of the Liquid.

i	j	Z^{i}_{ij}	Z^{j}_{ij}
Li	Li	6	6
Na	Na	6	6
K	K	6	6
Mg	Mg	6	6
Ca	Ca	6	6
Li	Na	6	6
Li	K	6	6
Li	Mg	3	6
Li	Ca	3	6
Na	K	6	6
Na	Mg	3	6
Na	Ca	3	6
K	Mg	3	6
K	Ca	3	6
Mg	Ca	6	6

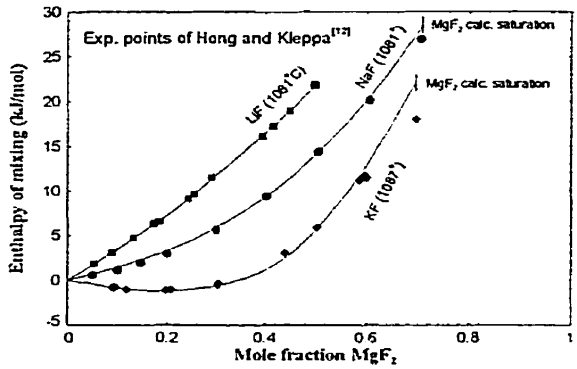

Fig. 1 – Calculated enthalpy of mixing of liquid alkali fluorides and solid MgF_2.

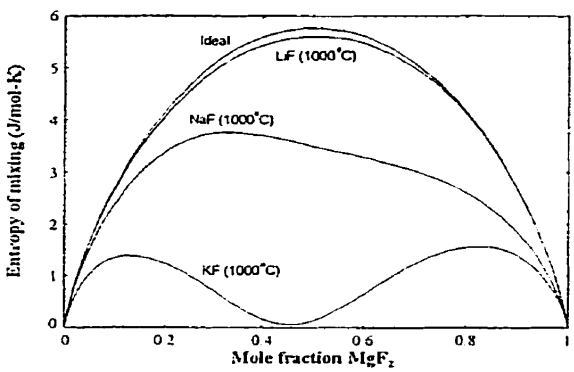

Fig. 2 – Calculated entropy of mixing of liquid alkali fluorides and (metastable) liquid MgF_2.

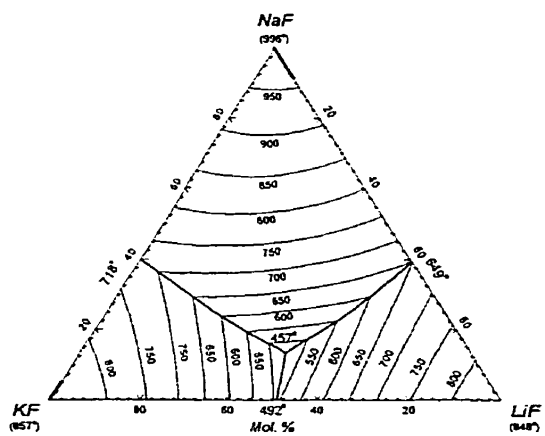

Fig. 3 – LiF-NaF-KF system : calculated liquidus projection.

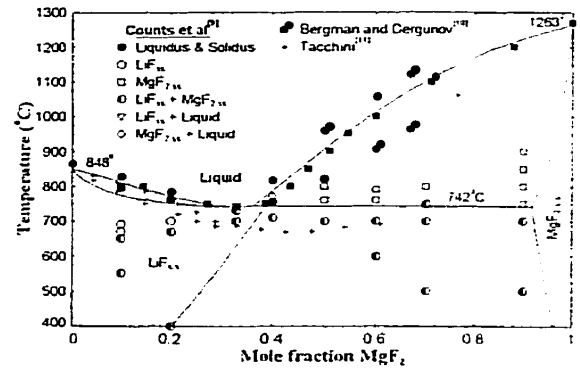

Fig. 4 – LiF-MgF_2 system : calculated phase diagram.

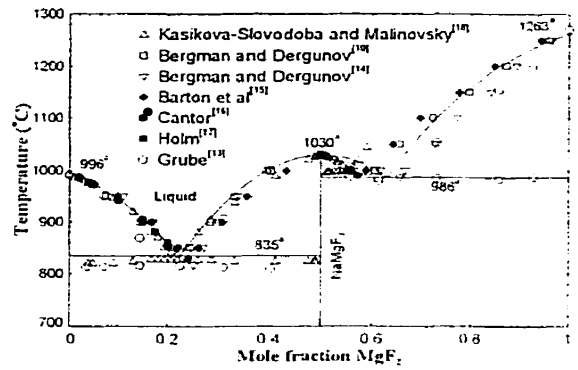

Fig. 5 – NaF-MgF_2 system : calculated phase diagram.

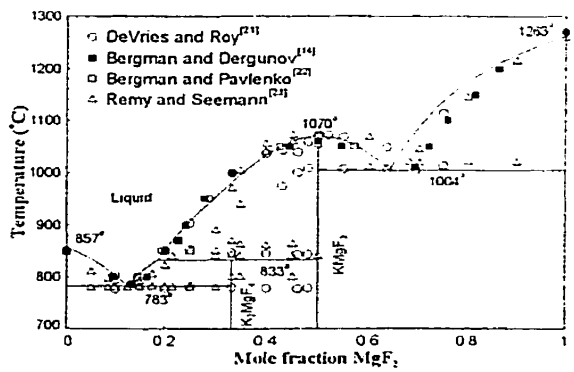

Fig. 6 – KF-MgF_2 system : calculated phase diagram.

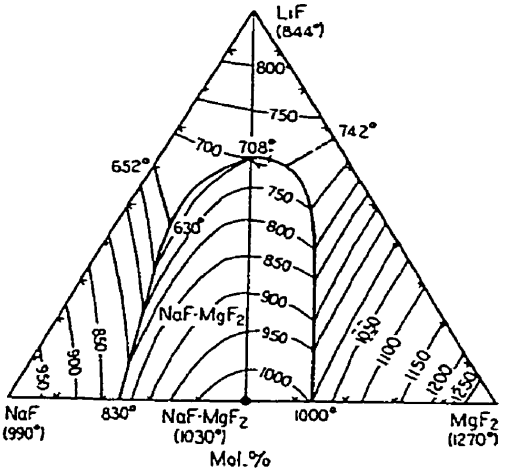

Fig. 7 – LiF-NaF-MgF_2 system : experimental liquidus projection of Bergman and Dergunov[10].

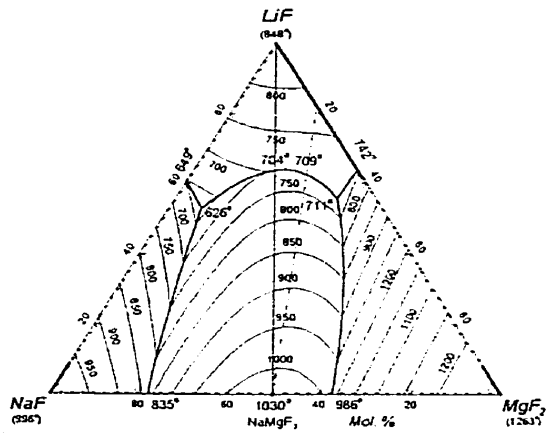

Fig. 8 – LiF-NaF-MgF_2 system : calculated liquidus projection.

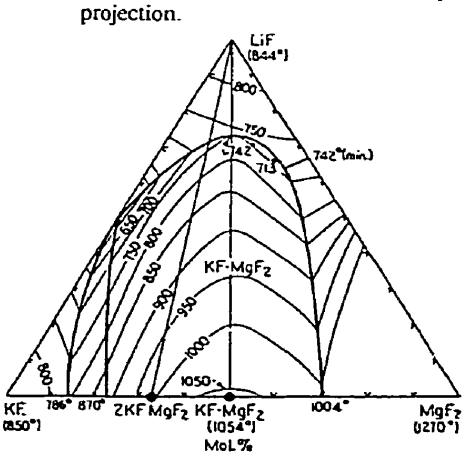

Fig. 9 – LiF-KF-MgF_2 system : experimental liquidus projection of Bergman and Pavlenko[22].

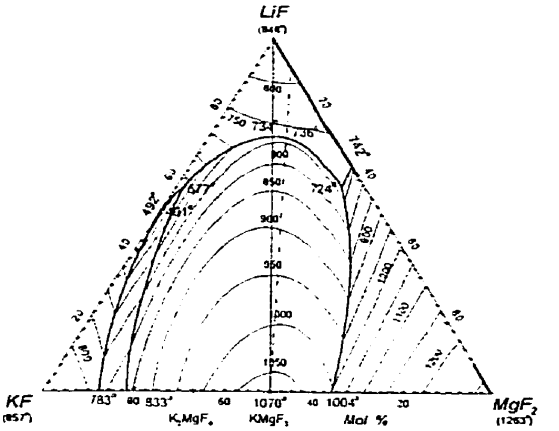

Fig. 10 – LiF-KF-MgF_2 system : calculated liquidus projection.

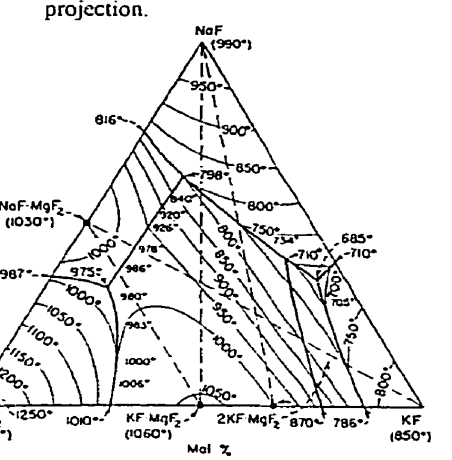

Fig. 11 – NaF-KF-MgF_2 system : experimental liquidus projection of Bergman and Dergunov[14].

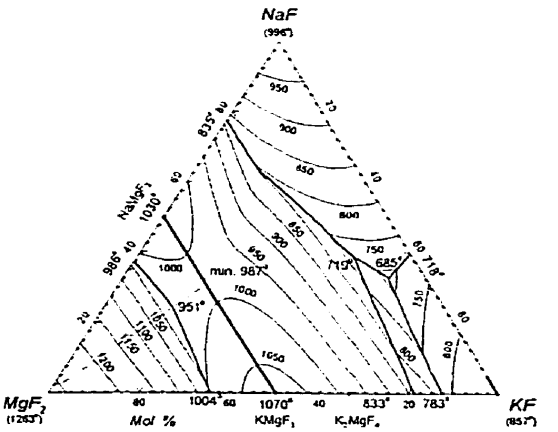

Fig. 12 – NaF-KF-MgF_2 system : calculated liquidus projection.

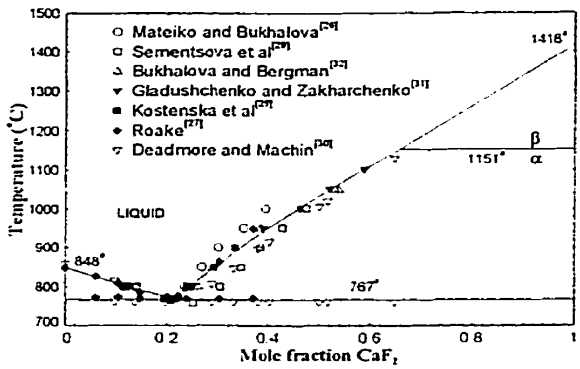

Fig. 13 – $LiF-CaF_2$ system : calculated phase diagram.

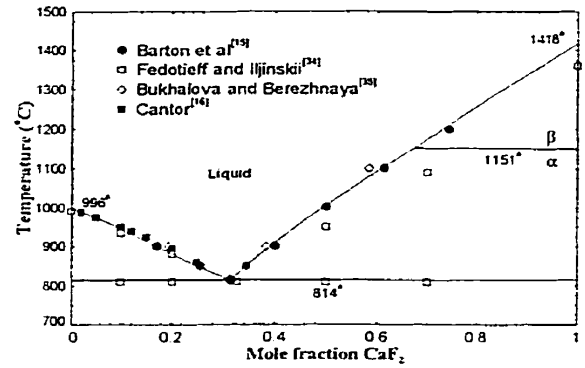

Fig. 16 – $NaF-CaF_2$ system : calculated phase diagram.

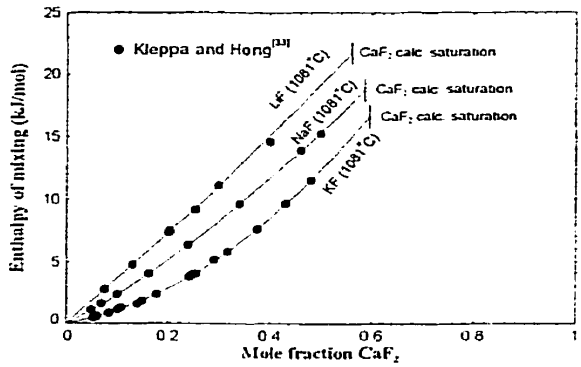

Fig. 14 – Calculated enthalpy of mixing of liquid alkali fluorides and solid CaF_2.

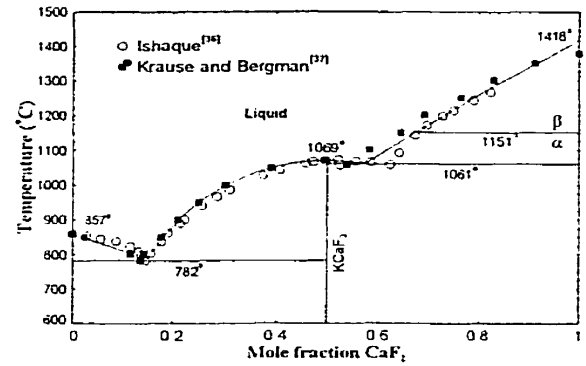

Fig. 17 – $KF-CaF_2$ system : calculated phase diagram.

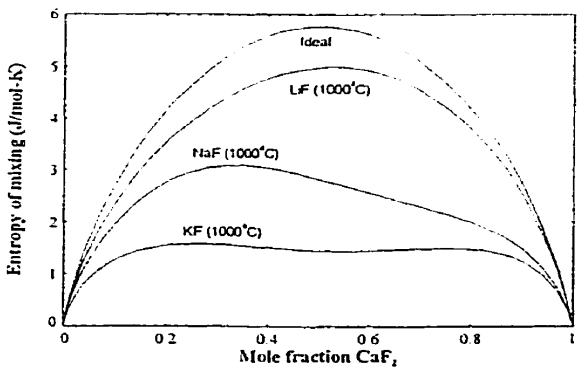

Fig. 15 – Calculated entropy of mixing of liquid alkali fluorides and (metastable) liquid CaF_2.

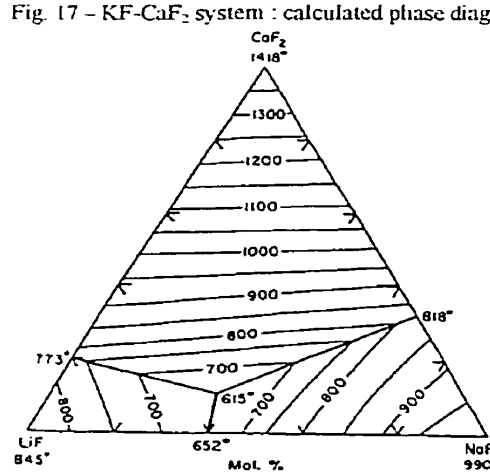

Fig. 18 – $LiF-NaF-CaF_2$ system : experimental liquidus projection of Barton *et al.*[15].

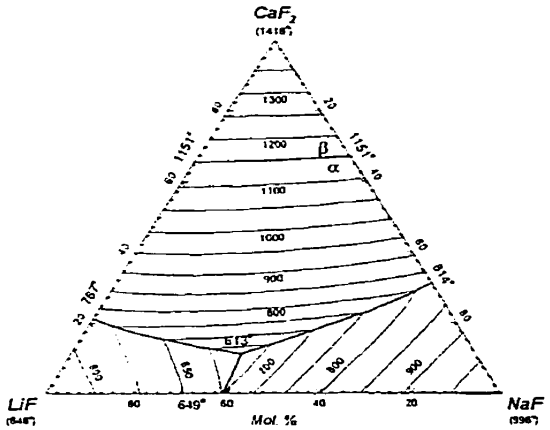

Fig. 19 – LiF-NaF-CaF_2 system : calculated liquidus projection.

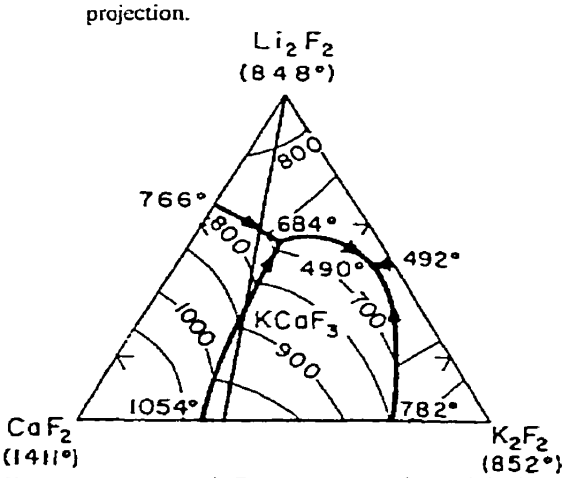

Fig. 20 – Li_2F_2-K_2F_2-CaF_2 system : experimental liquidus projection of Bukhalova and Berezhnaya[38] (mol.%).

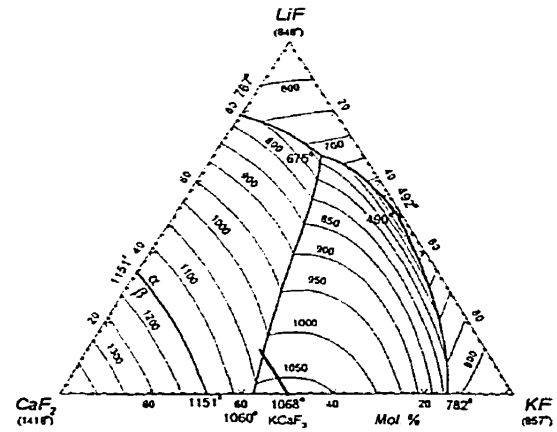

Fig. 21 – LiF-KF-CaF_2 system : calculated liquidus projection.

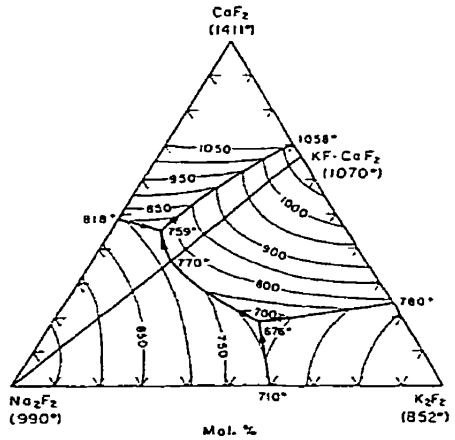

Fig. 22 – Na_2F_2-K_2F_2-CaF_2 system : experimental liquidus projection of Bukhalova and Berezhnaya[35].

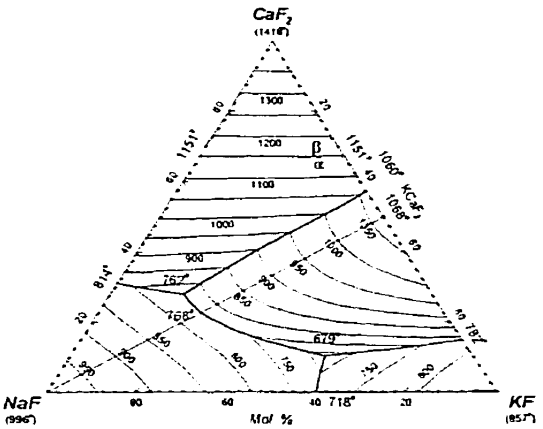

Fig. 23 – NaF-KF-CaF_2 system : calculated liquidus projection.

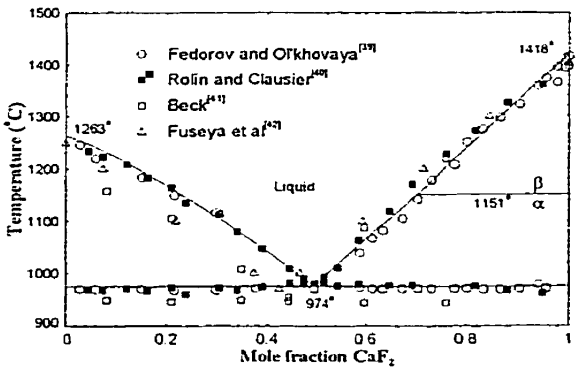

Fig. 24 – MgF_2-CaF_2 system : calculated phase diagram.

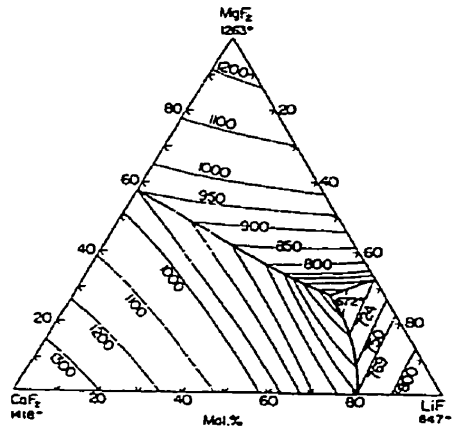

Fig. 25 – LiF-MgF_2-CaF_2 system : experimental liquidus projection of Roake[43].

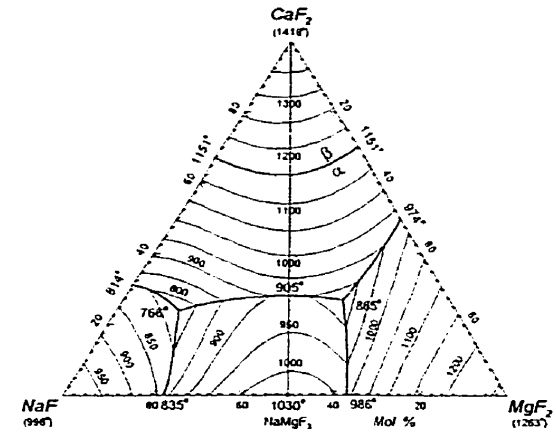

Fig. 28 – NaF-MgF_2-CaF_2 system : calculated liquidus projection.

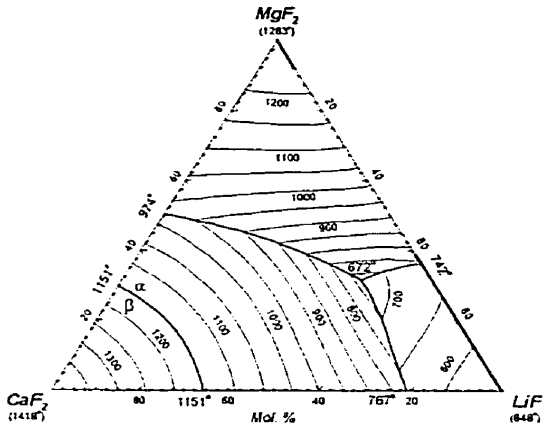

Fig. 26 – LiF-MgF_2-CaF_2 system : calculated liquidus projection.

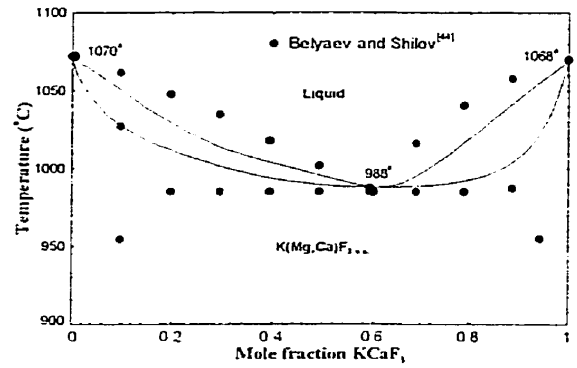

Fig. 29 – KF-MgF_2-CaF_2 system : calculated $KMgF_3$-$KCaF_3$ join with experimental points of Belyaev and Shilov[44].

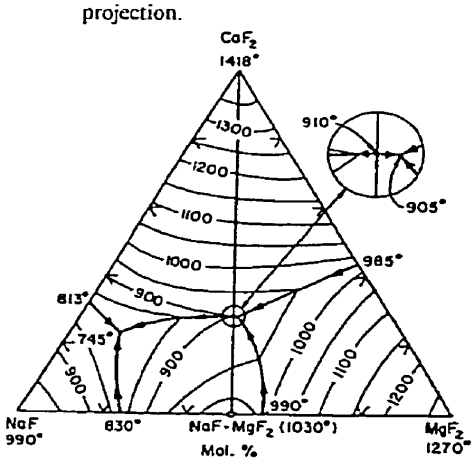

Fig. 27 – NaF-MgF_2-CaF_2 system : experimental liquidus projection of Barton *et al.*[15].

ANNEXE VIII

Article :

The Modified Quasichemical Model III – Two Sublattices

Patrice Chartrand et Arthur D. Pelton,

Soumis à *Metallurgical and Materials Transactions B*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel *FIGURE* développé par l'auteur de cette thèse durant ses études doctorales.

The Modified Quasichemical Model III – Two Sublattices

P. CHARTRAND and A.D. PELTON

The modified quasichemical model in the pair approximation for short-range ordering in liquids is extended to solutions with two sublattices. Short-range ordering of nearest-neighbor pairs is treated and the effect of second-nearest-neighbor interactions upon this ordering is taken into account. The model also applies to solid solutions if the number of lattice sites and coordination numbers are held constant. It may be combined with the Compound Energy Formalism to treat a wide variety of solution types. A significant computational simplification is achieved by formally treating the nearest-neighbor pairs as the "components" of the solution. The model is applied to an evaluation/optimization of the phase diagram of the Li, Na, K/F, Cl, SO_4 system.

I. INTRODUCTION

In the first two articles in the present series[1,2], the modified quasichemical model for short-range ordering in the pair approximation was described for solutions in which the species mix on only one lattice or sublattice. The present article extends the treatment to mixing on two sublattices. In solid solutions the existence of two sublattices is a manifestation of long-range ordering. For example, in a solid ionic solution one can distinguish anionic and cationic sublattices. In a liquid solution, on the other hand, there is no long-range ordering and, strictly speaking, it is incorrect to speak of sublattices. In molten NaCl, for example, the Na^+ and Cl^- ions should be treated as residing on one sublattice, but with a very high degree of short-range ordering such that the nearest-neighbors of Na^+ ions are almost exclusively Cl^- ions and vice-versa. Solutions of molten salts could thus be treated with the single-sublattice model described previously[1,2]. However in such solutions in which the degree of short-range ordering is very high, it is conceptually and mathematically simpler to treat the liquid solution as if it consisted of two distinct sublattices. This does not preclude the possibility of a small number of cation-cation or anion-anion nearest neighbors, since these can be treated within the two-sublattice model as substitutional defects (cations on anion sites and anions on cation sites).

In a solid solution, the ratio of the numbers of sites on the two sublattices is necessarily constant. However, in a liquid, this ratio can vary with composition. For example, in molten $NaCl$-$CaCl_2$ solutions the ratio of cation to anion sites varies from 1/1 to 1/2 as the composition varies from pure NaCl to pure $CaCl_2$.

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A two-sublattice model for multicomponent molten salt solutions was developed in an earlier article[3], but only for the case of random mixing of species on their respective sublattices. This was an extension and generalization of earlier work by Blander, Yosim and Saboungi [4–6]. Short-range ordering of first-nearest neighbors was introduced into the model by Dessureault and Pelton[7]. That is, account was taken of the fact that certain first-nearest neighbor ("cation-anion") pairs predominate. However, only reciprocal ternary systems (with only 2 species on each sublattice) were considered, and only for the case of an equal and constant number of sites on the two sublattices. In the present article this model is generalized. Simultaneous short-range ordering of first- and second-nearest neighbors is not treated by the present model since this is not possible within a pair approximation. However, this will be the subject of the next article in the present series.

II. THE MODEL

A. *Definitions, Coordination Numbers*

The solution consists of two sublattices, I and II. Let A, B, C, ... and X, Y, Z, ... be the species which reside on sublattices I and II respectively. In a salt solution, for example, A, B, C, . . . are the cations and X, Y, Z, . . . are the anions.

As another example, in a spinel solid solution, sublattices I and II would be associated with the tetrahedral and octahedral cationic sublattices. Although there is a third anionic sublattice, as long as this is occupied by only one species, O^{2-}, the present model can be applied. In other examples, lattice vacancies could also be considered as "species", or the same chemical species could occupy both sublattices. For example, in an ordered Cu-Au alloy, Cu and Au reside mainly on the I and II sublattices respectively. However, due to substitutional disordering, some Cu is found on the II sublattice and some Au on the I sublattice. That is, in this example A and X would both be Cu and B and Y would both be Au.

Let $Z^{A}_{A/X}$ be the nearest-neighbor coordination number of an A species when lattice II is occupied only by X, and let $Z^{X}_{A/X}$ be the coordination number of an X species when lattice I is occupied only by A.

In a solid solution, the numbers of sublattice I sites and sublattice II sites per mole are necessarily constant, independent of composition. Hence:

in solid solutions

$$Z^{A}_{A/X} = Z^{B}_{B/X} = Z^{A}_{A/Y} = Z^{B}_{B/Y} = \quad = \text{constant} = \\ = z_A = z_B = z_C = \ldots = z_I \qquad [1]$$

$$Z^{X}_{A/X} = Z^{X}_{B/X} = Z^{Y}_{A/Y} = Z^{Y}_{B/Y} = \quad = \text{constant} = \\ = z_X = z_Y = z_Z = \ldots = z_{II} \qquad [2]$$

In a liquid solution, on the other hand, the local structure is flexible, and the $Z^{i}_{i/j}$ and $Z^{j}_{i/j}$ can vary with composition.

The following mass balances apply:

$$z_A n_A = n_{A/X} + n_{A/Y} + n_{A/Z} + \ldots \qquad [3]$$

$$z_X n_X = n_{A/X} + n_{B/X} + n_{C/X} + \ldots \qquad [4]$$

$$\vdots$$

where z_A and z_X are the first-nearest-neighbor coordination numbers of A and X, n_i is the number of moles of species i in the solution, and $n_{i/j}$ is the number of moles of first-nearest-neighbor (i-j) pairs. Let:

$$\frac{1}{z_A} = \left(\frac{n_{A/X}}{Z^{A}_{A/X}} + \frac{n_{A/Y}}{Z^{A}_{A/Y}} + \frac{n_{A/Z}}{Z^{A}_{A/Z}} + \ldots\right)\left(\frac{1}{n_{A/X} + n_{A/Y} + n_{A/Z} + \ldots}\right) \qquad [5]$$

$$\frac{1}{z_X} = \left(\frac{n_{A/X}}{Z^{X}_{A/X}} + \frac{n_{B/X}}{Z^{X}_{B/X}} + \frac{n_{C/X}}{Z^{X}_{C/X}} + \ldots\right)\left(\frac{1}{n_{A/X} + n_{B/X} + n_{C/X} + \ldots}\right) \qquad [6]$$

Combining Eqs [3] to [6] gives:

$$n_A = n_{A/X}/Z^{A}_{A/X} + n_{A/Y}/Z^{A}_{A/Y} + n_{A/Z}/Z^{A}_{A/Z} + \ldots \qquad [7]$$

$$n_X = n_{A/X}/Z^{X}_{A/X} + n_{B/X}/Z^{X}_{B/X} + n_{C/X}/Z^{X}_{C/X} + \ldots \qquad [8]$$

$$\vdots$$

The composition dependence of Eqs [5,6] was chosen because it gives rise to the simple relationships of Eqs [7,8]. "Site fractions", X_i "pair fractions", $X_{i/j}$, and "coordination equivalent site fractions", Y_i, are defined as:

$$X_A = n_A/(n_A + n_B + \ldots) \\ X_X = n_X/(n_X + n_Y + \ldots) \qquad [9]$$

$$X_{i/j} = n_{i/j}/\sum n_{i/j} \qquad [10]$$

$$Y_A = z_A n_A/(z_A n_A + z_B n_B + \ldots) \\ Y_X = z_X n_X/(z_X n_X + z_Y n_Y + \ldots) \qquad [11]$$

Substitution into Eqs [7, 8] gives:

$$Y_A = X_{A/X} + X_{A/Y} + X_{A/Z} + \ldots \qquad [12]$$

$$Y_X = X_{A/X} + X_{B/X} + X_{C/X} + \ldots \qquad [13]$$

Restrictions on Z_{ij}

The restrictions on Z_{ij} for a solid solution were given in Eqs [1,2]. For a molten salt solution, these equations need not apply. However, it is necessary that

$$Z^{A}_{A/X}/Z^{X}_{A/X} = q_A/q_X \qquad [14]$$

where q_A and q_X are the absolute cationic and anionic charges. For example, in CaF_2, $Z^{Ca}_{Ca/F}/Z^{F}_{Ca/F} = 2/1$. Substitution of Eq [14] into Eqs [7,8] gives:

$$(q_A n_A + q_B n_B + \ldots) = (q_X n_X + q_Y n_Y + \ldots) \qquad [15]$$

which is the necessary charge neutrality condition.

A. Gibbs Energy Equation

We now define:

$$g^{o}_{A/X} = \left(\frac{q_A}{Z^{A}_{A/X}}\right) g^{o}_{A_{1/q_A} X_{1/q_X}} = \left(\frac{q_X}{Z^{X}_{A/X}}\right) g^{o}_{A_{1/q_A} X_{1/q_X}} \qquad [16]$$

where $g^{o}_{A_{1/q_A} X_{1/q_X}}$ is the standard Gibbs energy of the pure component. In the case of a salt, if q_A and q_X are the absolute cationic and anionic charges, then $g^{o}_{A_{1/q_A} X_{1/q_X}}$ is the standard Gibbs energy per charge equivalent. For Al_2O_3 for example,

$$g^{o}_{Al/O} = \left(3/Z^{Al}_{Al/O}\right) g^{o}_{Al_{1/3} O_{1/2}} = \left(2/Z^{O}_{Al/O}\right) g^{o}_{Al_{1/3} O_{1/2}} = \left(2/Z^{O}_{Al/O}\right) \frac{g^{o}_{Al_2O_3}}{6} \qquad [17]$$

That is, $g^{o}_{Al/O}$ is the standard Gibbs energy of Al_2O_3 per mole of Al-O pairs.

The Gibbs energy of the solution is given by the model as:

$$G = \left(n_{A/X} g^{o}_{A/X} + n_{A/Y} g^{o}_{A/Y} + n_{B/X} g^{o}_{B/X} + \ldots\right) - T\Delta S^{config}$$
$$+ \left(\sum n_{i/j}\right) \left[\frac{X_{A/X} X_{B/X}}{Y_X} \Delta g_{AB/X} + \frac{X_{A/Y} X_{B/Y}}{Y_Y} \Delta g_{AB/Y} + \frac{X_{A/X} X_{A/Y}}{Y_A} \Delta g_{A/XY} + \frac{X_{B/X} X_{B/Y}}{Y_B} \Delta g_{B/XY} + \ldots \right] \quad [18]$$
$$+ (\text{Reciprocal ternary terms})$$

where $\sum n_{i/j}$ is the total number of moles of pairs, and ΔS^{config} is the configurational entropy of mixing given by:

$$\Delta S^{config} = -R\left(n_{A/X} \ln X_{A/X} + n_{A/Y} \ln X_{A/Y} + n_{B/X} \ln X_{B/X} + \ldots\right)$$
$$+ R\left(n_{A/X} \ln Y_A Y_X + n_{A/Y} \ln Y_A Y_Y + n_{B/X} \ln Y_B Y_X + \ldots\right) \quad [19]$$
$$- R\left(n_A \ln X_A + n_B \ln X_B + \ldots + n_X \ln X_X + n_Y \ln X_Y + \ldots\right)$$

In Eq [18], the parameter $\Delta g_{AB/X}$ is related to the interaction of second-nearest-neighbor A-B pairs on lattice I when lattice II is occupied only by X, (a "cation-cation" interaction in the case of a salt solution). This parameter can be evaluated from experimental data for the AX-BX-CX . . .(abbreviated ABC . . /X) subsystem. This is discussed in detail in Section II D. The "reciprocal ternary terms" in Eq [18] are discussed in Section II E; these should be small and, in the first approximation, they are equal to zero.

The configurational entropy expression in Eq [19], for the distribution of the pairs over pair positions, is exact for a one-dimensional lattice and approximate for a three-dimensional lattice. Consider the limiting case of no short-range ordering (that is random mixing), when the interactions are very weak. The A, B, C, . . . species and the X, Y, Z, . . . species will then be randomly distributed over the sites of sublattices I and II respectively. Hence, $X_{ij} = Y_i Y_j$ and the first two terms of Eq [19] cancel each other, leaving only the third term, which is indeed the correct expression for a random mixture of A, B, C, . . . species on sublattice I and X, Y, Z, . . . species on sublattice II according to the Temkin[8] model for liquids in which the number of sites on a sublattice can vary with composition.

1. Minimization of G to Give the Equilibrium Pair Distribution

The numbers of moles n_{ij} of the pairs at equilibrium at a given overall composition are calculated by numerical minimization of G subject to the constraints of Eqs [7,8]. To illustrate how this results in short-range ordering, consider a simple case of a reciprocal ternary system AX-AY-BX-BY (abbreviated AB/XY) when the last two terms in Eq [18] are equal to zero. Setting $\partial G/\partial n_{ij} = 0$, subject to the constraints of Eqs [7,8], then gives the following "quasichemical equilibrium constant":

$$\frac{X_{A/Y} X_{B/X}}{X_{A/X} X_{B/Y}} = \exp\left(-\Delta g^{exchange}/RT\right) \quad [20]$$

for the pair exchange reaction:

$$(A-X) + (B-Y) = (A-Y) + (B-X) \quad [21]$$

where:

$$\Delta g^{exchange}_{AB/XY} = g^{o}_{A/Y} + g^{o}_{B/X} - g^{o}_{A/X} - g^{o}_{B/Y} \quad [22]$$

If $\Delta g^{exchange}$ is negative, for example, then reaction [21] is shifted to the right, and (A-Y) and (B-X) pairs predominate. If $\Delta g^{exchange}$ is zero, then the solution of Eqs [7,8,20] gives $X_{ij} = Y_i Y_j$ which is the limiting case for random mixing as discussed above. From Eqs [16,22], $\Delta g^{exchange}$ can be calculated solely from the standard Gibbs energies of the pure components.

B. Limiting Case of Random Mixing

Let us assume that the values of $\Delta g^{exchange}$ for all the pair exchange reactions are sufficiently small that the distribution of species on the sublattices is nearly random. Setting all $X_{ij} = Y_i Y_j$ in Eq [18] then gives:

$$G = \left(\sum n_{i/j}\right)\left(Y_A Y_X g^{o}_{A/X} + Y_A Y_Y g^{o}_{A/Y} + Y_B Y_X g^{o}_{B/X} + \ldots\right)$$
$$+ RT\left(n_A \ln X_A + n_B \ln X_B + \ldots + n_X \ln X_X + n_Y \ln X_Y + \ldots\right)$$
$$+ \left(\sum n_{i/j}\right)\left(Y_A Y_B Y_X \Delta g_{AB/X} + Y_A Y_B Y_Y \Delta g_{AB/Y} + Y_A Y_X Y_Y \Delta g_{A/XY} + Y_B Y_X Y_Y \Delta g_{B/XY} + \ldots\right)$$
$$+ (\text{reciprocal ternary terms}) \quad [23]$$

If Eq [23] is normalized per charge equivalent and if it is assumed, as was done previously [3], that $z_i = q_i z$ where z is a constant, then Eq [23] is identical to the expression given previously[3] for a molten salt solution with random mixing.

C. Second-Nearest-Neighbor Interaction Terms

As mentioned in Section II B, the third term in Eq [18] is related to the interactions of second-nearest-neighbor pairs on the same sublattice. In the ABC . . ./X subsystem, sublattice II is occupied only by X species; hence $Y_X = 1$ and $Y_Y = Y_Z = \ldots = 0$. Furthermore, $X_{AX} = Y_A$, $X_{BX} = Y_B$, etc.; $n_{AX} = Z^A_{A/X} n_A$, $n_{BX} = Z^B_{B/X} n_B$, etc.; while $n_{AY} = 0$, $X_{AY} = 0$, etc. Substitution into Eq [18] gives:

$$G = \left(n_A g^o_{AX} q_{X/q_A} + n_B g^o_{BX} q_{X/q_B} + \ldots \right) + RT\left(n_A \ln X_A + n_B \ln X_B + \ldots\right) + \left(\sum n_{i/j}\right)\left(Y_A Y_B \Delta g_{AB/X} + Y_B Y_C \Delta g_{BC/X} + Y_A Y_C \Delta g_{AC/X} + \ldots\right) \quad [24]$$

where $g^o_{AX} q_{X/q_A}$ is the standard Gibbs energy of the pure component per mole of A.

Eq. [24] is identical to the expression given previously[2] for the Gibbs energy of the ABC . . ./X solution when there is random mixing on sublattice I. If the parameters $\Delta g_{AB/X}$, $\Delta g_{BC/X}$, ... are independent of composition, for example, then Eq [24] is simply the expression for a regular solution.

The parameter $\Delta g_{AB/X}$ in Eq [24] may be equated [1] to the energy of the following second-nearest-neighbor pair exchange reaction:

$$(A - X - A) + (B - X - B) = 2(A - X - B) \quad [25]$$

and may be expanded as a polynomial such as [2]:

$$\Delta g_{AB/X} = \Delta g^o_{AB/X} + \sum_{(i+j)\geq 1} q^{ij}_{AB/X} Y^i_A Y^j_B + \sum_{\substack{j\geq 0\\ k\geq 1}} \left(\frac{Y_B}{Y_A + Y_B}\right)^j \left(q^{0jk}_{AB(C)/X} Y^k_C + q^{0jk}_{AB(D)/X} Y^k_D + \ldots\right) \quad [26]$$

where $\Delta g^o_{AB/X}$ and $'L_{AB,X}$ are composition-independent (although possibly temperature-dependent) coefficients obtained from fitting experimental data for binary AX-BX solutions. The remaining terms in Eq [26] are "ternary terms", which are all zero in the AX-BX binary system, and which give the effect of the presence of C, D, . . . upon the energy of reaction [25]. The constant coefficients $q^{0jk}_{AB(C)/X}$, for example, can be obtained from fitting experimental data for the A,B,C/X ternary subsystem. For further discussion of expansions of $\Delta g_{AB/X}$ as polynomials, see references [1,2].

Although Eq. [24] is identical to the expression for G given previously[2], in the previous equation Z_A and Z_B in the equivalent fraction expressions, $Y_A = Z_A/(n_A Z_A + n_B Z_B + \ldots)$, were second-nearest-neighbor coordination numbers. The present model thus requires that the ratios Z_B/Z_A, Z_C/Z_B, etc. of second-nearest-neighbor coordination numbers be the same as for the ratios z_B/z_A, z_C/z_B, etc. of corresponding first-nearest-neighbor coordination numbers. (Only the ratios need to be the same. The actual values of z_i for first- and Z_i for second-nearest-neighbors can be different as long as the parameters $\Delta g_{AB/X}$ etc. in Eq. [24] are expressed per mole of first-nearest-neighbor pairs.)

In the limit of random mixing, as shown in Eq [23], the term $Y_A Y_B \Delta g_{AB/X}$ in Eq [24] for the ABC . . ./X subsystem is simply multiplied by Y_X. That is, the contribution of reaction [25] to the Gibbs energy is decreased by the factor Y_X which is the probability, in a random mixture, that i =X in an (A-i-B) configuration. However, in the general non-random case when there is short-range-ordering, this is no longer true. Suppose that $\Delta g^{exchange}$ for reaction [25] is negative. The reaction is thus displaced to the right, with a resultant clustering of (A – Y) and (B – X) pairs. Hence, the probability of an (A – X – B) configuration is less than in a random mixture, and so the contribution of the (A – X – B) second-nearest-neighbor term to the Gibbs energy is less than in a random mixture. It was shown previously [7] that this effect can become very important when the absolute value of $\Delta g^{exchange}$ exceeds about 50 kJ. The use of the random mixing approximation in such cases can result in calculated phase diagrams which are greatly in error.

To account for this effect, the term $Y_A Y_B Y_X \Delta g_{AB/X}$ in Eq [23] for the AB . . ./X sub-system is replaced by $(X_{A/X} X_{B/X} / Y_X) \Delta g_{AB/X}$ in Eq [18]. That is, X_{AX} is the probability that a given pair is an (A – X) pair, and (X_{BX}/Y_X) is the conditional probability that a neighboring pair is a (B – X) pair, given that one member of this pair is an X. In a random mixture, where $X_{AX} = Y_A Y_X$ and $X_{BX} = Y_B Y_X$, this expression reduces to the limiting value, $Y_A Y_B Y_X \Delta g_{AB/X}$ as given in Eq [23].

Previously,[7] the expression for $\Delta g_{AB/X}$ from Eq [26] (or a similar polynomial) was substituted directly into Eq [18]. That is, it was assumed that $\Delta g_{AB/X}$ is constant along a surface of constant Y_A, Y_B, Y_C, . . . In the present model this has been modified somewhat. The factors Y_A, Y_B, . . . in Eq [26] are first replaced by X_{AX}/Y_X, X_{BX}/Y_X, . . . which are equal to Y_A, Y_B, . . . in the A BC . . ./X subsystem). Then Eq [26] is substituted into Eq [18]. From Eq [13] it can be seen that this is equivalent to assuming that $\Delta g_{AB/X}$ is constant along a surface of constant $X_{mX}/(X_{AX} + X_{BX} + \ldots)$, where m = A, B, C, . . . This is very similar to the previous[7] assumption, but has been found to give somewhat better results.

D. Reciprocal Ternary Terms

If the model is good, then Eq. [18] should give a reasonable prediction of the Gibbs energy of the solution, with no "reciprocal ternary terms". However, if experimental data, such as a phase diagram are available for an AB/XY reciprocal ternary subsystem, then these can be used to determine empirical coefficients of reciprocal ternary terms. The following very simple form is proposed:

$$\text{(Reciprocal ternary AB/XY terms)} = \left(\sum n_{i/j}\right) \sum_{\substack{i,j\neq 0 \\ \text{or } k,l\neq 0}} q^{ijkl}_{AB:XY} X^{i}_{A/X} X^{j}_{B/X} X^{k}_{A/Y} X^{l}_{B/X} \qquad [27]$$

where the $q^{ijkl}_{AB:XY}$ are empirical coefficients. In order that these terms be zero in all binary subsystems it is necessary either that i and j be both non-zero, or that k and l be both non-zero.

A more physically justifiable form for the reciprocal ternary terms could be proposed. This will be discussed with respect to the more general model in the next article in the present series.

E. The Lattice Stability Term

In Gibbs energy expressions such as Eq [18], the first term is often called the : "lattice stability term". In Eq [18], the standard Gibbs energy $g^{o}_{A/X}$ is weighted by the factor $n_{A:X}$, the number of first-nearest-neighbor pairs. The lattice stability term thus depends upon the degree of short-range ordering. At the other extreme, one might propose replacing this term by $\left(\sum n_{i/j}\right)\left(Y_A Y_X g^{o}_{A/X} + Y_B Y_X g^{o}_{B/X} + \ldots\right)$ which is independent of the short-range ordering. If this were done, then minimizing G would simply involve maximizing the entropy, and a random mixture would always result. However, experience has shown that, at least in the case of molten salts, the lattice stability term of Eq [18] yields predictions which agree closely with measurements.

Nevertheless, a more flexible equation could be proposed in which the lattice stability term is written as:

$$\left[n_{A/X}\left(g^{o}_{A/X} - g^{*}_{A/X}\right) + n_{A/Y}\left(g^{o}_{A/Y} - g^{*}_{A/Y}\right) + \ldots\right] + \left(\sum n_{i/j}\right)\left(Y_A Y_X g^{*}_{A/X} + Y_A Y_Y g^{*}_{A/Y} + \ldots\right) \qquad [28]$$

where the $g^{*}_{i/j}$ are additional adjustable parameters. In the ABC . . .//X subsystem, $n_{A/X} = \left(\sum n_{i/j}\right) Y_A Y_X$, and so all terms in $g^{*}_{i/j}$ disappear. However, within the reciprocal system it is now the term $(\Delta g^{exchange} - \Delta g^{*exchange})$ which appears in the exponential of Eq [20], and which affects the degree of short-range ordering. Note also that in a random mixture, $n_{A/X} = \left(\sum n_{i/j}\right) Y_A Y_X$, and all terms in $g^{*}_{i/j}$ disappear.

For molten salt systems, such as those presented in Section III, good results have been obtained with all $g^{*}_{i/j}$ set to zero (i.e. by using Eq [18]). However, the use of the lattice stability term of Eq. [28] may find application in solid solutions such as Ag-Au alloys in which Ag and Au can occupy both sublattices. In this case it can be shown that, in the first approximation the short-range ordering depends upon $\left(\Delta g^{exchange} - \Delta g^{*exchange}\right)$, while the long-range ordering depends upon $\Delta g^{*exchange}$.

F. Discussion

If Eq [18] is divided by $\sum n_{i/j}$ and if, furthermore, only the first term in Eq [19] for ΔS^{config} is used, then:

$$g\,(\text{per mole of bonds}) = \sum X_{i/j} g^{o}_{i/j} + RT \sum X_{i/j} \ln X_{i/j} + g^{E} \qquad [29]$$

where g^{E} can be written as a function only of the $X_{i/j}$ as:

$$g^{E} = \left(\frac{X_{A/X} X_{B/X}}{Y_X} \Delta g_{AB:X} + \frac{X_{A/Y} X_{B/Y}}{Y_Y} \Delta g_{AB:Y} + \ldots\right) + \sum q^{ijkl}_{AB:XY} X^{i}_{A/X} X^{j}_{B/Y} X^{k}_{A/Y} X^{l}_{B/X} \qquad [30]$$

with the Y_i given as functions of the $X_{i/j}$ by Eqs [12,13].

Eq [29] is identical to the Gibbs energy expression commonly used for a simple solution of the "species" (ij) with random mixing on a single lattice. That is, if the pairs (i-j) are formally considered to be the "components" of the solution, then the quasichemical model can be treated using currently available and relatively simple software. Only the two additional entropy terms of Eq [19] need to be added, and these can both be written as functions only of X_{ij} through use of Eqs [9-13]. A further computational simplification can be achieved by formally treating the pairs (A-X) as the "associates" or "molecules" $A_{1/Z^{A}_{A/X}} X_{1/Z^{X}_{A/X}}$. For example, if we chose $Z^{Na}_{Na/Cl} = Z^{Cl}_{Na/Cl} = 6$ for NaCl, then the "component" becomes $Na_{1/6}Cl_{1/6}$. In this case, the quasichemical mass balances of Eqs [7,8] become "true" chemical mass balances in that the numbers of moles of Na and Cl on each side of the equations are equal.

Furthermore, by considering the pairs as "components", the calculation of partial Gibbs energies and chemical activities is simplified. If $\mu_{A/X}$ is the "chemical potential of the A–X pairs":

$$\mu_{A/X} = \left(\partial G/\partial n_{A/X}\right)_{n_{i/j}} \qquad [31]$$

then substitution of Eq [18] into Eq [31] gives:

$$\mu_{A/X} = g^{o}_{A/X} + RT\left(\frac{\ln X_A}{Z^{A}_{A/X}} + \frac{\ln X_X}{Z^{X}_{A/X}} + \ln\frac{X_{A/X}}{Y_A Y_X}\right) + g^{E}_{A/X} \qquad [32]$$

where the partial excess term $g^{E}_{A/X}$ is calculated from the polynomial expression for g^E in Eq [30] in the usual way:

$$g^{E}_{A/X} = g^{E} + \left(\partial g^{E}/\partial X_{A/X}\right) - \sum_{(i,j \neq A,X)} X_{i/j}\left(\partial g^{E}/\partial X_{i/j}\right) \qquad [33]$$

where Eqs [12,13] are used to express the Y_i in terms of the X_{ij}.

The chemical potential of the actual pure component can then be calculated by the following equation which is similar to Eq [16]:

$$\mu_{A\,1/q_A\,X\,1/q_X} = \left(Z^{A}_{AX}/q_A\right)\mu_{A/X} = \left(Z^{X}_{X/A}/q_X\right)\mu_{A/X} \qquad [34]$$

The influence of $\Delta g^{exchange}$, Eq [22], upon the chemical potentials arises through the term $\ln(X_{AX}/Y_A Y_X)$ in Eq [32]. If $\Delta g^{exchange}$ is positive, then reaction[21] is shifted to the left, and X_{AX} becomes larger than $Y_A Y_X$ which is its value in a random mixture. This makes a positive contribution to μ_{AX} which will be greatest along the AX-BY "stable diagonal" of the composition square of the AB/XY reciprocal system, resulting in a tendency to immiscibility along this diagonal as illustrated in Section III.

III. OPTIMIZATION OF THE Li, Na, K/F, Cl, SO_4 SYSTEM

The model was applied to the liquid phase of the Li,Na,K/F,Cl,SO_4 system. This system was chosen because of the high exchange Gibbs energy, ~61 kJ/mol at 700°C, of the reaction

$$LiCl(\text{liq}) + KF(\text{liq}) = LiF(\text{liq}) + KCl(\text{liq}) \qquad [35]$$

which will result in significant first-nearest-neighbor short-range-ordering in liquid Li,K/F,Cl solutions; because deviations from ideal behavior in the binary common-ion subsystems are not large so that second-nearest-neighbor cation-cation and anion-anion short-range-ordering is small; and because all binary and most common-ion ternary subsystems have been previously evaluated and optimized.[9-11]

All coordination numbers $Z^{i}_{i/j}$ and $Z^{j}_{i/j}$ (i = Li, Na, K; j = F, Cl, SO_4) were set to 5.0 except for $Z^{SO_4}_{i/SO_4}$ (i = Li, Na, K) which were set to 10.0.

The thermodynamic properties (H^o, S^o, C_p) of the nine pure solid and liquid salts and of the compounds K_3FSO_4, $LiNaSO_4$ and $LiKSO_4$ were taken from the previous publications.[9-11] Slight adjustments were made to H^o_{298} of NaF, NaCl, KF and KCl as discussed in Section III B1. The properties of Na_3FSO_4 were modified slightly from the earlier work[11]. The revised value of the Gibbs energy of formation of Na_3FSO_4 from 2NaF(liq) and Na_2SO_4(liq) is : ΔG^o = (-57134.4 + 42.179 T) J/mol.

All available thermodynamic and phase diagram data for all common-ion binary subsystems were critically evaluated and optimized previously[9-11] with a random (Bragg-Williams) configurational entropy and polynomial expansions for the excess Gibbs energies. For example, the optimized[9] excess Gibbs energy of the LiF-Li_2SO_4 liquid solution is:

$$g^{E} = Y_F Y_{SO_4}\left(-629 - 2.352\,T - 718\,Y_{SO_4}\right) J/\,charge\ equivalent \qquad [36]$$

(where a "charge equivalent" is defined as usual as one mole of LiF or 0.5 moles of Li_2SO_4)
where:

$$Y_{SO_4} = \frac{Z_{SO_4} n_{SO_4}}{Z_{SO_4} n_{SO_4} + Z_F n_F} = \frac{10 n_{SO_4}}{10 n_{SO_4} + 5 n_F} = \frac{2X_{SO_4}}{2X_{SO_4} + X_F} \qquad [37]$$

Since $\sum n_{i/j} = 5$ moles of pairs per charge equivalent, the parameter $\Delta g_{Li/FSO_4}$ in Eq [18] is given by:

$$\Delta g_{Li/FSO_4} = \left(-629 - 2.352T - 718 Y_{SO_4}\right)/5 \qquad [38]$$

or, in the notation of Eq[26]: $\Delta g^{o}_{Li/FSO_4} = (-125.8 - 0.470\,T)$ and $q^{01}_{Li/FSO_4} = -143.6$. Similarly, expressions for the thermodynamic properties of all solid solutions were also obtained by optimization.[9-11]

A. Common-Ion Ternary Subsystems

For the common-ion ternary subsystems, a symmetric (Kohler) model was used when all three components are halides or sulfates, and an asymmetric (Toop) model was used when two components are halides and the third is a sulfate as described previously.[2]

The LiF-NaF-KF, and LiCl-NaCl-KCl subsystems were discussed previously.[12] No additional ternary parameters were required to reproduce the experimental ternary phase diagrams.

1. LiF-LiCl-Li_2SO_4 System

There is no reported experimental liquidus projection. It was assumed that no ternary terms are required for the liquid phase and that there are no ternary solid solutions. The calculated (predicted) liquidus projection is shown in Fig. 1.

2. NaF-NaCl-Na_2SO_4 System

Liquidus projections are reported from two studies.[13,14] That of Wolters [13] is shown in Fig. 2. It was assumed that there are no ternary solid solutions. A small ternary parameter $q^{001}_{Na/FCl(SO_4)}$ =1674 J (see Eq.[26]) was required in order to give the calculated liquidus surface shown in Fig. 3. From Eq.[18] it can be estimated that this term will give a maximum contribution of approximately 300 J/mol to the Gibbs energy of the liquid. That is, this is a very small term.

3. KF-KCl-K_2SO_4 System

The reported liquidus projection of Mukimov[14] is shown in Fig. 4 and the calculated projection is shown in Fig. 5. Ternary solid solubility was assumed negligible. A small ternary term $q^{001}_{K/FCl(SO_4)} = -2343$ J was required. Note that the composition scales of Figs. 4 and 5 are different.

4. Li_2SO_4-$NaSO_4$-K_2SO_4 System

The liquidus projection was measured by Akopov and Bergman[15] who reported eight ternary crystallization fields of unknown phases. The calculated liquidus surface of the $(Na, K)_2SO_4$ solid solution and the Li_2SO_4-rich solid solution agree well with the measurements without the introduction of any ternary parameters for the liquid.

B. Reciprocal Ternary Subsystems

1. The Li,Na/F,Cl, the Li,K/F,Cl and the Na,K/F,Cl Systems

The liquidus projection of the Li,Na/F,Cl system as reported by Bergman *et al*[16] is shown on Fig. 6. Gabcova and Malinovsky[17] reported the liquidus in the NaCl-NaF-LiF triangle, giving the eutectic at 604°C rather than at 582°C, and the LiF-NaCl pseudobinary eutectic at 686.5°C rather than at 670°C.

The liquidus surface of the Na,K/F,Cl system was measured in two studies.[18,19] That of Ishaque[18] is shown on Fig. 6.

The liquidus projection of the Li,K/F,Cl system as reported by Berezina *et al*[20] is shown on Fig. 6. Gabcova *et al*[21] measured the liquidus along the LiF-KCl join, reporting the pseudobinary eutectic at 719°C rather than at 710°C.

The calculated liquidus surfaces are also shown in Fig. 6. It was assumed that there is no ternary solid solubility. No reciprocal ternary parameters were required. However, in order to reproduce the reported liquidus surfaces, small adjustments of +250 J/mol were made H^{o}_{298} of NaCl and KCl, and of -250 J/mol to H^{o}_{298} of NaF and KF. These are all within the stated error limits [22] which vary from ±340 J/mol for NaCl to ±800 J/mol for NaF and KCl. The effect of these adjustments is to increase $\Delta g^{exchange}$ of the exchange reactions[35] and [39] by 500 J/mol, while leaving $\Delta g^{exchange}$ of reaction [40] unchanged.

$$LiCl(liq) + NaF(liq) = LiF(liq) + NaCl(liq) \qquad [39]$$

$$NaCl(liq) + KF(liq) = KCl(liq) + NaF(liq) \qquad [40]$$

As can be seen from Fig. 6, the reported liquidus surfaces are reproduced within experimental error limits except near the LiF-KCl join of the Li, K/F, Cl system which is the system with the largest $\Delta g^{exchange}$. It is believed that this is due to the fact that the present model neglects second-nearest-neighbor cation-cation short-range-ordering and its coupling with the first-nearest-neighbor ordering. This will be treated in the following article in the present series.

2. The Li,Na/F,SO_4 the Li,K/F,SO_4 and the Na, K/F, SO_4 Systems

The liquidus surfaces of the Na,K/F,SO_4 and Li,Na/F,SO_4 systems as reported by Bergman and Rubleva[23] and by Sperenskaya and Bergman[24] are shown in Fig. 7. No liquidus surface of the Li,K/F,SO_4 system has been reported.

The liquidus surface was calculated by assuming no ternary solid solubility, and with the following reciprocal ternary parameters as defined in Eq.[27]:

$$q^{001}_{NaK/FSO_4} = -335 \text{ J} \qquad q^{2100}_{LiNa/FSO_4} = 3347 \text{ J} \qquad [41]$$

The calculated liquidus surfaces in Fig. 7 agree with the measured surfaces within the experimental error limits.

3. The Li,Na/Cl, SO_4, the Li, K/Cl,SO_4 and the Na,K/Cl, SO_4 Systems

The liquidus projections of all three reciprocal ternary subsystems, as reported by Akopov and Bergman[25] are shown in Fig. 8. Phases "I, II, III" in the Na, K/Cl, SO_4 system were reported as "unknown phases". Rowe et al[26] measured the NaCl-K_2SO_4 join of this system and reported a crystallization field of K_3ClSO_4. None of these compounds were considered in the calculations which assumed no ternary solid solubility and which included the two ternary reciprocal parameters of Eq [42]. Agreement is within the experimental error limits.

$$q^{0021}_{LiK/ClSO_4} = -1674 \text{ J} \qquad q^{1100}_{NaK/ClSO_4} = -1255 \text{ J} \qquad [42]$$

C. *Quaternary Reciprocal Subsystems*

Reported[27] liquidus surface projections along the KF-LiCl-NaCl and LiCl-NaF-KF joins are compared with the calculated projections in Figs. 9 and 10. Agreement is within the experimental error limits. It is believed that the reported eutectic temperatures of 546°C and 514°C shown on Fig. 9a may be in error since these are inconsistent with the spacing of the isotherms at higher temperatures, and indicate an unlikely precipitous drop in the liquidus just near the eutectic.

Liquidus points along four composition planes in the $Li,Na,K/Cl,SO_4$ reciprocal quaternary subsystem were reported by Akopov and Bergman.[25,28,29] These are compared with calculations in Figs 11(a-d). Excellent agreement is obtained.

IV. CONCLUSIONS

A very general quasichemical model has been proposed for solutions with two sublattices. Short-range ordering of first-nearest-neighbor pairs is treated in the pair approximation. The effect of second-nearest-neighbor interactions upon this ordering is taken into account. The parameters of the model are determined from optimization of available experimental data for the binary and ternary subsystems.

The model has been used to calculate liquidus surfaces of ternary, ternary reciprocal and quaternary reciprocal subsystems of the $Li,Na,K/F,Cl,SO_4$ system. Quantitative agreement is obtained with measurements with only a very few small ternary parameters.

The model is suitable for liquid solutions where the ratio of the numbers of sites on the two sublattices can vary with composition. However, the model also applies to solid solutions if the numbers of lattice sites and the coordination numbers are kept constant. The model can thus be combined with the "compound energy formalism"[30,31] to treat a wide range of solution types (slags, mattes, salts, ceramics, alloys), order-disorder phenomena, non-stoichiometric phases, point defects etc. For a discussion of applications of the compound energy formalism see also references[32,33].

By formally treating the nearest-neighbor pairs as the "components" of the solution, a significant computational simplification is realized. The model can then be treated with currently available and relatively simple software.

A new proposal for the lattice stability term in this and similar models is proposed which may help in separating the driving forces for long-range and short-range ordering. Simultaneous short-range ordering of first- and second-nearest-neighbors is not treated by the present model since this is not possible within a pair approximation. This will be the subject of the next article in the present series.

ACKNOWLEDGEMENTS

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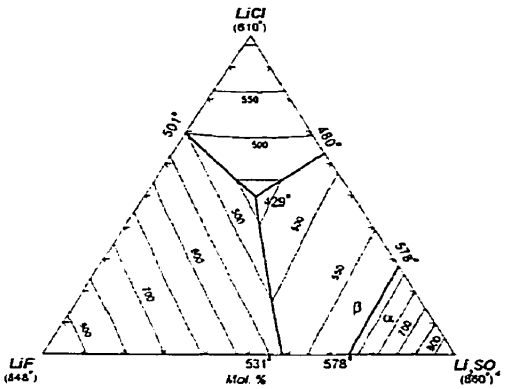

Fig. 1 - Calculated liquidus projection of the LiCl-LiF-Li_2SO_4 system (predicted).

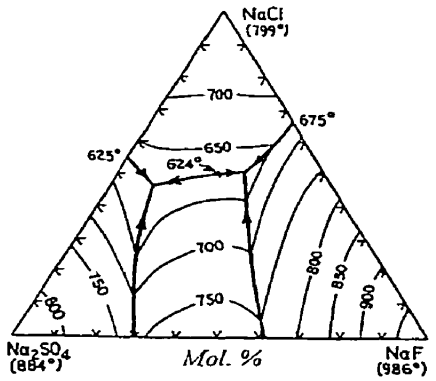

Fig. 2 - Measured NaCl-NaF-Na_2SO_4 liquidus projection of Wolters[13].projection.

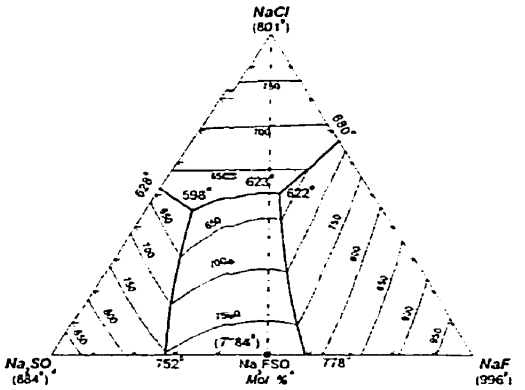

Fig. 3 - Calculated Na_2Cl_2-Na_2F_2-Na_2SO_4 liquidus projection

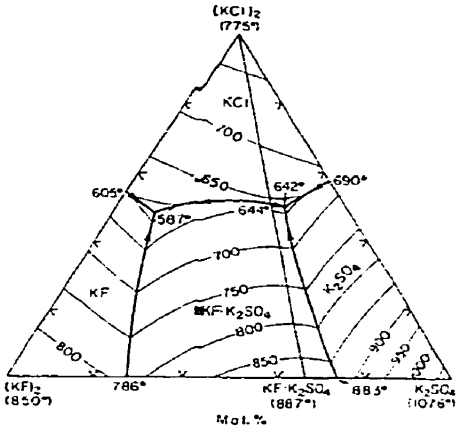

Fig. 4 - Measured K_2Cl_2-K_2F_2-K_2SO_4 liquidus projection of Mukimov[1-4].

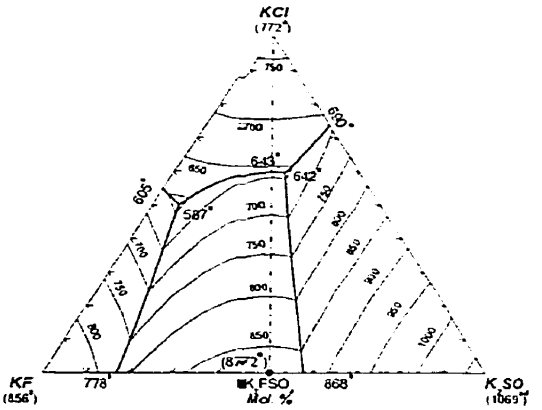

Fig. 5 - Calculated KCl–KF-K_2SO_4 liquidus projection.

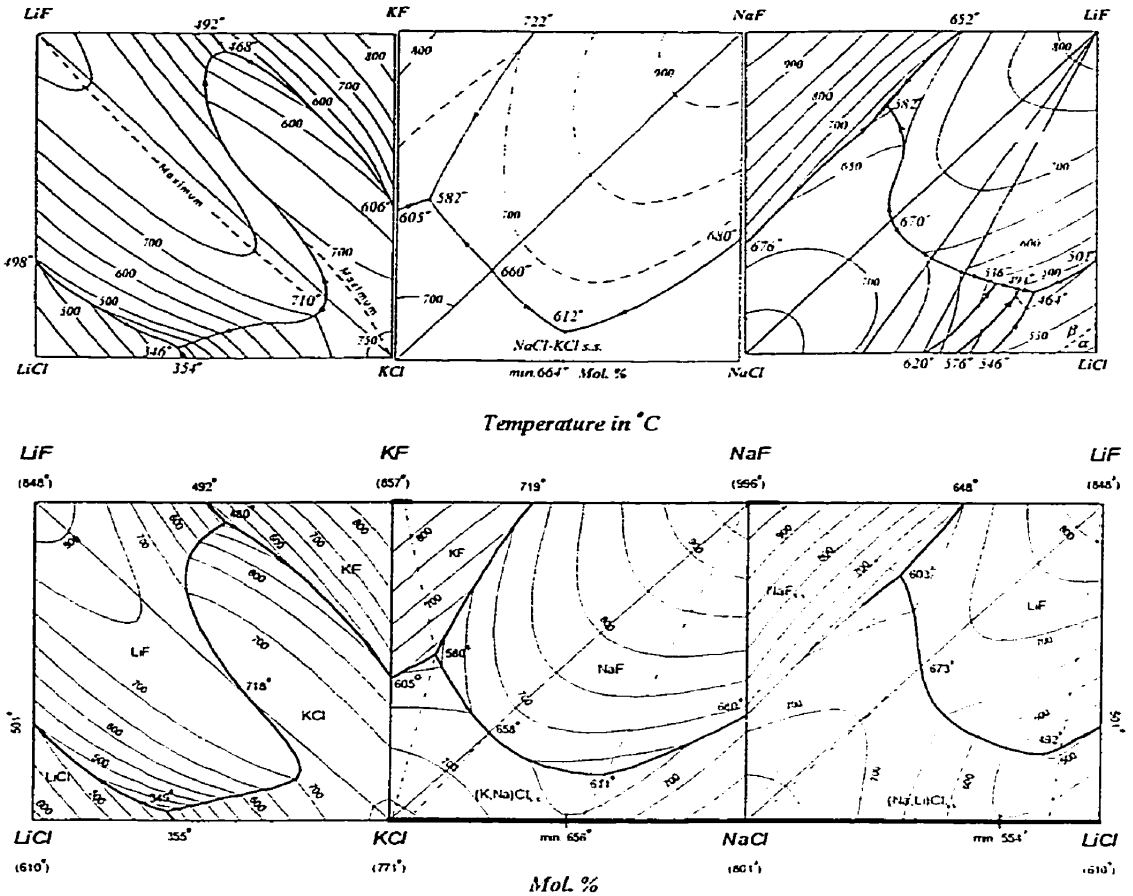

Figure 6. Top : Measured LiF-KF-LiCl-KC liquidus projection of Berezina et al.[20]; measured KF-NaF-KCl-NaCl liquidus projection of Ishaque[18]; measured NaF-LiF-NaCl-LiCl liquidus projection of Bergman et al.[16]. Bottom : calculated liquidus projections.

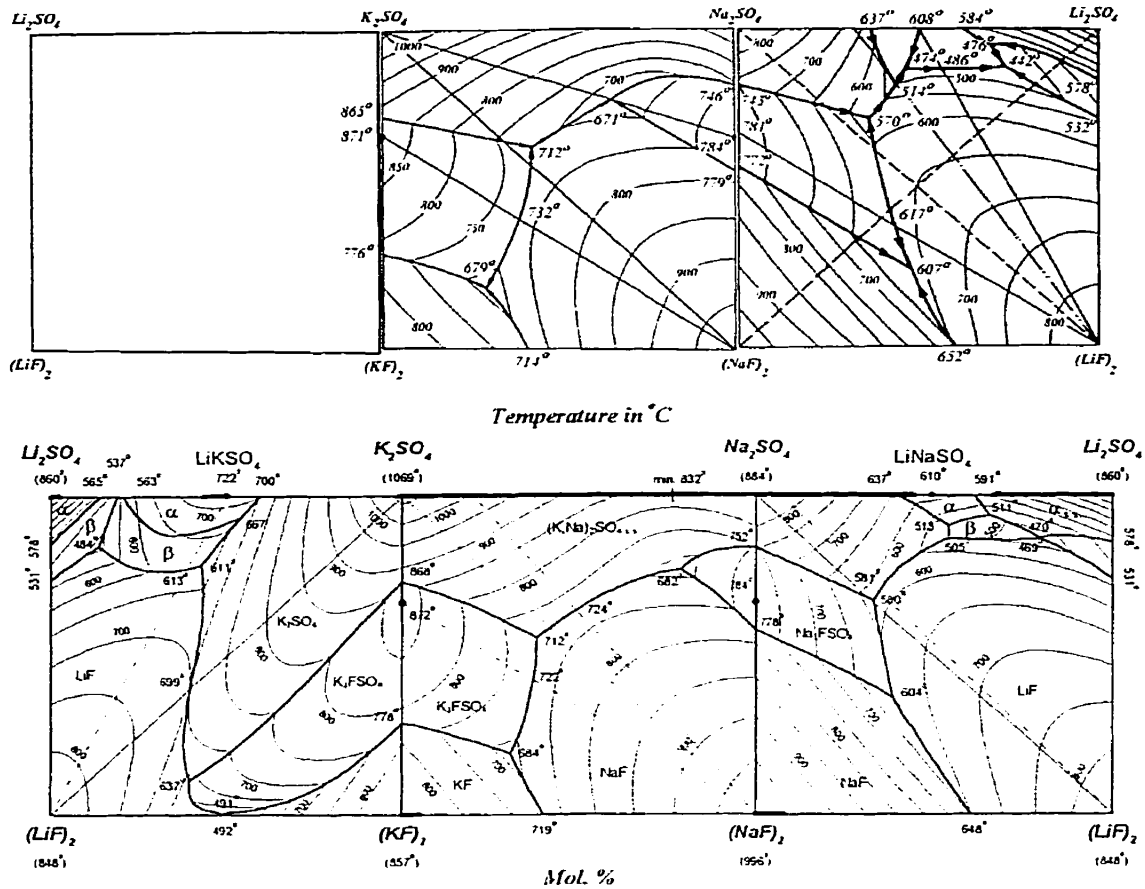

Figure 7. Top : Measured K_2SO_4-Na_2SO_4-$(KF)_2$-$(NaF)_2$ liquidus projection of Bergman and Rubleva[23] ; measured Na_2SO_4-Li_2SO_4-$(NaF)_2$-$(LiF)_2$ liquidus projection of Sperenskaya and Bergman[24]. Bottom: calculated liquidus projections.

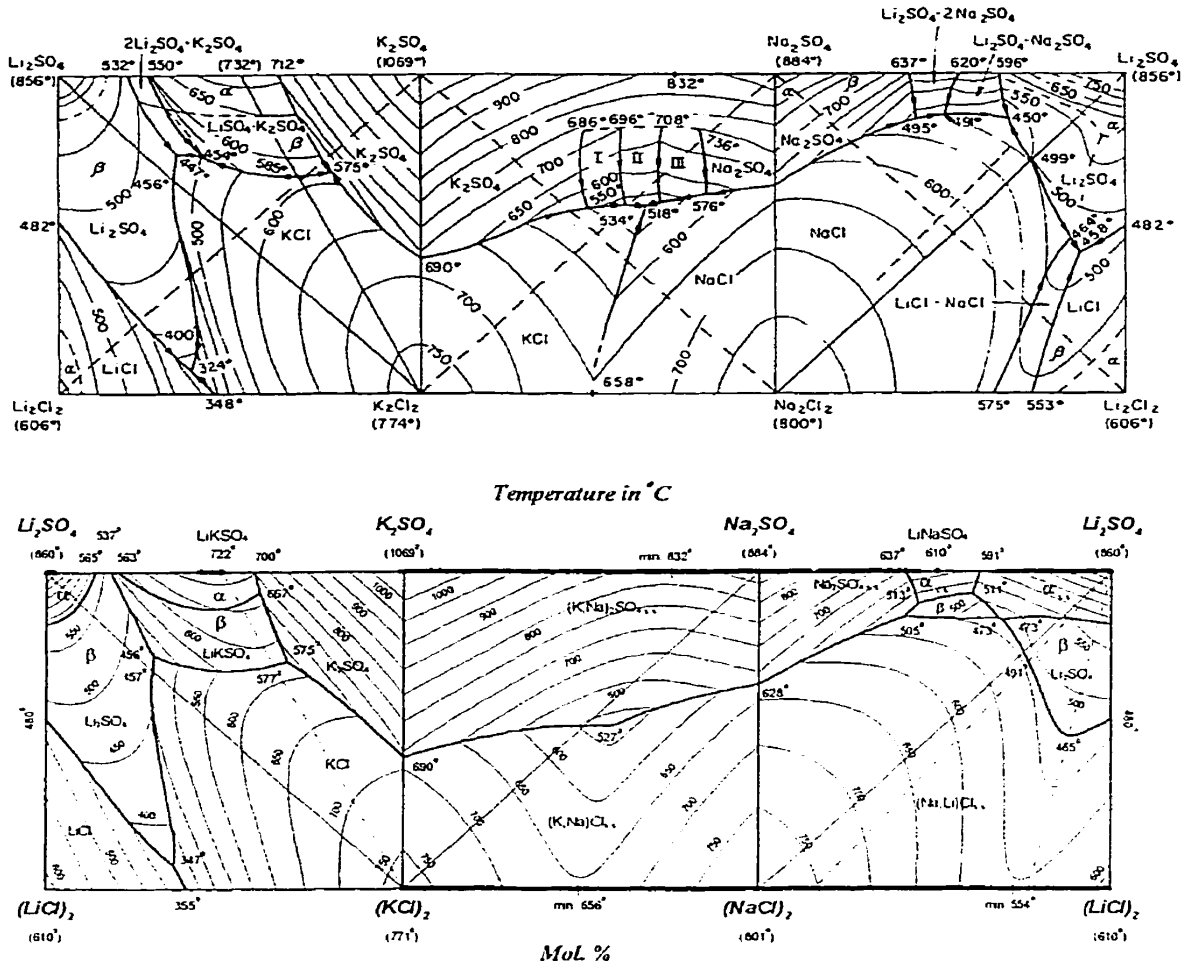

Figure 8. Top : Measured Li,Na,K/Cl,SO_4 liquidus projection of Akopov and Bergman[23] Bottom : calculated liquidus projection of the Li,Na,K/Cl,SO_4 system.

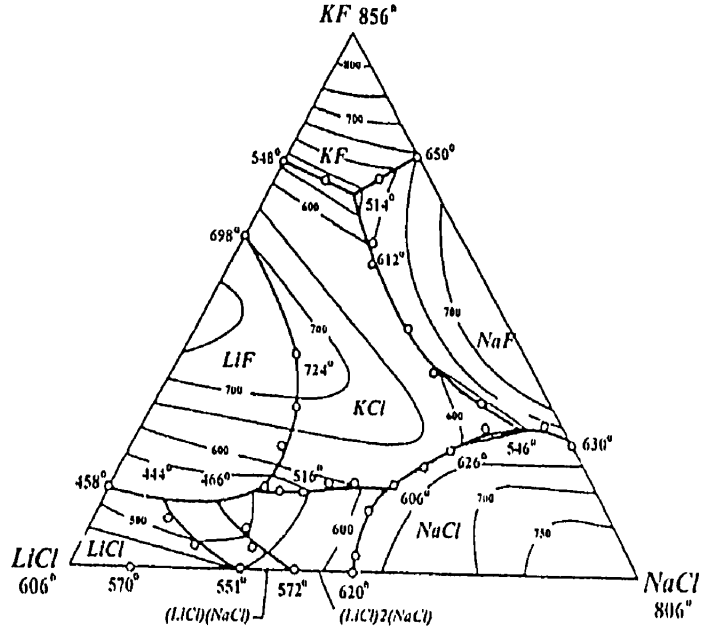

Figure 9a. Measured KF-LiCl-NaCl liquidus projection from Bergman et al.[27] (T in °C).

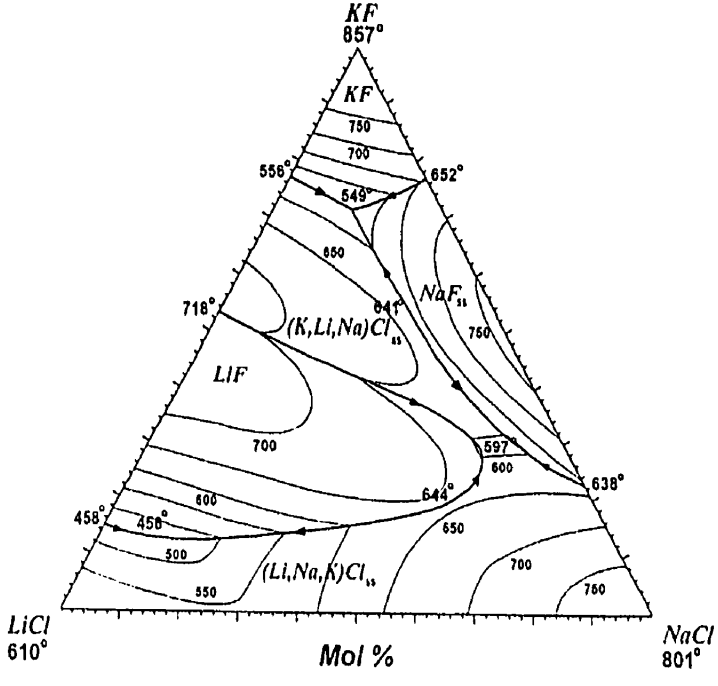

Figure 9b. Calculated KF-LiCl-NaCl liquidus projection (T in °C).

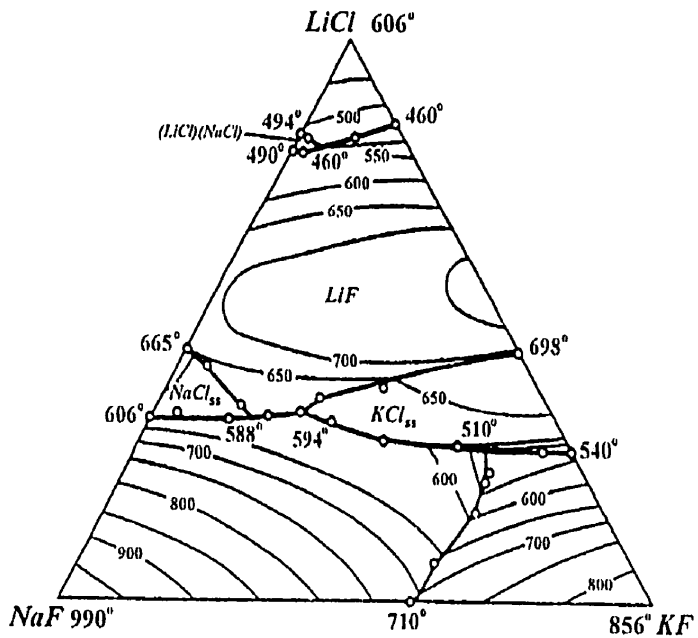

Figure 10a Measured LiCl-NaF-KF liquidus projection from Bergman et al.[27] (T in °C).

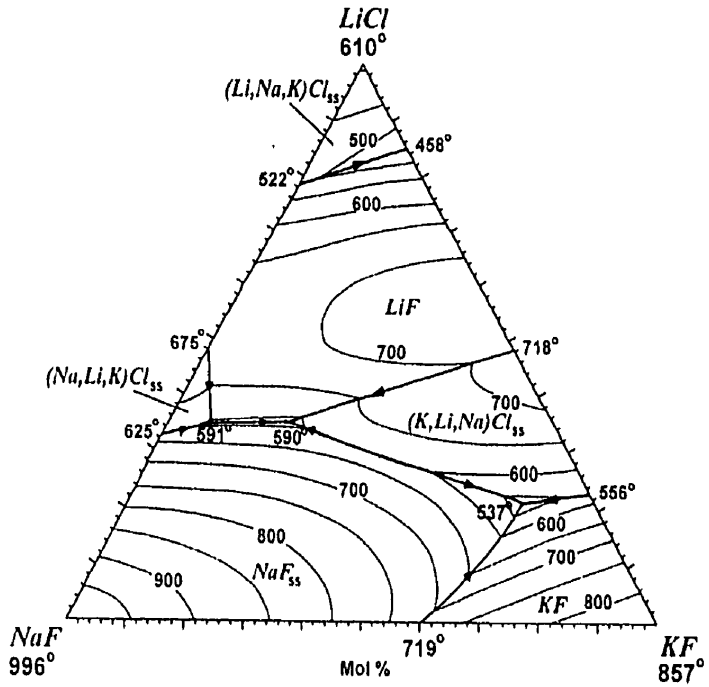

Figure 10b. Calculated LiCl-NaF-KF liquidus projection (T in °C).

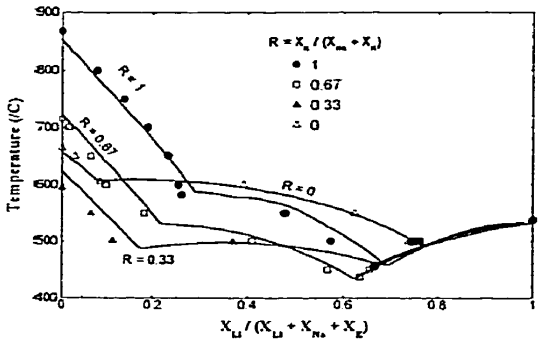

Fig. 11a - Calculated $0.3Li_2SO_4$-$0.7(LiCl)_2$-$0.3Na_2SO_4$-$0.7(NaCl)_2$-$0.3K_2SO_4$-$0.7(KCl)_2$ liquidus at different K/Na ratios with experimental pointsfrom Akopov and Bergman[20].

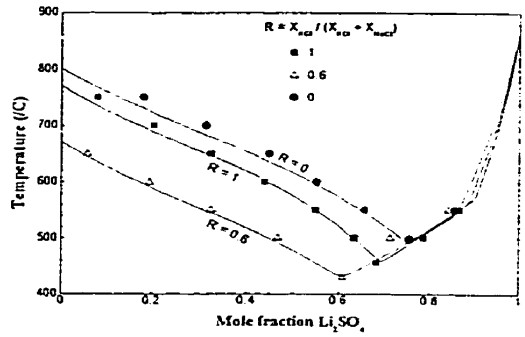

Fig. 11b - Calculated Li_2SO_4-$(NaCl)_2$-$(KCl)_2$ liquidus at different KCl/NaCl ratios with experimental liquidus points from Akopov and Bergman[29]

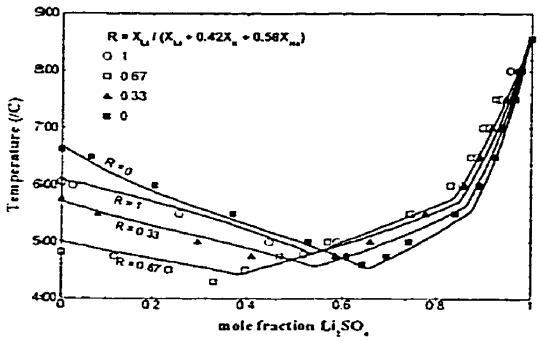

Fig. 11c - Calculated Li_2SO_4-$(LiCl)_2$-$(0.42KCl$-$0.58NaCl)_2$ liquidus at different Li/(Na+K) ratios with experimental points from Akopov and Bergman[28].

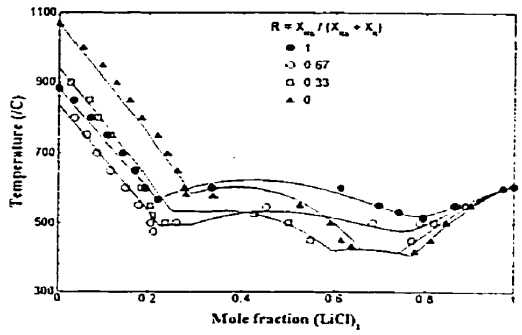

Fig. 11d - Calculated $(LiCl)_2$-Na_2SO_4-K_2SO_4 liquidus at different Na/K ratios with experimental points from Akopov and Bergman[20]

ANNEXE IX

Article :

Thermodynamic Phase Diagram Calculations and Cryoscopic Measurements in the $NaCl$-$CaCl_2$-$MgCl_2$-CaF_2 System

Heidi Mediaas, Patrice Chartrand, Olga Tkatcheva,
Arthur D. Pelton et Terje Østvold,
Accepté dans *Canadian Metallurgical Quarterly*,
2000.

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THERMODYNAMIC PHASE DIAGRAM CALCULATIONS AND CRYOSCOPIC MEASUREMENTS IN THE $NaCl-CaCl_2-MgCl_2-CaF_2$ SYSTEM.

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Abstract - Investigations of the quaternary phase diagram of the $NaCl-CaCl_2-MgCl_2-CaF_2$ system have been performed by thermodynamic phase diagram calculations and cryoscopy. A limited concentration region of the system is used as a flux medium for liquid magnesium metal in connection with the casting process. In this connection the knowledge of liquidus temperatures is important to avoid precipitation from the liquid flux, and thereby composition and property changes. Cryoscopic measurements were performed in the composition range of 40-60 wt% NaCl and $CaCl_2$, 0-15 wt% $MgCl_2$ and 0-10 wt% CaF_2. A thermodynamic model has been developed for multicomponent reciprocal molten salt solutions. The parameters of the model were obtained by critical evaluation and optimization of available thermodynamic data of the pure components, and of 9 binary and 5 ternary subsystems. This thermodynamic model makes it possible to calculate crystallization temperatures in this quaternary reciprocal system. These calculated crystallization temperatures agree reasonably well with measured temperatures. An average deviation of 11°C was observed between calculated and measured data while the uncertainty in the calculated data was estimated to be ±15 °C. This shows that it is possible to obtain reliable calculated crystallization temperatures in multicomponent molten salt systems. In view of the large amount of experimental work needed to measure such data in the whole composition volume of the multicomponent system, this is very promising.

Résumé - Le système réciproque quaternaire $NaCl-CaCl_2-MgCl_2-CaF_2$ a été étudié expérimentalement par cryoscopie, et un modèle thermodynamique a été développé pour reproduire les propriétés thermodynamiques et l'équilibre des phases dans ce système. Une petite région de composition de ce système est utilisée comme flux métallurgique pour la coulée et le moulage du magnésium liquide. La connaissance des températures du liquidus est donc importante pour éviter la précipitation du flux qui impliquerait un changement de sa composition et de ses propriétés. Des mesures cryoscopiques ont été faites pour une région de composition de 40% à 60% poids NaCl et $CaCl_2$, de 0% à 15% poids $MgCl_2$ et de 0% à 10% poids CaF_2. Un modèle thermodynamique a été développé pour les solutions de sels fondus multicomposantes réciproques. Les paramètres du modèle ont été obtenus par une analyse critique et l'évaluation des données thermodynamiques expérimentales pour les composants purs, les 9 sous-systèmes binaires et les 5 sous-systèmes ternaires. Ce modèle thermodynamique permet le calcul des températures de cristallisation dans ce système quaternaire réciproque. Les températures de cristallisation données par le modèle sont en accord avec les températures mesurées. Une déviation moyenne de 11 °C est observée entre les données calculées et les données expérimentales. L'incertitude sur les températures calculées à d'autres compositions que celles mesurées est estimée à ±15 °C, ce qui montre qu'il est possible d'obtenir des calculs fiables de températures de cristallisation d'un mélange multicomposant réciproque de sels fondus. Face à la quantité d'expériences nécessaires à la caractérisation de l'équilibre des phases pour la totalité du champ de composition d'un système multicomposant, cette approche est très prometteuse.

INTRODUCTION

A limited concentration region of the $NaCl-CaCl_2-MgCl_2-CaF_2$ system is used as a flux medium for liquid magnesium metal in connection with the casting process. In this connection the knowledge of liquidus temperatures is important to avoid precipitation from the liquid flux, and thereby composition and property changes.

Thermodynamic calculations of multicomponent phase diagrams have been possible to perform with good results in recent years due to useful thermodynamic models of the liquid phase. The first step in such calculations is the optimisation of all available phase diagrams and thermodynamic data for binary subsystems. In this step, least-squares analysis is used to obtain parameters of equations for the thermodynamic properties of all binary phases that best reproduce the binary phase diagrams and

thermodynamic properties simultaneously. In the next step, the solution model is used to estimate the Gibbs energy surface of the ternary subsystem solutions, and the ternary phase diagrams are calculated. Any available ternary phase diagram data can be used in order to refine the model through the introduction of small empirical ternary parameters. This approach is used regularly to calculate the phase diagrams of a wide variety of ternary systems. However, very few calculations have ever been performed for reciprocal salt systems like the quaternary $NaCl$-$MgCl_2$-$CaCl_2$-NaF-MgF_2-CaF_2 system which is discussed in the present paper. The present paper begins with a summary of the thermodynamic data used for the pure salts and the 9 common ion binary systems formed among the six salt components of the quaternary system. The optimisation of binary salt systems has been described in detail previously [1]. Ideal mixing terms for the liquid phase are given by the Temkin model [2], and excess Gibbs energies are expressed as empirical polynomial expansions in terms of the equivalent ionic fractions.

Following this, the optimizations of the common-ion ternary systems $NaCl$-$MgCl_2$-$CaCl_2$ and NaF-MgF_2-CaF_2 are treated. The excess Gibbs energy of each ternary liquid can be obtained from the excess Gibbs energies of the liquid phase in the three binary sub-systems by the "Toop" interpolation technique [1]. In the case of the fluoride system, an empirical ternary parameter was added in order to better reproduce the available ternary data.

The next step is to treat the calculation of the reciprocal ternary systems Na,Mg/F,Cl, Mg,Ca/F,Cl and Na,Ca/F,Cl. For two of these systems, empirical reciprocal ternary parameters were required to reproduce the available data. Finally, phase equilibria are calculated for the present reciprocal quaternary system and compared with measured data. No additional empirical parameters were added in this last calculation. The experimental data were obtained in a limited volume of the composition prism of the quaternary system. This concentration volume was of particular interest since a liquid salt flux of composition in this volume is used during casting of liquid Mg. For this application especially the liquidus temperatures were important.

The aim of the project was to determine if calculations of liquidus temperatures in complex molten salt solutions can give reasonable and useful results.

EXPERIMENTAL

Chemicals:

$CaCl_2$ and $MgCl_2$ were dehydrated from $CaCl_2 \cdot 2H_2O$ (p.a., E. Merck A.G) and $MgCl_2 \cdot 6H_2O$ (p.a., E. Merck A.G.) in a stream of HCl (g) while heated to 500 °C. Dehydrated $MgCl_2$ was distilled under vacuum at 1000 °C as explained elsewhere [3]. Dehydrated $CaCl_2$ was zone refined for 4 days. The purified $CaCl_2$(s) and the pure distilled $MgCl_2$(s) contained 0.005 wt% oxygen. The oxygen content was analyzed by carbothermal reduction analysis using a LECO TC-436 Nitrogen and Oxygen Analyzer [4]. NaCl (p.a., E. Merck A.G.) was dried under vacuum for 4 hrs at 400 °C and then recrystallised twice in a platinum crucible at a cooling rate of 3 °C/hr under inert atmosphere. CaF_2 (suprapur, E. Merck A.G) and MgF_2 (fibergrade, E. Merck A.G) were dried under vacuum in a Pt crucible at 400 °C for 5 hrs.

Procedure:

Cryoscopic measurements were carried out in an argon filled glove box with a water content < 1 ppm and an oxygen content < 5 ppm. The furnace with the experimental platinum crucible contained in a silica cell positioned in a Kanthal tube tightly connected to the glove box is shown in Fig. 1. The platinum crucible used as melt container was filled with weighed amounts of the salts to be studied. Alsint (sintered Al_2O_3) radiation shields having holes to accommodate the Alsint stirring rod, quartz salt charger, and thermocouple were positioned above the experimental cell to reduce the temperature gradient over the cell. The thermocouple was contained in a platinum protected Alsint tube and placed directly in the melt. The stirring rod had a platinum cover around the part immersed in the melt. In some experiments the Pt, Pt10%Rh thermocouple wire was immersed directly in the melt with no protection. The second thermocouple was positioned just above the melt and its signal was subtracted from that of the thermocouple in the melt. This gave a DTA-like output signal, which was used as an extra phase change indicator. This was sometimes needed when the phase changes which occurred during cooling were difficult to observe from the cooling curves alone. The temperature was measured with a calibrated Pt, Pt10%Rh thermocouple using a differential voltmeter equipped with a strip-chart recorder. The molten mixtures were stirred and equilibrated well above what was believed to be the liquidus temperature for 12 hrs before the liquidus temperature was measured. About 45 g of the $NaCl$-$CaCl_2$ binary mixture was used as an initial melt batch for each experiment. The composition of the melt was changed by additions of $MgCl_2$ and CaF_2 through a charging tube. The crystallization temperature of the new melt composition was then determined. The cooling rate was 1-3 ^{o}C/min. Small pieces of Pt or crystals of NaCl were added to the melt at the expected liquidus temperature to prevent super- cooling. The reproducibility of these melting point measurements was within ± 0.5 °C and the accuracy was within ± 2 °C.

For the $NaCl$-MgF_2 system about 45 g of NaCl was used and MgF_2 was added through the charging tube. The cooling rate was 1-3°C/min. Small crystals of NaCl or MgF_2, <0.005g depending on the liquidus line measured, were added to the melt at the expected freezing point temperature to prevent super- cooling. The accuracy of the freezing point determination was not satisfactory at the

MgF_2 rich side of the binary. This was due to a very sharp increase in the liquidus temperature with composition, and the very small enthalpy of fusion of MgF_2.This was so even if the Pt,Pt10%Rh thermocouple was immersed directly in the melt. The accuracy of the solidus temperature was ±1 °C.

Liquid melt samples were therefore withdrawn in the NaCl- MgF_2 melt containing excess $MgF_2(s)$ at given temperatures. This was done by a specially designed graphite ladle, where the inlet was located 15 mm above the bottom to avoid solids in the sample. This graphite ladle was threaded and screwed onto a steel shaft. The sampling device was slowly lowered to the last radiation shield and preheated just above the melt before sampling. In this way the melt temperature was kept constant during sampling. Samples were quenched at room temperature and analyzed by ICP for Mg^{2+} to determine the mole fractions of MgF_2 and NaCl in the liquid sample(the amount of NaCl was best determined from the amount added to the cell corrected for the NaCl in the samples removed). MgF_2 has a low solubility in common solvents as normally used for ICP analysis. The melt samples were therefore mixed with KOH and heated to 400°C for 2 hours in a glassy carbon crucible to remove the fluorides. The final melt was quenched and dissolved in ion distilled water containing 5% concentrated HNO_3. This solution was used for ICP analysis.

THE MOLTEN SALT MODEL

The original sub-lattice model developed by Blander, Førland and others has been generalized and extended to multicomponent solutions [5]. However, in this model, deviations from an ideal random Temkin distribution of the ions are treated only approximately. When these deviations become large, the model is unsatisfactory. An improvement to account more correctly for non-randomness in reciprocal ternary systems containing only univalent ions has been published [6]. This model has recently been further extended to multicomponent solutions and to solutions with ions of different charge [7].

For the present system, the Gibbs energy of one equivalent of the quaternary reciprocal molten salt solution, G, is given by the equation

$$
\begin{aligned}
G\ (J/\ equivalent) &= x_{Na/F}G^{o}_{Na/F} + x_{Na/Cl}G^{o}_{Na/Cl} + x_{Mg/F}G^{o}_{Mg/F} + x_{Mg/Cl}G^{o}_{Mg/Cl} + x_{Ca/F}G^{o}_{Ca/F} + x_{Ca/Cl}G^{o}_{Ca/Cl} + \\
&+ \frac{RT}{(q_{Na}x_{Na} + q_{Mg}x_{Mg} + q_{Ca}x_{Ca})}(x_{Na}\ln x_{Na} + x_{Mg}\ln x_{Mg} + x_{Ca}\ln_{Ca}) \\
&+ \frac{RT}{(q_F x_F + q_{Cl}x_{Cl})}(x_F \ln x_F + x_{Cl}\ln x_{Cl}) \qquad (1) \\
&+ ZRT\left(x_{Na/F}\ln\frac{x_{Na/F}}{y_{Na}y_F} + x_{Na/Cl}\ln\frac{x_{Na/Cl}}{y_{Na}y_{Cl}} + x_{Mg/F}\ln\frac{x_{Mg/F}}{y_{Mg}y_F} + x_{Mg/Cl}\ln\frac{x_{Mg/Cl}}{y_{Mg}y_{Cl}} + x_{Ca/F}\ln\frac{x_{Ca/F}}{y_{Ca}y_F} + x_{Ca/Cl}\ln\frac{x_{Ca/Cl}}{y_{Ca}y_{Cl}}\right) \\
&+ G^{E}_{Fluorides} + G^{E}_{Chlorides} + G^{E}_{Common\text{-}Cation} + G^{E}_{Recip}
\end{aligned}
$$

Where:

R	gas constant (8.31451 J/mol-K)
T	temperature in Kelvin
Z	co-ordination number = 6
x_i	ionic mole fraction of ion i
y_i	equivalent ionic fraction of ion i
q_i	absolute value of charge of ion i (Na = 1, Mg = 2, Ca = 2, F = 1 and Cl = 1)
$x_{c/a}$	mole fraction of a given set of *cation - anion* nearest - neighbor pairs (see Appendix).
$G^{o}_{c/a}$	Gibbs energy of one equivalent of a given pure salt $(c_{\frac{1}{q_c}}a_{\frac{1}{q_a}})$

x_i and y_i are defined as

For cations $x_c = \dfrac{n_c}{\sum_{all\ cations} n_i}$ for anions $x_a = \dfrac{n_a}{\sum_{all\ anions} n_i}$

For cations: $y_c = \dfrac{q_c n_c}{\sum_{all\ cations} q_i n_i}$ for anions: $y_a = \dfrac{q_a n_a}{\sum_{all\ anions} q_i n_i}$

where n_i is the number of moles of ion, i, in the solution.

Equations for the G^E terms are given in the Appendix of this paper. The numerical parameters in the G^E terms are parameters obtained from the binary and ternary optimizations.

RESULTS AND DISCUSSION

Pure salts

Thermodynamic properties for the pure components are listed in Table 1. The data are taken from "JANAF Thermochemical Tables" and "Thermochemical Properties of Inorganic Substances" [8,9]. The standard enthalpy of formation of $CaF_2(s)$ at 298.15 K is an optimized value, which differs from JANAF by 3186 J/mol. The standard entropy of formation of $CaCl_2(s)$ at 298.15 K is also an optimized value, which differs from JANAF by 0.8449 J/mol-K. These minor changes, well within JANAF's estimated error limits, are necessary to calculate the ternary reciprocal subsystems. For the solids, CaFCl, $NaMgF_3$, $NaMgCl_3$ and Na_2MgCl_4, ΔH^0_{298} and ΔS^0_{298} were obtained from the binary optimizations, while C_p data were estimated from the pure compounds. For example, $C_p(CaFCl(s)) = 1/2[C_p(CaF_2(\alpha)) + C_p(CaCl_2(s))]$ and $C_p(Na_2MgCl_4(s)) = 2C_p(NaCl(s)) + C_p(MgCl_2(s))$.

Binary systems

Phase diagrams and activity data for the 9 binary systems which were available for the present multicomponent system were used together with the data for the pure components to obtain optimized equations for the excess Gibbs energy function for each binary. These optimized equations were used to obtain the first three G^E terms in eqn.(1). Detailed data are given in the Appendix, eqns.(A1-A3). The data for the 3 common- fluoride and 3 common-chloride systems were taken from references [10-21] and [22-49], respectively. The data for the common-cation systems were taken from [49-54]. Full details of the optimizations of many of these binary systems have been published elsewhere(Talley [49] and Sangster [54]). Accurate data for the $NaCl-CaCl_2$ binary subsystem is most important for a reliable calculation of crystallization temperatures in the composition range where measurements were performed since $MgCl_2$ and CaF_2 were added to this binary. The calculated (optimized) phase diagram, enthalpy of mixing of the liquid and activity of NaCl at 825 °C for this binary are therefore shown in Figs. 2, 3 and 4.

The ternary systems

$NaX - MgX_2 - CaX_2$ (X=F or Cl): The fluoride system has a saddle point between $NaMgF_3$ and CaF_2 at 910 °C and at 28 mol% CaF_2, 36 mol% NaF and 36 mol% MgF_2. The temperature of the $NaF-NaMgF_3-CaF_2$ eutectic is at 745 °C, while the $MgF_2-NaMgF_3-CaF_2$ eutectic is at 905 °C. The experimental phase diagram is shown in Fig. 5 [13]. The « Toop » interpolation method [1] was used with NaF as the « asymmetric » component to calculate the same phase diagram. One ternary excess parameter, given by eqn.(2), was introduced in order to bring the calculated liquidus as shown in Fig. 6 into closer agreement with the reported. Without this term, the calculated eutectic and saddle points are about 20 °C lower. This is the final term in eqn.(A2) in the Appendix.

$$G^E = G^E_{Toop} + 28000\, y_{NaF}\, y_{MgF_2}\, y_{CaF_2} \quad \text{J/equiv.} \qquad (2)$$

An experimental liquidus projection of the $NaCl-MgCl_2-CaCl_2$ system was not found. The activity of NaCl at 850 °C was, however, measured by an e.m.f. technique for $x_{MgCl_2}/(x_{MgCl_2} + x_{CaCl_2})$ ratios of 0.129, 0.344, 0.517, 0.718 and 0.796 [39]. The activity of $MgCl_2$ at 800 °C was measured by the e.m.f. method for $x_{NaCl}/(x_{NaCl} + x_{CaCl_2})$ ratios of 0.25, 0.50 and 0.75 [55]. Calculations were again performed with the « Toop » interpolation technique with NaCl as the « asymmetric » component. Ternary terms were not used. Calculated and measured activity data for the $NaCl-MgCl_2-CaCl_2$ system are compared, with very good results, in Figs. 7 and 8. The predicted $NaCl-MgCl_2-CaCl_2$ phase diagram is presented in Fig. 9.

Reciprocal Ternary Systems

The influence of the ternary exchange Gibbs energies on the thermodynamic properties of reciprocal liquid solutions may often be very significant. Very strong nearest-neighbor interactions (more than 50 kJ/equiv.) sometimes coupled with complexation make modeling of reciprocal solutions a challenge. For the quaternary system Na,Mg,Ca/F,Cl, strong ternary exchange Gibbs energies are found for two of the three ternary reciprocal subsystems:

$$NaF(l) + \tfrac{1}{2}MgCl_2(l) \Leftrightarrow \tfrac{1}{2}MgF_2(l) + NaCl(l) \qquad \Delta G^o \approx -77 \text{ kJ/equiv.} \quad (3)$$

$$NaF(l) + \tfrac{1}{2}CaCl_2(l) \Leftrightarrow \tfrac{1}{2}CaF_2 + NaCl(l) \qquad \Delta G^o \approx -53 \text{ kJ/equiv.} \quad (4)$$

$$\tfrac{1}{2}CaF_2(l) + \tfrac{1}{2}MgCl_2(l) \Leftrightarrow \tfrac{1}{2}MgF_2(l) + \tfrac{1}{2}CaCl_2(l) \qquad \Delta G^o \approx -24 \text{ kJ/equiv.} \quad (5)$$

A calculated reciprocal ternary phase diagram is very sensitive to $\Delta G°$. Altering these values even within small experimental error limits can often have a major influence on the liquidus lines.

The large negative values of $\Delta G°$ in eqns.(3-5) indicate strong nearest-neighbor interactions and, consequently, large deviations from a random Temkin distribution. Moreover, the $NaCl-MgCl_2$ subsystem exhibits $MgCl_4^{2-}$ complexation. It has also been shown that the $NaF-MgF_2$ subsystem exhibits limited complexation [19]. The quasichemical model for reciprocal solutions used to construct eqn.(1) does not explicitly take into account such complexation on the same lattice, and probably oversimplifies the variation of the co-ordination numbers with composition as well. Consequently, the fit of the liquidus surface of the three ternary reciprocal subsystems must be made by slightly adjusting the exchange Gibbs energies. Only two of the three exchange equations (3-5) are independent. We may therefore modify the exchange

Gibbs energies by modifying the enthalpy of formation at 298.15 K of CaF_2 (the enthalpy error given for that salt is the highest of all salts considered [8]), and the entropy of formation at 298.15 K of $CaCl_2$ (the entropy error given for that salt is the highest of all salts considered [8]) by small values within the probable error limits. This proved to be necessary as a first step to fit the liquidus surfaces. Ternary reciprocal excess Gibbs energy parameters were then required for two of the reciprocal ternary subsystems, as discussed below.

The NaF-NaCl-MgF_2-$MgCl_2$ liquidus points on the stable diagonal NaCl-MgF_2 have been measured by DTA and by an equilibration and sampling technique both in this work and by Sharma and Johnson [51]. In the composition region of primary crystallization of MgF_2, the liquidus is very steep. Hence, the amount of solid MgF_2, which precipitates per degree of under-cooling below the liquidus, is very small. Consequently, the thermal effect is also very small and large under-cooling may occur before it is detected by the DTA technique. This led us to believe that DTA data could not be trusted. Careful equilibrium measurements with excess MgF_2 in the solution were performed. The data obtained in this way deviated considerably from the data of Sharma and Johnson [51], and also agreed better with the calculations. In order to reproduce our data, reciprocal ternary terms were required. Equation (6) is the optimized expression for the ternary reciprocal parameters obtained using these liquidus data. The calculated and measured liquidus along the NaCl-MgF_2 are shown in Figure 10.

$$G^E = x_{Na/Cl}x_{Mg/F}(-61000+41.84T) - 50208x^3_{Na/Cl}x_{Mg/F} \quad \text{J/equiv.} \qquad (6)$$

The NaF-NaCl-CaF_2-$CaCl_2$ liquidus projection has been published [14] and liquidus points along the stable diagonal NaCl-CaF_2 in the NaCl-rich (eutectic) region based on measurements have been reported [41]. A NaCl-CaF_2 eutectic at 779.5 °C at 4.5 mol% CaF_2 [41] and at 4 mol% CaF_2 at 775 °C [14] are given. In order to reproduce the liquidus projection, ternary reciprocal excess parameters were required. Equation (7) is the optimized expression for the ternary reciprocal parameters.

$$G^E = -12552x_{Na/Cl}x_{Ca/F} - 25104x^3_{Na/Cl}x_{Ca/F} \quad \text{J/equiv.} \qquad (7)$$

Figs. 11 and 12 show the measured and calculated liquidus projection of the Na,Ca/F,Cl system. Equations (6) and (7) are used to make up the G^E_{recip} term of eqn.(1) and eqn.(A4) in the Appendix.

MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ liquidus points on the stable diagonal $CaCl_2$-MgF_2 were measured by DTA and by an equilibration and sampling technique by Sharma and Johnson [51]. Ternary reciprocal parameters were not required to fit the liquidus. Only the modification of the Gibbs energies of the pure salts, CaF_2 and $CaCl_2$, as discussed before was needed to give a good reproduction of the measurements.

Quaternary Calculations

The composition region of interest for the present experimental study is shown in Figure 13. DTA measurements were carried out as discussed in the experimental section of this paper at 24 quaternary compositions. In Table 2, calculated (eqn.(1)) and experimental crystallization temperatures are compared. The calculated crystallization temperatures agree reasonably well with DTA measurements. An average deviation of 7.6 °C over 46 data points was observed. For the 25 primary crystallization temperatures an average deviation of 11.3 °C was found, while the secondary crystallization temperatures agreed within an average deviation of 3.0 °C. In the composition region of primary crystallization of MgF_2, the liquidus is very steep, the enthalpy of fusion of MgF_2 is small, and the same arguments as presented previously are valid. Consequently large under-cooling may occur before it is detected by the DTA technique. It can be observed from the data in Table 2 that most of the experimental primary crystallization temperatures are lower than the calculated ones in agreement with this assumption. Absolute accuracy of model liquidus calculations over this composition region is estimated as ±15 °C at a given composition when the liquidus is relatively flat, and ±3 mol% at a given temperature when the liquidus is steep. These error limits apply for temperatures up to 900 °C. Error limits on the calculated secondary crystallization temperatures are estimated as ±10 °C at a given composition.

CONCLUSIONS

From optimized model parameters based on activity and binary and ternary phase diagram data, it has been possible to calculate crystallization temperatures in the NaCl-$MgCl_2$-$CaCl_2$-CaF_2 quaternary reciprocal system. These temperatures agree reasonably well with measurements over the composition range of interest for the flux used for industrial liquid Mg casting. An average deviation of 8 °C was observed between calculated and measured data while the uncertainty in the calculated data was estimated as ±15 °C. This shows that it is possible to obtain reliable calculated crystallization temperatures in multicomponent molten salt systems where binary and ternary data are available to model the Gibbs energy of the complex multicomponent molten salt. In view of the large amount of experimental work needed to measure such data in the whole composition volume of the multicomponent system, this is very promising.

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APPENDIX

$$G^E_{Chlorides} = \frac{x_{Na/Cl}x_{Mg/Cl}}{y_{Cl}} [-11962 - 1.60327\,T + (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})(-35843 + 13.721\,T)$$
$$+ (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})^2 (34447 - 15.593\,T) - 8470.5 (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})^3]$$
$$+ \frac{x_{Na/Cl}x_{Ca/Cl}}{y_{Cl}} [-10069 + 4.3966\,T + (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})(-5300 - 4.9883\,T)$$
$$+ 12368 (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})^2 - 11016 (\frac{x_{Mg/Cl} + x_{Ca/Cl}}{x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl}})^3]$$
$$+ \frac{x_{Mg/Cl}x_{Ca/Cl}}{y_{Cl}} [3640 - 2.751\,T + (\frac{x_{Ca/Cl}}{x_{Mg/Cl} + x_{Ca/Cl}})(-8440 + 6.992\,T)$$
$$+ (\frac{x_{Ca/Cl}}{x_{Mg/Cl} + x_{Ca/Cl}})^2 (4436 - 5.436\,T)] \qquad \text{(A1)}$$

$$G^E_{Fluorides} = \frac{x_{Na/F}x_{Mg/F}}{y_F} [-25163 + 6.1183\,T + (\frac{x_{Mg/F} + x_{Ca/F}}{x_{Na/F} + x_{Mg/F} + x_{Ca/F}})(-10642 + 16.664\,T)$$
$$- 22896 (\frac{x_{Mg/F} + x_{Ca/F}}{x_{Na/F} + x_{Mg/F} + x_{Ca/F}})^2]$$
$$+ \frac{x_{Na/F}x_{Ca/F}}{y_F} [-7672.7 + 2.44918\,T + (\frac{x_{Mg/F} + x_{Ca/F}}{x_{Na/F} + x_{Mg/F} + x_{Ca/F}})(-10577.25 + 12.171\,T)]$$
$$+ \frac{x_{Mg/F}x_{Ca/F}}{y_F} [-7721 + 5661 (\frac{x_{Ca/F}}{x_{Mg/F} + x_{Ca/F}})] + 28000 \frac{x_{Na/F}x_{Mg/F}x_{Ca/F}}{y_F^2} \qquad \text{(A2)}$$

$$G^E_{common-cation} = \frac{x_{Na/F}x_{Na/Cl}}{y_{Na}} [1416 + 1283 (\frac{x_{Na/F}}{x_{Na/F} + x_{Na/Cl}})] + (\frac{x_{Mg/F} + x_{Mg/Cl}}{y_{Mg}} [-1290.5 + 25 (\frac{x_{Mg/F}}{x_{Mg/F} + x_{Mg/Cl}})]$$
$$+ \frac{x_{Ca/F}x_{Ca/Cl}}{y_{Ca}} [-3380.5 + 4598 (\frac{x_{Ca/F}}{x_{Ca/F} + x_{Ca/Cl}})] \qquad \text{(A3)}$$

$$G^E_{recip} = x_{Na/Cl}x_{Mg/F}(-61000 + 41.84T - 50208x^2_{Na/Cl}) + x_{Na/Cl}x_{Ca/F}(-12552 - 25104x^2_{Na/Cl}) \qquad \text{(A4)}$$

where:

$$y_F = x_{Na/F} + x_{Mg/F} + x_{Ca/F} \qquad \text{(A5)}$$
$$y_{Cl} = x_{Na/Cl} + x_{Mg/Cl} + x_{Ca/Cl} \qquad \text{(A6)}$$
$$y_{Na} = x_{Na/F} + x_{Na/Cl} \qquad \text{(A7)}$$
$$y_{Mg} = x_{Mg/F} + x_{Mg/Cl} \qquad \text{(A8)}$$
$$y_{Ca} = x_{Ca/F} + x_{Ca/Cl} \qquad \text{(A9)}$$

The numerical parameters in the G^E terms of eqns.(A1-A4) are the parameters from the binary and ternary optimizations.

The Gibbs energy, G, at any overall composition (given by x_i or y_i) is obtained by minimizing G of eqn (1) with respect to the $x_{c/a}$ variables subject to the constraints of Equations (A5-A9).

Table 1. Thermodynamic Properties of Pure Salts

Phase	T range (K)	ΔH°_{298} (J/mol)	S°_{298} (J/mol-K)	Cp (J/mol-K)
NaF(s)	298-2500	-573626.40	51.29584	$46.58884+0.009899344T-212965.6T^{-2}$
NaF(l)	298-2500	-556784.35	51.157608	70.567344
NaCl(s)	298-2000	-411119.84	72.13216	45.94032+0.0163176T
NaCl(l)	298-1500	-394956.03	76.076101	77.763824-0.0075312T
	1500-2000	-390090.09	84.505492	66.944
*MgF_2(s)	298-1536	-1124241.00	57.255	$94.5209323 - 0.006621697411T + 217229.898T^{-2} + 2.435541\times10^{-6}T^{2} - 10040.6082/T$
	1536-3000	-1145206.71	25.201983	94.922
*MgF_2(l)	298-1536	-1065539.00	95.472448	$94.5209323 - 0.006621697411T + 217229.898T^{-2} + 2.435541\times10^{-6}T^{2} - 10040.6082/T$
	1536-3000	-1086504.71	63.419431	94.922
*$MgCl_2$ (s)	298-987	-641616.00	89.629	$54.5843433 + 0.0214212731T - 1112119.22T^{-2} - 2.3566724\times10^{-6}T^{2} + 399.176723T^{-0.5}$
	987-2500	-649982.44	73.634468	92.048
*$MgCl_2$ (l)	298-987	-598521.00	133.291614	$54.5843433 + 0.0214212731T - 1112119.22T^{-2} - 2.3566724\times10^{-6}T^{2} + 399.176723T^{-0.5}$
	987-2500	-606887.44	117.297082	92.048
**CaF_2(α)	298-1423	-1222725.68	68.572	$122.822373 + 0.02848021T - 6489901.1T^{-2} + 72535.4528/T - 4023.10681T^{-0.5}$
	1423-1691	-1257026.02	16.747386	$107.989026 + 0.0104599903T$
	1691-4000	-1231288.56	45.330618	99.914
**CaF_2(β)	298-1423	-1217955.68	71.921719	$122.822373 + 0.02848021T - 6489901.1T^{-2} + 72535.4528/T - 4023.10681T^{-0.5}$
	1423-1691	-1252256.02	20.097105	$107.989026 + 0.0104599903T$
	1691-4000	-1226518.56	48.680337	99.914
*CaF_2(l)	298-1423	-1188174.00	89.576786	$122.822373 + 0.02848021T - 6489901.1T^{-2} + 72535.4528/T - 4023.10681T^{-0.5}$
	1423-1691	-1222550.03	37.664221	$107.989026 + 0.0104599903T$
	1691-4000	-1196812.56	66.247458	99.914
*$CaCl_2$(s)	298-1045	-795797.00	105.447953	$-338.821819 + 0.1092566449T + 7960390.64T^{-2} - 179502.014/T + 15395.4603T^{-0.5}$
	1045-3000	-812974.79	75.081985	102.533
*$CaCl_2$(l)	298-1045	-767254.00	132.761829	$-338.821819 + 0.1092566449T + 7960390.64T^{-2} - 179502.014/T + 15395.4603T^{-0.5}$
	1045-3000	-784431.79	102.39586	102.533
$CaFCl_4$(s)	298-1500	-1032275.84	69.088349	$-108 + 0.068868428T + 735244.8T^{-2} - 53483.2806/T + 5686.17675T^{-0.5}$
$NaMgF_3$(s)	298-1536	-1679280.23	138.429495	$141.109772 + 0.003277646591T + 4264.29824T^{-2} + 2.43554085\times10^{-6}T^{2} - 10040.6082/T$
	1536-3000	-1700122.15	106.540411	$141.41084 + 0.009899344T - 212965.6T^{-2}$
$NaMgCl_3$(s)	298-987	-1024875.96	205.664305	$100.524663 + 0.037738873T - 1112119.22T^{-2} - 2.3566724\times10^{-6}T^{2} + 399.176723T^{-0.5}$
Na_2MgCl_4(s)	298-987	-1415842.97	307.266928	$146.464983 + 0.054056473T - 1112119.22T^{-2} - 2.3566724\times10^{-6}T^{2} + 399.176723T^{-0.5}$

* In order to avoid extrapolation errors, C_p of the liquid phase is set equal to C_p of the solid phase below T^0_{fusion} and C_p of the solid phase is set equal to C_p of the liquid phase above T^0_{fusion}.

** In order to avoid extrapolation errors, C^l_p is set equal to C^β_p below T^0_{fusion} and above $T^0_{\alpha-\beta}$ and equal to C^α_p below $T^0_{\alpha-\beta}$. C^α_p is set equal to C^l_p above T^0_{fusion} and equal to C^β_p between $T^0_{\alpha-\beta}$ and T^0_{fusion}. C^β_p is set equal to C^l_p above T^0_{fusion} and equal to C^α_p below $T^0_{\alpha-\beta}$.

Table 2. Experimental and calculated primary, secondary and tertiary crystallization temperatures. System: $NaCl-CaCl_2-MgCl_2-CaF_2$.

Ex. No	Composition [wt%]				Experimental T/°C			Calculated T/°C			Calculated Phase
	$CaCl_2$	NaCl	$MgCl_2$	CaF_2	T_1	T_2	T_3	T_1	T_2	T_3	
1a	59.84	40.15	0	0	561			568	503		NaCl(ss)
1b	59.82	40.18	0.00	0.00	556	499		568	503		-
2a	56.85	38.14	5.00	0	527			533			NaCl(ss)
2b	56.80	38.19	5.01	0.00	518			533			-
3a	53.99	36.23	4.75	5.03		541		642	540		MgF_2+NaCl(ss)
3b	53.91	36.31	4.75	5.03	651	535		642	540		-
4a	51.11	34.29	4.50	10.09		574		728	567	548	MgF_2+CaFCl
4b	51.03	34.37	4.50	10.10	700	570	553	729	567	549	-
5a	48.16	32.31	10.01	9.51		517		766	518	489	MgF_2+NaCl(ss)
5b	48.17	32.34	10.01	9.48	748	514	484	765	518	489	-
6a	45.48	30.51	15.03	8.98		483		762	490	486	MgF_2+CaFCl+NaCl
6b	45.46	30.57	15.03	8.95	753	483	481	761	490	486	-
7	39.98	60.02	0	0	683			689			NaCl(ss)
8	37.95	56.98	5.07	0	654			662			NaCl(ss)
9	37.56	56.38	5.02	1.05	654			661			NaCl(ss)
10	37.19	55.84	4.97	2.00	657			660			NaCl(ss)
11	36.07	54.17	4.81	4.94	696			667			MgF_2
12	35.11	52.71	4.69	7.49	726			730			MgF_2
13	34.11	51.28	4.56	9.99	736			767			MgF_2
14	32.22	48.37	9.98	9.43		640		803	636		MgF_2+NaCl(ss)
15	30.42	45.67	15.00	8.90		610		792	603		MgF_2+NaCl(ss)
16a	50.08	49.92	0	0	627			634			NaCl(ss)
16b	50.09	49.91	0.00	0.00	626			634			-
17	47.57	47.42	5.01	0	594			603			NaCl(ss)
18	47.04	46.89	4.95	1.11	596			602			NaCl(ss)
19	46.60	46.45	4.90	2.05	598			602			NaCl(ss)
20a	45.20	45.05	4.76	5.00		603		653	604		MgF_2+NaCl(ss)
20b	45.20	45.06	4.74	4.99	671	602		653	604		-
21a	44.01	43.87	4.63	7.48		607		709	607		MgF_2+NaCl(ss)
21b	44.01	43.90	4.62	7.48	705	606		709	607		-
22a	42.79	42.65	4.50	10.05		609		745	607		MgF_2+NaCl(ss)
22b	42.77	42.69	4.49	10.05	714	609		745	607		-
23a	40.29	40.16	10.09	9.46		581		783	581		MgF_2+NaCl(ss)
23b	40.24	40.19	10.12	9.45	767	581		783	581		-
24a	38.07	37.95	15.04	8.94		547		776	546		MgF_2+NaCl(ss)
24b	38.03	38.01	15.03	8.93	766	544		775	547		-

a) The thermocouple immersed in the melt had a platinum covered alsint protection tube. In some experiments the starting temperature for cooling was too low to record the first crystallization.

b) The thermocouple immersed in the melt had no protection on the Pt/Pt10%Rh wire.

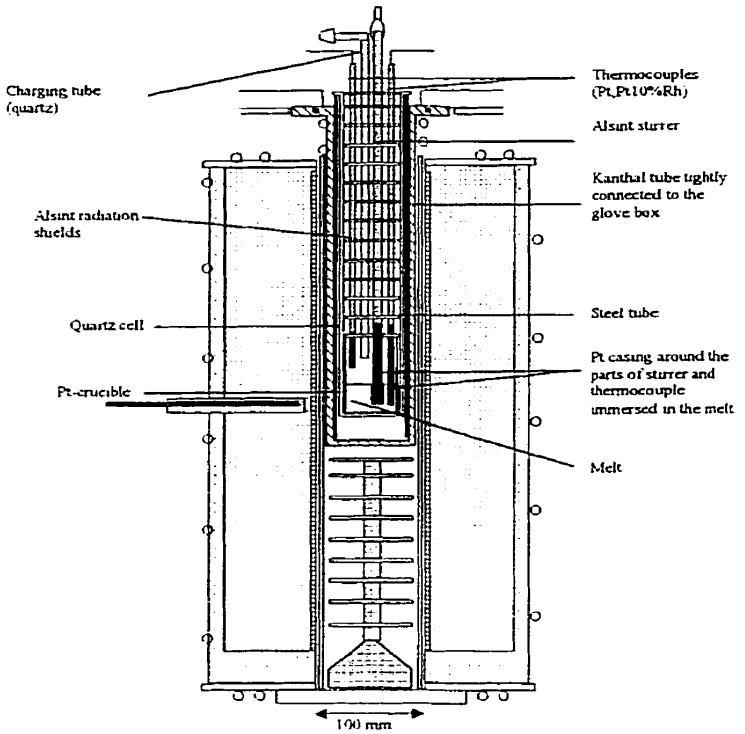

Fig.1 : Experimental cell and furnace mounted to glove box.

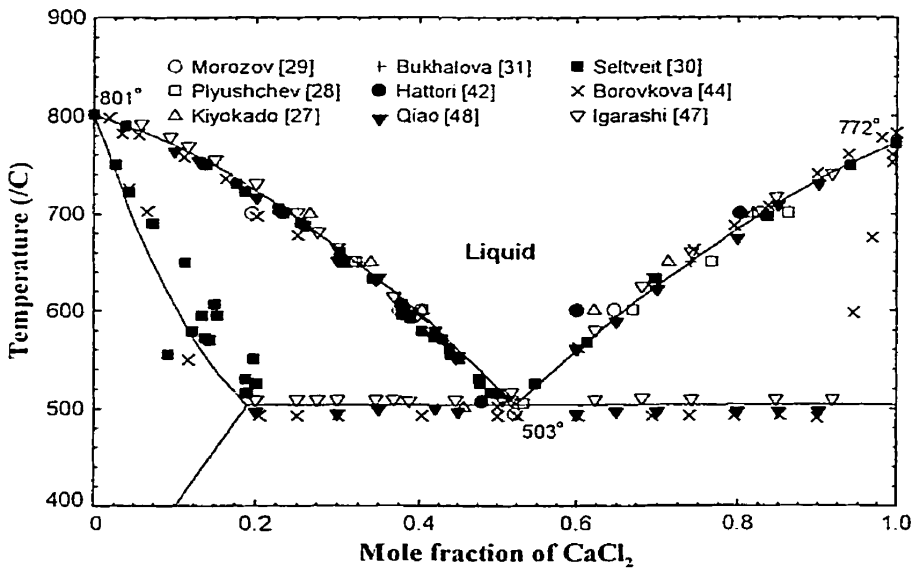

Fig.2 : The experimental and calculated NaCl-$CaCl_2$ phase diagram.

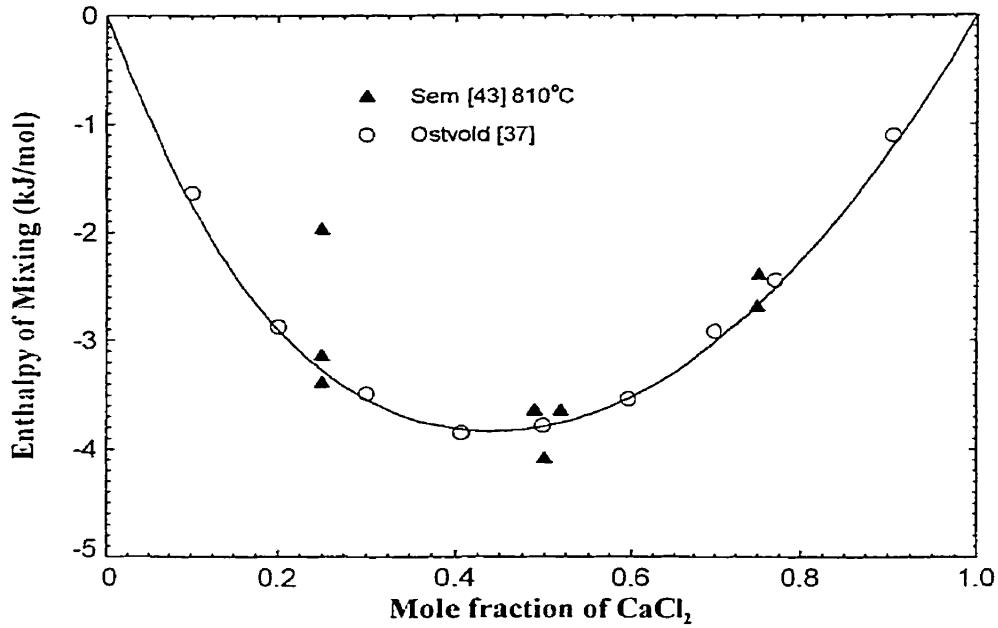

Fig.3 : Experimental and calculated enthalpy of mixing for the liquid NaCl-$CaCl_2$ binary.

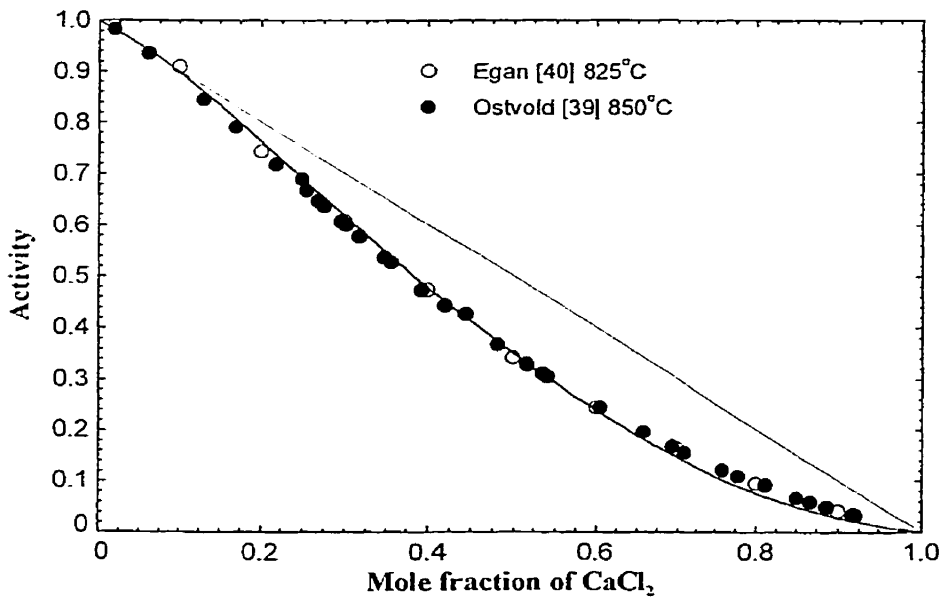

Fig. 4 : Experimental and calculated NaCl activities for the NaCl-$CaCl_2$ binary.

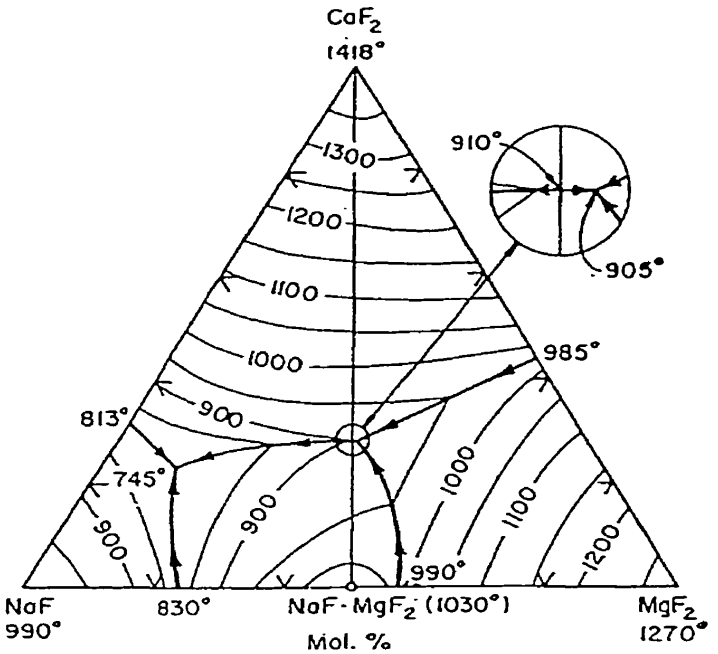

Fig.5 : The experimental $NaF-CaF_2-MgF_2$ phase diagram [13].

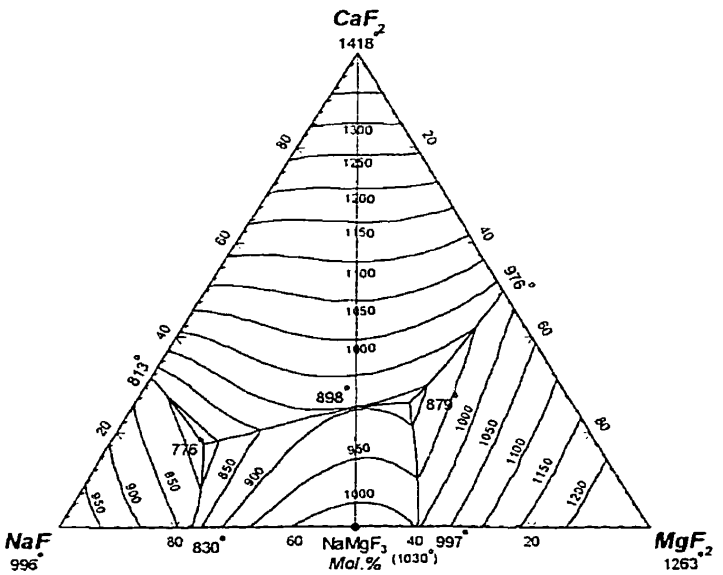

Fig.6 : Calculated phase diagram of the $NaF-CaF_2-MgF_2$ system.

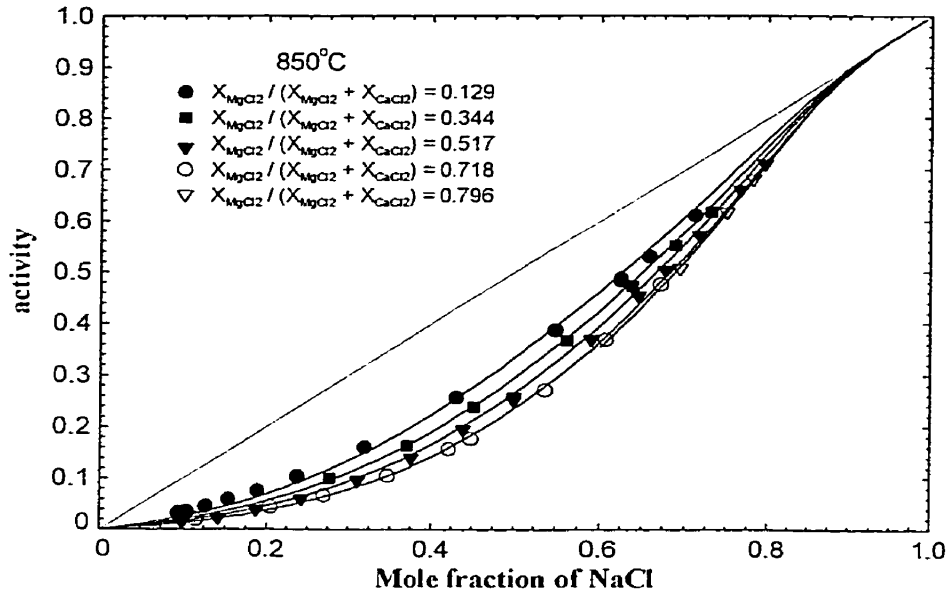

Fig.7 : Experimental [39] and calculated NaCl activities for the NaCl-$CaCl_2$-$MgCl_2$ ternary at 850°C.

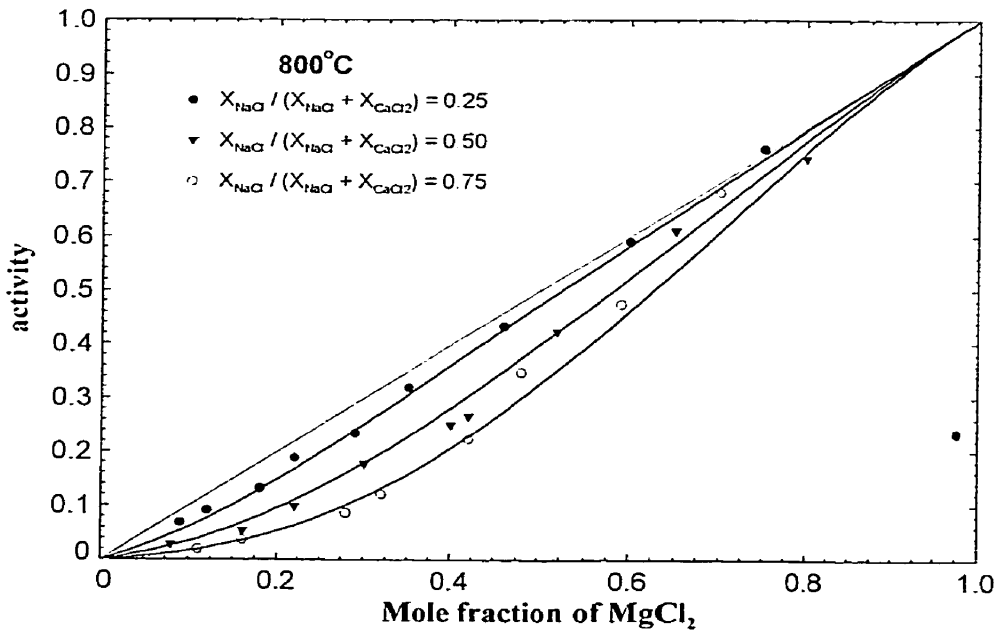

Fig.8 : Experimental [55] and calculated $MgCl_2$ activities in the NaCl-$CaCl_2$-$MgCl_2$ ternary at 850 °C.

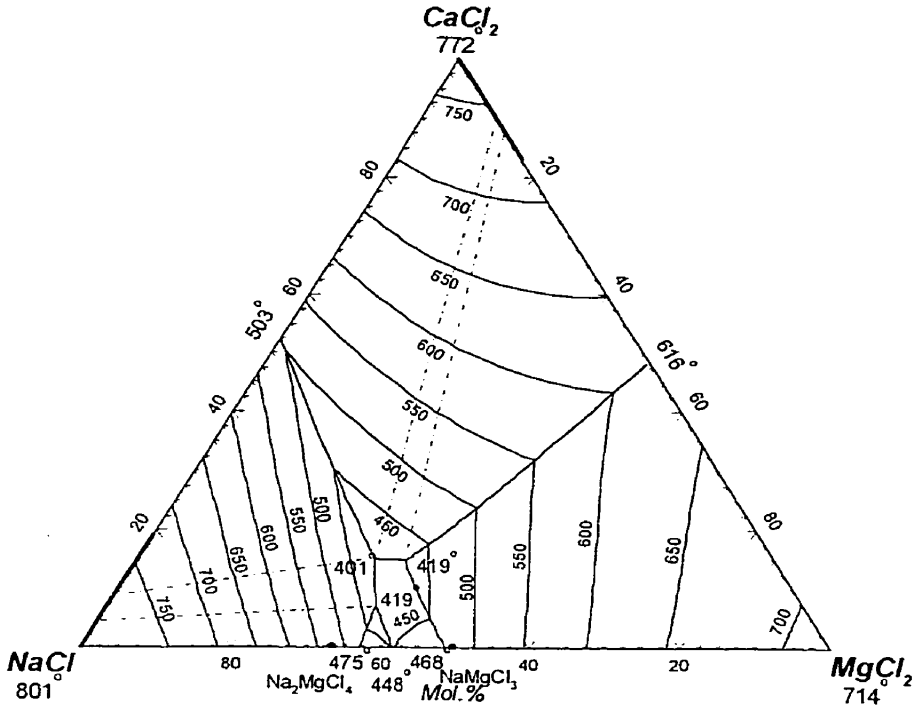

Fig.9 : The calculated NaCl-$CaCl_2$-$MgCl_2$ phase diagram.

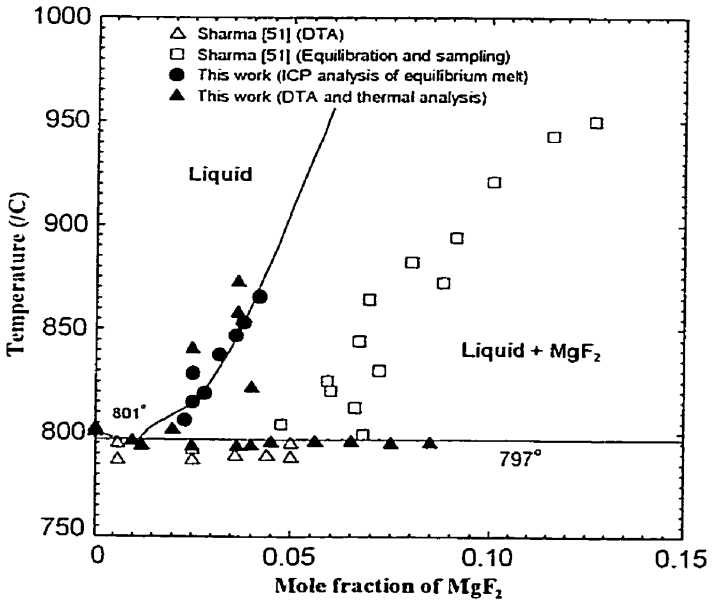

Fig. 10 : Experimental (points) and calculated (lines) transition temperatures for the NaCl – MgF_2 system.

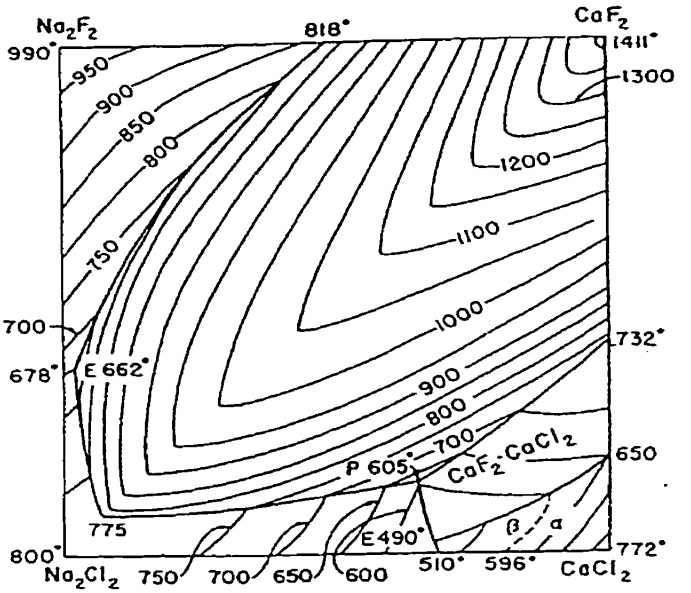

Fig. 11 : The experimental NaF-NaCl-CaF_2-$CaCl_2$ phase diagram [14].

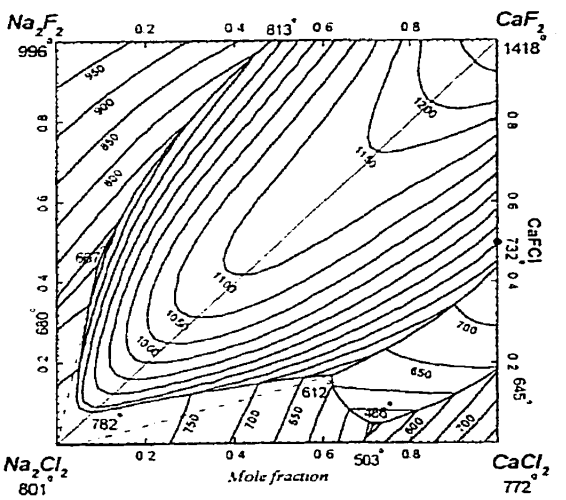

Fig. 12 : The calculated NaF-NaCl-CaF_2-$CaCl_2$ phase diagram.

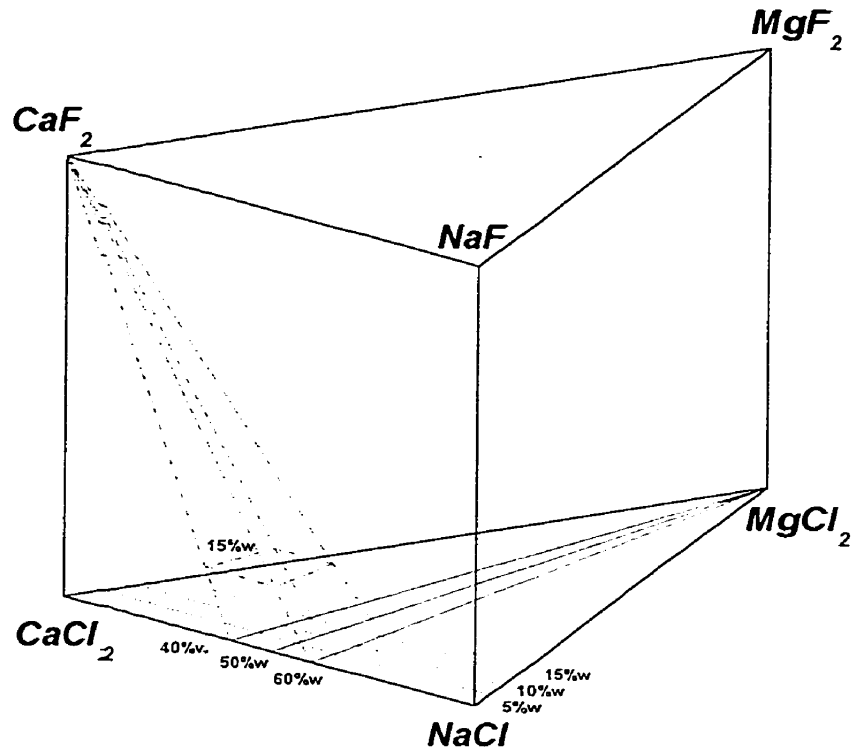

Fig. 13 : The experimentally studied composition volume which is also of interest for industrial fluxes during liquid Mg casting.

ANNEXE X

Article :

The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation

Arthur D. Pelton, Patrice Chartrand et Gunnar Eriksson,

Soumis à *Metallurgical and Materials Transactions B*,
2000.

Note : Les figures dans cet article ont été produites, éditées et imprimées par le logiciel *FIGURE* développé par l'auteur de cette thèse durant ses études doctorales.

The Modified Quasichemical Model IV – Two Sublattice Quadruplet Approximation

Arthur D. PELTON, Patrice CHARTRAND and Gunnar ERIKSSON

The modified quasichemical model is further extended, in the quadruplet approximation, to treat, simultaneously, first-nearest-neighbor and second-nearest-neighbor short-range ordering in solutions with two sublattices. When one sublattice is occupied by only one species, or is empty, the model reduces to the modified quasichemical model for one sublattice in the pair approximation. The coordination numbers and the ratio of the numbers of sites on the two sublattices are permitted to vary with composition, thereby making the model ideally suited to the treatment of liquid solutions such as molten salts. The model also applies to solid solutions if the numbers of sites and coordination numbers are held constant, and may be combined with the Compound Energy Formalism to treat short-range ordering in a wide variety of types of solution. A significant computational simplification is achieved by formally treating the quadruplets as the "components" of the solution.

I. INTRODUCTION

In the first two articles in the present series[1,2] the modified quasichemical model for short-range ordering (s.r.o.) in the pair approximation was developed for solutions in which the species mix on only one lattice or sublattice. The application of the model was illustrated in two accompanying articles by the evaluation and optimization of all available thermodynamic and phase equilibrium data for the common-anion systems Li,Na,K,Rb,Cs,Mg,Ca//Cl[3] and Li,Na,K,Mg,Ca//F[4]. The next article in the series[5] developed the model, in the pair approximation, for s.r.o. involving first-nearest-neighbor (1st-n.-n.) pairs in solutions with two sublattices. The present article extends the treatment, in the quadruplet approximation, to take account, simultaneously, of 1st-n.-n. s.r.o. between sublattices and of second-nearest-neighbor (2nd-n.-n.) s.r.o. within a sublattice.

In solid solutions the existence of two sublattices is a manifestation of long-range ordering. For example, in a solid ionic solution one can distinguish anionic and cationic sublattices. In a liquid solution, on the other hand, there is no long-range ordering and strictly speaking, it is incorrect to speak of sublattices. In molten NaCl, for example, the Na^+ and Cl^- ions should be treated as residing on one sublattice, but with a very high degree of short-range ordering, such that the nearest-neighbors of Na^+ ions are almost exclusively Cl^- ions and *vice-versa*. Solutions of molten salts could thus in principle be treated with a single-sublattice model. However in such solutions in which the degree of short-range ordering is very high, it is conceptually and mathematically simpler to treat the liquid solution as if it consisted of two distinct sublattices. This does not preclude the possibility of a small number of cation-cation or anion-anion nearest neighbors, since these can be treated within the two-sublattice model as substitutional defects (cations on anion sites and anions on cation sites).

In a solid solution, the ratio of the numbers of sites on the two sublattices is necessarily constant. However, in a liquid, this ratio can vary with composition. For example, in molten $NaCl-CaCl_2$ solutions the ratio of cation to anion sites varies from 1/1 to 1/2 as the composition varies from pure NaCl to pure $CaCl_2$.

It is an important feature of the present model that the ratio of the numbers of sites on the two sublattices is permitted to vary with composition. Further flexibility is also provided by permitting coordination numbers to vary with composition. The model is thus ideally suited to describing molten ionic solutions.

In an accompanying article [6] the use of the model is illustrated by application to the thermodynamic evaluation/optimization of the Li,Na,K,Mg,Ca/F,Cl system.

II. THE MODEL

A. Definitions, Coordination Numbers

The solution consists of two sublattices, I and II. Let A,B,C,... and X,Y,Z,... be the species which reside on sublattices I and II respectively. In a salt solution, for example, A,B,C,... are the cations and X,Y,Z,... are the anions, and in the present article we shall refer to them as "cations" and "anions". However the model is also applicable to other solutions. For example, in a solid spinel solution, sublattices I and II would be associated with the tetrahedral and octahedral cationic sublattices. Although there is a third anionic sublattice, as long as this is occupied by only one species, O^{2-}, the present model can be applied. In other examples, lattice vacancies could also be considered as "species", or the same chemical species could

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occupy both sublattices. For instance, in an ordered Cu-Au alloy, Cu and Au reside mainly on the I and II sublattices respectively. However, due to substitutional disordering, some Cu is found on the II sublattice and some Au on the I sublattice. That is, in this example A and X would both be Cu, and B and Y would both be Au.

When sublattice II is occupied only by X species, then the model, as developed in the previous publications[1-4], considered the formation of 2nd-n.-n. (A-[X]-B) pairs from 2nd-n.-n. (A-[X]-A) and (B-[X]-B) pairs according to:

$$\text{(A-[X]-A)} + \text{(B-[X]-B)} = 2\text{(A-[X]-B)} \qquad \Delta g_{AB/X} \qquad [1]$$

The entropy expression was obtained[1,2] by distributing the pairs over "pair positions". $\Delta g_{AB/X}$ is an empirical parameter of the model, which may be composition dependent. If $\Delta g_{AB/X} = 0$, then ideal random mixing results. If $\Delta g_{AB/X} < 0$, then reaction [1] is displaced to the right and s.r.o. results with (A-[X]-B) pairs becoming predominant. Similarly, when sublattice I is occupied only by A species, the model considered the formation of (X-[A]-Y) 2nd-n.-n. pairs according to:

$$\text{(X-[A]-X)} + \text{(Y-[A]-Y)} = 2\text{(X-[A]-Y)} \qquad \Delta g_{A/XY} \qquad [2]$$

In the next article in the present series[5], the following exchange reaction among 1st-n.-n. pairs was considered :

$$\text{(A-X)} + \text{(B-Y)} = \text{(A-Y)} + \text{(B-X)} \qquad \Delta g^{exchange}_{AB/XY} \qquad [3]$$

and the 1st-n.n. pairs were distributed over pair positions. If $\Delta g^{exchange}_{AB/XY} < 0$, then there is s.r.o. of 1st-n.-n. pairs with (A-X) and (B-Y) pairs predominating. As a result, the probability of an (A-[X]-B) pair is less than in a random mixture, and so the contribution of the (A-[X]-B) 2nd-n.-n. energy $\Delta g_{AB/X}$ to the total Gibbs energy of the solution is reduced. It was shown[5] that this effect becomes very important when $\left|\Delta g^{exchange}\right|$ is greater than about 50 kJ/mol.

Since the previous article[5] considered the quasichemical model only in the pair approximation, it was not possible to treat both 1st-n.-n. and 2nd-n.-n. s.r.o. simultaneously. For systems such as K, Mg//Cl,F a large degree of 2nd-n.-n. s.r.o. is observed in the binary KCl-$MgCl_2$ and KF-MgF_2 subsystems, and this cannot be neglected in a quantitative model. In the present article we consider the distribution, not of pairs, but of "quadruplets": A_2X_2, ABX_2, A_2XY, ABXY, etc. As illustrated in Figure 1, each quadruplet consists of two 2nd-n.-n. cations and two 2nd-n.-n. anions, the cations and anions being mutual first-nearest-neighbors. Both 1st-n.-n. and 2nd-n.-n. s.r.o. can thereby be treated simultaneously.

In a solid all the various possible configurations of the quadruplets on the sublattices could be considered, as is done in the Cluster Variation Method (CVM)[7], and this is necessary for the full quantitative modelling of order-disorder phenomena. However, this additional complexity is neither necessary nor possible in the case of liquid solutions, and can also be neglected in the modelling of solid solutions with a limited amount of s.r.o.

Let n_i (i = A,B,...X,Y...) be the number of moles of species i; $n_{A/X}$ the number of moles of 1st-n.-n. (A-X) pairs; and n_{A_2/X_2}, n_{AB/X_2}, $n_{AB/XY}$, etc. the numbers of moles of A_2X_2, ABX_2, ABXY etc. quadruplets. (Note that n_{AB/X_2} and n_{BA/X_2} represent the same quantity and can be used interchangeably.) Let Z_A be the 2nd-n.-n. coordination number of A (i.e. the number of 2nd-n.-n. pairs emanating from an A). Since each quadruplet contains just one 2nd-n.-n. pair, Z_A is also the number of quadruplets emanating from and A. Z_X is defined similarly. Then:

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \ldots \qquad [4]$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \ldots \qquad [5]$$

Overall mole (or site) fractions X_i, 1st-n.-n. pair fractions X_{ij}, and quadruplet fractions $X_{ij,kl}$ are defined as:

$$X_A = n_A/(n_A + n_B + \ldots) \quad X_X = n_X/(n_X + n_Y + \ldots) \qquad [6]$$

$$X_{A/X} = n_{A/X}/(n_{A/X} + n_{B/X} + n_{A/Y} \ldots) \qquad [7]$$

$$X_{AB/XY} = n_{AB/XY}/\sum n_{ij/kl} \qquad [8]$$

where $\left(\sum n_{ij/kl}\right)$ is the total number of moles of quadruplets. From Eqs [4,5]:

$$2\left(\sum n_{ij/kl}\right) = (Z_A n_A + Z_B n_B + \ldots) = (Z_X n_X + Z_Y n_Y + \ldots) \qquad [9]$$

"Coordination equivalent site fraction", Y_i are defined as:

$$Y_A = Z_A n_A/(Z_A n_A + Z_B n_B + \ldots)$$
$$Y_X = Z_X n_X/(Z_X n_X + Z_Y n_Y + \ldots) \qquad [10]$$

These are called "coordination equivalent" fractions to distinguish them from the more usual "charge equivalent" fractions in which the n_i are multiplied by the ionic charges rather than by the coordination numbers. It may be noted that the Y_i as defined in Eq.[10] are identical to those defined in the previous publications.[1,2] Substitution into Eqs. [4,5] gives:

$$Y_A = X_{A_2/X_2} + X_{A_2/Y_2} + X_{A_2/XY} + \tfrac{1}{2}X_{AB/X_2} + \tfrac{1}{2}X_{AB/XY} + \ldots \qquad [11]$$

$$Y_X = X_{A_2/X_2} + X_{B_2/X_2} + X_{AB/X_2} + \tfrac{1}{2}X_{A_2/XY} + \tfrac{1}{2}X_{AB/XY} + \ldots \qquad [12]$$

In a solid solution it is clearly required that $Z_A=Z_B=Z_C=...$ and that $Z_X=Z_Y=Z_Z=...$ However, in a liquid this is not necessary and, furthermore, the coordination numbers can vary with composition. As shown previously,[1-5] the use of variable coordination numbers is an important feature of the present model which provides the necessary flexibility to fix the compositions of maximum s.r.o. in each subsystem.

Let $Z^{A}_{AB/XY}$ be the 2nd-n.-n coordination number of an A species when (hypothetically) all A species exist in ABXY quadruplets. We then let :

$$\frac{1}{Z_A} = \frac{\frac{2n_{A_2/X_2}}{Z^{A}_{A_2/X_2}} + \frac{2n_{A_2/Y_2}}{Z^{A}_{A_2/Y_2}} + \frac{2n_{A_2/XY}}{Z^{A}_{A_2/XY}} + \frac{n_{AB/X_2}}{Z^{A}_{AB/X_2}} + \frac{n_{AB/XY}}{Z^{A}_{AB/XY}} + \ldots}{2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/XY} + \ldots} \qquad [13]$$

$$\frac{1}{Z_X} = \frac{\frac{2n_{A_2/X_2}}{Z^{X}_{A_2/X_2}} + \frac{2n_{B_2/X_2}}{Z^{X}_{B_2/X_2}} + \frac{2n_{AB/X_2}}{Z^{X}_{AB/X_2}} + \frac{n_{A_2/XY}}{Z^{X}_{A_2/XY}} + \frac{n_{AB/XY}}{Z^{X}_{AB/XY}} + \ldots}{2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{AB/XY} + \ldots} \qquad [14]$$

This composition dependence is chosen because substitution of Eqs. [13,14] into Eqs.[4,5] yields the following simple relations:

$$n_A = \frac{2n_{A_2/X_2}}{Z^{A}_{A_2/X_2}} + \frac{2n_{A_2/Y_2}}{Z^{A}_{A_2/Y_2}} + \frac{2n_{A_2/XY}}{Z^{A}_{A_2/XY}} + \frac{n_{AB/X_2}}{Z^{A}_{AB/X_2}} + \frac{n_{AB/XY}}{Z^{A}_{AB/XY}} + .. \qquad [15]$$

$$n_X = \frac{2n_{A_2/X_2}}{Z^{X}_{A_2/X_2}} + \frac{2n_{B_2/X_2}}{Z^{X}_{B_2/X_2}} + \frac{2n_{AB/X_2}}{Z^{X}_{AB/X_2}} + \frac{n_{A_2/XY}}{Z^{X}_{A_2/XY}} + \frac{n_{AB/XY}}{Z^{X}_{AB/XY}} + .. \qquad [16]$$

Note that in the A,B,C,...//X subsystem, where sublattice II is occupied only by X species, the Z^{i}_{y/X_2} are identical to the 2nd-n.-n. coordination numbers $Z^{i}_{y/X}$ defined in the previous articles[1-4].

As in the previous article,[5] we may also define a 1st-n.-n. coordination number z_A as the number of 1st-n.n. pairs emanating from an A, and similarly for z_X. Let $\zeta/2$ be the ratio of 2nd-n.-n. to 1st-n.-n. pairs:

$$Z_i/z_i = \zeta/2 \qquad [17]$$

In the general case, the ratios Z_A/z_A , Z_B/z_B , Z_C/z_C, etc. could all be different and could even depend upon composition. However, this would make the model unnecessarily complex, particularly for the case of liquids. Hence, it is assumed that the ratio Z_i/z_i is the same for all species i.

It follows that the coordination equivalent fractions defined in Eq [10] are also given by:

$$Y_A = z_A n_A / (z_A n_A + z_B n_B + \ldots) \qquad [18]$$

and similarly for Y_X, and that the total numbers of pairs and quadruplets are related by:

$$\sum n_{i/j} = (4/\zeta) \sum n_{y/kl} \qquad [19]$$

Each quadruplet contains one 2nd-n.-n. pair and two 1st-n.-n. pairs emanating from a given ion. Hence, ζ is equal to the number of quadruplets emanating from, or containing, a 1st-n.-n. pair. Therefore:

$$\zeta\ n_{A/X} = 4n_{A_2/X_2} + 2n_{AB/X_2} + 2n_{A_2/XY} + n_{AB/XY} + \ldots \qquad [20]$$

and so from Eq.[19]:

$$X_{A/X} = X_{A_2/X_2} + \tfrac{1}{2} X_{AB/X_2} + \tfrac{1}{2} X_{A_2/XY} + \tfrac{1}{4} X_{AB/XY} + \ldots \qquad [21]$$

B. Formal treatment of Quadruplets as "Complexes" or Molecules"

The quadruplet ABXY may be treated formally as the "complex" or "molecule" $A_{1/Z^{A}_{AB/XY}} B_{1/Z^{B}_{AB/XY}} X_{1/Z^{X}_{AB/XY}} Y_{1/Z^{Y}_{AB/XY}}$. Similarly, an A_2X_2 quadruplet is formally treated as $A_{2/Z^{A}_{A_2/X_2}} X_{2/Z^{X}_{A_2/X_2}}$, etc. For example, in molten $KCl-MgCl_2$ solutions, if we were to choose $Z^{K}_{KMg/Cl_2} = 3$, $Z^{Mg}_{KMg/Cl_2} = 6$, and $Z^{Cl}_{KMg/Cl_2} = 3$, then the quadruplet $KMgCl_2$ is formally treated as a $K_{1/3}Mg_{1/6}Cl_{2/3}$ complex.

It must be stressed that this is only a formalism. The entropy expression in the quasichemical model (see Section II D) is not obtained by distributing the quadruplets as if they were molecules (as is, in fact, done in various "associate models"). It is not essential that this formalism be used. However, it aids in the conceptualization and in many derivations. For example, if n_{A_2/X_2} , $n_{A_2/XY}$, etc. in Eq.[15] are replaced by $n_{A_{2/Z^{A}_{A_2/X_2}}/X_{2/Z^{X}_{A_2/X_2}}}$,

$n_{A_{2/Z^A_{A_2/XY}}X_{1/Z^X_{A_2/XY}}Y_{1/Z^Y_{A_2/XY}}}$ etc., then the number of moles of A is the same on both sides of the equation which thereby becomes a "normal" mass balance equation.

Furthermore, it can be seen that all quadruplets such as $K_{1/3}Mg_{1/6}Cl_{2/3}$ in a molten salt solution must be electrically neutral. This stoichiometry represents the composition of a hypothetical solution formed exclusively of these quadruplets and containing one mole of quadruplets. That is, one mole of $KMgCl_2$ quadruplets contains 1/3 mol K^+, 1/6 mol Mg^{2+} and 2/3 mol Cl^-.

In general, for a molten salt solution, if q_A, q_B, ... , q_X, q_Y, ... are the absolute cationic and anionic charges then the charge neutrality condition for ABXY (*i.e.* $A_{1/Z^A_{AB/XY}}B_{1/Z^B_{AB/XY}}X_{1/Z^X_{AB/XY}}Y_{1/Z^Y_{AB/XY}}$) quadruplets is as follows:

$$\frac{q_A}{Z^A_{AB/XY}}+\frac{q_B}{Z^B_{AB/XY}} = \frac{q_X}{Z^X_{AB/XY}}+\frac{q_Y}{Z^Y_{AB/XY}} \qquad [22]$$

This equation also holds when A=B and/or when X=Y. The previous example of $K^+_{1/3}Mg^{2+}_{1/6}Cl^-_{2/3}$ clearly satisfies Eq.[22]. In the most general form of the model, it is not essential for Eq.[22] to apply. However, in practice, for liquid solutions which can be described as consisting of two "sublattices", this equation will almost always be satisfied.

Figure 2 shows a traditional composition square of a reciprocal ternary A,B//X,Y system. One charge equivalent of each pure component is shown at each corner. For example, in the Na,Ca//F, SO_4 system, where the absolute ionic charges are q_A = 1, q_B = 2, q_X = 1, q_Y = 2, the components would be NaF, $Ca_{1/2}F$, $Na(SO_4)_{1/2}$ and $Ca_{1/2}(SO_4)_{1/2}$. The axes are the usual "charge equivalent" fractions Y'_A and Y'_X (not to be confused with Y_A and Y_X in Eq. [10]). The formal compositions of quadruplets such as $A_{2/Z^A_{A_2/X_2}}X_{2/Z^X_{A_2/X_2}}$ are at the corners. (Note that, from Eq.[22], the ratio $Z^A_{A_2/X_2}/Z^X_{A_2/X_2}$ is the same as the ratio (q_A/q_X).) The formal compositions of quadruplets such as $A_{1/Z^A_{AB/X_2}}B_{1/Z^B_{AB/X_2}}X_{2/Z^X_{AB/X_2}}$ are found on the sides of the square as shown in Figure 2.

1. Choice of $Z^m_{ij/kl}$

For a solid solution it is required that all catonic coordination numbers $Z^i_{ij/kl}$ be equal and that all anionic coordination numbers $Z^k_{ij/kl}$ be equal. For liquid solutions on the other hand, Z^A_{AB/X_2} and Z^B_{AB/X_2} are chosen to correspond to the composition of maximum 2nd-n.n. s.r.o. in the A,B//X binary sub-system as discussed previously.[1-4] For example, for KCl-$MgCl_2$ solutions, s.r.o. is at a maximum near the composition K_2MgCl_4. Hence, we set $Z^{Mg}_{KMg/Cl_2}/Z^K_{KMg/Cl_2} = 2.0$.

Since the quasichemical expression for the entropy (see Section II D) is, of necessity, only approximate, it is not necessary that the values of $Z^m_{ij/kl}$ used in the model correspond exactly to the actual coordination numbers. In fact, it is found that better representations are frequently obtained with intentionally non-physical values of $Z^m_{ij/kl}$ since one can thereby partially compensate for the error caused by the entropy approximation. However, it is important that the ratios of the $Z^m_{ij/kl}$ correspond to the compositions of maximum s.r.o. as discussed above.

In principle, the coordination numbers $Z'_{AB/XY}$ for the "reciprocal" ABXY quadruplets (A ≠ B, X ≠ Y) could be chosen to reflect a tendency to s.r.o. at some particular composition in the reciprocal A,B//X,Y solutions. However, in most cases there will be no such tendency and one can set the value of $Z'_{AB/XY}$ as an "average" of the values in the A_2XY, B_2XY, ABX_2 and ABY_2 quadruplets. It is suggested that this be done by defining the "composition" of the ABXY quadruplets as lying at the average of the values of Y'_X of the quadruplets A_2XY and B_2XY and at the average of the values of Y'_A of the quadruplets ABX_2 and ABY_2 as illustrated on Figure 2. This construction corresponds to the following "default" values:

$$\frac{1}{Z^A_{AB/XY}} = \left(\frac{Z^X_{AB/X_2}}{q_X Z^A_{AB/X_2}}+\frac{Z^Y_{AB/Y_2}}{q_Y Z^A_{AB/Y_2}}\right)F$$
$$\frac{1}{Z^X_{AB/XY}} = \left(\frac{Z^A_{A_2/XY}}{q_A Z^X_{A_2/XY}}+\frac{Z^B_{B_2/XY}}{q_B Z^X_{B_2/XY}}\right)F \qquad [23]$$

and similarly for $Z^B_{AB/XY}$ and $Z^Y_{AB/XY}$, where:

$$F = \frac{1}{8}\left(\frac{q_X}{Z^X_{AB/X_2}}+\frac{q_Y}{Z^Y_{AB/Y_2}}+\frac{q_A}{Z^A_{A_2/XY}}+\frac{q_B}{Z^B_{B_2/XY}}\right) \qquad [24]$$

C. Gibbs Energy Equation

We now define:

$$g^o_{A_2/X_2} = \left(\frac{2q_A}{Z^A_{A_2/X_2}}\right)g^o_{A_{1/q_A}X_{1/q_X}} = \left(\frac{2q_X}{Z^X_{A_2/X_2}}\right)g^o_{A_{1/q_A}X_{1/q_X}} \qquad [25]$$

where $g^o_{A_{1/q_A}X_{1/q_X}}$ is the standard Gibbs energy of the pure component per charge equivalent. For Al_2O_3, for example:

$$g^{o}_{Al_2/O_2} = \left(\frac{6}{Z^{Al}_{Al_2/O_2}}\right) g^{o}_{Al_{1/3}O_{1/2}} = \left(\frac{4}{Z^{O}_{Al_2/O_2}}\right) g^{o}_{Al_{1/3}O_{1/2}} \qquad [26]$$

That is, $g^{o}_{Al_2/O_2}$ is the standard Gibbs energy of Al_2O_3 per mole of Al_2O_2 quadruplets.

Previously,[5] $g^{o}_{A/X}$ was defined as the standard Gibbs energy per mole of 1st-n.-n. pairs. Therefore:

$$g^{o}_{A_2/X_2} = (4/\zeta) g^{o}_{A/X} \qquad [27]$$

The Gibbs energy of the solution is given by the model as:

$$\begin{aligned} G = & \left(n_{A_2/X_2} g^{o}_{A_2/X_2} + n_{B_2/X_2} g^{o}_{B_2/X_2} + n_{A_2/Y_2} g^{o}_{A_2/Y_2} + \ldots\right) \\ & + \left(n_{AB/X_2} g_{AB/X_2} + n_{AB/Y_2} g_{AB/Y_2} + n_{A_2/XY} g_{A_2/XY} + \ldots\right) \\ & + \left(n_{AB/XY} g_{AB/XY} + \ldots\right) \\ & - T\,\Delta S^{config} \end{aligned} \qquad [28]$$

where g_{AB/X_2}, $g_{AB/XY}$ etc. are the Gibbs energies of one mole of the quadruplets.

Let us consider the following reaction for the formation of quadruplets:

$$(A_2X_2)_{quad} + (B_2X_2)_{quad} = 2(ABX_2)_{quad} \qquad \Delta g_{AB/X_2} \quad [29]$$

for which the Gibbs energy change is $\Delta g_{AB/X_2}$. If we do not use the shorthand notation, then Eq.[29] is written:

$$\left(\frac{Z^{A}_{A_2/X_2}}{Z^{A}_{AB/X_2}}\right) A_{2/Z^{A}_{A_2/X_2}} X_{2/Z^{X}_{A_2/X_2}} + \left(\frac{Z^{B}_{B_2/X_2}}{Z^{B}_{AB/X_2}}\right) B_{2/Z^{B}_{B_2/X_2}} X_{2/Z^{X}_{B_2/X_2}} = 2A_{1/Z^{A}_{AB/X_2}} B_{1/Z^{B}_{AB/X_2}} X_{2/Z^{X}_{AB/X_2}} \qquad [30]$$

When $\Delta g_{AB/X_2} = 0$, the binary A,B//X system is ideal. In this case:

$$2g_{AB/X_2} = \left(\frac{Z^{A}_{A_2/X_2}}{Z^{A}_{AB/X_2}}\right) g^{o}_{A_2/X_2} + \left(\frac{Z^{B}_{B_2/X_2}}{Z^{B}_{AB/X_2}}\right) g^{o}_{B_2/X_2} \qquad [31]$$

Now $\Delta g_{AB/X_2}$ is an empirical parameter of the model. It may be expressed as:

$$\Delta g_{AB/X_2} = \Delta g^{o}_{AB/X_2} + \left(\Delta g_{AB/X_2} - \Delta g^{o}_{AB/X_2}\right) \qquad [32]$$

where $\Delta g^{o}_{A_2/X_2}$ is a constant, independent of composition, and $\left(\Delta g_{AB/X_2} - \Delta g^{o}_{AB/X_2}\right)$ is expanded as an empirical polynomial in the quadruplet fractions $X_{ij\,kl}$

As discussed below in Section II E. $\Delta g_{AB/X_2}$ in the A,B,C,...//X subsystem is identical to $\Delta g_{AB/X}$ of reaction [1] in this subsystem, and $\Delta g^{o}_{AB/X_2}$ and the coefficients of the polynomial expansion of $(\Delta g_{AB/X_2} - \Delta g^{o}_{AB/X_2})$ are all numerically equal to the coefficients obtained from optimization of data in this subsystem as described previously[2,3,4].

We now define the "standard molar Gibbs energy of the ABX_2 quadruplets" as:

$$2g^{o}_{AB/X_2} = \left(\frac{Z^{A}_{A_2/X_2}}{Z^{A}_{AB/X_2}}\right) g^{o}_{A_2/X_2} + \left(\frac{Z^{B}_{B_2/X_2}}{Z^{B}_{AB/X_2}}\right) g^{o}_{B_2/X_2} + \Delta g^{o}_{AB/X_2} \qquad [33]$$

Similarly, for the quadruplet formation reaction:

$$(A_2X_2)_{quad} + (A_2Y_2)_{quad} = 2(A_2XY)_{quad} \qquad \Delta g_{A_2/XY} \quad [34]$$

we define:

$$2g^{o}_{A_2/XY} = \left(\frac{Z^{X}_{A_2/X_2}}{Z^{X}_{A_2/XY}}\right) g^{o}_{A_2/X_2} + \left(\frac{Z^{Y}_{A_2/Y_2}}{Z^{Y}_{A_2/XY}}\right) g^{o}_{A_2/Y_2} + \Delta g^{o}_{A_2/XY} \qquad [35]$$

To now define $\Delta g^{o}_{AB/XY}$ for the reciprocal ABXY quadruplet, consider that in an ideal solution, $g_{AB/XY}$ (when normalized per charge equivalent) would vary linearly with composition on Figure 2 between points x and y and between points a and b. To this linear variation is added the sum of $\Delta g^{o}_{AB/X_2}$, $\Delta g^{o}_{AB/Y_2}$, $\Delta g^{o}_{A_2/XY}$ and $\Delta g^{o}_{B_2/XY}$ (which were included in Eqs.[33,35]) corrected to the same molar basis, and finally we add the composition-independent term $\Delta g^{o}_{AB/XY}$ of the Gibbs energy change $\Delta g^{o}_{AB/XY}$ of the quadruplet formation reaction:

$$\begin{aligned} \tfrac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) &= 2(ABXY) \\ \Delta g_{AB/XY} &= \Delta g^{o}_{AB/XY} + \left(\Delta g_{AB/XY} - \Delta g^{o}_{AB/XY}\right) \end{aligned} \qquad [36]$$

$\Delta g_{AB/XY}$ is an empirical parameter of the model, obtained from optimization of data on the reciprocal A,B//X,Y system as discussed in Section II E. In the ideal case, $\Delta g_{AB/XY} = 0$. The resultant definition of $\Delta g^{o}_{AB/XY}$ is:

$$\Delta g^{o}_{AB/XY} = \left(\frac{q_X}{Z^X_{AB/XY}} + \frac{q_Y}{Z^Y_{AB/XY}}\right)^{-1}\left[\frac{q_X Z^A_{A_2/X_2}}{2Z^A_{AB/XY}Z^X_{AB/XY}}\cdot g^{o}_{A_2/X_2} + \frac{q_X Z^B_{B_2/X_2}}{2Z^B_{AB/XY}Z^X_{AB/XY}}\cdot g^{o}_{B_2/X_2} + \frac{q_Y Z^A_{A_2/Y_2}}{2Z^A_{AB/XY}Z^Y_{AB/XY}}\cdot g^{o}_{A_2/Y_2} + \frac{q_Y Z^B_{B_2/Y_2}}{2Z^B_{AB/XY}Z^Y_{AB/XY}}\cdot g^{o}_{B_2/Y_2}\right]$$
$$+ \frac{1}{4}\left[\frac{Z^X_{AB/X_2}}{Z^X_{AB/XY}}\Delta g^{o}_{AB/X_2} + \frac{Z^Y_{AB/Y_2}}{Z^Y_{AB/XY}}\Delta g^{o}_{AB/Y_2} + \frac{Z^A_{A_2/XY}}{Z^A_{AB/XY}}\Delta g^{o}_{A_2/XY} + \frac{Z^B_{B_2/XY}}{Z^B_{AB/XY}}\Delta g^{o}_{B_2/XY}\right] + \Delta g^{o}_{AB/XY} \qquad [37]$$

Note that Eq.[22] applies, and that the definition in Eq.[37] holds, even if one does not choose to define $Z^{i}_{AB/XY}$ as in Eqs.[23,24].

Substitution of Eqs.[33,35,37] into Eq.[28], gives:

$$\begin{aligned} G = {} & \left[n_{A_2/X_2}g^{o}_{A_2/X_2} + \ldots + n_{AB/X_2}g^{o}_{AB/X_2} + n_{A_2/XY}g^{o}_{A_2/XY} + \ldots + n_{AB/XY}g^{o}_{AB/XY} + \ldots\right] \\ & + \frac{1}{2}\left[n_{AB/X_2} + \frac{Z^X_{AB/X_2}}{2}\left(\frac{n_{AB/XY}}{Z^X_{AB/XY}} + \frac{n_{AB/XZ}}{Z^X_{AB/XZ}} + \ldots\right)\right]\left(\Delta g_{AB/X_2} - \Delta g^{o}_{AB/X_2}\right) \\ & + \frac{1}{2}\left[n_{A_2/XY} + \frac{Z^A_{A_2/XY}}{2}\left(\frac{n_{AB/XY}}{Z^A_{AB/XY}} + \frac{n_{AC/XY}}{Z^A_{AC/XY}} + \ldots\right)\right]\left(\Delta g_{A_2/XY} - \Delta g^{o}_{A_2/XY}\right) \\ & + \frac{1}{2}\ldots \\ & + \frac{1}{2}\left[n_{AB/XY}\left(\Delta g_{AB/XY} - \Delta g^{o}_{AB/XY}\right) + n_{AB/YZ}\left(\Delta g_{AB/YZ} - \Delta g^{o}_{AB/YZ}\right) + \ldots\right] \\ & - T\ \Delta S^{config} \end{aligned} \qquad [38]$$

D. *The Configurational Entropy*

In Eq.[38], ΔS^{config} is given by distributing all the quadruplets randomly over "quadruplet positions". Unfortunately, an exact mathematical expression for this is unknown, and so approximations must be made. Letting ΔS^{config} equal $-R\sum\left(n_{ij/kl}\ln X_{ij/kl}\right)$ would clearly overcount the number of possible configurations. The following expression is proposed:

$$\begin{aligned} \left(-\Delta S^{config}/R\right) = {} & \left(n_A \ln Y_A + n_B \ln X_B + \ldots + n_X \ln X_X + n_Y \ln Y_Y + \ldots\right) + \left(n_{A/X}\ln\frac{X_{A/X}}{Y_A Y_X} + n_{B/X}\ln\frac{X_{B/X}}{Y_B Y_X} + n_{A/Y}\ln\frac{X_{A/Y}}{Y_A Y_Y} + \ldots\right) \\ & + \left(n_{A_2/X_2}\ln\frac{X_{A_2/X_2}}{X^4_{A/X}/Y^2_A Y^2_X} + \ldots + n_{AB/X_2}\ln\frac{X_{AB/X_2}}{2X^2_{A/X}X^2_{B/X}/Y_A Y_B Y^2_X} + n_{A_2/XY}\ln\frac{X_{A_2/XY}}{2X^2_{A/X}X^2_{A/Y}/Y^2_A Y_X Y_Y} + \ldots + n_{AB/XY}\ln\frac{X_{AB/XY}}{4X_{A/X}X_{B/X}X_{A/Y}X_{B/Y}/Y_A Y_B Y_X Y_Y} + \ldots\right) \end{aligned} \qquad [39]$$

Consider the case when all $\Delta g_{ij/kl}$ for reactions [32,34,36] are zero and also when all (reaction [33]) are zero. In this case the distribution $\Delta g^{exchange}_{ij/kl}$s of A, B, C,... and X, Y, Z,... on each sublattice are completely random. There is neither 1st-n.-n. nor 2nd.-n.-n. s.r.o. Hence, the probability of finding an A-X 1st-n.-n. pair is equal to $(Y_A X_X)$, that is:

$$X_{i/j} = Y_i Y_j \qquad [40]$$

Furthermore, the probability of finding an ABXY quadruplet is given, with reference to Figure 1, by the probability that pair 1 is an A-X pair, times the conditional probabilities that pairs 2, 3 and 4 are A-Y, Y-B, and B-X pairs respectively, times 4.0 which is the number of possible permutations of this order of bonds. Hence:

$$X_{AB/XY} = 4X_{A/X}\left(X_{A/Y}/Y_A\right)\left(X_{B/Y}/Y_Y\right)\left(X_{B/X}/Y_B Y_X\right) \qquad [41]$$

Similarly one can derive:

$$X_{AB/X_2} = 2X^2_{A/X}X^2_{B/X}/\left(Y_A Y_B Y^2_X\right) \text{ and } X_{A_2/X_2} = X^4_{A/X}/Y^2_A Y^2_X \qquad [42]$$

Substitution of Eqs.[40-42] into Eq. [39] gives the correct ideal (Temkin) entropy: $-R\left(n_A \ln X_A + n_B \ln X_B + \ldots + n_X \ln X_X + n_Y \ln X_Y + \ldots\right)$. Also, for this ideal case, substitution of Eqs.[20,27,33,35,37] into Eq.[38] gives the correct expression for an ideal solution:

$$G = \left(n_{A/X} g^{o}_{A/X} + n_{A/Y} g^{o}_{A/Y} + \ldots\right) + RT\left(n_A \ln X_A + n_B \ln X_B + n_X \ln X_X + \ldots\right) \quad [43]$$

Consider next the case where the values of $\Delta g^{exchange}_{ij/kl}$ of reaction [3] are not all zero, so that there is 1st-n.-n. s.r.o. In this case, Eq.[40] does not hold. Equations [41,42] hold exactly in subsystems such as A,B,C,...//X or A//X,Y,Z,... where one sublattice is occupied exclusively by one species, but do not hold exactly in general because they were derived under the assumption of random distribution of 1st-n.-n. pairs. Nevertheless, calculations show that Eqs.[41,42] still hold approximately and their use results in errors of only a few percent for absolute values of $\Delta g^{exchange}_{ij/kl}$ as large as 100 kJ/mol. The approximation, of course, becomes exact as $\Delta g^{exchange}_{ij/kl}$ approaches zero. Substitution of Eqs.[41,42] into Eq.[39] gives the expression:

$$\left(-\Delta S^{config}/R\right) = \left(n_A \ln X_A + n_B \ln X_B + \ldots\right) + \left(n_X \ln X_X + n_Y \ln X_Y + \ldots\right) + \left(n_{A/X} \ln \frac{X_{A/X}}{Y_A Y_X} + n_{B/Y} \ln \frac{X_{B/Y}}{Y_B Y_Y} + \ldots\right) \quad [44]$$

which is identical to that given previously [5] for the two-sublattice quasichemical model with 1st-n.-n., but no 2nd-n.-n., s.r.o.

E. Second-Nearest-Neighbor Interaction Terms

$\Delta g_{AB/X_2}$ is an empirical parameter of the model, obtained by optimization of data in the A,B,C,...//X subsystem, which is related to the Gibbs energy of formation of 2nd-n.-n. pairs according to reaction[29] or reaction [1]. As in Eq.[30] of the previous publication,[2] in the A,B,C,...//X subsystem $\Delta g_{AB/X_2}$ is expanded as:

$$\Delta g_{AB/X_2} = \Delta g^{o}_{AB/X_2} + \sum_{(i+j)\geq 1} \chi^{i}_{AB/X_2} \chi^{j}_{BA/X_2} g^{ij}_{AB/X_2} + \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi^{i}_{AB/X_2} \chi^{j}_{BA/X_2} \left[\sum_{l} g^{ijk}_{AB(l)/X_2} Y_l \left(1 - \xi_{AB/X_2} - \xi_{BA/X_2}\right)^{k-1} + \sum_{m} g^{ijk}_{AB(m)/X_2} \left(\frac{Y_m}{\xi_{BA/X_2}}\right)\left(1 - \frac{Y_B}{\xi_{BA/X_2}}\right)^{k-1} + \sum_{n} g^{ijk}_{AB(n)/X_2} \left(\frac{Y_n}{\xi_{AB/X_2}}\right)\left(1 - \frac{Y_A}{\xi_{AB/X_2}}\right)^{k-1} \right] \quad [45]$$

where the summations over l, m and n are as described previously[2]. Equation [45] may be compared to Eq.[32]. The empirical coefficients $\Delta g^{o}_{AB/X_2}$ and g^{ij}_{AB/X_2} are found by optimization of data in the A,B//X binary system, the other terms in Eq.[45] all being equal to zero in this binary system. For example, if all g^{ij}_{AB/X_2} are zero and if $\Delta g^{o}_{AB/X_2}$ is small, then the model approaches regular solution behavior, with $\Delta g^{o}_{AB/X_2}$ as the regular solution parameter. The coefficients $\Delta g^{ijk}_{AB(C)/X_2}$ are ternary parameters, which should not be large, which give the influence of the presence of a third cation, C, upon the energy of formation of 2nd-n.-n. (A-[X]-B) pairs. These are found by optimization of available data in the A,B,C//X ternary subsystem. In the absence of such data, these coefficients can be set to zero. The variables, Y_i, χ_{AB/X_2}, χ_{BA/X_2}, ξ_{AB/X_2}, ξ_{BA/X_2} were defined previously[2]. They are functions of the quadruplet fractions X_{ij/X_2}, which are equal to the 2nd-n.-n. bond fractions in the A,B,C,...//X subsystem.

The coefficients $\Delta g^{o}_{AB/X_2}$, g^{ij}_{AB/X_2} and $g^{ijk}_{AB(C)/X_2}$ are identical to the coefficients Δg^{o}_{AB}, g^{ij}_{AB} and $g^{ijk}_{AB(C)}$ of the previous articles [2,3,4] in which the quasichemical model was developed and applied for the case where sublattice II is occupied solely by X species.

Equation [45] holds for the A,B,C...//X subsystem. The composition variables χ_{AB/X_2} and χ_{BA/X_2} were defined in Eq.[27] of the previous article[2] in terms of ratios of the quadruplet fractions X_{ij/X_2}. For example, if the symmetric (Kohler) model is used in all ternary subsystems (see reference[2]) then $\chi_{AB/X_2} = \left(X_{A_2/X_2} / \left(X_{A_2/X_2} + X_{AB/X_2} + X_{B_2/X_2}\right)\right)$. In the multicomponent A,B,C,...//X,Y,Z,... system we assume that $\Delta g_{AB/X_2}$ is constant along composition paths where these ratios are constant. Hence, the factors χ_{AB/X_2} and χ_{BA/X_2} in Eq.[45] remain unchanged in the multicomponent system.

In the A,B,C,...//X subsystem, from Eq.[11] the equivalent fraction Y_i is equal to $\left(X_{i_2/X_2} + \frac{1}{2}\left(X_{iA/X_2} + X_{iB/X_2} + \ldots\right)\right)$ which, from Eq.[21], is equal to X_{iX} in this subsystem. In the multicomponent system we assume that the ternary terms in Eq.[45] are constant along lines of constant X_{iX}/Y_X (where $Y_X = 1$ in the A,B,C,...//X subsystem). Therefore, the factors Y_i in Eq.[45] are replaced by X_{iX}/Y_X. The factors ξ_{AB/X_2} and ξ_{BA/X_2} were defined previously[2] as sums of Y_A, Y_B, Y_C ... Hence, in Eq.[45] these are replaced by the corresponding sums of X_{AX}/Y_X, X_{BX}/Y_X, X_{CX}/Y_X, etc.

Finally, then, $\Delta g_{AB/X_2}$ is given in the multicomponent system by:

$$\Delta g_{AB/X_2} = \Delta g^{o}_{AB/X_2} + \sum_{(i\neq j)\geq 1} \chi'_{AB/X_2}\chi'_{BA/X_2} g^{y}_{AB/X_2}$$
$$+ \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi'_{AB/X_2}\chi'_{BA/X_2}\left[\sum_{l} g^{yk}_{AB(l)/X_2}\frac{X_{l/X}}{Y_X}\left(1-\xi_{AB/X_2}-\xi_{BA/X_2}\right)^{k-1}\right.$$
$$+ \sum_{m} g^{yk}_{AB(m)/X_2}\left(\frac{X_{m/X}}{Y_X\xi_{BA/X_2}}\right)\left(1-\frac{X_{B/X}}{Y_X\xi_{BA/X_2}}\right)^{k-1}$$
$$+ \sum_{n} g^{yk}_{AB(n)/X_2}\left(\frac{X_{n/X}}{Y_X\xi_{AB/X_2}}\right)\left(1-\frac{X_{A/X}}{Y_X\xi_{AB/X_2}}\right)^{k-1}$$
$$\left.+ \sum_{Y\neq X} g^{yk}_{AB/X_2(Y)} Y_Y\left(1-Y_X\right)^{k-1}\right] \qquad [46]$$

where χ_{AB/X_2} and χ_{BA/X_2} are ratios of X_{ij/X_2} as defined previously[2] and where ξ_{AB/X_2} and ξ_{BA/X_2}, defined previously[2] as sums of $Y_A, Y_B, Y_C, \ldots$ are now the corresponding sums of X_{AX}/Y_X, X_{BX}/Y_X, etc.

The final term in Eq.[46] is zero in theA,B,C,...//X subsystem. The empirical coefficients $g^{yk}_{AB/X_2(Y)}$ are reciprocal ternary coefficients giving the effect of the presence of a Y anion upon the energy of formation of ABX_2 quadruplets. These coefficients, which should not be large, are found by optimization of available data for the A,B//X,Y reciprocal ternary subsystem. In the absence of such data, these coefficients may be set to zero.

A similar expansion of $\Delta g_{A_2/XY}$ for the formation of A_2XY quadruplets may be written:

$$\Delta g_{A_2/XY} = \Delta g^{o}_{A_2/XY} + \sum_{(i\neq j)\geq 1} \chi'_{A_2/XY}\chi'_{A_2/YX} g^{y}_{A_2/XY}$$
$$+ \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}} \chi'_{A_2/XY}\chi'_{A_2/YX}\left[\sum_{l} g^{yk}_{A_2/XY(l)}\frac{Y_{A/l}}{Y_A}\left(1-\xi_{A_2/XY}-\xi_{A_2/YX}\right)^{k-1}\right.$$
$$+ \sum_{m} g^{yk}_{A_2/XY(m)}\left(\frac{X_{A/m}}{Y_A\xi_{A_2/YX}}\right)\left(1-\frac{X_{A/Y}}{Y_Y\xi_{A_2/YX}}\right)^{k-1}$$
$$+ \sum_{n} g^{yk}_{A_2/XY(n)}\left(\frac{X_{A/n}}{Y_A\xi_{A_2/XY}}\right)\left(1-\frac{X_{A/X}}{Y_A\xi_{A_2/XY}}\right)^{k-1}$$
$$\left.+ \sum_{B\neq A} g^{yk}_{A_2(B)/XY} Y_B\left(1-Y_A\right)^{k-1}\right] \qquad [47]$$

In Eq.[45], $\Delta g_{AB/X_2}$ in the A,B,C,...//X subsystem is expanded as a polynomial in the quadruplet fractions X_{ij/X_2} which are equal to the 2nd-n.-n. pair fractions in this subsystem. In earlier versions of the quasichemical model, $\Delta g_{AB/X_2}$ was expanded in terms of the equivalent fractions $Y_A, Y_B, Y_C \ldots$ The general expression is [2]:

$$\Delta g_{AB/X_2} = \Delta g^{o}_{AB/X_2} + \sum_{(i\neq j)\geq 1}\left(\frac{\xi_{AB/X_2}}{\xi_{AB/X_2}+\xi_{BA/X_2}}\right)^{i}\left(\frac{\xi_{BA/X_2}}{\xi_{AB/X_2}+\xi_{BA/X_2}}\right)^{j} q^{y}_{AB/X_2}$$
$$+ \sum_{\substack{i\geq 0\\ j\geq 0\\ k\geq 1}}\left(\frac{\xi_{AB/X_2}}{\xi_{AB/X_2}+\xi_{BA/X_2}}\right)^{i}\left(\frac{\xi_{BA/X_2}}{\xi_{AB/X_2}+\xi_{BA/X_2}}\right)^{j}\left[\sum_{l} q^{yk}_{AB(l)/X_2} Y_l\left(1-\xi_{AB/X_2}-\xi_{BA/X_2}\right)^{k-1}\right.$$
$$\left.+ \sum_{m} q^{yk}_{AB(m)/X_2}\left(\frac{X_m}{\xi_{BA/X_2}}\right)\left(1-\frac{X_B}{\xi_{BA/X_2}}\right)^{k-1} + \sum_{n} q^{yk}_{AB(n)/X_2}\left(\frac{X_n}{\xi_{AB/X_2}}\right)\left(1-\frac{X_A}{\xi_{AB/X_2}}\right)^{k-1}\right] \qquad [48]$$

This equation is clearly very similar to Eq.[45]. If the A,B,C,...//X subsystem was optimized using this expansion, then Eq.[48] can be substituted into Eq.[38] after first replacing all Y_i by X_{iX}/Y_X, replacing all ξ_{AB/X_2} and ξ_{BA/X_2} by the corresponding sums of X_{iX}/Y_X , and after adding reciprocal ternary terms if required, just as was done in Eq.[46].

In order to provide more flexibility in optimizing data in reciprocal systems, the parameter $\Delta g_{AB/XY}$ for reaction[36] can also be expanded as follows and substituted into Eq.[38]:

$$\Delta g_{AB/XY} = \Delta g^{o}_{AB/XY} + \sum_{i\geq 1}\left(g'_{AB/XY(AX)}X'_{A_2/X_2} + g'_{AB/XY(BX)}X'_{B_2/X_2} + g'_{AB/XY(AY)}X'_{A_2/Y_2} + g'_{AB/XY(BY)}X'_{B_2/Y_2}\right) \qquad [49]$$

where $\Delta g^{o}_{AB/XY}$, $g'_{AB/XY(AX)}$, etc. are additional empirical parameters obtainable by optimization of available data for the reciprocal ternary A,B//X,Y system. In the absence of such data, these terms should be set to zero.

F. The Quasichemical Model in the "Complex" Formalism

As discussed in Section II B, if the quadruplets ABXY are formally treated as "complexes" or "molecules" $A_{1/Z^A_{AB/XY}} B_{1/Z^B_{AB/XY}} X_{1/Z^X_{AB/XY}} Y_{1/Z^Y_{AB/XY}}$, then the mass balances of Eq.[15] become "normal" mass balances. Furthermore, all the parameters $\Delta g_{ij/kl}$ in Eq.[38] have been shown in Section II E to be expressible solely in terms of the quadruplet fractions $X_{ij/kl}$. (The pair fractions X_{ij} and equivalent fractions of Eqs.[46,47] can be expanded in terms of the $X_{ij/kl}$ through use of Eqs.[11,12,21].) Hence, apart from the ($-T\Delta S^{config}$) term, Eq.[38] is of the same form as an expression for the Gibbs energy of a mixture of molecules $A_{1/Z^A_{AB/XY}} B_{1/Z^B_{AB/XY}} X_{1/Z^X_{AB/XY}} Y_{1/Z^Y_{AB/XY}}$ on a single lattice, with the non-cofigurational "excess" terms expressed as polynomials in the mole fractions $X_{AB/XY}$ of these molecules. Hence, the same existing algorithms and computer subroutines which are commonly used for simple polynomial solution models can be usesd directly for the quasichemical model merely by including the additional configurational entropy terms.

Furthermore, the fact that Eq.[38] can be written solely in terms of the fractions $X_{ij/kl}$ of the quadruplet "components" permits the chemical potentials to be calculated easily in closed explicit form. By the same argument as that leading to Eq.[36] of reference[1], the chemical potential of the actual component $A_{1/q_A} X_{1/q_X}$ is given in terms of the "chemical potential μ_{A_2/X_2} of the quadruplet A_2X_2" by:

$$\mu_{A_{1/q_A} X_{1/q_X}} = \mu_{A_2/X_2}\left(Z^A_{A_2/X_2}/2q_A\right) = \mu_{A_2/X_2}\left(Z^X_{A_2/X_2}/2q_X\right) \qquad [50]$$

where

$$\mu_{A_2/X_2} = \left(\partial G/\partial n_{A_2/X_2}\right)_{n_{ij/kl}} \qquad [51]$$

Substitution of Eq.[38] into Eq.[51] then gives:

$$\mu_{A_2/X_2} = g^o_{A_2/X_2} + RT\left(\frac{2\ln X_A}{Z^A_{A_2/X_2}} + \frac{2\ln X_X}{Z^X_{A_2/X_2}} + \ln\frac{X_{A_2/X_2}}{\left(Y^1_{A/X}/\left(Y^2_A Y^2_X\right)\right)} + \frac{4}{\zeta}\ln\frac{X_{A/X}}{Y_A Y_X}\right) + g^E_{A_2/X_2} \qquad [52]$$

where $g^E_{A_2/X_2}$ is calculated from the non-configurational "g^E" polynomial terms of Eq[38] in the usual way:

$$g^E_{A_2/X_2} = g^E + \left(\partial g^E/\partial X_{A_2/X_2}\right) - \sum_{ij/kl \neq A_2/X_2} X_{ij/kl}\left(\partial g^E/\partial X_{ij/kl}\right) \qquad [53]$$

III. DISCUSSION

Many binary and ternary common-ion systems A,B,C,...//X have already been evaluated and optimized, by using a random mixing (Bragg Williams) expression for ΔS^{config}, and by expanding the excess Gibbs energy as a simple polynomial in the mole fractions. For example, in a binary A,B//X system, this is equivalent to writing:

$$G = \left(n_{A/X} g^o_{A/X} + n_{B/X} g^o_{B/X}\right) + RT\left(n_A \ln X_A + n_B \ln X_B\right) + n_{AB/X_2}\Delta g_{AB/X_2} \qquad [54]$$

with n_{AB/X_2} now equal to $\left(\sum n_{ij/kl}\right) Y_{A/X} X_{B/X}$ and with $\Delta g_{AB/X_2}$ expanded as:

$$\Delta g_{AB/X_2} = \Delta g^o_{AB/X_2} + \sum_{(i+j)\geq 1} q^{ij}_{AB/X_2} Y^i_A Y^j_B \qquad [55]$$

For example, if all q^{ij}_{AB/X_2} coefficients are zero, then this is a simple regular solution. Ideally, of course, all these systems should be re-optimized with the quasichemical model. However, this entails a great deal of work. For systems in which $\Delta g_{AB/X_2}$ is relatively small, the neglect of s.r.o. involving 2nd-n.-n. (A-[X]-B) pairs will give rise only to small errors. Hence, it would be very useful to be able to combine the large existing databases of evaluated simple polynomial coefficients for such subsystems with the quasichemical coefficients obtained by optimization of other subsystems where s.r.o. is more important, in order to produce one large database for the multicomponent solution. It has been shown previously[1-4] how this combination of coefficients can easily be achieved for A,B,C,...//X systems. In the present case, if a binary A,B//X system has been optimized using a simple Bragg-Williams entropy and a polynomial expansion as in Eq.[55], then the coefficients of Eq[55] can be substituted directly into Eq.[48]. (This is also true for simple polynomial ternary coefficients as described previously.[2]) It is required that $Z^A_{AB/X_2} = Z^A_{A_2/X_2}$ and that $Z^B_{AB/X_2} = Z^B_{B_2/X_2}$. The term $\frac{1}{2}\left(n_{AB/X_2} + \frac{Z^X_{AB/X_2}}{2}\left(\frac{n_{AB/XY}}{Z^X_{AB/XY}} + \ldots\right)\right)\left(\Delta g_{AB/X_2} - \Delta g^o_{AB/X_2}\right)$ in Eq.[38] is replaced by $\left(\sum n_{ij/kl}\right)\left(\frac{X_{A/X} X_{B/X}}{Y_X}\right)\Delta g_{AB/X_2}$, and the term $\Delta g^o_{AB/X_2}$ must be removed from Eqs.[33] and [37]. It is also recommended that if any binary subsystem of the A,B,//X,Y system has been optimized with a simple polynomial expansion, then all coefficients in the expansion for $\Delta g_{AB/XY}$ in Eq.[49] be set to zero.

IV. CONCLUSIONS

A quasichemical model for treating short-range-ordering (s..r.o.) in the quadruplet approximation has been proposed for solutions with two sublattices. Both s.r.o. of first-nearest-neighbor pairs and s.r.o. of second-nearest-neighbor pairs are taken into account. If one sublattice is occupied by only one species, or is empty, then the present model reduces exactly to the quasichemical model for s.r.o. on one sublattice in the pair approximation as developed previously.[1-4] Also, by means of a minor alteration to the entropy expression, the Gibbs energy expression can be made identical to that of a randomly-mixed (Bragg Williams) solution with a simple polynomial expansion for the excess Gibbs energy. This is of much practical importance because the large existing databases of evaluated simple polynomial coefficients of certain subsystems can thereby be combined in one datbase with the quasichemical coefficients of other subsystems, in order to produce one large database for a multicomponent solution.

The model is well suited to liquid solutions where the ratio of the numbers of sites on the two sublattices can vary with composition. Further flexibility is provided by permitting coordination numbers to vary with composition. Nevertheless, the model also applies to solid solutions if the numbers of lattice sites and coordination numbers are held constant. The model can thus be combined with the "Compound Energy Formalism[8,9] to treat a wide range of types of solution (slags, mattes, ceramics, salts, alloys), point defects, order-disorder phenomena, non-stoichiometric phases, etc. For a discussion of applications of the Compound Energy Formalism, see also references [10,11]. If s.r.o. is not included (by assuming Bragg-Williams random-mixing entropy as just mentioned), the model reduces exactly to the Compound Energy Formalism for two (or one) sublattices.

That is several different models are limiting cases of the present model. These models can thus all be treated with the same algorithms; the coefficients can all be stored in the same multicomponent databases; and different models for different subsystems can be combined in many cases.

By formally treating the quadruplets as the "components" of the solution, a significant computational simplification is realized. The model can then be treated with currently available and relatively simple software.

The model has been applied to the molten salt phase in an evaluation/optimization of the Li,Na,K,Mg,Ca//F,Cl system using the F*A*C*T [12] thermodynamic computing system. This work is presented in an accompanying article.[6]

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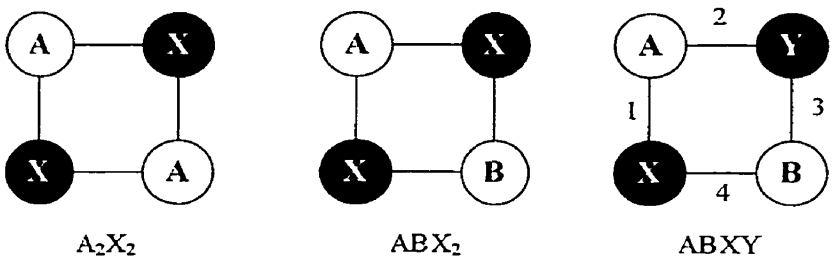

Figure 1. Some quadruplets

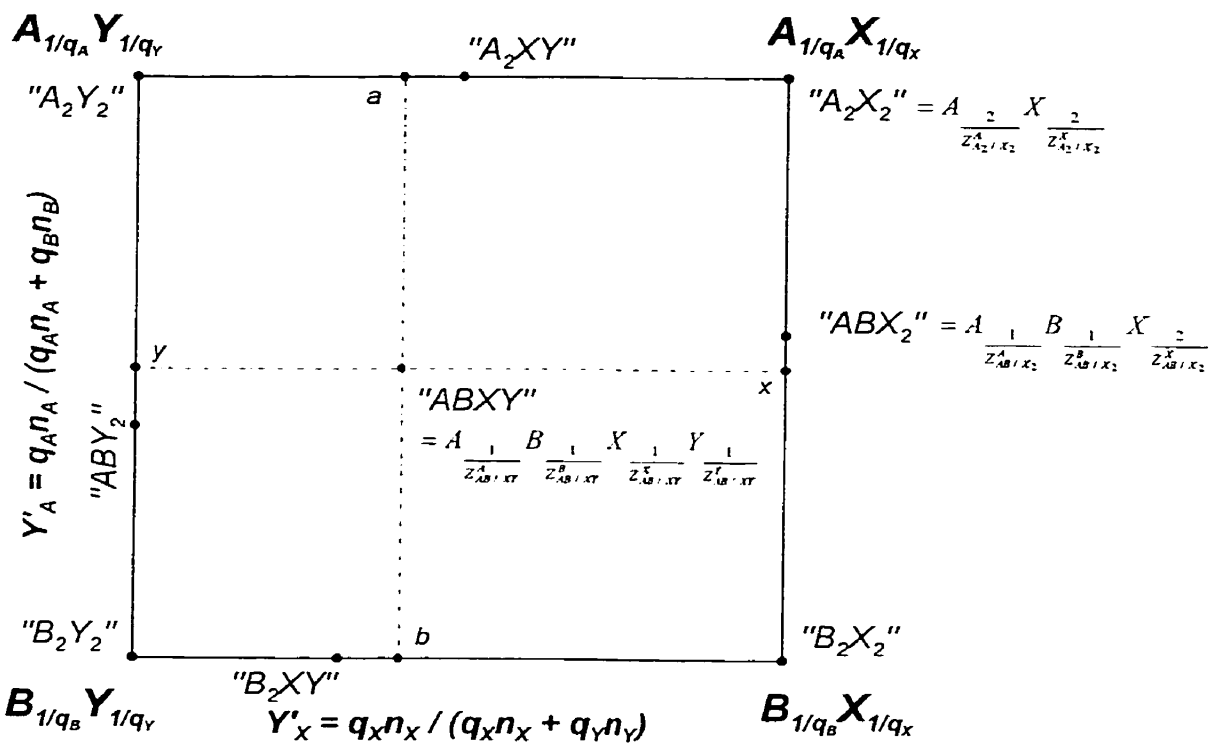

Figure 2. Composition square of the A,B//X,Y reciprocal ternary system showing formal "compositions" of the various quadruplets

ANNEXE XI

Article :

Thermodynamic Evaluation and Optimization of the Li,Na,K,Mg,Ca//F,Cl Reciprocal System Using the Modified Quasichemical Model

Patrice Chartrand et Arthur D. Pelton,

Soumis à *Metallurgical and Materials Transactions B*,
2000.

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Thermodynamic Evaluation and Optimization of the Li,Na,K,Mg,Ca//F,Cl Reciprocal System Using the Modified Quasichemical Model

PATRICE CHARTRAND and ARTHUR D. PELTON

A complete critical evaluation and quantitative optimization of all available ternary reciprocal phase diagram data has been performed for all condensed phases of the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ system. The model parameters obtained for ternary reciprocal subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent reciprocal system. The modified quasichemical model in the quadruplet approximation, for short-range ordering of first- and second-nearest-neighbors, was used for the molten salt phase.

I. INTRODUCTION

Molten salts used in metallurgical applications are often based on alkali alkaline-earth chloride fluoride mixtures. For example, the electrolytes used for Mg production are based mainly on NaCl, $CaCl_2$, and $MgCl_2$ salts, which can also be used as fluxes for Mg casting; NaCl, KCl, $MgCl_2$, NaF and KF are used extensively as fluxing agents for liquid aluminum treatment; alkali chlorides and fluorides can be used as fluxes for the gas welding of light metals; electro-deposition of refractory metals (Nb,Ta) can be made from these solutions; and NaF, CaF_2, LiF, and MgF_2 are important bath components in the Hall-Heroult electrolysis cells for Al production. Developing a thermodynamic model for the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ system will contribute to the understanding, calculation and simulation of many present and future metallurgical applications.

In reciprocal molten salt solutions (*i.e.* solutions with more than one cation and more than one anion) large deviations from ideal mixing can occur due to the strong first-nearest-neighbor (cation-anion) interactions. Modeling such solutions is a challenge. If, simultaneously, there is also strong second-nearest-neighbor (cation-cation) short-range ordering, the solution becomes even more difficult to model.

The binary common-ion systems KCl-$MgCl_2$ and KF-MgF_2 exhibit extensive short-range ordering which has been associated with the formation of $MgCl_4^{2-}$ and MgF_4^{2-} "complex ions". To a lesser, but still appreciable extent, the NaCl-$MgCl_2$, NaF-CaF_2 and KF-CaF_2 systems also exhibit such short-range ordering. In a previous publication[1] we presented a modified quasichemical model, in the pair approximation, in which this ordering is described in terms of the following equilibrium among second-nearest-neighbor cation-cation pairs :

$$(A-[X]-A) + (B-[X]-B) = 2(A-[X]-B) \qquad \Delta g_{AB/X} \quad [1]$$

where A, B = Li, Na, K, Mg or Ca and X = F or Cl. If $\Delta g_{AB/X}$ is negative, reaction [1] is shifted to the right, (A-[X]-B) pairs predominate, and short-range ordering results. The amount of this ordering depends upon the magnitude of the Gibbs energy change, $\Delta g_{AB/X}$ of reaction [1] which is a parameter of the model that can be expressed as a function of composition by an empirical polynomial expression.

In earlier publications[2,3] all available phase diagram and thermodynamic data for the LiCl-NaCl-KCl-$MgCl_2$-$CaCl_2$ and LiF-NaF-KF-MgF_2-CaF_2 common-anion systems were critically evaluated and optimized to obtain empirical coefficients which reproduce all the data within the experimental error limits. At the same time, similar optimized model equations for all solid solution phases in these systems were obtained.

When reciprocal salt solutions are formed containing both chlorides and fluorides, first-nearest-neighbor short-range ordering can occur, the extent of which is related to the Gibbs energy of the exchange reaction :

$$AF + BCl = ACl + BF \qquad \Delta g^{exchange}_{AB/FCl} \qquad [2]$$

If $\Delta g^{exchange}_{AB/FCl}$ is negative, then A-Cl and B-F nearest-neighbor pairs predominate. In several of the reciprocal ternary subsystems (systems with 2 cations and 2 anions), $\Delta g^{exchange}_{AB/FCl}$ is very negative as can be seen in Table I. These systems thus exhibit such ordering to a large extent.

In another recent publication[4] the modified quasichemical model, in the pair approximation, was developed for treating such first-nearest-neighbor short-range ordering. However, since the pair approximation was used this model could not simultaneously take account of first-nearest-neighbor and second-nearest-neighbor ordering.

Recently[5] we have proposed a new modified quasichemical model in the quadruplet approximation

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which incorporates the previous models[1-4] as limiting cases. A quadruplet A_2X_2, ABX_2, A_2XY, or $ABXY$ consists of two second-nearest-neighbor cations and two second-nearest-neighbor anions which are mutual first-nearest-neighbors. The parameters of the model are the energies of the quadruplet-formation reactions, similar to reaction [1]. However, in common-ion systems such as $LiCl$-$NaCl$-KCl-$MgCl_2$-$CaCl_2$, the quadruplets ABX_2 are identical to the second-nearest-neighbor (A-[X]-B) pairs, so that the optimized parameters obtained previously for this system[2] and for the common-ion fluoride system[3] can be used directly in the new model.

To a much lesser extent, second-nearest-neighbor anion-anion ordering can play a role, and this is determined by the pair formation energies $\Delta g_{A/FCl}$ of the reaction :

$$(F-[A]-F) + (Cl-[A]-Cl) = 2(F-[A]-Cl) \qquad \Delta g_{A/FCl} \qquad [3]$$

The same model is used. In the present case, optimized parameters obtained from evaluation of data for the AF-ACl binary systems (A = Li, Na, K, Mg or Ca) are required. These evaluations are given in the Appendix.

In the present article, the modified quasichemical model in the quadruplet approximation[5] is applied to the Li,Na,K,Mg,Ca//F,Cl system with the parameters from the common-ion systems taken from the previous publications[2,3] and from the Appendix. To obtain quantitative fits, small empirical "reciprocal ternary parameters" are included. As described previously[5] these parameters represent the Gibbs energies of formation of the ABXY quadruplets from the binary quadruplets according to :

$$\tfrac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2ABXY \qquad \Delta g_{AB/XY} \qquad [4]$$

where $\Delta g_{AB/XY}$ is expanded as an empirical polynomial in the fractions X_{A_2/X_2}, X_{A_2/Y_2}, X_{B_2/X_2} and X_{B_2/Y_2} of the A_2X_2, A_2Y_2, B_2X_2 and B_2Y_2 quadruplets as follows :

$$\Delta g_{AB/XY} = \Delta g^{o}_{AB:XY} + \sum_{i\geq 1} \left[g'_{AB/XY(AX)} X'_{A_2/X_2} + g'_{AB/XY(BX)} X'_{B_2/X_2} + g'_{AB/XY(AY)} X'_{A_2/Y_2} + g'_{AB/XY(BY)} X'_{B_2/Y_2} \right] \qquad [5]$$

The empirical parameters $\Delta g^{o}_{AB/XY}$ and $g'_{AB/XY(AX)}$, etc. should all be small, and this is in fact the case in this system.

The Li,Na,K,Mg,Ca//F,Cl system presents a severe test of the model because first- and second-nearest-neighbor short-range ordering are both present to a large extent.

II. THERMODYNAMIC DATA

All common-ion binary and ternary liquid model parameters can be found in previous publications[2,3], and in the Appendix, along with all second-nearest-neighbor coordination numbers and Gibbs energies of pure compounds. Also in these publications[2,3] are the optimized model parameters for the (Li,Na,K,[Mg])Cl, (Mg,[Li])Cl_2, (Li,[Mg])F, (Mg,[Li])F_2, (Na,[Li])F, ([Na],K)F, (Li,Na,K)(Mg,Ca)F_3, (Li,Na,K)(Mg,Ca)Cl_3 and $(Li,Na,K)_2(Mg,Ca)Cl_4$ solid solutions, and the optimized thermodynamic properties ($\Delta H^{o}_{298.15K}$, $S^{o}_{298.15K}$ and C_p) of all binary and ternary compounds. From the thermodynamic properties of the pure liquid salts, $\Delta g^{exchange}_{AB/FCl}$ of reaction [2] for all ternary reciprocal subsystems can be calculated. Mean values over the temperature range 400°C < T < 1200°C are given in Table I.

In the previous publication[5], "default values" of the coordination numbers of the ABXY quadruplets were proposed (Eq.[23] of reference [5]). These values are used here with the following exceptions $Z^{Li}_{LiK/FCl} = Z^{K}_{LiK/FCl} = Z^{F}_{LiK/FCl} = Z^{Cl}_{LiK/FCl} = 8$, $Z^{Li}_{LiCa/FCl} = Z^{F}_{LiCa/FCl} = Z^{Cl}_{LiCa/FCl} = 3$ and $Z^{Ca}_{LiCa/FCl} = 6$, $Z^{Na}_{NaMg/FCl} = Z^{F}_{NaMg/FCl} = Z^{Cl}_{NaMg/FCl} = 3$ and $Z^{Mg}_{NaMg/FCl} = 6$, and $Z^{K}_{KCa/FCl} = Z^{F}_{KCa/FCl} = Z^{Cl}_{KCa/FCl} = 2$ and $Z^{Ca}_{KCa/FCl} = 4$. These values are close to the "default" values, but were found to give slightly better optimizations than the "default" values. Furthermore, it is necessary to propose a value of ζ, defined in Eq.[23] of reference [5] as :

$$\zeta = 2Z/z \qquad [6]$$

where z and Z are the first-nearest-neighbor and second-nearest-neighbor coordination numbers. In the present case we have taken $\zeta = 2.4$.

Table I. Mean Exchange Gibbs Energies ($\Delta g^{exchange}_{AB/FCl}$) for Reaction [2] for Liquid Salts over the Range 400°C < T < 1200°C.

System A,B/F,Cl	$\Delta g^{exchange}_{AB/FCl}$ (kJ / charge equivalent)
LiCl + NaF = LiF + NaCl	≈ -38
LiCl + KF = LiF + KCl	≈ -61
LiF + ½ $MgCl_2$ = LiCl + ½ MgF_2	≈ -40
LiF + ½ $CaCl_2$ = LiCl + ½ CaF_2	≈ -18
NaCl + KF = NaF + KCl	≈ -23
NaF + ½ $MgCl_2$ = NaCl + ½ MgF_2	≈ -80
NaF + ½ $CaCl_2$ = NaCl + ½ CaF_2	≈ -58
KF + ½ $MgCl_2$ = KCl + ½ MgF_2	≈ -100
KF + ½ $CaCl_2$ = KCl + ½ CaF_2	≈ -78
½ CaF_2+ ½ $MgCl_2$=½ $CaCl_2$ + ½ MgF_2	≈ -22

III. TERNARY RECIPROCAL SUBSYSTEMS

A. *The LiF-LiCl-NaF-NaCl System*

The liquidus projection has been measured[6] (Figure 1). Gabcova and Malinovsky[7] measured the NaCl-NaF-LiF liquidus projection, reporting the eutectic at 604°C instead of 582°C[6]. The LiF-NaCl join has also been measured[6-11] (Figure 2). The liquidus surface is calculated (Figure 3) with a very small ternary reciprocal parameter :

$$\Delta g_{LiNa/FCl} = 1882.8 X_{Li_2/F_2} \quad \text{J/mol} \qquad [7]$$

B. *The LiF-LiCl-KF-KCl System*

The liquidus projection has been measured[12] (Figure 4). The LiF-KCl join has been reported[9,12,13] (Figure 5) with the eutectic at 719°C[13], 713°C[9] or 710°C[12]. Zsigrai *et al.*[14] previously calculated the ternary liquidus projection with a sublattice model which neglected all ordering. (See comments in Chartrand and Pelton[4]). The calculated liquidus projection, using the following ternary reciprocal excess terms, is shown in Figure 6, and the calculated LiF-KCl join is shown in Figure 5 :

$$\Delta g_{LiK/FCl} = -2928.8 + 2.9288T - 3347.2 X_{K_2/Cl_2} + 2092.0 X_{Li_2/F_2} \quad \text{J/mol} \qquad [8]$$

Without these ternary reciprocal terms, the calculated LiF-KCl eutectic is 12°C higher with a 2 mol% displacement in composition, while the ternary eutectic temperatures are increased by 2 to 3°C. That is, these terms give only a small correction. Even without these terms, the model predictions are very good. This is also true in all the other systems reported in this article. Significantly improved precision is obtained with the present model compared to the previous calculation[4] which accounted for first-nearest-neighbor , but neglected second-nearest-neighbor ordering. First-nearest-neighbor ordering is high in this system due to the large exchange Gibbs energy (reaction [2]) of –61 kJ/mol (Table I).

C. *The LiF-LiCl-MgF_2-$MgCl_2$ System*

No reported liquidus projection has been found for the Li,Mg//F,Cl system. The calculated LiCl-MgF_2 join is shown in Figure 7 with no additional reciprocal parameters.

D. *The LiF-LiCl-CaF_2-$CaCl_2$ System*

The liquidus projection has been measured[15] (Figure 8). The liquidus projection is calculated (Figure 9) assuming no reciprocal ternary solid solubility, with the following small excess ternary terms :

$$\Delta g_{LiCa/FCl} = -5506.0 + 4.184T \quad \text{J/mol} \qquad [9]$$

E. *The NaF-NaCl-KF-KCl System*

The liquidus projection has been measured[16,17] (Figure 10[16]). The calculated liquidus projection is shown in Figure 11. No ternary terms were necessary and no reciprocal ternary solid solubility is assumed.

F. *The NaF-NaCl-MgF_2-$MgCl_2$ System*

The liquidus along the NaCl-MgF_2 join has been measured[18,19]. There is disagreement between these authors on the MgF_2 liquidus on the NaCl-rich side. Sharma and Johnson[18] reported a higher MgF_2 solubility than Mediaas *et al.*[19]. The exchange Gibbs energy for this system is large (see Table I).

The NaCl-MgF_2 phase diagram was calculated previously[18] using the quasichemical model[4] in the pair-approximation which accounts for first-nearest-neighbor ordering, but neglects second-nearest-neighbor ordering. The calculated NaCl-MgF_2 phase diagram, with the present model for the liquid phase, is shown in Figure 12. No excess ternary term is required. No reciprocal ternary solid solubility is assumed. Calculations predict a liquid-liquid miscibility gap above 1000°C.

G. *The NaF-NaCl-CaF_2-$CaCl_2$ System*

The liquidus projection has been measured[20] (Figure 13). Malinovsky and Gregorcokova[21] measured the NaCl liquidus along the NaCl-CaF_2 join reporting the eutectic at 4.5 mol.% CaF_2 at 779.5°C. The exchange Gibbs energy for this system is moderately large (Table I). The NaF-NaCl-CaF_2-$CaCl_2$ liquidus projection was calculated previously[19] using the quasichemical model[4] in the pair approximation (neglecting second-nearest-neighbor ordering). The calculated liquidus projection of the present work is shown in Figure 14. A very small empirical ternary excess term was included :

$$\Delta g_{NaCa/FCl} = -2092 \quad \text{J/mol} \qquad [10]$$

The calculated eutectic on the NaCl-CaF_2 join is at 3.7 mol.% CaF_2 at 783°C. No reciprocal ternary solid solubility was assumed.

H. *The KF-KCl-MgF_2-$MgCl_2$ System*

No reported thermodynamic nor phase diagram data were found for this system. The exchange Gibbs energy for this system is very large (Table I). Since there are no reported data for this system, no excess ternary terms were added to the liquid model. Because the exchange Gibbs energy is very large, and because second-nearest-neighbor ordering is very strong in the KCl-$MgCl_2$ subsystem[5] and in the KF-MgF_2 subsystem[3], a ternary term is most probably necessary to obtain a good prediction. A few well chosen experimental liquidus measurements in this system would permit these coefficients to be determined.

I. *The KF-KCl-CaF_2-$CaCl_2$ System*

The liquidus projection has been measured[16,22] (Figures 15[22] and 16[16]). Desyatnik *et al.*[23] measured the KCl-$CaCl_2$-CaF_2 liquidus projection (Figure 17). A strong disagreement can be seen between the liquidus projections of Krause[22] and Ishaque[16] at least for the liquidus along the KCl-CaF_2 join, although the reported invariant points agree very well in temperature. However, reported invariant point temperatures of Desyatnik[23] are around 20°C lower than those reported by the other authors except for the KCl-CaF_2-$KCaCl_3$ eutectic. The exchange Gibbs energy is very large (-78 kJ/equiv) for this system (Table I). One small ternary term was used :

$$\Delta g_{KCa/FCl} = -4.184T \quad \text{J/mol} \qquad [11]$$

The calculated liquidus projection below 900°C is shown in Figure 18. A liquid-liquid miscibility gap is calculated along the KCl-CaF_2 join for temperatures above 950°C. Because of the large differerences between the two measured diagrams and between the measured and the calculated digrams in this region, the calculations are not shown in Figure 18. One can note that the calculated ternary invariant points are in good agreement in temperature with the reported points[16]. $KCaCl_3$ and $KCaF_3$ were assumed immiscible, and this assumption permits a good fit of the $KCaCl_3$ liquidus and related invariant points. The calculated $KCaCl_3$-CaF_2 join is shown in Figure 17.

J. *The MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ System*

The MgF_2-$CaCl_2$ join has been measured[18] (Figure 19). The phase diagram was calculated previously[24] with a model[25] for the liquid phase assuming random mixing of ions on their respective sublattices. Because first-nearest-neighbor ordering was ignored, a large ternary reciprocal excess term was required to reproduce the experimental liquidus. The MgF_2-$CaCl_2$ join, calculated with the present model with the following small excess terms, and assuming no ternary solid solubility, is shown in Figure 19 :

$$\Delta g_{MgCa/FCl} = -7305.0 + 8.3680T \quad \text{J/mol} \qquad [12]$$

IV. MULTICOMPONENT SYSTEMS

The thermodynamic properties of the multicomponent liquid phase calculated by the model are obtained solely from binary, ternary and ternary reciprocal optimized parameters. There is no additional higher order parameter added to the liquid model. Hence, the calculated values in this sections are predictions of the model from optimized subsystem data.

For most of the experimental work described in this section, the "visual-polythermal" method was used. The accuracy of this method is low. Only liquidus temperatures are actually measured and errors on these are large. All univariant and invariant temperatures and compositions are found by interpolation, and errors are even larger.

A. *The Li,Na,K//F,Cl System*

The LiCl-NaCl-KF and LiCl-NaF-KF liquidus projections were measured[26] by the visual-polythermal method. The calculated liquidus lines of the LiCl-NaF-KF system along constant NaF/(NaF+KF) molar ratios are shown in Figure 20. The calculated liquidus lines of the LiCl-NaCl-KF system along constant LiCl/KF molar ratios are shown in Figure 21.

The LiF-NaF-KCl liquidus has been measured by the visual-polythermal method[27] and by thermal analysis[28]. The LiF-NaCl-KCl liquidus projection has also been measured[27,29]. Univariant line compositions and temperatures of the LiF-NaF-KCl[27,28] and LiF-NaCl-KCl[27,29] systems are given in Tables II and III with the corresponding calculated points. These measured[27-29] points were obtained by starting with a mixture of two salts and then adding a third salt progressively and observing the liquidus temperatures until the univariant line (secondary crystallization) was observed. The calculations simulate this procedure. The calculated liquidus lines of the LiF-NaCl-KCl system along constant NaCl/KCl molar ratios are shown in Figure 22. The liquidus of the Li,Na,K//F,Cl system is well reproduced by calculations, essentially within the experimental error limits.

Table II : Points on Univariant Line in the LiF-NaF-KCl Liquidus Projection.

composition (mol.%)			T(°C)	Ref
LiF	NaF	KCl		
26.5	16.5	57.0	664	[27]
~29	~16	~55	?	[28]*
32.1	15.3	52.6	676	This work
23.5	12.2	64.3	676	[27]
~27	~12	~61	?	[28]*
28.9	11.4	59.7	688	This work
21.5	7.9	70.6	690	[27]
~24	~8	~68	?	[28]*
25.9	7.4	66.7	699	This work
8.6	31.0	60.4	628	[27]
~9	~31	~60	?	[28]*
8.5	32.0	59.5	645	This work
12.8	32.5	54.7	620	[27]
~13	~32	~55	?	[28]*
12.6	33.9	53.5	639	This work
31.6	21.0	47.4	648	[27]
~32	~20	~48	?	[28]*
33.3	16.7	50.0	672	This work
36.8	26.5	36.8	634	[27]
~36	~29	~36	?	[28]*
38.3	23.5	38.3	650	This work
41.9	33.0	25.1	615	[27]
~39	~38	~23	?	[28]*
41.6	33.4	25.0	611	This work
51.9	39.0	9.1	601	[27]
~51	~40	~9	?	[28]*
51.3	39.7	9.0	614	This work

*extracted from figure

Table III : Points on Univariant Line in the LiF-NaCl-KCl Liquidus Projection.

composition (mol.%)			T(°C)	Ref
LiF	NaCl	KCl		
31.0	58.7	10.4	650	[27]
~32	~58	~10	?	[29]*
30.5	59.1	10.4	659	This work
20.0	56.0	24.0	627	[27]
~19	~57	~24	?	[29]*
20.4	55.7	23.9	630	This work
15.0	40.4	44.6	608	[27]
~12	~42	~46	?	[29]*
13.9	40.9	45.2	616	This work
16.5	35.5	48.0	618	[27]
~12	~37	~51	?	[29]*
14.8	36.2	49.0	628	This work
19.0	24.3	56.7	650	[27]
~15	~26	~59	?	[29]*
17.4	24.8	57.8	659	This work
20.0	12.0	68.0	679	[27]
~18	~12	~70	?	[29]*
20.3	12.0	67.7	691	This work

* extracted from figure

B. *The Na,K,Ca//F,Cl System*

The $(NaF)_2$-$(KCl)_2$-$KCaF_3$ and the $(NaF)_2$-$(KCl)_2$-CaF_2 liquidus projections have been measured[30] by the visual-polythermal method (Figures 23 and 24). The calculated liquidus lines for corresponding compositions are also shown in Figures 23 and 24.

Litvinova and Bukhalova[31] measured five liquidus projections for constant $X_F/(X_F+X_{Cl})$ ratios by the visual polythermal method (Figure 25), and reported quaternary invariant points (Table IV). The corresponding calculated liquidus curves are shown in Figure 25, and the calculated quaternary invariant points are given in Table IV. Calculated quaternary invariant points are generally slightly higher in temperature (by around 5 to 20°C) than the experimental points. This is within the experimental uncertainty. In general, agreement in the Na,K,Ca//F,Cl system is good in most cases, particularly when one considers the uncertainties in the experimental data surrounding the K,Ca//F,Cl system (Figures 15-18).

Table IV -Experimental and Calculated Major Invariant Points of the Quaternary Reciprocal Na,K,Ca//F,Cl System.

Solid phases in equilibrium with liquid	T(°C)	
	Exp.	Calc.
$KCaCl_3$ + $CaCl_2$ + CaFCl	570[22,31], 584[16]	585.8
(Na,[K,Ca])Cl_{ss} + $KCaCl_3$ + CaFCl	530[31]	542.6
(Na,[Ca])Cl_{ss} + $CaCl_2$ + CaFCl	490[31]	486.0
(Na,[K,Ca])Cl_{ss} + $KCaCl_3$ + $CaCl_2$	465[31], 504[32]	477.1
$KCaCl_3$ + CaFCl + CaF_2	652[22,31], 656[16]	647.3
(Na,[K,Ca])Cl_{ss} + $KCaCl_3$ + CaFCl	527[31]	515.4
(Na,[Ca])Cl_{ss} + CaFCl + CaF_2	605[31]	601.4
(Na,[K,Ca])Cl_{ss} +$KCaCl_3$+CaF_2+CaFCl	533[31]	542.6
(Na,[K,Ca])$_{ss}$ + $KCaCl_3$ + CaFCl + $CaCl_2$	460[31]	464.5
(Na,K)Cl_{ss} + $KCaCl_3$ + CaF_2	506[31]	525.4
KCl + $KCaCl_3$ + CaF_2	572[22,31], 582[16]	586.4
(Na,K)Cl_{ss} + $KCaCl_3$ (min.)	513[31]	535.6
(K,Na)Cl_{ss} + $KCaF_3$ + NaF + CaF_2	652[31]	648.2
(Na,K)Cl_{ss} + NaF + CaF_2	590[31]	605.9
NaF + NaCl + CaF_2	662[26,31]	663.8
(Na,K)Cl_{ss} + NaF (min.)	606[31], 612[16]	610.0
$KCaF_3$ + NaF + CaF_2	758[31], 759[33]	761.7
KCl + $KCaF_3$ + CaF_2	602[22,31], 722[16]	722.3
(K,[Na])F_{ss} +(Na,K)Cl_{ss} +$KCaF_3$+NaF	564[31], 574*	573.4
KF + KCl + $KCaF_3$	600[22,31], 600[16]	599.3
(K,[Na])F_{ss} + (Na,K)Cl_{ss} + NaF	570[31], 582[16]	580.4
(K,[Na])F_{ss} + $KCaF_3$ + NaF	683[31], 676[33]	678.7

* A thermal arrest at 574°C is also reported by Litvinova[31].

C. *The Li,K,Ca//F,Cl System*

Various quaternary reciprocal sections of the Li,K,Ca//F,Cl have been measured[34,35] by the visual-polythermal method. Points extracted from reported liquidus projections[34,35] on these sections are shown in Figures 26 to 30. Agreement is acceptable except in composition regions where the CaF_2 liquidus is very steep such that a small change in the Ca/K ratio corresponds to a large change in liquidus temperature. Considering the large exchange Gibbs energies of the K,Ca//F,Cl and Li,K//F,Cl subsystems (Table I), the model gives results of acceptable accuracy.

D. *The Li,Na,Ca//F,Cl System*

Various quaternary reciprocal sections of the Li,Na,Ca//F,Cl systems have been measured[36] by the visual-polythermal method. Points extracted from reported liquidus projections[36] on these sections are shown in

Figures 31 to 33. Agreement is good except in composition regions where the CaF_2 liquidus is very steep such that a small change in the Ca/Na ratio corresponds to a relatively large change in liquidus temperature.

Khardikova *et al.*[37] measured, by the visual-polythermal method, the temperature and the liquid composition of the quaternary invariant points of the Li,Na,Ca//F,Cl system (Table V). The calculated quaternary invariant points are also given in Table V. Note that the $LiNaCl_2$ and $LiNa_2Cl_3$ compounds reported by Khardikova[37] were not considered to be stable compounds in the thermodynamic evaluation[2] of the LiCl-NaCl system, but instead, a complete solid solution between LiCl and NaCl was proposed. Consequently, the reported invariant points of Khardikova[37] in Table V noted with a "*" are calculated as minima of univariant quaternary lines. The model gives better results for higher Cl/F ratios, and the calculated points are generally higher than the reported values.

Table V – Experimental[37] and Calculated Quaternary Invariant Points of the Li,Na,Ca//F,Cl System.

Solid phases in equilibrium with liquid	Exp.[37] T (°C)	Calc. T (°C)
$(Na,[Li])F_{ss}$ + $(Na,[Li])Cl_{ss}$ + LiF + CaF_2	542	584.9
$(Li,Na)Cl_{ss}$ + LiF + CaF_2	432	463.2
$(Li,Na)Cl_{ss}$ + LiF + CaF_2	451*	475.4 (min)
$(Li,Na)Cl_{ss}$ + LiF + CaF_2	469*	479.0 (min)
$(Li,Na)Cl_{ss}$ + CaFCl + CaF_2	420	480.1
$(Li,Na)Cl_{ss}$ + CaFCl + CaF_2	435*	481.0 (min)
$(Li,Na)Cl_{ss}$ + CaFCl + CaF_2	455*	482.3
$(Li,Na)Cl_{ss}$ + CaFCl + $CaCl_2$	410	422.8
$(Li,Na)Cl_{ss}$ + CaFCl + $CaCl_2$	423*	421.5 (min)
$(Li,Na)Cl_{ss}$ + CaFCl + $CaCl_2$	437*	421.5 (min)

* $LiNaCl_2$ and $LiNa_2Cl_3$ pure solids are reported[37] instead of the (Li,Na)Cl solid solution as used for calculations. Calculated temperatures are minima of univariant lines.

E. *The Na,Mg,Ca//F,Cl System*

Mediaas *et al.*[19] measured by cryoscopy-DTA the first and second crystallization temperatures of 24 mixtures in the $NaCl$-$MgCl_2$-$CaCl_2$-CaF_2 system, and also performed calculations using the quasichemical model[4] in the pair approximation (accounting for first-nearest-neighbor ordering, but neglecting second-nearest-neighbor ordering). Calculations of the present model (which takes into account both first- and second-nearest-neighbor ordering) are given in Table VI along with the experimental points[19]. The calculations are in very good agreement with the experiments, especially for secondary crystallization temperatures.

V. CONCLUSIONS

The modified quasichemical model in the quadruplet approximation[5] has been applied to the liquid phase of the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ system. Model parameters obtained previously[2,3] from evaluation/optimization of the common-ion chloride and fluoride systems were used along with parameters for the cation-cation binary systems reported in the Appendix to the present article.

Phase diagrams of the ternary and quaternary reciprocal systems were calculated. Small empirical reciprocal ternary parameters were required in some cases for precise reproduction of experimental phase equilibria. However, in all cases these parameters are small and their inclusion only changes the calculated liquidus temperatures and compositions by the order of 10°C to 20°C and 1 to 2 mol.% or less. All experimental ternary reciprocal phase equilibria are reproduced by the model within experimental error limits. This is generally also the case for the reciprocal quaternary equilibria. In the case of the quaternary systems, no additional empirical terms were used.

The model takes into account, simultaneously, both first-nearest-neighbor and second-nearest-neighbor short-range ordering. Calculations were performed previously in these systems using the quasichemical model in the pair approximation which takes account only of first-nearest-neighbor ordering. The present model gives significantly improved predictions over those obtained previously.

The model predictions for the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ system are very satisfactory considering that (1) the Gibbs energies for the first-nearest-neighbor exchange reactions (Table I) are very negative in many cases, thereby inducing a large degree of first-nearest-neighbor short-range ordering, and (2) several binary systems (such as KCl-$MgCl_2$) exhibit strong second-nearest-neighbor short-range ordering. That is, the LiF-LiCl-NaF-NaCl-KF-KCl-MgF_2-$MgCl_2$-CaF_2-$CaCl_2$ system provides a severe test of the model.

The model parameters are stored in the database of the F*A*C*T[44] computer system along with the optimized parameters for the solid phases. This database can be used, along with the other databases and Gibbs energy minimization software, to calculate the conditions of multicomponent multiphase equilibria of interest in processes involving these salts. It is planned to extent the database, through further evaluations/optimizations, to include other anions (NO_3^-, OH^-, CO_3^{2-}, SO_4^{2-}, O^{2-}, Br^-, I^-) and cations (Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, Fe^{2+}, Cd^{2+}, ..., Al^{3+}, La^{3+}, ...). In the case of larger anions, and many of the larger and/or multivalent cations, the strong interionic interactions result in a large degree of short-range ordering in the molten salt solution.

Table VI- Experimental[19] and Calculated Primary, Secondary and Tertiary Crystallization Temperatures of the $NaCl-CaCl_2-MgCl_2-CaF_2$ System.

Composition (wt%)				T_{exp} (°C)			T_{calc} (°C)			Calculated Precipitating Phases
$CaCl_2$	NaCl	$MgCl_2$	CaF_2	T_1	T_2	T_3	T_1	T_2	T_3	
59.84	40.15	0	0	561			572	504	-	$NaCl_{ss}$
59.82	40.18	0	0	556	499		573	504	-	$NaCl_{ss}$
56.85	38.14	5.00	0	527			534	488	-	$NaCl_{ss}$
56.80	38.19	5.01	0	518			535	488	-	$NaCl_{ss}$
53.99	36.23	4.75	5.03		541		641	547	488	MgF_2+ $NaCl_{ss}$
53.91	36.31	4.75	5.03	651	535		641	548	488	MgF_2+ $NaCl_{ss}$
51.11	34.29	4.50	10.09		574		689	567	556	MgF_2+CaFCl
51.03	34.37	4.50	10.10	700	570	553	689	567	556	MgF_2+CaFCl
48.16	32.31	10.01	9.51		517		734	523	488	MgF_2+ $NaCl_{ss}$
48.17	32.34	10.01	9.48	748	514	484	734	524	488	MgF_2+ $NaCl_{ss}$
45.48	30.51	15.03	8.98		483		736	486	484	MgF_2+CaFCl+$NaCl_{ss}$
45.46	30.57	15.03	8.95	753	483	481	736	486	484	MgF_2+CaFCl+$NaCl_{ss}$
39.98	60.02	0	0	683			690	504	-	$NaCl_{ss}$
37.95	56.98	5.07	0	654			665	470	-	$NaCl_{ss}$
37.56	56.38	5.02	1.05	654			665	547	472	$NaCl_{ss}$
37.19	55.84	4.97	2.00	657			665	611	479	$NaCl_{ss}$
36.07	54.17	4.81	4.94	696			690	667	492	MgF_2
35.11	52.71	4.69	7.49	726			716	668	564	MgF_2
34.11	51.28	4.56	9.99	736			722	669	589	MgF_2
32.22	48.37	9.98	9.43		640		770	646	494	MgF_2+$NaCl_{ss}$
30.42	45.67	15.00	8.90		610		772	616	477	MgF_2+$NaCl_{ss}$
50.08	49.92	0	0	627			639	504	-	$NaCl_{ss}$
50.09	49.91	0	0	626			638	504	-	$NaCl_{ss}$
47.57	47.42	5.01	0	594			608	482	-	$NaCl_{ss}$
47.04	46.89	4.95	1.11	596			609	514	481	$NaCl_{ss}$
46.60	46.45	4.90	2.05	598			610	576	485	$NaCl_{ss}$
45.20	45.05	4.76	5.00		603		664	614	487	MgF_2+$NaCl_{ss}$
45.20	45.06	4.74	4.99	671	602		663	614	486	MgF_2+$NaCl_{ss}$
44.01	43.87	4.63	7.48		607		693	616	545	MgF_2+$NaCl_{ss}$
44.01	43.90	4.62	7.48	705	606		693	616	545	MgF_2+$NaCl_{ss}$
42.79	42.65	4.50	10.05		609		704	617	576	MgF_2+$NaCl_{ss}$
42.77	42.69	4.49	10.05	714	609		704	617	576	MgF_2+$NaCl_{ss}$
40.29	40.16	10.09	9.46		581		751	591	487	MgF_2+$NaCl_{ss}$
40.24	40.19	10.12	9.45	767	581		751	591	487	MgF_2+$NaCl_{ss}$
38.07	37.95	15.04	8.94		547		753	557	481	MgF_2+$NaCl_{ss}$
38.03	38.01	15.03	8.93	766	544		753	557	481	MgF_2+$NaCl_{ss}$

List of Symbols

$\Delta g_{AB/X}$ Gibbs energy of the common-anion pair-exchange reaction :
$(A-[X]-A)+(B-[X]-B)=2(A-[X]-B)$

$\Delta g_{A/FCl}$ Gibbs energy of the common-cation pair-exchange reaction :
$(F-[A]-F)+(Cl-[A]-Cl)=2(F-[A]-Cl)$

$\Delta g^{exchange}_{AB/FCl}$ Gibbs energy of the exchange reaction :
$AF+BCl=ACl+BF$

$\Delta g_{AB/XY}$ Gibbs energy of formation of ABXY quadruplet from ABX_2, ABY_2, A_2XY and B_2XY quadruplets :
$\frac{1}{2}(ABX_2+ABY_2+A_2XY+B_2XY)=2ABXY$

$g^{i}_{AB/XY(AX)}$ parameter giving the influence of first-nearest-neighbor A-X pairs on the Gibbs energy of formation of ABXY quadruplet ($\Delta g_{AB/XY}$).

T absolute temperature (K)

X_{A_2/X_2} mole fraction of A_2X_2 "unary" quadruplets

X_{AB/X_2} mole fraction of ABX_2 "binary" quadruplets

$X_{A_2/XY}$ mole fraction of A_2XY "binary" quadruplets

$X_{AB/XY}$ mole fraction of ABXY "reciprocal" quadruplets

z_i 1st nearest-neighbor coordination number of ion i

Z_i 2nd nearest-neighbor coordination number of ion i

Z^{A}_{ABXY} 2nd nearest-neighbor coordination number of ion A in a hypothetical solution formed only by $ABXY$ quadruplets.

ζ number of quadruplets emanating from a pair (2.4 in this work).

χ_{FCl} $\chi_{FCl} = X_{A_2F_2}$

χ_{ClF} $\chi_{ClF} = X_{A_2Cl_2}$

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APPENDIX

Evaluation/Optimization of Common-cation Binary Systems

The LiF-LiCl, NaF-NaCl, KF-KCl, MgF_2-$MgCl_2$ and CaF_2-$CaCl_2$ systems were optimized previously[24,38] with a random-mixing (Bragg-Williams) entropy and a polynomial expansion for the excess Gibbs energy. They are re-optimized here with the quasichemical model. Second-nearest-neighbor coordination numbers are $Z^{F}_{FCl} = Z^{Cl}_{FCl} = 6$ for common-alkali systems and $Z^{F}_{FCl} = Z^{Cl}_{FCl} = 3$ for common-alkaline-earth systems. As defined previously[1], in these binary systems χ_{FCl} and

χ_{ClF} are equal to the second-nearest-neighbor pair fractions. In all systems, solid solubility is assumed to be negligible.

A. *The LiF-LiCl System*

The phase diagram has been measured[10] (Figure 34). Calorimetric measurements are available[39] (Figure 35). Figures 34 and 35 show the phase diagram and thermodynamic properties. The optimized energy of formation of *F-Li-Cl* second-nearest-neighbor pairs is :

$$\Delta g_{Li/FCl} = -736.4 + 0.2802T + 740.6\chi_{FCl} + 236.1\chi_{ClF} \quad \text{J/mol} \quad [A\text{-}1]$$

B. *The NaF-NaCl System*

The phase diagram has been measured[40,41] (Figure 36). Calorimetric measurements are available[39] (Figure 35). Figures 35 and 36 show the phase diagram and thermodynamic properties. The optimized energy of formation of *F-Na-Cl* second-nearest-neighbor pairs is :

$$\Delta g_{Na/FCl} = 174.0 + 0.4623T + 611.2\chi_{FCl} - 222.6\chi_{ClF} \quad \text{J/mol} \quad [A\text{-}2]$$

C. *The KF-KCl System*

The phase diagram has been measured[42] (Figure 37). Calorimetric measurements are available[39] (Figure 35). Figures 35 and 37 show the phase diagram and thermodynamic properties. The optimized energy of formation of *F-K-Cl* second-nearest-neighbor pairs is :

$$\Delta g_{K/FCl} = -107.6 - 0.2880T + 437.3\chi_{FCl} + (-96.2 + 1.3362T)\chi_{ClF} \quad \text{J/mol} \quad [A\text{-}3]$$

D. *The MgF_2-$MgCl_2$ System*

The phase diagram has been measured[18] (Figure 38). The calculated phase diagram is shown in Figure 38. The optimized energy of formation of *F-Mg-Cl* second-nearest-neighbor pairs is :

$$\Delta g_{Mg/FCl} = 272.0 - 73.6\chi_{FCl} - 383.1\chi_{ClF} \quad \text{J/mol} \quad [A\text{-}4]$$

E. *The CaF_2-$CaCl_2$ System*

The phase diagram has been measured[15,20,22,23,43] (Figure 39). The calculated phase diagram is shown in Figure 39. The optimized energy of formation of *F-Ca-Cl* second-nearest-neighbor pairs is:

$$\Delta g_{Ca/FCl} = -646.1 \quad \text{J/mol} \quad [A\text{-}5]$$

The optimized Gibbs energy of formation of CaFCl from $CaCl_{2\,(S)}$ and $CaF_{2\,(\alpha)}$ is as follows. (ΔC_p of formation is assumed to be 0)

$$\tfrac{1}{2}CaCl_{2(S)} + \tfrac{1}{2}CaF_{2(S)} = CaFCl \quad \Delta G^o = -14026.2 + 9.866T \quad \text{J/mol} \quad [A\text{-}6]$$

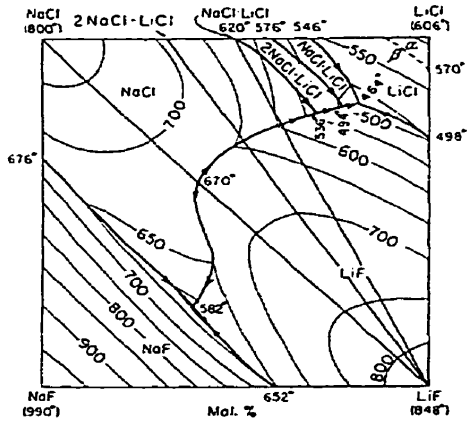

Fig. 1- Li,Na//F,Cl system : experimental liquidus projection of Bergman *et al.*[6].

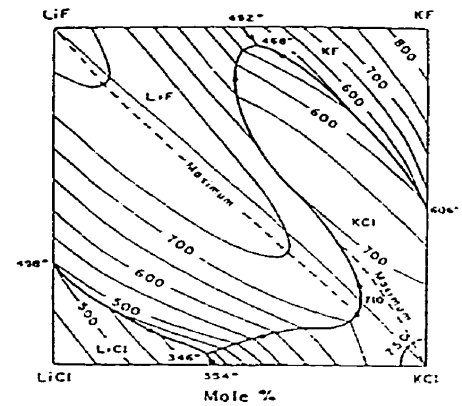

Fig. 4 –Li,K//F,Cl system : experimental liquidus projection of Berezina *et al.*[12].

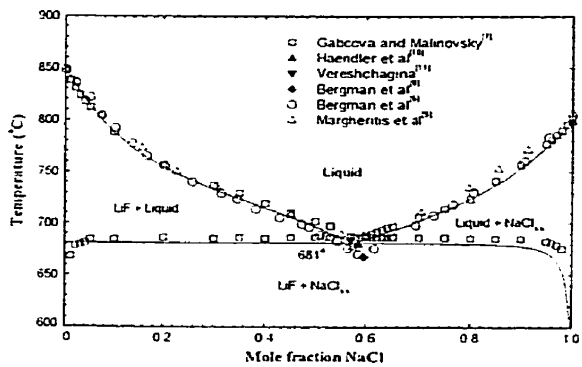

Fig. 2 - Li,Na//F,Cl system : calculated LiF-NaCl join.

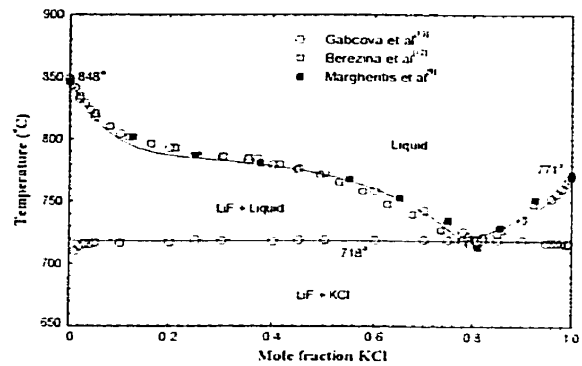

Fig. 5 - Li,K//F,Cl system : calculated LiF-KCl join.

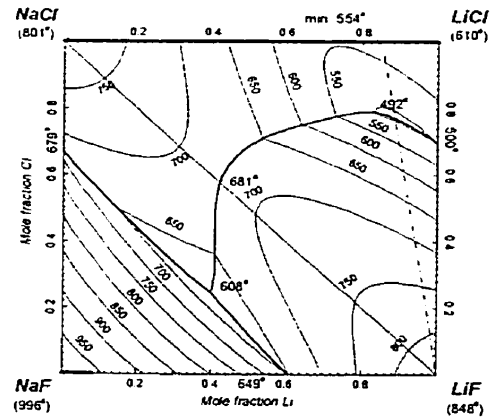

Fig. 3 - Li,Na//F,Cl system : calculated liquidus projection.

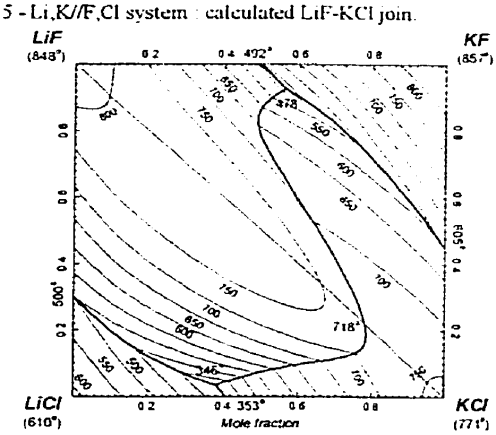

Fig. 6 – Li,K//F,Cl system : calculated liquidus projection.

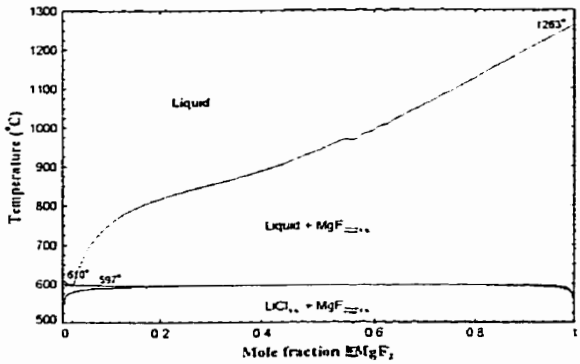

Fig. 7 – Li,Mg//F,Cl system : calculated LiCl-MgF_2 join.

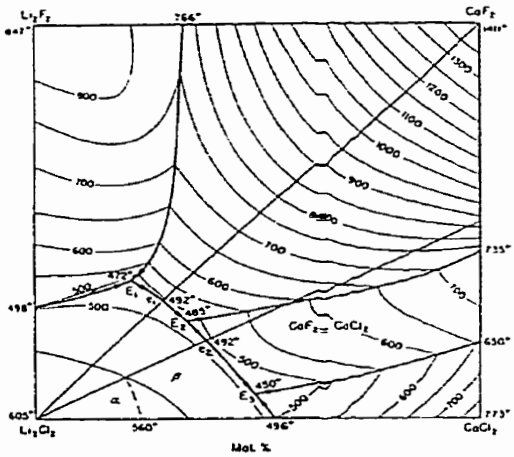

Fig. 8 – Li,Ca//F,Cl system : experimental Li_2Cl_2-Li_2F_2-$CaCl_2$-CaF_2 liquidus projection of Bukhalova and Bergman[15]

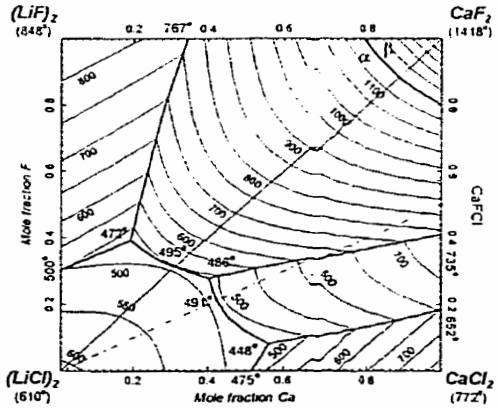

Fig. 9 – Li,Ca//F,Cl system : calculated Liquidus projection.

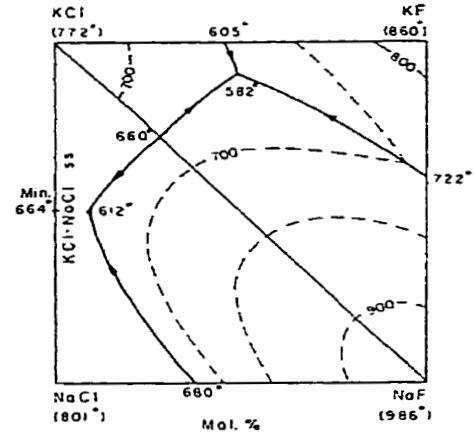

Fig. 10 – Na,K//F,Cl system : experimental liquidus projection of Ishaque[10]

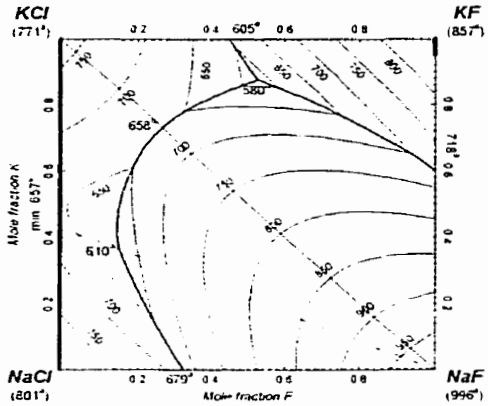

Fig. 11 – Na,K//F,Cl system : calculated liquidus projection.

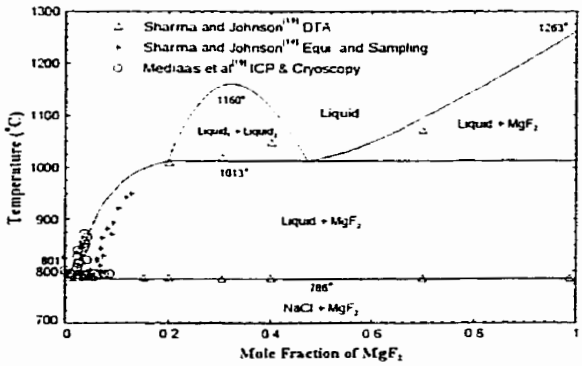

Fig. 12 – Na,Mg//F,Cl system : calculated NaCl-MgF_2 join

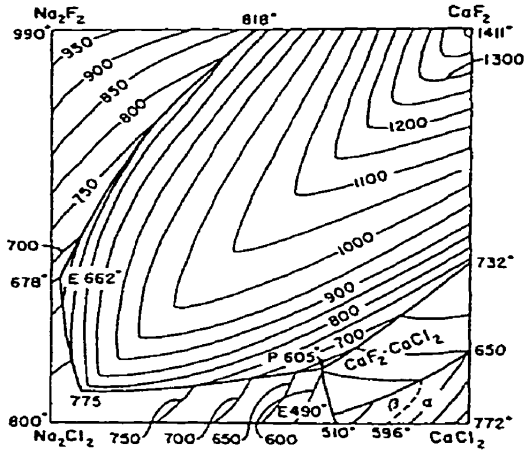

Fig. 13 – Na,Ca//F,Cl system : experimental Na_2F_2-Na_2Cl_2-CaF_2-$CaCl_2$ liquidus projection of Bukhalova[20].

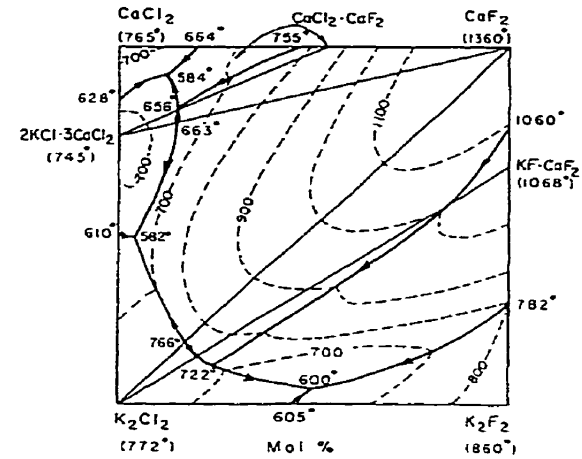

Fig. 16 – K,Ca//F,Cl system : experimental K_2F_2-K_2Cl_2-CaF_2-$CaCl_2$ liquidus projection of Ishaque[16].

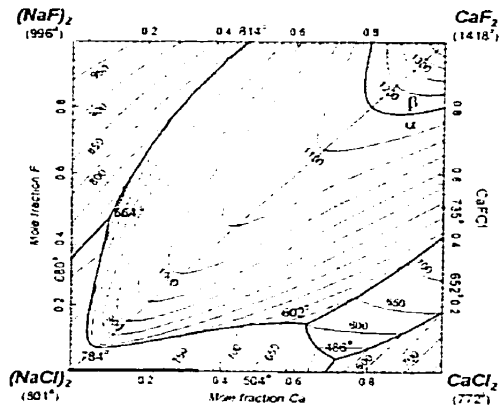

Fig. 14 – Na,Ca//F,Cl system : calculated liquidus projection.

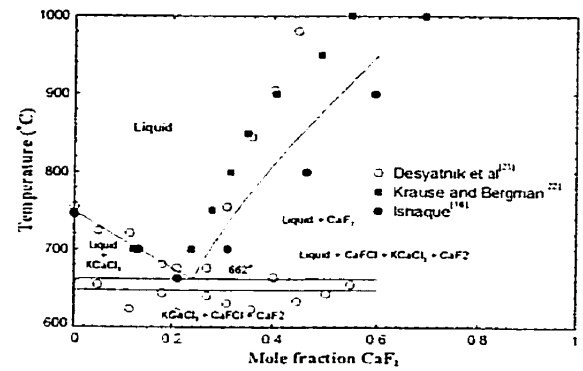

Fig. 17 – K,Ca//F,Cl system : calculated $KCaCl_3$-CaF_2 join (partial).

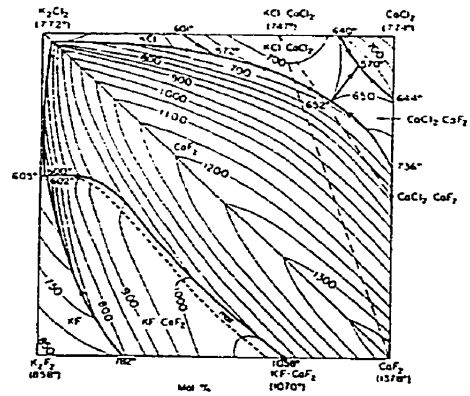

Fig. 15 – K,Ca//F,Cl system : experimental K_2F_2-K_2Cl_2-CaF_2-$CaCl_2$ liquidus projection of Krause and Bergman[22].

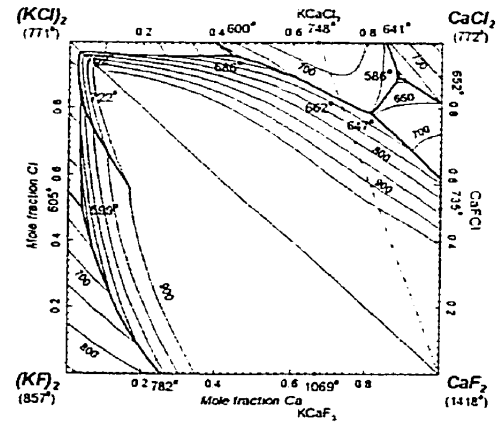

Fig. 18 – K,Ca//F,Cl system : calculated liquidus projection (below 900°C).

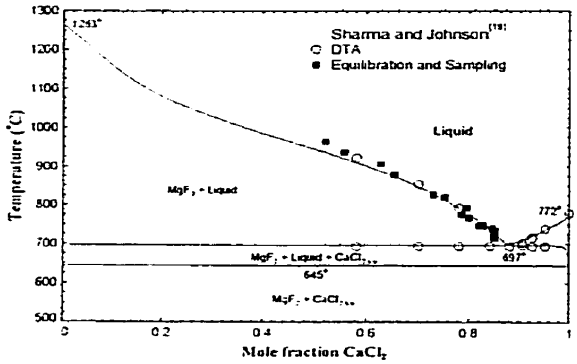

Fig. 19 – Mg,Ca//F,Cl system : calculated MgF_2-$CaCl_2$ join.

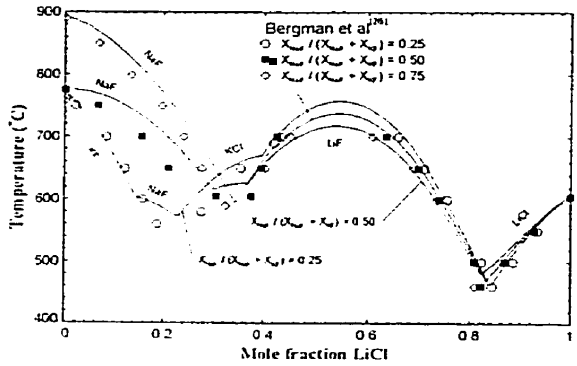

Fig. 20 – Li,Na,K//F,Cl system : calculated liquidus lines of the LiCl-NaF-KF isopleth for constant NaF/(NaF+KF) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

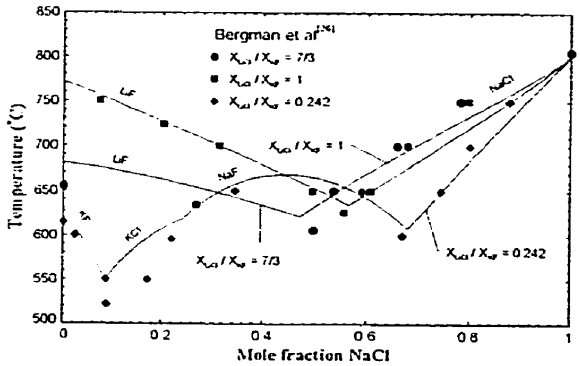

Fig. 21 – Li,Na,K//F,Cl system : calculated liquidus lines of the LiCl-NaCl-KF isopleth for constant LiCl / KF molar ratios of 7/3, 1.0 and 0.242. (Labels on lines indicate the primary solid phases).

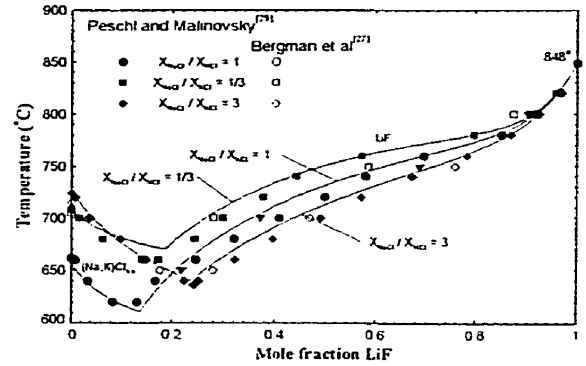

Fig. 22 – Li,Na,K//F,Cl system : calculated liquidus lines of the LiF-NaCl-KCl isopleth for constant NaCl / KCl molar ratios of 1/3, 1.0 and 3. (Labels on lines indicate the primary solid phases).

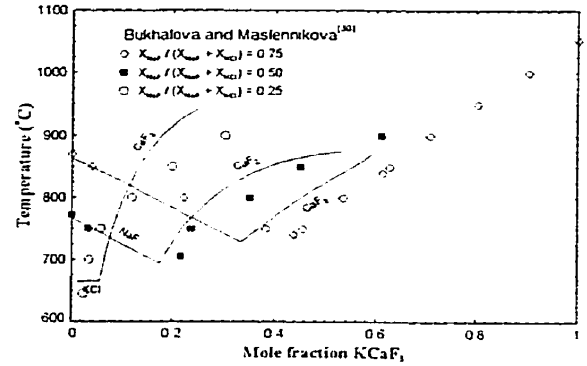

Fig. 23 – Na,K,Ca//F,Cl system : calculated liquidus lines of the $(NaF)_2$-$(KCl)_2$-$KCaF_3$ isopleth for constant NaF/(NaF+KCl) molar ratios of 0.25, 0.50 and 0.75 (Labels on lines indicate the primary solid phases).

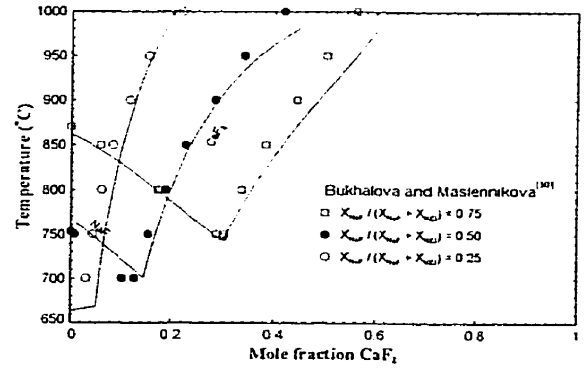

Fig. 24 – Na,K,Ca//F,Cl system : calculated liquidus lines of the $(NaF)_2$-$(KCl)_2$-CaF_2 isopleth for constant NaF/(NaF+KCl) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

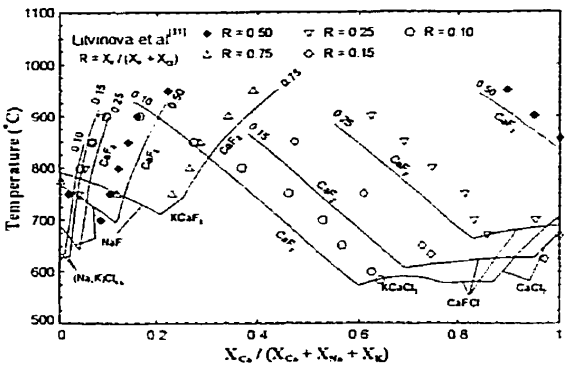

Fig. 25 - Na,K,Ca//F,Cl system : calculated liquidus lines on constant F/(F+Cl) molar ratio isopleths of 0.10, 0.15, 0.25, 0.50 and 0.75 along the (NaX+KX) – CaX_2 join (with X = F, Cl). (Labels on lines indicate the primary solid phases).

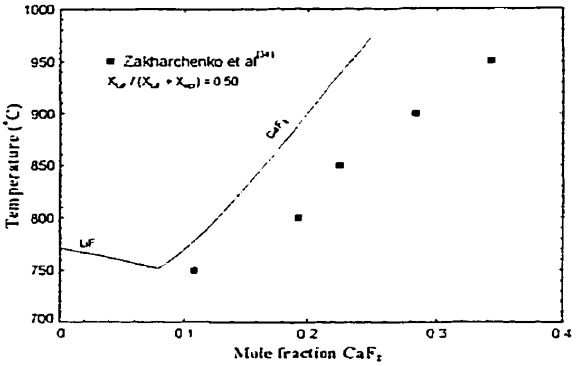

Fig. 28 – Li,K,Ca//F,Cl system : calculated liquidus line of the $(LiF)_2$-$(KCl)_2$-CaF_2 isopleth for constant LiF/(LiF+KCl) molar ratio of 0.5. (Labels on lines indicate the primary solid phases).

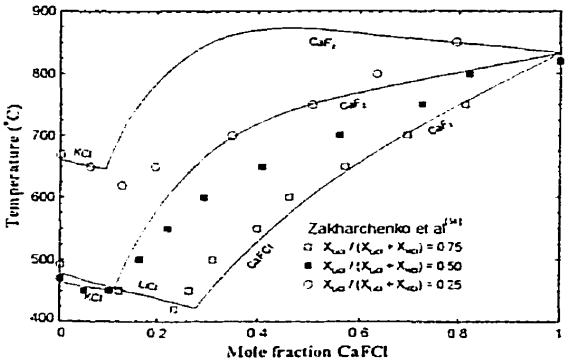

Fig. 26 – Li,K,Ca//F,Cl system : calculated liquidus lines of the $(LiCl)_2$-$(KCl)_2$-CaFCl isopleth for constant LiCl/(LiCl+KCl) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

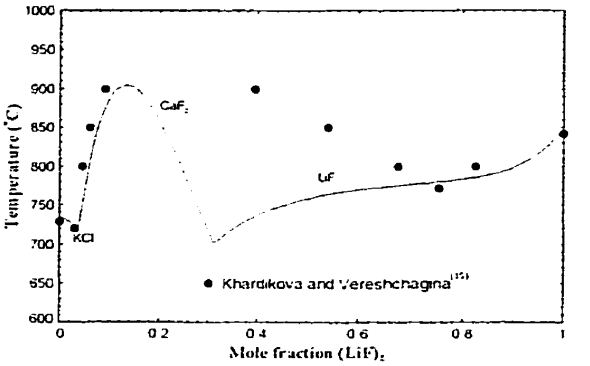

Fig. 29 - Li,K,Ca//F,Cl system: calculated [15%$CaCl_2$+85%K_2Cl_2] -$(LiF)_2$ liquidus. (Labels on lines indicate the primary solid phases).

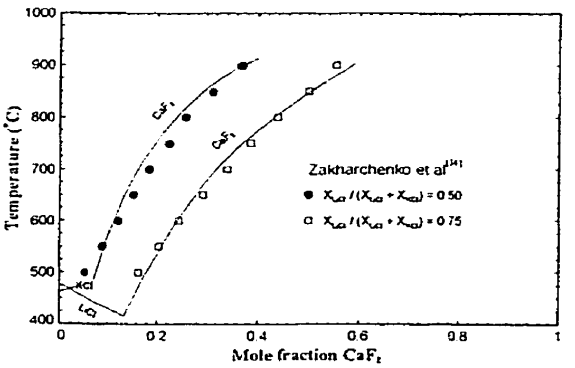

Fig. 27 – Li,K,Ca//F,Cl system : calculated liquidus lines of the $(LiCl)_2$-$(KCl)_2$-CaF_2 isopleth for constant LiCl/(LiCl+KCl) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

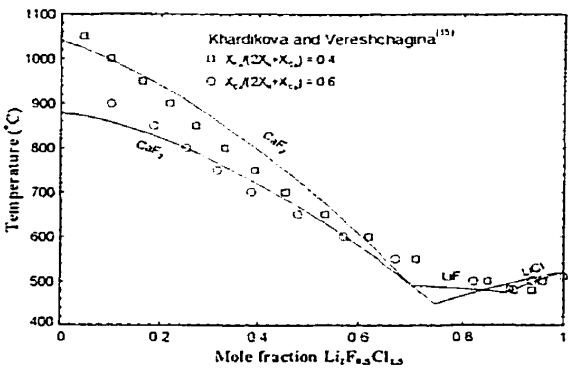

Fig. 30 - Li,K,Ca//F,Cl system : calculated liquidus lines of the F/(F+Cl) constant 0.25 molar ratio isopleth for constant Ca/(Ca+2K) molar ratios of 0.4 and 0.6. (Labels on lines indicate the primary solid phases).

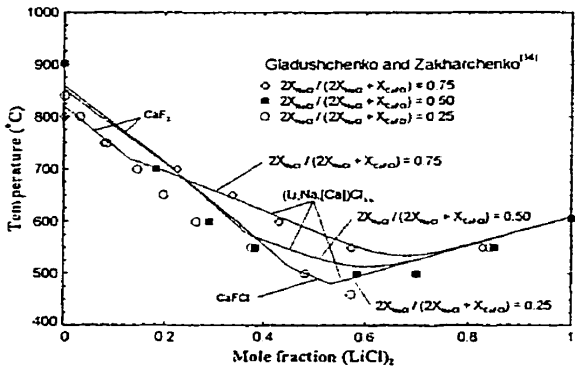

Fig. 31 – Li,Na,Ca//F,Cl system : calculated liquidus lines of the $(LiCl)_2$-$(NaCl)_2$-CaFCl isopleth for constant Ca/(Ca+2Na) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

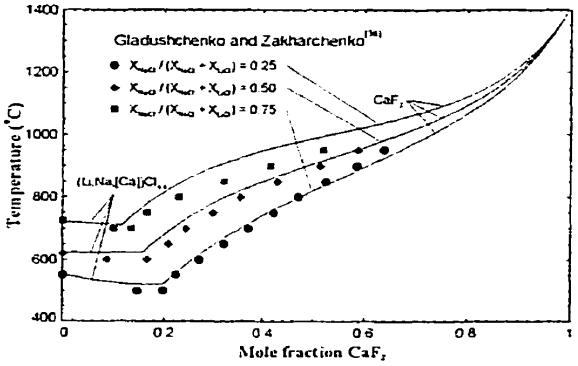

Fig. 32 – Li,Na,Ca//F,Cl system : calculated liquidus lines of the $(LiCl)_2$-$(NaCl)_2$-CaF_2 isopleth for constant LiCl/(LiCl+NaCl) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

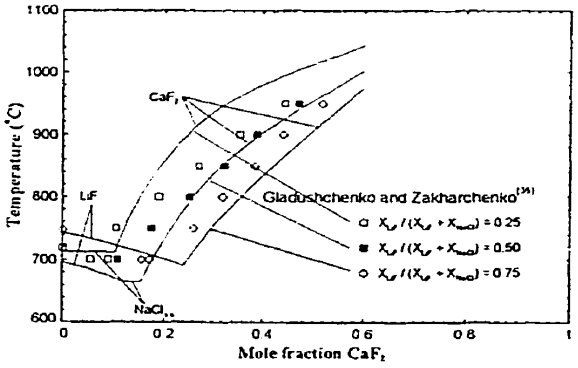

Fig. 33 – Li,Na,Ca//F,Cl system : calculated liquidus lines of the $(LiF)_2$-$(NaCl)_2$-CaF_2 isopleth for constant LiF/(LiF+NaCl) molar ratios of 0.25, 0.50 and 0.75. (Labels on lines indicate the primary solid phases).

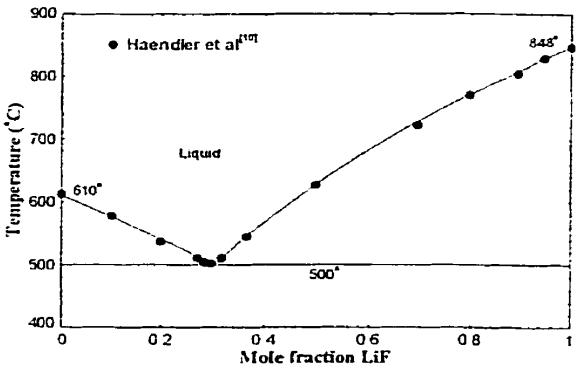

Fig. 34 – LiCl-LiF system : calculated phase diagram.

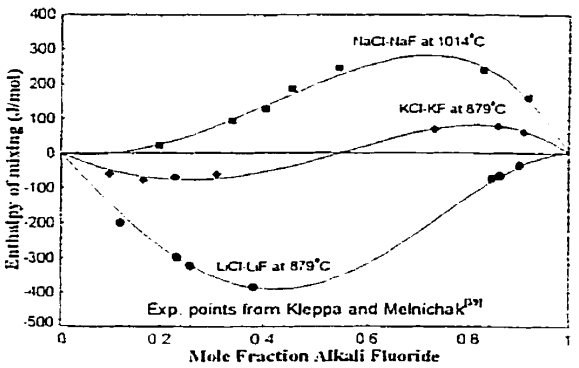

Fig. 35 – Alkali chloride – alkali fluoride systems : calculated enthalpy of mixing of the liquid with experimental points of Kleppa and Melnichak[39].

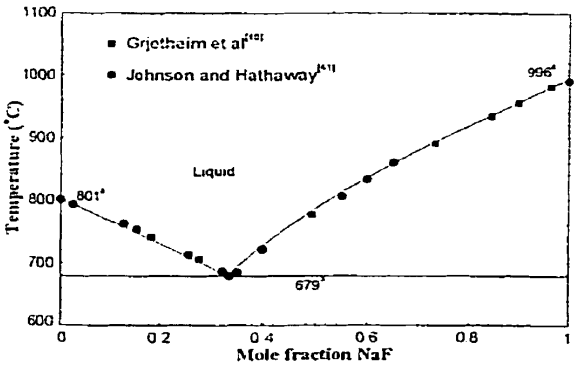

Fig. 36 - NaCl-NaF system : calculated phase diagram.

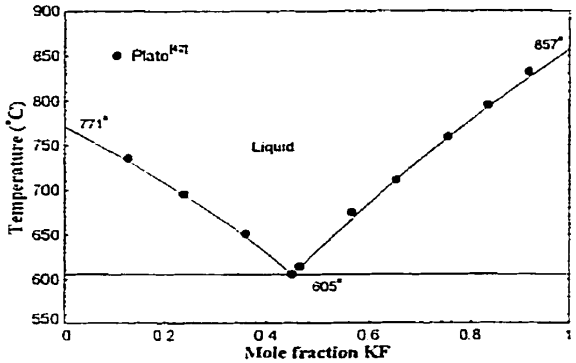

Fig. 37 - KCl-KF system : calculated phase diagram.

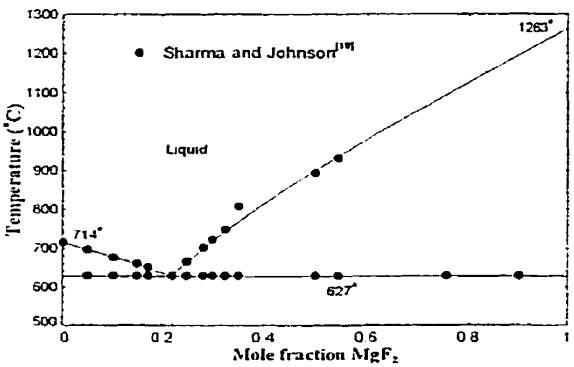

Fig. 38 - $MgCl_2$-MgF_2 system : calculated phase diagram.

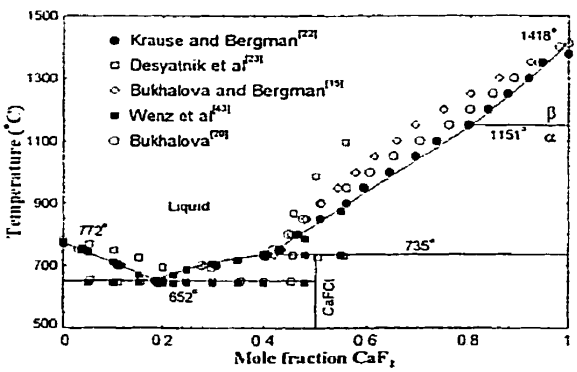

Fig. 39 - $CaCl_2$-CaF_2 system : calculated phase diagram.

ANNEXE XII

Conversion des coefficients optimisés pour l'expansion compositionnelle de l'énergie de formation des paires des modèles polynomial et quasichimique modifié aux coefficients du modèle quasichimique amélioré avec expansion des paires.

Pour un modèle thermodynamique avec entropie configurationnelle de type Bragg-Williams (BW) et expansion de l'énergie en excès sous forme d'un polynôme de puissances des fractions équivalentes, l'énergie de formation des paires *A-B* à partir des paires *A-A et B-B* est :

$$\Delta\omega_{AB}^{(BW)} = \Delta\omega_{AB}^{00(BW)} + \Delta\omega_{AB}^{10(BW)} Y_A + \Delta\omega_{AB}^{20(BW)} Y_A^2 + \Delta\omega_{AB}^{01(BW)} Y_B + \Delta\omega_{AB}^{02(BW)} Y_B^2 + \ldots \tag{1}$$

où les paramètres $\Delta\omega_{AB}^{ij(BW)}$ sont les paramètres optimisés pour ce modèle. Pour le modèle quasichimique modifié de Pelton et Blander, 1984 (QM) une expansion similaire peut être utilisée :

$$\Delta\omega_{AB}^{(QM)} = \Delta\omega_{AB}^{00(QM)} + \Delta\omega_{AB}^{10(QM)} Y_A + \Delta\omega_{AB}^{20(QM)} Y_A^2 + \Delta\omega_{AB}^{01(QM)} Y_B + \Delta\omega_{AB}^{02(QM)} Y_B^2 + \ldots \tag{2}$$

où les paramètres $\Delta\omega_{AB}^{ij(QM)}$ sont les paramètres optimisés pour ce modèle. Il est possible de convertir exactement les paramètres $\Delta\omega_{AB}^{ij(QM)}$ en paramètres pour le modèle quasichimique amélioré. Il est aussi possible de convertir approximativement les paramètres $\Delta\omega_{AB}^{ij(BW)}$ en paramètres pour le modèle quasichimique amélioré. Cette approximation est meilleure plus la valeur des paramètres tend vers 0 car alors le mélange s'approche d'un mélange aléatoire des espèces tel qu'imposé par l'entropie de Bragg-Williams. Les termes $\Delta\omega_{AB}^{ij(QM)}$ et $\Delta\omega_{AB}^{ij(BW)}$ correspondent exactement l'un à l'autre et sont notés $\Delta\omega_{AB}^{ij}$ dès maintenant dans cette annexe.

Sachant que, du bilan de masse des espèces, on a :

$$Y_A = X_{AA} + \tfrac{1}{2} X_{AB} \tag{3}$$

$$Y_B = X_{BB} + \tfrac{1}{2} X_{AB} \tag{4}$$

et

$$X_{AB} = 1 - X_{AA} - X_{BB} \tag{5}$$

pour les 3 modèles considérés et pour un système binaire. Alors on a que :

$$\begin{aligned}\Delta\omega_{AB} = {} & \Delta\omega_{AB}^{00} + \tfrac{1}{2}\Delta\omega_{AB}^{10}\left(1 + X_{AA} - X_{BB}\right) + \tfrac{1}{2}\Delta\omega_{AB}^{01}\left(1 + X_{BB} - X_{AA}\right) \\ & + \tfrac{1}{4}\Delta\omega_{AB}^{20}\left(1 + 2X_{AA} - 2X_{BB} - 2X_{AA}X_{BB} + X_{AA}^2 + X_{BB}^2\right) \\ & + \tfrac{1}{4}\Delta\omega_{AB}^{02}\left(1 + 2X_{BB} - 2X_{AA} - 2X_{AA}X_{BB} + X_{AA}^2 + X_{BB}^2\right)\end{aligned} \tag{6}$$

Ce qui équivaut à :

$$\begin{aligned}\Delta\omega_{AB} = {} & \left(\Delta\omega_{AB}^{00} + \tfrac{1}{2}\Delta\omega_{AB}^{10} + \tfrac{1}{2}\Delta\omega_{AB}^{01} + \tfrac{1}{4}\Delta\omega_{AB}^{20} + \tfrac{1}{4}\Delta\omega_{AB}^{02}\right) \\ & + \left(\tfrac{1}{2}\Delta\omega_{AB}^{10} - \tfrac{1}{2}\Delta\omega_{AB}^{01} + \tfrac{1}{2}\Delta\omega_{AB}^{20} - \tfrac{1}{2}\Delta\omega_{AB}^{02}\right)X_{AA} \\ & + \left(\tfrac{1}{2}\Delta\omega_{AB}^{01} - \tfrac{1}{2}\Delta\omega_{AB}^{10} + \tfrac{1}{2}\Delta\omega_{AB}^{02} - \tfrac{1}{2}\Delta\omega_{AB}^{20}\right)X_{BB} \\ & + \left(\tfrac{1}{4}\Delta\omega_{AB}^{20} + \tfrac{1}{4}\Delta\omega_{AB}^{02}\right)X_{AA}^2 + \left(\tfrac{1}{4}\Delta\omega_{AB}^{02} + \tfrac{1}{4}\Delta\omega_{AB}^{20}\right)X_{BB}^2 \\ & - \left(\tfrac{1}{2}\Delta\omega_{AB}^{20} + \tfrac{1}{2}\Delta\omega_{AB}^{02}\right)X_{AA}X_{BB}\end{aligned} \tag{7}$$

L'expansion compositionnelle pour le modèle quasichimique amélioré (QA) est :

$$\begin{aligned}\Delta\omega_{AB}^{(QA)} = {} & \Delta\omega_{AB}^{00(QA)} + \Delta\omega_{AB}^{10(QA)}X_{AA} + \Delta\omega_{AB}^{01(QA)}X_{BB} \\ & + \Delta\omega_{AB}^{20(QA)}X_{AA}^2 + \Delta\omega_{AB}^{02(QA)}X_{BB}^2 + \Delta\omega_{AB}^{11(QA)}X_{AA}X_{BB}\end{aligned} \tag{8}$$

Ce qui donne la conversion suivante :

$$\Delta\omega_{AB}^{00(QA)} = \Delta\omega_{AB}^{00} + \tfrac{1}{2}\left(\Delta\omega_{AB}^{10} + \Delta\omega_{AB}^{01}\right) + \tfrac{1}{4}\left(\Delta\omega_{AB}^{20} + \Delta\omega_{AB}^{02}\right) \tag{9}$$

$$\Delta\omega_{AB}^{10(QA)} = \tfrac{1}{2}\left(\Delta\omega_{AB}^{10} - \Delta\omega_{AB}^{01} + \Delta\omega_{AB}^{20} - \Delta\omega_{AB}^{02}\right) \tag{10}$$

$$\Delta\omega_{AB}^{01(QA)} = \tfrac{1}{2}\left(\Delta\omega_{AB}^{01} - \Delta\omega_{AB}^{10} + \Delta\omega_{AB}^{02} - \Delta\omega_{AB}^{20}\right) \tag{11}$$

$$\Delta\omega_{AB}^{20(Q\cdot 1)} = \Delta\omega_{AB}^{02(Q\cdot 1)} = \tfrac{1}{4}\left(\Delta\omega_{AB}^{20} + \Delta\omega_{AB}^{02}\right) \tag{12}$$

$$\Delta\omega_{AB}^{11(Q\cdot 1)} = -\tfrac{1}{2}\left(\Delta\omega_{AB}^{20} + \Delta\omega_{AB}^{02}\right) \tag{13}$$

Une approche similaire peut être utilisée pour les puissances plus élevées.

Une conversion des paramètres des fonctions Y_i (quasichimique modifié et polynomial) en paramètres des fonctions X_{ij} (quasichimique amélioré) est donc possible pour l'intégration des bases de données courantes des 2 premiers modèles à une base de données du nouveau modèle quasichimique amélioré.