

# Thermodynamic Evaluation and Optimization of the Li, Na, K, Mg, Ca//F, Cl Reciprocal System Using the Modified Quasi-chemical Model

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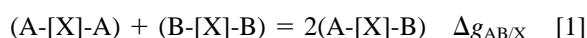
A complete critical evaluation of all available ternary reciprocal phase diagram data has been performed for all condensed phases of the LiF-LiCl-NaF-NaCl-KF-KCl-MgF<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> system and optimized model parameters have been found. The model parameters obtained for ternary reciprocal subsystems can be used to predict thermodynamic properties and phase equilibria for the multicomponent reciprocal system. The modified quasi-chemical model in the quadruplet approximation was used for the molten salt phase. This model takes into account, simultaneously, both first-nearest-neighbor (FNN) and second-nearest-neighbor (SNN) short-range-ordering (SRO) and the coupling between them. The predictions are significantly better than those obtained with previous models.

## 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<sub>2</sub>, and MgCl<sub>2</sub> salts, which can also be used as fluxes for Mg casting; NaCl, KCl, MgCl<sub>2</sub>, 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; electrodeposition of refractory metals (Nb, Ta) can be made from these solutions; and NaF, CaF<sub>2</sub>, LiF, and MgF<sub>2</sub> 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<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> system will contribute to the understanding, calculation, and simulation of many present and future metallurgical applications.

In reciprocal molten salt solution (*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 (FNN) (cation-anion) interactions. Modeling such solutions is a challenge. If, simultaneously, there is also strong second-nearest-neighbor SNN (cation-cation) short-range ordering (SRO), the solution becomes even more difficult to model.

The binary common-ion systems KCl-MgCl<sub>2</sub> and KF-MgF<sub>2</sub> exhibit extensive SRO, which has been associated with the formation of MgCl<sub>4</sub><sup>2-</sup> and MgF<sub>4</sub><sup>2-</sup> “complex ions.” To a lesser, but still appreciable, extent the NaCl-MgCl<sub>2</sub>, NaF-CaF<sub>2</sub>, and KF-CaF<sub>2</sub> systems also exhibit such SRO. In a previous publication,<sup>[1]</sup> we presented a modified quasi-chemical model, in the pair approximation, in which this ordering is described in terms of the following equilibrium among SNN cation-cation pairs:



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 SNN SRO 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<sup>[2,3]</sup> all available phase diagram and thermodynamic data for the LiCl-NaCl-KCl-MgCl<sub>2</sub>-CaCl<sub>2</sub> and LiF-NaF-KF-MgF<sub>2</sub>-CaF<sub>2</sub> common-anion systems were critically evaluated to obtain optimized 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, FNN SRO can occur, the extent of which is related to the Gibbs energy of the exchange reaction:



If  $\Delta g_{AB/FCI}^{exchange}$  is negative, then A-Cl and B-F nearest-neighbor-pairs predominate. In several of the reciprocal ternary subsystems (systems with two cations and two anions),  $\Delta g_{AB/FCI}^{exchange}$  is very negative, as can be seen in Table I. These systems thus exhibit such ordering to a large extent.

In another recent publication,<sup>[4]</sup> the modified quasi-chemical model, in the pair approximation, was developed for treating such FNN SRO. However, since the pair approximation was used, this model could not simultaneously take account of FNN and SNN ordering.

Recently,<sup>[5]</sup> we have proposed a new modified quasi-chemical model in the quadruplet approximation, which incorporates the previous models.<sup>[1-4]</sup> as limiting cases. A quadruplet A<sub>2</sub>X<sub>2</sub>, ABX<sub>2</sub>, A<sub>2</sub>XY, or ABXY consists of two SNN cations and two SNN 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<sub>2</sub>-CaCl<sub>2</sub>, the quadruplets ABX<sub>2</sub> are identical to the SNN (A-[X]-B) pairs, so that the optimized parameters obtained previously for this system<sup>[2]</sup> and for the common-ion fluoride system<sup>[3]</sup> can be used directly in the new model.

To a much lesser extent, SNN anion-anion ordering can

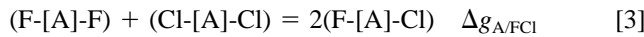
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**Table I. Average Exchange Gibbs Energies ( $\Delta g_{AB/FCI}^{\text{exchange}}$ ) for Reaction [2] for Liquid Salts over the Range 400 °C <  $T < 1200$  °C**

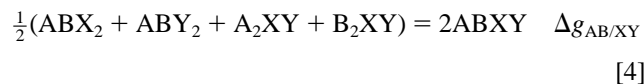
System A,B/FCI	$\Delta g_{AB/FCI}^{\text{exchange}}$ (kJ / Charge Equivalent)
LiCl + NaF = LiF + NaCl	$\approx -38$
LiCl + KF = LiF + KCl	$\approx -61$
LiF + 0.5MgCl <sub>2</sub> = LiCl + 0.5MgF <sub>2</sub>	$\approx -40$
LiF + 0.5CaCl <sub>2</sub> = LiCl + 0.5CaF <sub>2</sub>	$\approx -18$
NaCl + KF = NaF + KCl	$\approx -23$
NaF + 0.5MgCl <sub>2</sub> = NaCl + 0.5MgF <sub>2</sub>	$\approx -80$
NaF + 0.5CaCl <sub>2</sub> = NaCl + 0.5CaF <sub>2</sub>	$\approx -58$
KF + 0.5MgCl <sub>2</sub> = KCl + 0.5MgF <sub>2</sub>	$\approx -100$
KF + 0.5CaCl <sub>2</sub> = KCl + 0.5CaF <sub>2</sub>	$\approx -78$
0.5CaF <sub>2</sub> + 0.5MgCl <sub>2</sub> = 0.5CaCl <sub>2</sub> + 0.5MgF <sub>2</sub>	$\approx -22$

play a role, and this is determined by the pair formation energies  $\Delta g_{A/FCI}$  of the reaction



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 quasi-chemical model in the quadruplet approximation<sup>[5]</sup> is applied to the Li, Na, K, Mg, Ca//F, Cl system with the parameters for the common-ion systems taken from the previous publications<sup>[2,3]</sup> and from the Appendix. To obtain quantitative fits, small empirical “reciprocal ternary parameters” are included. As described previously,<sup>[5]</sup> these parameters represent the Gibbs energies of formation of the ABXY quadruplets from the binary quadruplets according to



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:

$$\begin{aligned} \Delta g_{AB/XY} = & \Delta g_{AB/XY}^0 + \sum_{i \geq 1} [g_{AB/XY(AX)}^i X_{A_2/X_2}^i \\ & + g_{AB/XY(BX)}^i X_{B_2/X_2}^i + g_{AB/XY(AY)}^i X_{A_2/Y_2}^i \quad [5] \\ & + g_{AB/XY(BY)}^i X_{B_2/Y_2}^i] \end{aligned}$$

The empirical parameters  $\Delta g_{AB/XY}^0$  and  $g_{AB/XY(AX)}^i$ , 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 FNN and SNN SRO 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,<sup>[2,3]</sup> and in the Appendix, along with all SNN coordination numbers and Gibbs energies of pure compounds. Also in these publications<sup>[2,3]</sup> are the optimized model parameters for the (Li, Na,

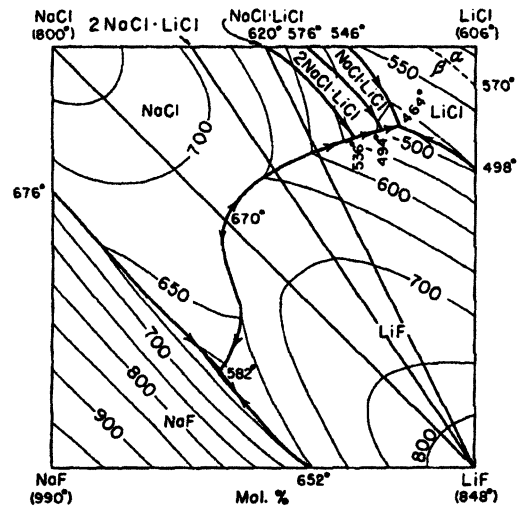


Fig. 1—Li, Na/F, Cl system: experimental liquidus projection of Bergman *et al.*<sup>[6]</sup>

K, [Mg]Cl, (Mg, [Li])Cl<sub>2</sub>, (Li, [Mg])F, (Mg, [Li])F<sub>2</sub>, (Na, [Li])F, ([Na], K)F, (Li, Na, K)(Mg, Ca)F<sub>3</sub>, (Li, Na, K)(Mg, Ca)Cl<sub>3</sub>, and (Li, Na, K)<sub>2</sub>(Mg, Ca)Cl<sub>4</sub> solid solutions and the optimized thermodynamic properties ( $\Delta H_{298.15K}^0$ ,  $S_{298.15K}^0$ , and  $C_p$ ) of all binary and ternary compounds. From the thermodynamic properties of the pure liquid salts,  $\Delta g_{AB/FCI}^{\text{exchange}}$  of reaction [2] for all ternary reciprocal subsystems can be calculated. Average values over the temperature range 400 °C <  $T < 1200$  °C are given in Table I.

In the previous publication,<sup>[5]</sup> “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:  $Z_{LiK/FCI}^{Li} = Z_{LiK/FCI}^{K} = Z_{LiK/FCI}^{F} = Z_{LiCa/FCI}^{Li} = 8$ ,  $Z_{LiCa/FCI}^{Ca} = Z_{LiCa/FCI}^{F} = Z_{LiCa/FCI}^{Cl} = 3$ , and  $Z_{LiCa/FCI}^{Ca} = 6$ ;  $Z_{NaMg/FCI}^{Na} = Z_{NaMg/FCI}^{F} = Z_{NaMg/FCI}^{Cl} = 3$  and  $Z_{NaMg/FCI}^{Mg} = 6$ ; and  $Z_{KCa/FCI}^{K} = Z_{KCa/FCI}^{F} = Z_{KCa/FCI}^{Cl} = 2$  and  $Z_{KCa/FCI}^{Ca} = 4$ . 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  $\zeta$ , defined in Eq. [23] of Reference 5 as

$$\zeta = 2Z/z \quad [6]$$

where  $z$  and  $Z$  are the FNN and SNN coordination numbers. In the present case, we have taken  $\zeta = 2.4$ .

## III. TERNARY RECIPROCAL SUBSYSTEMS

### A. The LiF-LiCl-NaF-NaCl System

The liquidus projection has been measured<sup>[6]</sup> (Figure 1). Gabcova and Malinovsky<sup>[7]</sup> measured the NaCl-NaF-LiF liquidus projection, reporting the eutectic at 604 °C instead of 582 °C.<sup>[6]</sup> The LiF-NaCl join has also been measured<sup>[6-11]</sup> and calculated (Figure 2). The liquidus surface is calculated (Figure 3) with a very small ternary reciprocal parameter:

$$\Delta g_{LiNa/FCI} = 1882.8X_{Li_2/F_2} \quad \text{J/mol} \quad [7]$$

### B. The LiF-LiCl-KF-KCl System

The liquidus projection has been measured<sup>[12]</sup> (Figure 4). The LiF-KCl join has been reported<sup>[9,12,13]</sup> (Figure 5) with

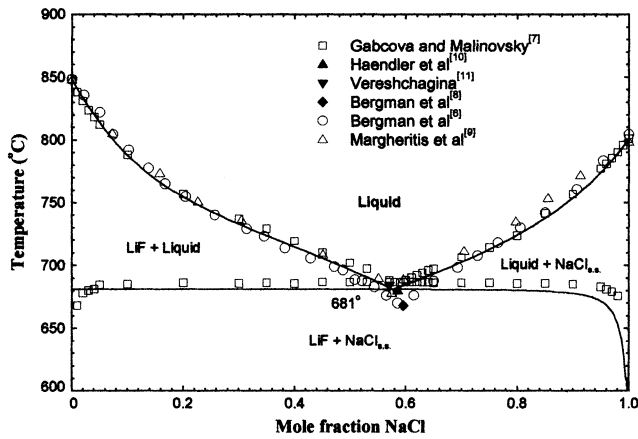


Fig. 2—Li, Na/F, Cl system: calculated LiF-NaCl join.

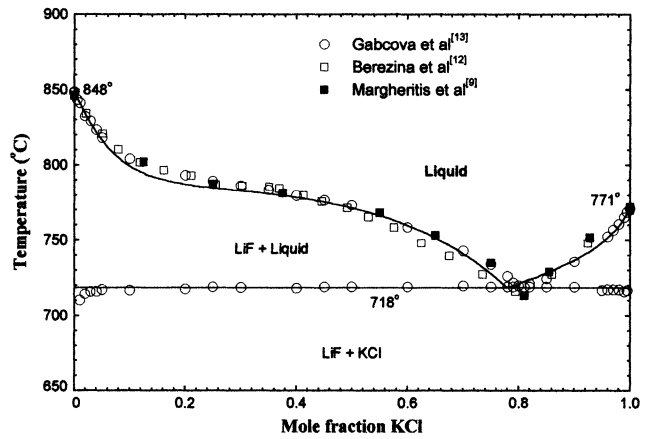


Fig. 5—Li, K/F, Cl system: calculated LiF-KCl join.

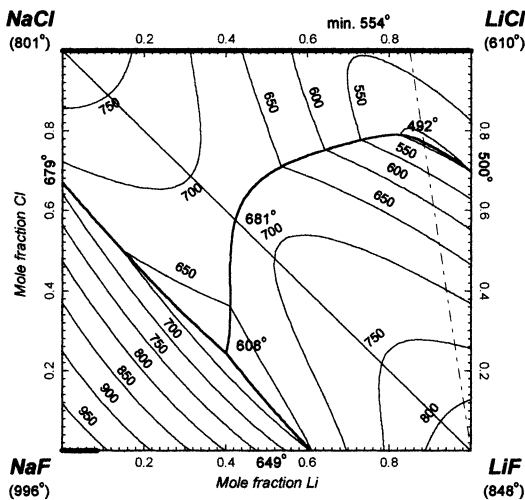


Fig. 3—Li, Na/F, Cl system: calculated liquidus projection.

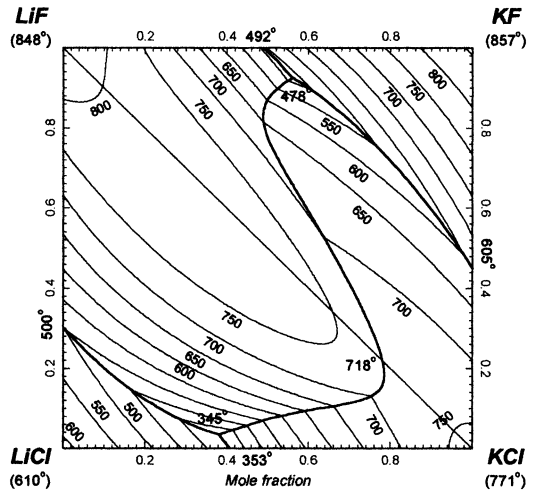


Fig. 6—Li, K/F, Cl system: calculated liquidus projection.

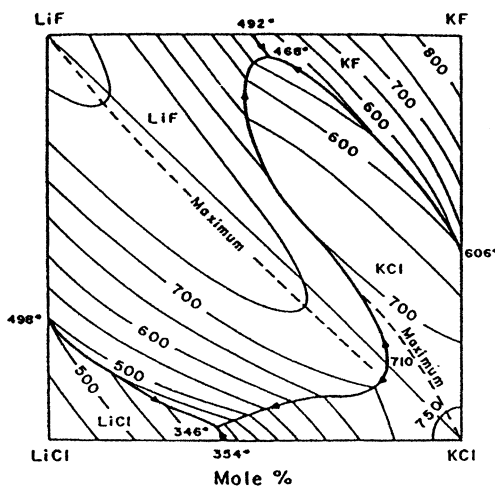


Fig. 4—Li, K/F, Cl system: experimental liquidus projection of Berezina *et al.*<sup>[12]</sup>

the eutectic at 719 °C,<sup>[13]</sup> 713 °C,<sup>[9]</sup> or 710 °C.<sup>[12]</sup> Zsigrai *et al.*<sup>[14]</sup> previously calculated the ternary liquidus projection with a sublattice model, which neglected all ordering (refer to the comments in Chartrand and Pelton<sup>[4]</sup>). 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:

$$\Delta g_{\text{LiK/FCI}} = -2928.8 + 2.9288T - 3347.2X_{\text{K}_2\text{Cl}_2} + 2092.0X_{\text{Li}_2\text{F}_2} \text{ J/mol} \quad [8]$$

Without these ternary reciprocal terms, the calculated LiF-KCl eutectic is 12 °C higher with a 2 mol pct displacement in composition, while the ternary eutectic temperatures are increased by 2 °C 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,<sup>[4]</sup> which accounted for FNN, but neglected SNN 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<sub>2</sub>-MgCl<sub>2</sub> System

No reported liquidus projection has been found for the Li, Mg/F, Cl system. The calculated LiCl-MgF<sub>2</sub> join is shown in Figure 7 with no additional reciprocal parameters.

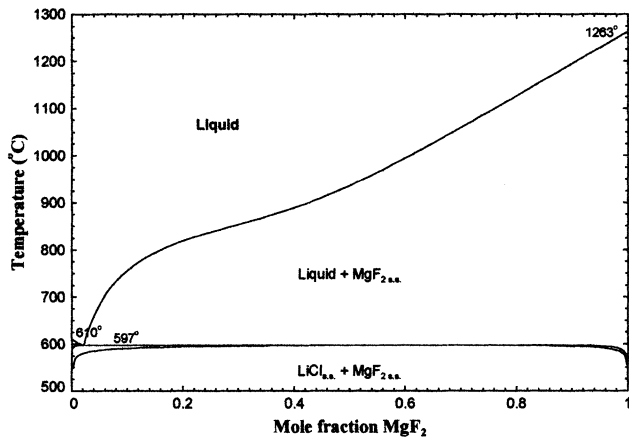


Fig. 7—Li, Mg/F, Cl system: calculated LiCl-MgF<sub>2</sub> join.

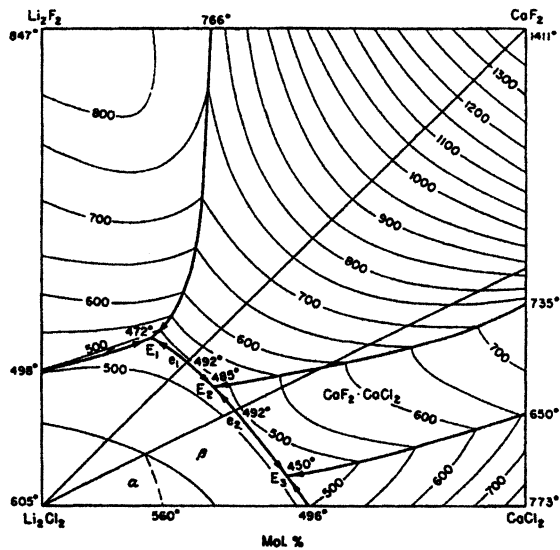


Fig. 8—Li, Ca/F, Cl system: experimental Li<sub>2</sub>Cl<sub>2</sub>-Li<sub>2</sub>F<sub>2</sub>-CaCl<sub>2</sub>-CaF<sub>2</sub> liquidus projection of Bukhalova and Bergman.<sup>[15]</sup>

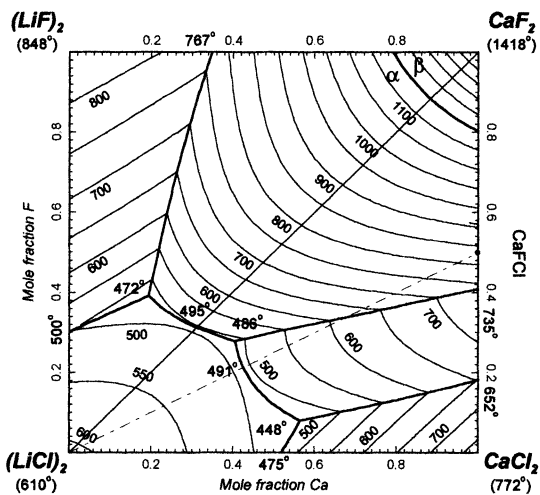


Fig. 9—Li, Ca/F, Cl system: calculated liquidus projection.

#### D. The LiF-LiCl-CaF<sub>2</sub>-CaCl<sub>2</sub> System

The liquidus projection has been measured<sup>[15]</sup> (Figure 8). The liquidus projection is calculated (Figure 9) assuming

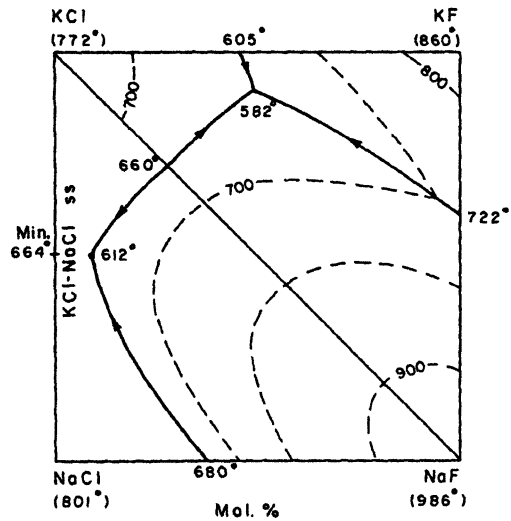


Fig. 10—Na, K/F, Cl system: experimental liquidus projection of Ishaque.<sup>[16]</sup>

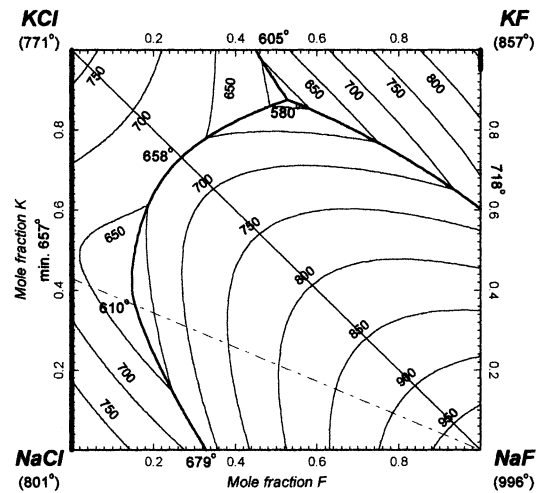


Fig. 11—Na, K/F, Cl system: calculated liquidus projection.

no reciprocal ternary solid solubility, with the following small excess ternary terms:

$$\Delta g_{\text{LiCa/FCI}} = -5506.0 + 4.184T \text{ J/mol} \quad [9]$$

#### E. The NaF-NaCl-KF-KCl System

The liquidus projection has been measured<sup>[16,17]</sup> (Figure 10<sup>[16]</sup>). 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<sub>2</sub>-MgCl<sub>2</sub> System

The liquidus along the NaCl-MgF<sub>2</sub> join has been measured.<sup>[18,19]</sup> There is disagreement between these authors on the MgF<sub>2</sub> liquidus on the NaCl-rich side. Sharma and Johnson<sup>[18]</sup> reported a higher MgF<sub>2</sub> solubility than Mediaias *et al.*<sup>[19]</sup> The exchange Gibbs energy for this system is large (Table I).

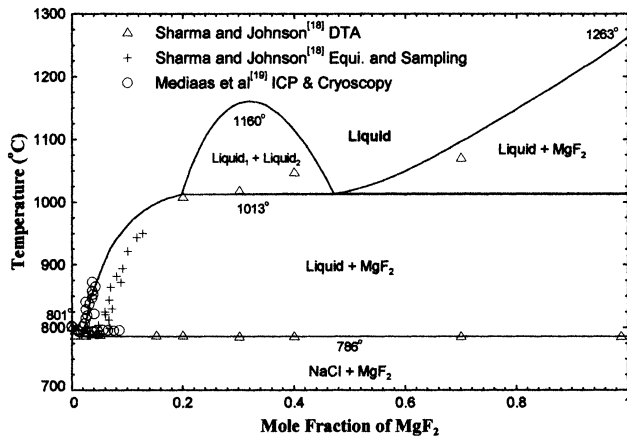


Fig. 12—Na, Mg/F, Cl system: calculated NaCl-MgF<sub>2</sub> join.

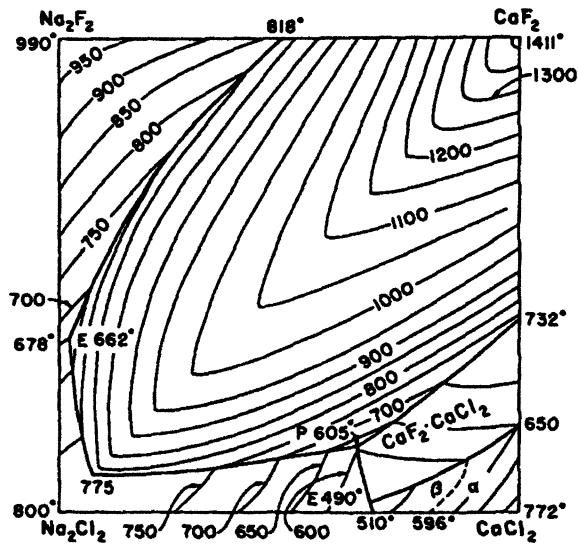


Fig. 13—Na, Ca/F, Cl system: experimental Na<sub>2</sub>F<sub>2</sub>-Na<sub>2</sub>Cl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> liquidus projection of Bukhalova.<sup>[20]</sup>

The NaCl-MgF<sub>2</sub> phase diagram was calculated previously<sup>[18]</sup> using the quasi-chemical model<sup>[4]</sup> in the pair approximation which accounts for FNN ordering, but neglects SNN ordering. The calculated NaCl-MgF<sub>2</sub> phase diagram, with the present model for the liquid phase, is shown in Fig. 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<sub>2</sub>-CaCl<sub>2</sub> System

The liquidus projection has been measured<sup>[20]</sup> (Figure 13). Malinovsky and Gregorcokova<sup>[21]</sup> measured the NaCl liquidus along the NaCl-CaF<sub>2</sub> join reporting the eutectic at 4.5 mol pct CaF<sub>2</sub> at 779.5 °C. The exchange Gibbs energy for this system is moderately large (Table I). The NaF-NaCl-CaF<sub>2</sub>-CaCl<sub>2</sub> liquidus projection was calculated previously<sup>[19]</sup> using the quasi-chemical model<sup>[4]</sup> in the pair approximation (neglecting SNN ordering). The calculated liquidus projection of the present work is shown in Figure 14. A very small empirical ternary excess term was included:

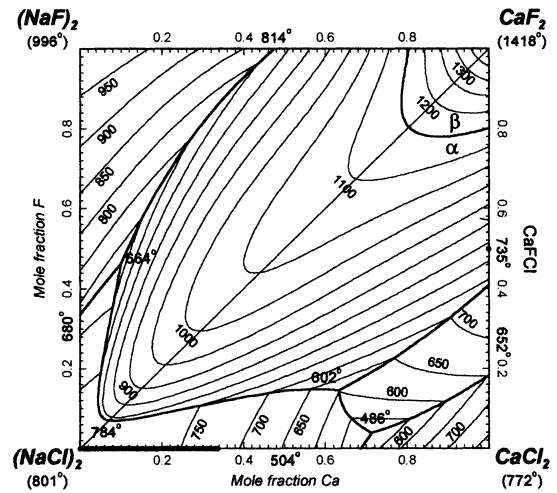


Fig. 14—Na, Ca/F, Cl system: calculated liquidus projection.

$$\Delta g_{\text{NaCa/FCI}} = -2092 \text{ J/mol} \quad [10]$$

The calculated eutectic on the NaCl-CaF<sub>2</sub> join is at 3.7 mol pct CaF<sub>2</sub> at 783 °C. No reciprocal ternary solid solubility was assumed.

#### H. The KF-KCl-MgF<sub>2</sub>-MgCl<sub>2</sub> 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 SNN ordering is very strong in the KCl-MgCl<sub>2</sub> subsystem<sup>[2]</sup> and in the KF-MgF<sub>2</sub> subsystem,<sup>[3]</sup> 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<sub>2</sub>-CaCl<sub>2</sub> System

The liquidus projection has been measured<sup>[16,22]</sup> (Figures 15<sup>[22]</sup> and 16<sup>[16]</sup>). Desyatnik *et al.*<sup>[23]</sup> measured the KCl-CaCl<sub>2</sub>-CaF<sub>2</sub> liquidus projection (Figure 17). A strong disagreement can be seen between the liquidus projections of Krause and Bergman<sup>[22]</sup> and Ishaque<sup>[16]</sup> at least for the liquidus along the KCl-CaF<sub>2</sub> join, although the reported invariant points agree very well in temperature. However, reported invariant point temperatures of Desyatnik<sup>[23]</sup> are around 20 °C lower than those reported by the other authors except for the KCl-CaF<sub>2</sub>-KCaCl<sub>3</sub> eutectic. The exchange Gibbs energy is very large (-78 kJ/equiv) for this system (Table I). One small ternary term was used:

$$\Delta g_{\text{KCa/FCI}} = -4.184T \text{ J/mol} \quad [11]$$

The calculated liquidus projection below 900 °C is shown in Figure 18. A liquid-liquid miscibility gap is calculated along the KCl-CaF<sub>2</sub> join for temperatures above 950 °C. Because of the large differences between the two measured diagrams and between the measured and the calculated diagrams in this region, the calculations above 950 °C are not shown in Figure 18. One can note that the calculated ternary

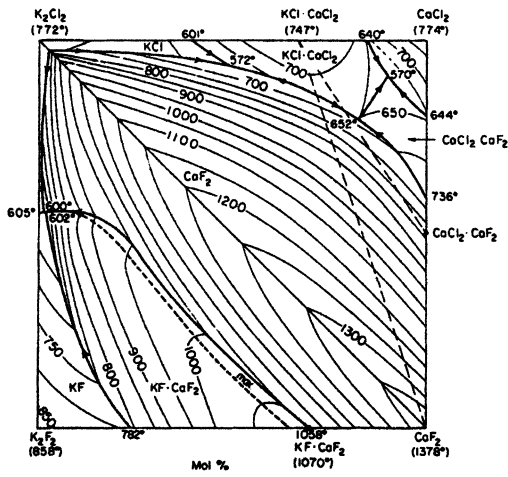


Fig. 15—K, Ca/F, Cl system: experimental  $K_2F_2$ - $K_2Cl_2$ - $CaCl_2$  liquidus projection of Krause and Bergman.<sup>[22]</sup>

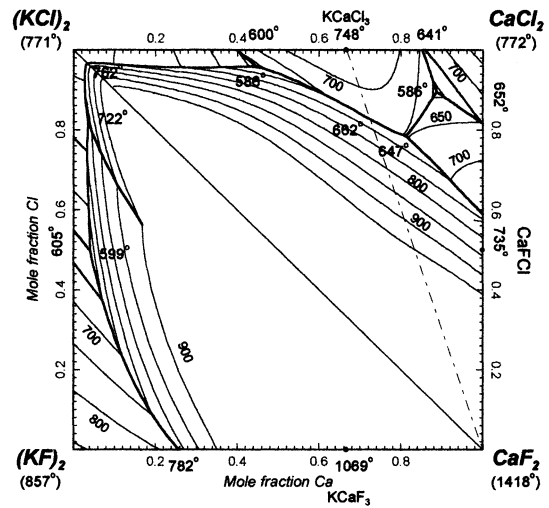


Fig. 18—K, Ca/F, Cl system: calculated liquidus projection (below 900 °C).

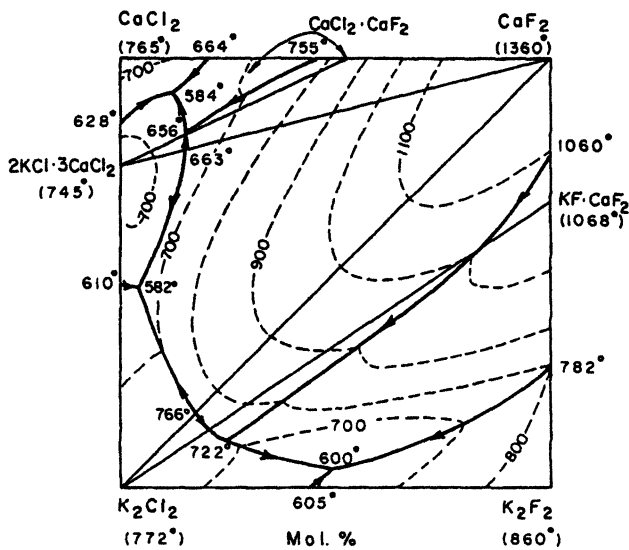


Fig. 16—K, Ca/F, Cl system: experimental  $K_2F_2$ - $K_2Cl_2$ - $CaF_2$ - $CaCl_2$  liquidus projection of Ishaque.<sup>[16]</sup>

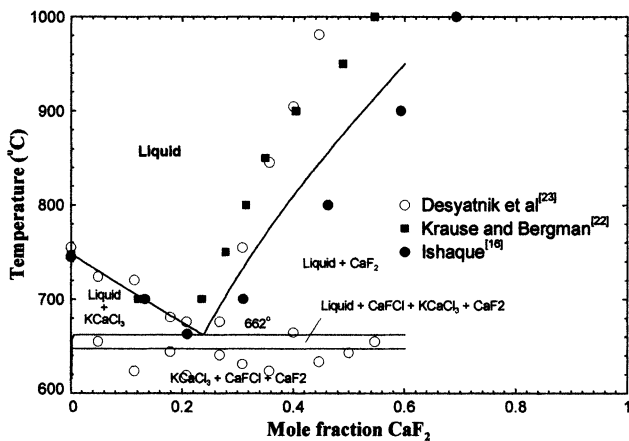


Fig. 17—K, Ca/F, Cl system: calculated  $KCaCl_3$ - $CaF_2$  join (partial).

invariant points are in good agreement in temperature with the reported points.<sup>[16]</sup>  $KCaCl_3$  and  $KCaF_3$  were assumed

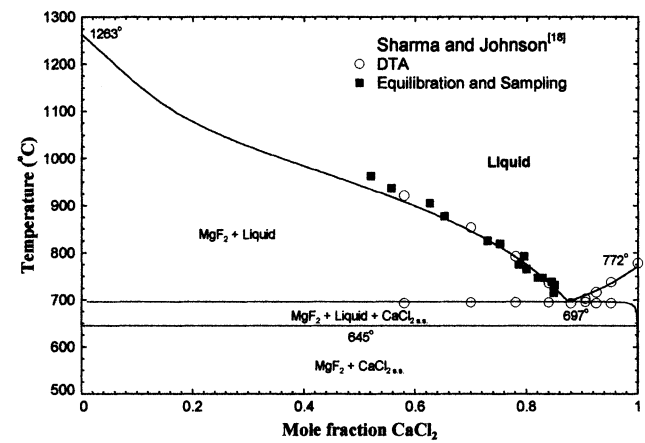


Fig. 19—Mg, Ca/F, Cl system: calculated  $MgF_2$ - $CaCl_2$  join.

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<sup>[18]</sup> (Figure 19). The phase diagram was calculated previously<sup>[24]</sup> with a model<sup>[25]</sup> for the liquid phase assuming random mixing of ions on their respective sublattices. Because FNN 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:

$$\Delta g_{MgCa/Cl} = -7305.0 + 8.3680T \text{ J/mol} \quad [12]$$

### 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

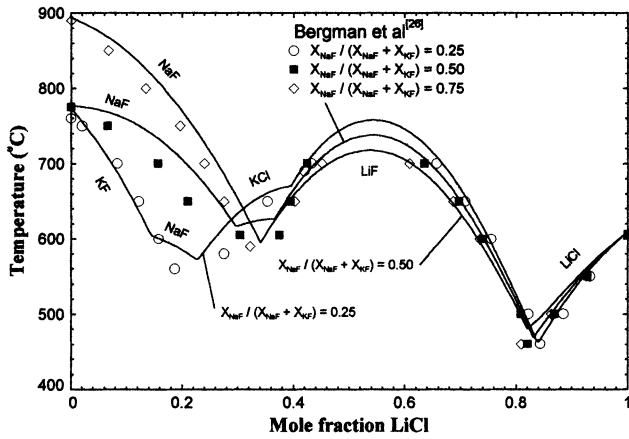


Fig. 20—Li, Na, K/F, Cl system: calculated liquidus lines of the LiCl-NaF-KF isopleth for constant NaF/(NaF + KF) molar ratios of 0.25, 0.50, and 0.75.

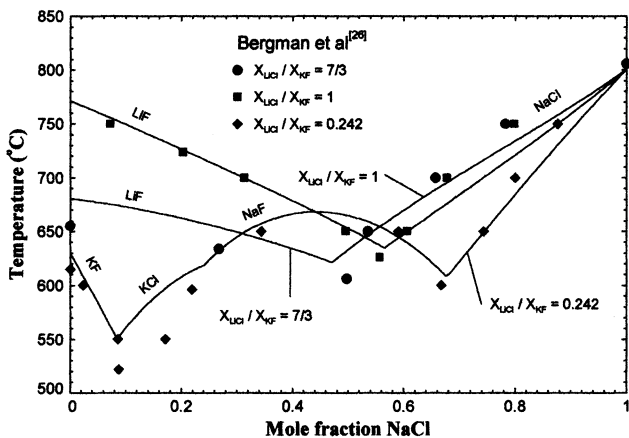


Fig. 21—Li, Na, K/F, Cl system: calculated liquidus lines of the LiCl-NaCl-KF isopleth for constant LiCl/KF molar ratios of 7/3, 1.0, and 0.242 (labels on lines indicate the primary solid phases).

liquid model. Hence, the calculated values in this section 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<sup>[26]</sup> 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<sup>[27]</sup> and by thermal analysis.<sup>[28]</sup> The LiF-NaCl-KCl liquidus projection has also been measured.<sup>[27,29]</sup> Univariant line compositions and temperatures of the LiF-NaF-KCl<sup>[27,28]</sup> and LiF-NaCl-KCl<sup>[27,29]</sup> systems

Table II. Points on Univariant Line in the LiF-NaF-KCl Liquidus Projection

Composition (Mol Pct)				Reference
LiF	NaF	KCl	T (°C)	
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 Pct)				Reference
LiF	NaCl	KCl	T (°C)	
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.

are given in Tables II and III with the corresponding calculated points. These measured<sup>[27,28,29]</sup> points were obtained by starting with a mixture of two salts and then adding a

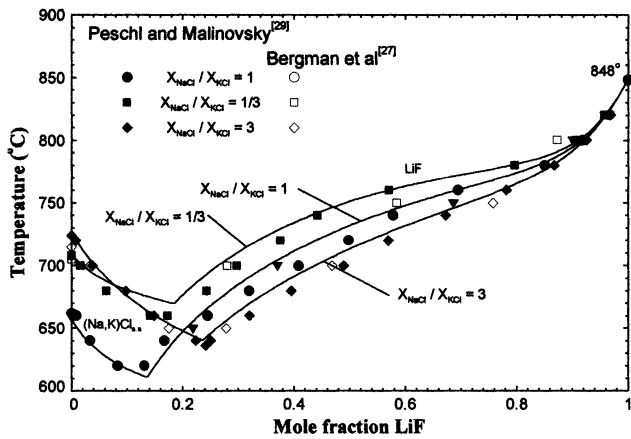


Fig. 22—Li, Na, K/F, Cl system: calculated liquidus lines of the LiF-NaCl-KCl isopleth for constant NaCl / KCl molar ratios of 1/3, 1.0, and 3 (labels on lines indicate the primary solid phases).

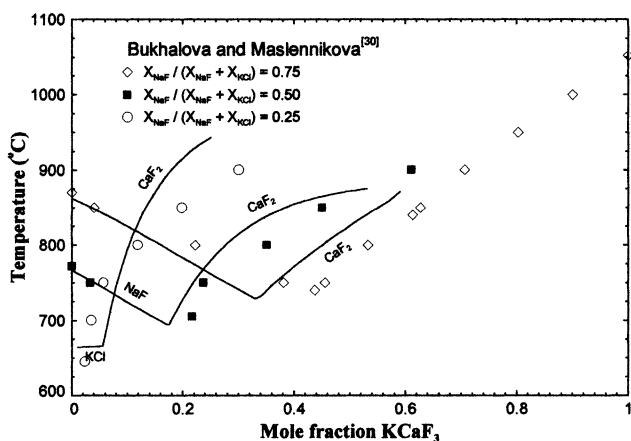


Fig. 23—Na, K, Ca/F, Cl system: calculated liquidus lines of the (NaF)<sub>2</sub>-(KCl)<sub>2</sub>-KCaF<sub>3</sub> isopleth for constant NaF/(NaF + KCl) molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

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 the calculations, essentially within the experimental error limits.

### B. The Na, K, Ca//F, Cl System

The (NaF)<sub>2</sub>-(KCl)<sub>2</sub>-KCaF<sub>3</sub> and the (NaF)<sub>2</sub>-(KCl)<sub>2</sub>-CaF<sub>2</sub> liquidus projections have been measured<sup>[30]</sup> 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<sup>[31]</sup> 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

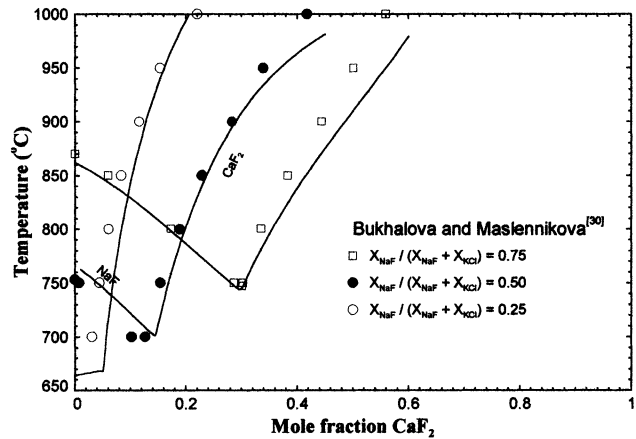


Fig. 24—Na, K, Ca/F, Cl system: calculated liquidus lines of the (NaF)<sub>2</sub>-(KCl)<sub>2</sub>-CaF<sub>2</sub> isopleth for constant NaF/(NaF + KCl) molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

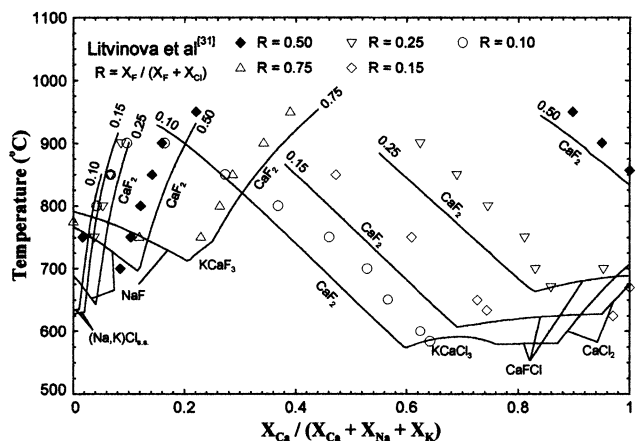


Fig. 25—Na, K, Ca/F, Cl system: calculated liquidus lines on constant F/(F + Cl) molar ratio isopleths of 0.10, 0.15, 0.25, 0.50, and 0.75 along the (NaX + KX) - CaX<sub>2</sub> join (with X = F, Cl) (labels on lines indicate the primary solid phases).

temperature (by around 5 °C 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 through 18).

### C. The Li, K, Ca//F, Cl System

Various quaternary reciprocal sections of the Li, K, Ca//F, Cl system have been measured<sup>[34,35]</sup> by the visual-polythermal method. Points extracted from reported liquidus projections<sup>[34,35]</sup> on these sections are shown in Figures 26 through 30. Agreement is acceptable except in composition regions where the CaF<sub>2</sub> 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<sup>[36]</sup> by the visual-polythermal



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)	
	Experimental	Calculated
KCaCl <sub>3</sub> + CaCl <sub>2</sub> + CaFCl	570, <sup>[22,31]</sup> 584 <sup>[16]</sup>	585.8
(Na, [K,Ca])Cl <sub>ss</sub> + KCaCl <sub>3</sub> + CaFCl	530 <sup>[31]</sup>	542.6
(Na, [Ca])Cl <sub>ss</sub> + CaCl <sub>2</sub> + CaFCl	490 <sup>[31]</sup>	486.0
(Na, [K,Ca])Cl <sub>ss</sub> + KCaCl <sub>3</sub> + CaCl <sub>2</sub>	465, <sup>[31]</sup> 504 <sup>[32]</sup>	477.1
KCaCl <sub>3</sub> + CaFCl + CaF <sub>2</sub>	652, <sup>[22,31]</sup> 656 <sup>[16]</sup>	647.3
(Na, [K,Ca])Cl <sub>ss</sub> + KCaCl <sub>3</sub> + CaFCl	527 <sup>[31]</sup>	515.4
(Na, [Ca])Cl <sub>ss</sub> + CaFCl + CaF <sub>2</sub>	605 <sup>[31]</sup>	601.4
(Na, [K,Ca])Cl <sub>ss</sub> + KCaCl <sub>3</sub> + CaF <sub>2</sub> + CaFCl	533 <sup>[31]</sup>	542.6
(Na, [K,Ca]) <sub>ss</sub> + KCaCl <sub>3</sub> + CaFCl + CaCl <sub>2</sub>	460 <sup>[31]</sup>	464.5
(Na, K)Cl <sub>ss</sub> + KCaCl <sub>3</sub> + CaF <sub>2</sub>	506 <sup>[31]</sup>	525.4
KCl + KCaCl <sub>3</sub> + CaF <sub>2</sub>	572, <sup>[22,31]</sup> 582 <sup>[16]</sup>	586.4
(Na, K)Cl <sub>ss</sub> + KCaCl <sub>3</sub> (min)	513 <sup>[31]</sup>	535.6
(K, Na)Cl <sub>ss</sub> + KCaF <sub>3</sub> + NaF + CaF <sub>2</sub>	652 <sup>[31]</sup>	648.2
(Na, K)Cl <sub>ss</sub> + NaF + CaF <sub>2</sub>	590 <sup>[31]</sup>	605.9
NaF + NaCl + CaF <sub>2</sub>	662 <sup>[20,31]</sup>	663.8
(Na, K)Cl <sub>ss</sub> + NaF (min)	606, <sup>[31]</sup> 612 <sup>[16]</sup>	610.0
KCaF <sub>3</sub> + NaF + CaF <sub>2</sub>	758, <sup>[31]</sup> 759 <sup>[33]</sup>	761.7
KCl + KCaF <sub>3</sub> + CaF <sub>2</sub>	602, <sup>[22,31]</sup> 722 <sup>[16]</sup>	722.3
(K, [Na])F <sub>ss</sub> + (Na, K)Cl <sub>ss</sub> + KCaF <sub>3</sub> + NaF	564, <sup>[31]</sup> 574*	573.4
KF + KCl + KCaF <sub>3</sub>	600, <sup>[22,31]</sup> 600 <sup>[16]</sup>	599.3
(K, [Na])F <sub>ss</sub> + (Na, K)Cl <sub>ss</sub> + NaF	570, <sup>[31]</sup> 582 <sup>[16]</sup>	580.4
(K, [Na])F <sub>ss</sub> + KCaF <sub>3</sub> + NaF	683, <sup>[31]</sup> 676 <sup>[33]</sup>	678.7

\*A thermal arrest at 574 °C is also reported by Litvinova.<sup>[31]</sup>

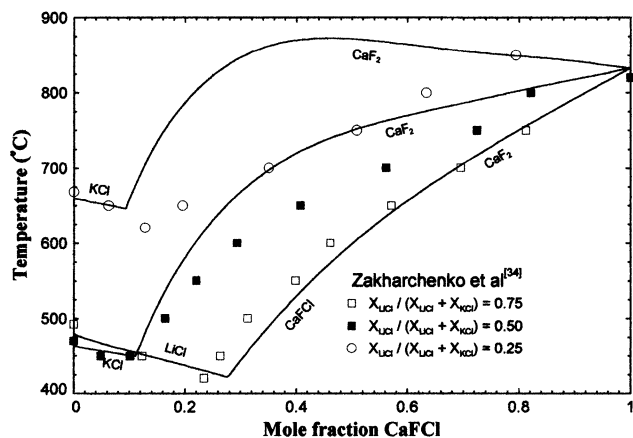


Fig. 26—Li, K, Ca/F, Cl system: calculated liquidus lines of the (LiCl)<sub>2</sub>-(KCl)<sub>2</sub>-CaFCl isopleth for constant LiCl/(LiCl + KCl) molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

method. Points extracted from reported liquidus projections<sup>[36]</sup> on these sections are shown in Figures 31 through 33. Agreement is good except in composition regions where the CaF<sub>2</sub> liquidus is very steep such that a small change in the Ca/Na ratio corresponds to a relatively large change in liquidus temperature.

Khaidikova *et al.*<sup>[37]</sup> 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<sub>2</sub> and LiNa<sub>2</sub>Cl<sub>3</sub> compounds reported by Khaidikova *et al.*<sup>[37]</sup> were not considered to be stable compounds in the thermodynamic evaluation<sup>[2]</sup> of the LiCl-NaCl system, but instead, a complete solid solution between LiCl and NaCl was proposed. Consequently, the reported invariant points of Khaidikova *et al.*<sup>[37]</sup>

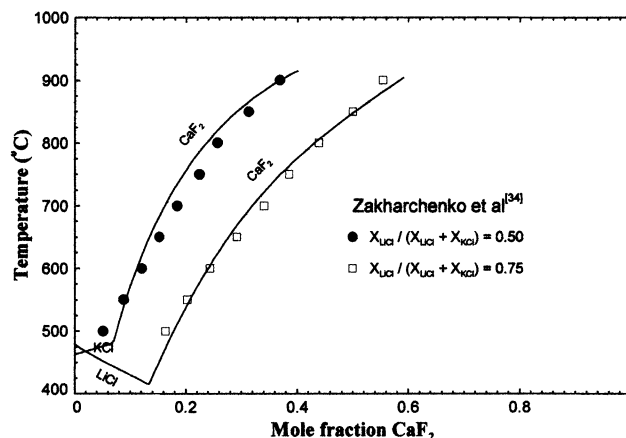


Fig. 27—Li, K, Ca/F, Cl system: calculated liquidus lines of the (LiCl)<sub>2</sub>-(KCl)<sub>2</sub>-CaF<sub>2</sub> isopleth for constant LiCl/(LiCl + KCl) molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

in Table V noted with an asterisk 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.

#### E. The Na, Mg, Ca/F, Cl System

Mediaas *et al.*<sup>[19]</sup> measured by cryoscopy-differential thermal analysis the first and second crystallization temperatures of 24 mixtures in the NaCl-MgCl<sub>2</sub>-CaCl<sub>2</sub>-CaF<sub>2</sub> system, and also performed calculations using the quasi-chemical model<sup>[4]</sup> in the pair approximation (accounting for FNN ordering, but neglecting SNN ordering). Calculations of the present model (which takes into account both FNN and SNN ordering) are given in Table VI along with the experimental

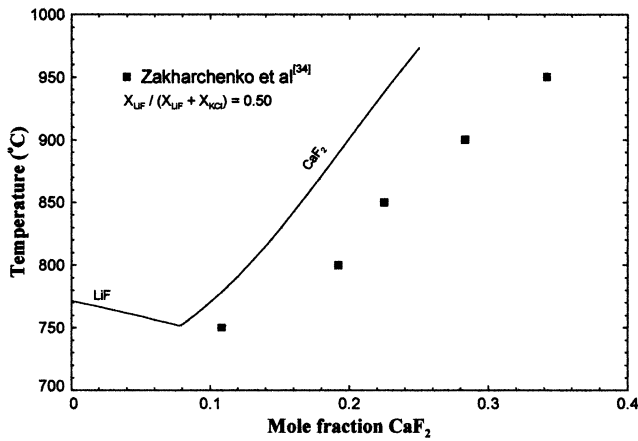


Fig. 28—Li, K, Ca/F, Cl system: calculated liquidus line of the  $(\text{LiF})_2$ - $(\text{KCl})_2$ - $\text{CaF}_2$  isopleth for constant  $\text{LiF}/(\text{LiF} + \text{KCl})$  molar ratio of 0.5 (labels on lines indicate the primary solid phases).

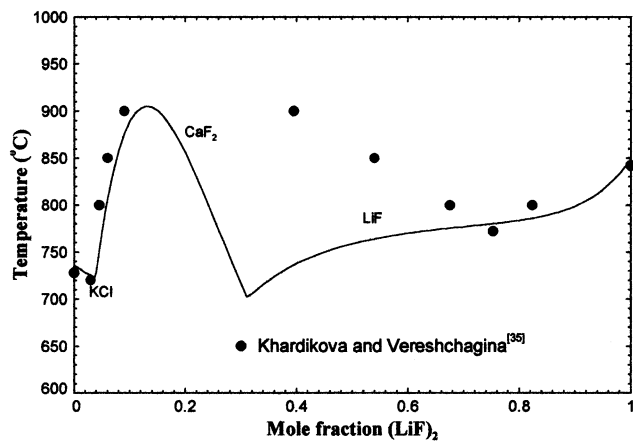


Fig. 29—Li, K, Ca/F, Cl system: calculated [15 pct  $\text{CaCl}_2$  + 85 pct  $\text{K}_2\text{Cl}_2$ ]- $(\text{LiF})_2$  liquidus (labels on lines indicate the primary solid phases).

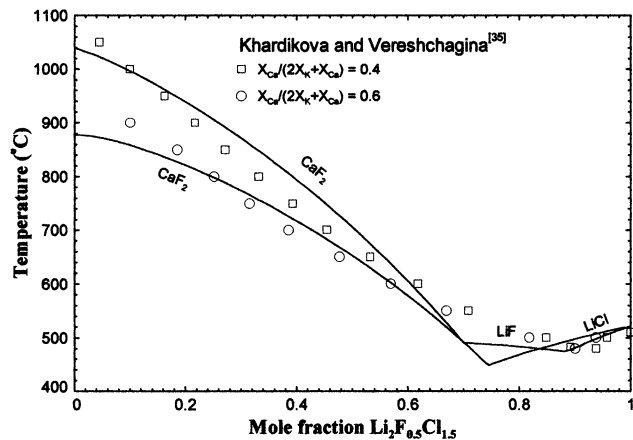


Fig. 30—Li, K, Ca/F, Cl system: calculated liquidus lines of the  $\text{F}/(\text{F} + \text{Cl})$  constant 0.25 molar ratio isopleth for constant  $\text{Ca}/(\text{Ca} + \text{K})$  molar ratios of 0.4 and 0.6 (labels on lines indicate the primary solid phases).

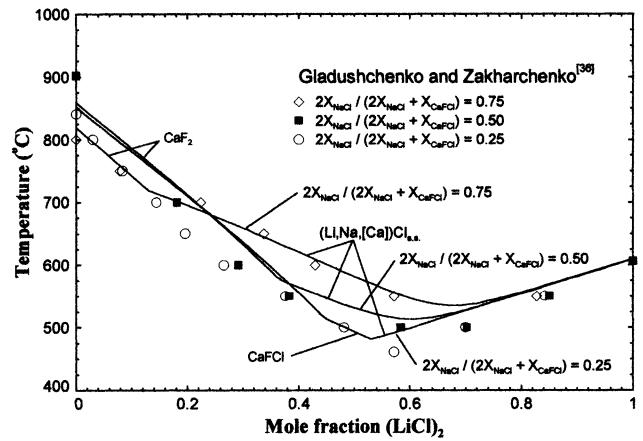


Fig. 31—Li, Na, Ca/F, Cl system: calculated liquidus lines of the  $(\text{LiCl})_2$ - $(\text{NaCl})_2$ - $\text{CaFCl}$  isopleth for constant  $\text{Ca}/(\text{Ca} + 2\text{Na})$  molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

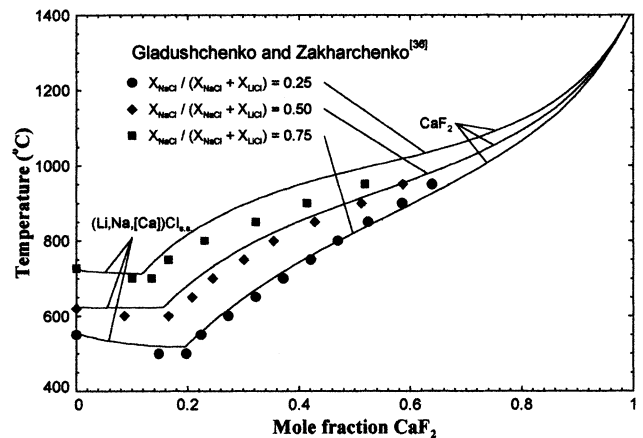


Fig. 32—Li, Na, Ca/F, Cl system: calculated liquidus lines of the  $(\text{LiCl})_2$ - $(\text{NaCl})_2$ - $\text{CaF}_2$  isopleth for constant  $\text{LiCl}/(\text{LiCl} + \text{NaCl})$  molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

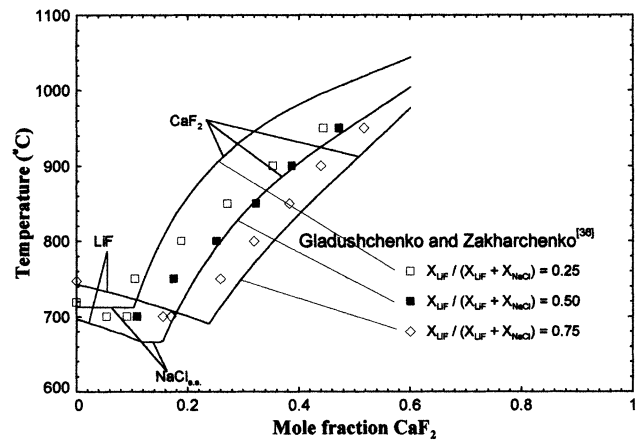


Fig. 33—Li, Na, Ca/F, Cl system: calculated liquidus lines of the  $(\text{LiF})_2$ - $(\text{NaCl})_2$ - $\text{CaF}_2$  isopleth for constant  $\text{LiF}/(\text{LiF} + \text{NaCl})$  molar ratios of 0.25, 0.50, and 0.75 (labels on lines indicate the primary solid phases).

points.<sup>[19]</sup> The calculations are in very good agreement with the experiments, especially for secondary crystallization temperatures.

## V. CONCLUSIONS

The modified quasi-chemical model in the quadruplet approximation<sup>[5]</sup> has been applied to the liquid phase of

**Table V. Experimental<sup>[37]</sup> and Calculated Quaternary Invariant Points of the Li, Na, Ca/F, Cl System**

Solid Phases in Equilibrium with Liquid	Experimental <sup>[37]</sup> $T$ (°C)	Calculated $T$ (°C)
(Na, [Li])F <sub>ss</sub> + (Na, [Li])Cl <sub>ss</sub> + LiF + CaF <sub>2</sub>	542	584.9
(Li, Na)Cl <sub>ss</sub> + LiF + CaF <sub>2</sub>	432	463.2
(Li, Na)Cl <sub>ss</sub> + LiF + CaF <sub>2</sub>	451*	475.4 (min)
(Li, Na)Cl <sub>ss</sub> + LiF + CaF <sub>2</sub>	469*	479.0 (min)
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaF <sub>2</sub>	420	480.1
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaF <sub>2</sub>	435*	481.0 (min)
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaF <sub>2</sub>	455*	482.3
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaCl <sub>2</sub>	410	422.8
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaCl <sub>2</sub>	423*	421.5 (min)
(Li, Na)Cl <sub>ss</sub> + CaFCl + CaCl <sub>2</sub>	437*	421.5 (min)

\*LiNaCl<sub>2</sub> and LiNa<sub>2</sub>Cl<sub>3</sub> pure solids are reported<sup>[37]</sup> instead of the (Li, Na)Cl solid solution as used for calculations. Calculated temperatures are minima of univariant lines.

**Table VI. Experimental<sup>[19]</sup> and Calculated Primary, Secondary, and Tertiary Crystallization Temperatures of the NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub> System**

Composition (Wt pct)				$T_{exp}$ (°C)			$T_{calc}$ (°C)			Calculated Precipitating Phases
CaCl <sub>2</sub>	NaCl	MgCl <sub>2</sub>	CaF <sub>2</sub>	$T_1$	$T_2$	$T_3$	$T_1$	$T_2$	$T_3$	
59.84	40.15	0	0	561	—	—	572	504	—	NaCl <sub>ss</sub>
59.82	40.18	0	0	556	499	—	573	504	—	NaCl <sub>ss</sub>
56.85	38.14	5.00	0	527	—	—	534	488	—	NaCl <sub>ss</sub>
56.80	38.14	5.01	0	518	—	—	535	488	—	NaCl <sub>ss</sub>
53.99	36.23	4.75	5.03	—	541	—	641	547	488	MgF <sub>2</sub> + NaCl <sub>ss</sub>
53.91	36.31	4.75	5.03	651	535	—	641	548	488	MgF <sub>2</sub> + NaCl <sub>ss</sub>
51.11	34.29	4.50	10.09	—	574	—	689	567	556	MgF <sub>2</sub> + CaFCl
51.03	34.37	4.50	10.10	700	570	553	689	567	556	MgF <sub>2</sub> + CaFCl
48.16	32.31	10.01	9.51	—	517	—	734	523	488	MgF <sub>2</sub> + NaCl <sub>ss</sub>
48.17	32.34	10.01	9.48	748	514	484	734	524	488	MgF <sub>2</sub> + NaCl <sub>ss</sub>
45.48	30.51	15.03	8.98	—	483	—	736	486	484	MgF <sub>2</sub> + CaFCl + NaCl <sub>ss</sub>
45.46	30.57	15.03	8.95	753	483	481	736	486	484	MgF <sub>2</sub> + CaFCl + NaCl <sub>ss</sub>
39.98	60.02	0	0	683	—	—	690	504	—	NaCl <sub>ss</sub>
37.95	56.98	5.07	0	654	—	—	665	470	—	NaCl <sub>ss</sub>
37.56	56.38	5.02	1.05	654	—	—	665	547	472	NaCl <sub>ss</sub>
37.19	55.84	4.97	2.00	657	—	—	665	611	479	NaCl <sub>ss</sub>
36.07	54.17	4.81	4.94	696	—	—	690	667	492	MgF <sub>2</sub>
35.11	52.71	4.69	7.49	726	—	—	716	668	564	MgF <sub>2</sub>
34.11	51.28	4.56	9.99	736	—	—	722	669	589	MgF <sub>2</sub>
32.22	48.37	9.98	9.43	—	640	—	770	646	494	MgF <sub>2</sub> + NaCl <sub>ss</sub>
30.42	45.67	15.00	8.90	—	610	—	772	616	477	MgF <sub>2</sub> + NaCl <sub>ss</sub>
50.08	49.92	0	0	627	—	—	639	504	—	NaCl <sub>ss</sub>
50.09	49.91	0	0	626	—	—	638	504	—	NaCl <sub>ss</sub>
47.57	47.42	5.01	0	594	—	—	608	482	—	NaCl <sub>ss</sub>
47.04	46.89	4.95	1.11	596	—	—	609	514	481	NaCl <sub>ss</sub>
46.60	46.45	4.90	2.05	598	—	—	610	576	485	NaCl <sub>ss</sub>
45.20	45.05	4.76	5.00	—	603	—	664	614	487	MgF <sub>2</sub> + NaCl <sub>ss</sub>
45.20	45.06	4.74	4.99	671	602	—	663	614	486	MgF <sub>2</sub> + NaCl <sub>ss</sub>
44.01	43.87	4.63	7.48	—	607	—	693	616	545	MgF <sub>2</sub> + NaCl <sub>ss</sub>
44.01	43.90	4.62	7.48	705	606	—	693	616	545	MgF <sub>2</sub> + NaCl <sub>ss</sub>
42.79	42.65	4.50	10.05	—	609	—	704	617	576	MgF <sub>2</sub> + NaCl <sub>ss</sub>
42.77	42.69	4.49	10.05	714	609	—	704	617	576	MgF <sub>2</sub> + NaCl <sub>ss</sub>
40.29	40.16	10.09	9.46	—	581	—	751	591	487	MgF <sub>2</sub> + NaCl <sub>ss</sub>
40.24	40.19	10.12	9.45	767	581	—	751	591	487	MgF <sub>2</sub> + NaCl <sub>ss</sub>
38.07	37.95	15.04	8.94	—	547	—	753	557	481	MgF <sub>2</sub> + NaCl <sub>ss</sub>
38.03	38.01	15.03	8.93	766	544	—	753	557	481	MgF <sub>2</sub> + NaCl <sub>ss</sub>

the LiF-LiCl-NaF-NaCl-KF-KCl-MgF<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> system. Model parameters obtained previously<sup>[2,3]</sup> 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 pct 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 FNN and SNN SRO and the coupling between them. Calculations were performed previously in these systems using the quasi-chemical model in the pair approximation, which takes account only of FNN ordering. The present model gives significantly improved predictions over those obtained previously.

The model predictions for the LiF-LiCl-NaF-NaCl-KF-KCl-MgF<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> system are very satisfactory considering that (1) the Gibbs energies for the FNN exchange reactions (Table I) are very negative in many cases, thereby inducing a large degree of FNN SRO and (2) several binary systems (such as KCl-MgCl<sub>2</sub>) exhibit strong SNN SRO. That is, the LiF-LiCl-NaF-NaCl-KF-KCl-MgF<sub>2</sub>-MgCl<sub>2</sub>-CaF<sub>2</sub>-CaCl<sub>2</sub> system provides a severe test of the model.

The model parameters are stored in the database of the F\*A\*C\*T<sup>[44]</sup> 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 extend the database, through further evaluations/optimizations, to include other anions (NO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, O<sup>2-</sup>, Br<sup>-</sup>, I<sup>-</sup>) and cations (Rb<sup>+</sup>, Cs<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Cd<sup>2+</sup>, . . . , Al<sup>3+</sup>, La<sup>3+</sup>, . . .). 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 SRO in the molten salt solution.

### 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)
$\Delta g_{A/FCI}$	Gibbs energy of the common-cation pair-exchange reaction: (F - [A] - F) + (Cl - [A] - Cl) = 2 (F - [A] - Cl)
$\Delta g_{AB/FCI}^{\text{exchange}}$	Gibbs energy of the exchange reaction: AF + BCl = ACl + BF
$\Delta g_{AB/XY}$	Gibbs energy of formation of ABXY quadruplet from ABX <sub>2</sub> , ABY <sub>2</sub> , A <sub>2</sub> XY, and B <sub>2</sub> XY, quadruplets: 1/2(ABX <sub>2</sub> + ABY <sub>2</sub> + A <sub>2</sub> XY + B <sub>2</sub> XY) = 2ABXY
$g_{AB/XY(Ax)}^i$	parameter giving the influence of FNN 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 <sub>2</sub> X <sub>2</sub> "unary" quadruplets
$X_{AB/X_2}$	mole fraction of ABX <sub>2</sub> "binary" quadruplets
$X_{A_2/XY}$	mole fraction of A <sub>2</sub> XY "binary" quadruplets
$X_{AB/XY}$	mole fraction of ABXY "reciprocal" quadruplets
$z_i$	FNN coordination number of ion <i>i</i>
$Z_i$	SNN coordination number of ion <i>i</i>
$Z_{ABXY}^A$	SNN coordination number of ion A in a hypothetical solution formed only of ABXY quadruplets

$\zeta$	number of quadruplets emanating from a pair ( $\zeta = 2.4$ in this work)
$\chi_{FCI}$	$\chi_{FCI} = X_{A_2F_2}$
$\chi_{CIF}$	$\chi_{CIF} = X_{A_2Cl_2}$

### ACKNOWLEDGMENTS

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### APPENDIX

#### Evaluation/Optimization of Common-Cation Binary Systems

The LiF-LiCl, NaF-NaCl, KF-KCl, MgF<sub>2</sub>-MgCl<sub>2</sub>, and CaF<sub>2</sub>-CaCl<sub>2</sub> systems were optimized previously<sup>[24,38]</sup> with a random-mixing (Bragg-Williams) entropy and a polynomial expansion for the excess Gibbs energy. They are reoptimized here with the quasi-chemical model. Second-nearest-neighbor coordination numbers are  $Z_{FCI}^F = Z_{FCI}^{Cl} = 6$  for common-alkali systems and  $Z_{FCI}^F = Z_{FCI}^{Cl} = 3$  for common-alkaline-earth systems. As defined previously,<sup>[1]</sup> in these binary systems,  $\chi_{FCI}$  and  $\chi_{CIF}$  are equal to the SNN pair fractions. In all systems, solid solubility is assumed to be negligible.

#### A. The LiF-LiCl System

The phase diagram has been measured<sup>[10]</sup> (Figure 34). Calorimetric measurements are available<sup>[39]</sup> (Figure 35). Figures 34 and 35 show the phase diagram and thermodynamic properties. The optimized energy of formation of F-Li-Cl SNN pairs is

$$\Delta g_{Li/FCI} = -736.4 + 0.2802T + 740.6\chi_{FCI} + 236.1\chi_{CIF} \quad \text{J/mol} \quad [A1]$$

#### B. The NaF-NaCl System

The phase diagram has been measured<sup>[40,41]</sup> (Figure 36). Calorimetric measurements are available<sup>[39]</sup> (Figure 35). Figures 35 and 36 show the phase diagram and thermodynamic properties. The optimized energy of formation of F-Na-Cl SNN pairs is

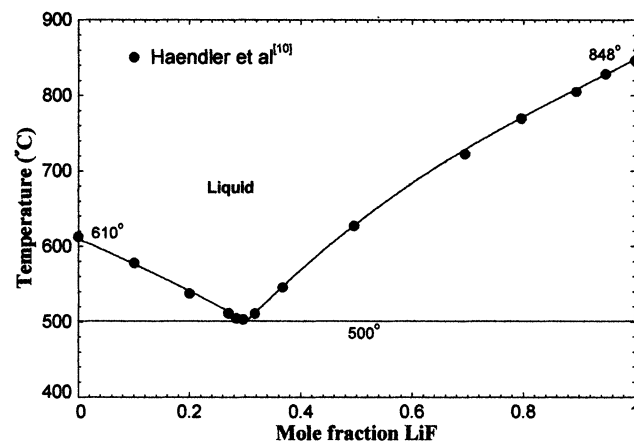


Fig. 34—LiCl-LiF system: calculated phase diagram.

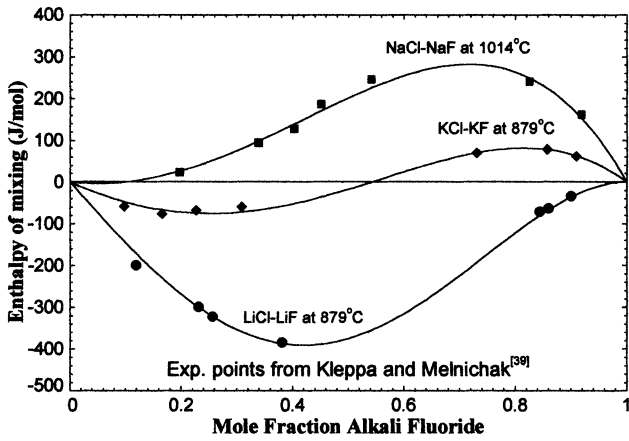


Fig. 35—Alkali chloride-alkali fluoride systems: calculated enthalpy of mixing of the liquid with experimental points of Kleppa and Melnichak.<sup>[39]</sup>

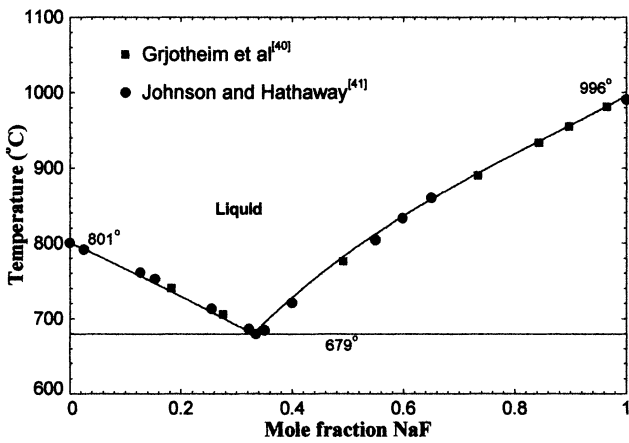


Fig. 36—NaCl-NaF system: calculated phase diagram.

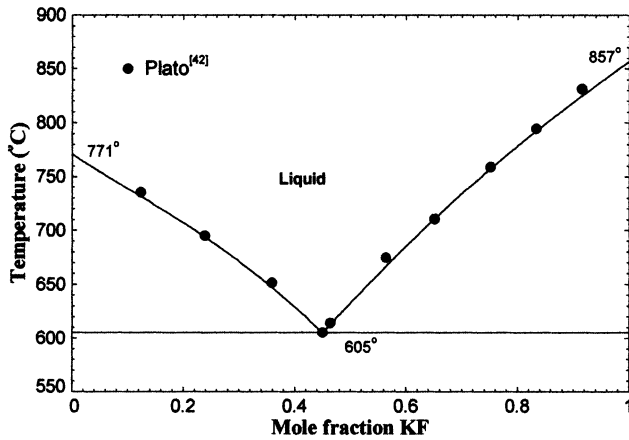


Fig. 37—KCl-KF system: calculated phase diagram.

$$\Delta g_{\text{Na/FCI}} = 174.0 + 0.4623T + 611.2\chi_{\text{FCI}} - 222.6\chi_{\text{CIF}} \quad \text{J/mol} \quad [\text{A2}]$$

### C. The KF-KCl System

The phase diagram has been measured<sup>[42]</sup> (Figure 37). Calorimetric measurements are available<sup>[39]</sup> (Figure 35). Figures 35 and 37 show the phase diagram and thermodynamic

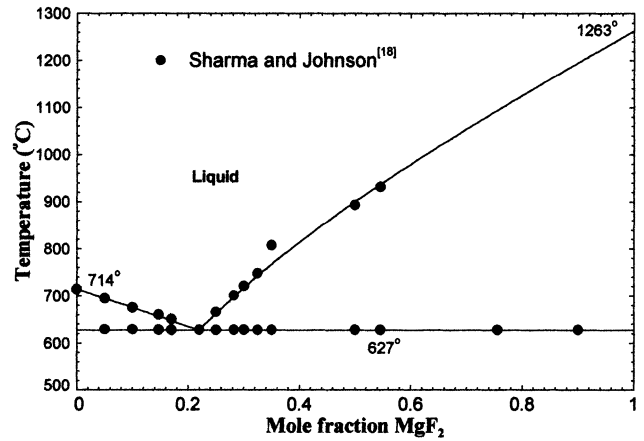


Fig. 38—MgCl<sub>2</sub>-MgF<sub>2</sub> system: calculated phase diagram.

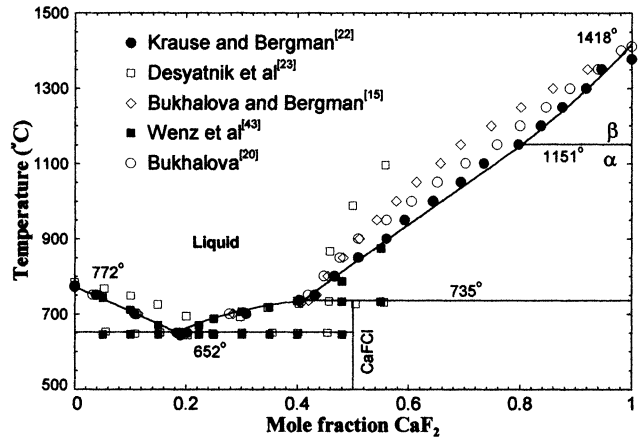


Fig. 39—CaCl<sub>2</sub>-CaF<sub>2</sub> system: calculated phase diagram.

properties. The optimized energy of formation of F-K-Cl SNN pairs is

$$\Delta g_{\text{K/FCI}} = -107.6 - 0.2880T + 437.3\chi_{\text{FCI}} + (-96.2 + 1.3362T)\chi_{\text{CIF}} \quad \text{J/mol} \quad [\text{A3}]$$

### D. The MgF<sub>2</sub>-MgCl<sub>2</sub> System

The phase diagram has been measured<sup>[18]</sup> (Figure 38). The calculated phase diagram is shown in Figure 38. The optimized energy of formation of F-Mg-Cl SNN pairs is

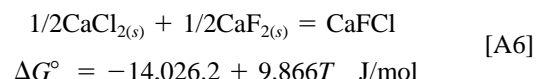
$$\Delta g_{\text{Mg/FCI}} = 272.0 - 73.6\chi_{\text{FCI}} - 383.1\chi_{\text{CIF}} \quad \text{J/mol} \quad [\text{A4}]$$

### E. The CaF<sub>2</sub>-CaCl<sub>2</sub> System

The phase diagram has been measured<sup>[15,20,22,23,43]</sup> (Figure 39). The calculated phase diagram is shown in Figure 39. The optimized energy of formation of F-Ca-Cl SNN pairs is

$$\Delta g_{\text{Ca/FCI}} = -646.1 \quad \text{J/mol} \quad [\text{A5}]$$

The optimized Gibbs energy of formation of CaFCl from CaCl<sub>2(s)</sub> and CaF<sub>2(α)</sub> is as follows. ( $\Delta C_p$  of formation is assumed to be 0)



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