

Calculation of Charge Asymmetric Additive Ternary Phase Diagrams with and without Compound Formation

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Liquidus temperatures have been calculated for fourteen ternary additive charge asymmetric molten salt systems. The second-order terms of the conformal ionic solution theory have been used, replacing mol fractions with equivalent fractions of the ions. The calculations indicate that this simple representation of the excess Gibbs energy of mixing in most cases gives a satisfactory representation of the phase diagrams. A method is shown for calculation of ternary additive phase diagrams where a congruently melting compound is formed in one of the constituting binaries.

I. INTRODUCTION

The conformal ionic solution theory (CIS)¹ has been extended and applied to calculate liquidus temperatures and liquid-liquid miscibility gaps for reciprocal molten salt systems.^{2–5} Although the CIS theory has been extended to additive ternary molten salt systems up to fourth-order terms,⁶ a representation of the excess Gibbs energy of mixing on the basis of the second-order terms is known to be satisfactory for systems with monovalent ions, where deviations from ideality are small.⁷ By use of second-order terms only, it is assumed that the deviation from ideality in the binaries may be described by one parameter, not allowing for asymmetry of the excess Gibbs energy of mixing.

Charge asymmetric ternary systems have been calculated on the basis of a different theoretical approach.⁸ For this type of systems, the formation of binary compounds has been taken into account.⁹ Calculation of ternary phase diagrams also has been performed in metallic systems.¹⁰

Expressing the excess Gibbs energy of mixing by the second-order terms derived from CIS theory,

with equivalent fractions instead of mol fractions, we will calculate phase diagrams for ternary additive molten mixtures of the salts AX_{q_A} , BX_{q_B} and CX_{q_C} , where q_i represents the absolute value of the charge of the cation. The same approach also is applied in calculations of ternary additive systems where a compound is formed in one of the constituting binaries.

II. THEORY

The basic set of equations needed to express the excess Gibbs energy of mixing is derived from conformal ionic solution theory.¹ When only second-order terms are used, the excess Gibbs energy of mixing per equivalent for the binary systems may be expressed by:

$$\Delta G^E(AX_{q_A} - BX_{q_B}) = X'_A X'_B \lambda_{AB}$$

$$\Delta G^E(BX_{q_B} - CX_{q_C}) = X'_B X'_C \lambda_{BC} \quad (1)$$

$$\Delta G^E(AX_{q_A} - CX_{q_C}) = X'_A X'_C \lambda_{AC}$$

where $X'_i = q_i X_i / (\sum_j q_j X_j)$

X_i is the ionic fraction, and q_i is the absolute value of the charge of the i 'th ion. The summation is over all ions with charges of the same sign.

Eqn. (1) corresponds to a regular solution model. The λ_{ij} 's are the binary interaction parameters, which are determined experimentally for a number of systems with one common ion.

The activity coefficient of AX_{q_A} in a molten mixture of AX_{q_A} and BX_{q_B} is given by:

$$RT \ln \gamma(\text{AX}_{q_A}) = \frac{\partial(n_{\text{tot}} \Delta G_m^E)}{\partial n(\text{AX}_{q_A})} = q_A X_B'^2 \lambda_{AB} \quad (2)$$

where ΔG_m^E is the excess Gibbs energy of formation of the mixture from the pure liquid compounds, and n_{tot} is the total number of equivalents in the mixture. $n(\text{AX}_{q_A})$ is the number of mol of AX_{q_A} in the mixture. When the heat of fusion of the salts. ΔH_f , is temperature independent, and the heat capacity difference between liquid and solid at constant pressure is negligible, the activity of AX_{q_A} in the binary mixture may be expressed by:

$$R \ln a(\text{AX}_{q_A}) = -\Delta H_f(\text{AX}_{q_A}) \left[\frac{1}{T} - \frac{1}{T^\circ(\text{AX}_{q_A})} \right] \\ = R \ln X_A X_X^{q_A} \gamma(\text{AX}_{q_A}) \quad (3)$$

where $T^\circ(\text{AX}_{q_A})$ is the melting point of AX_{q_A} . X_X is the ionic fraction of the common ion, hence $X_X = 1$. For simplicity, X_X is omitted from the following equations. Combination of eqns. (2) and (3), applied to each component of the binary, yields:

$$T[\Delta H_f(\text{AX}_{q_A})/T^\circ(\text{AX}_{q_A}) - R \ln X_A] - \Delta H_f(\text{AX}_{q_A}) \\ = q_A X_B'^2 \lambda_{AB} \quad (4) \\ T[\Delta H_f(\text{BX}_{q_B})/T^\circ(\text{BX}_{q_B}) - R \ln X_B] - \Delta H_f(\text{BX}_{q_B}) \\ = q_B X_A'^2 \lambda_{AB}$$

From these equations the binary interaction parameter, λ_{AB} , may be calculated.

The excess Gibbs energy of mixing per equivalent for the ternary system is expressed as:

$$\Delta G_m^E = X'_A X'_B \lambda_{AB} + X'_B X'_C \lambda_{BC} + X'_A X'_C \lambda_{AC} \quad (5)$$

The pure liquid compounds are chosen as standard state for the salts. The activity coefficients of the salts in the ternary mixture are calculated by combining eqn. (2) and eqn. (5).

$$RT \ln \gamma(\text{AX}_{q_A}) = q_A (X'_B + X'_C) X'_B \lambda_{AB} - q_A X'_B X'_C \lambda_{BC} \\ + q_A (X'_B + X'_C) X'_C \lambda_{AC} \\ RT \ln \gamma(\text{BX}_{q_B}) = q_B (X'_A + X'_C) X'_A \lambda_{AB} + \\ + q_B (X'_A + X'_C) X'_C \lambda_{BC} - q_B X'_A X'_C \lambda_{AC} \quad (6)$$

$$RT \ln \gamma(\text{CX}_{q_C}) = -q_C X'_A X'_B \lambda_{AB} + q_C (X'_A + X'_B) X'_B \lambda_{BC} \\ + q_C (X'_A + X'_B) X'_A \lambda_{AC}$$

The expressions for the activity coefficients are introduced in eqn. (3), and the set of equations is solved, giving the liquidus temperatures in the primary phase fields of the three components:

$$T(\text{AX}_{q_A}) = \{ \Delta H_f(\text{AX}_{q_A}) + q_A [(X'_B + X'_C) X'_B \lambda_{AB} - \\ - X'_B X'_C \lambda_{BC} + (X'_B + X'_C) X'_C \lambda_{AC}] \} / [\Delta H_f(\text{AX}_{q_A}) / \\ T^\circ(\text{AX}_{q_A}) - R \ln X_A] \\ T(\text{BX}_{q_B}) = \{ \Delta H_f(\text{BX}_{q_B}) + q_B [(X'_A + X'_C) X'_A \lambda_{AB} \\ + (X'_A + X'_C) X'_C \lambda_{BC} - X'_A X'_C \lambda_{AC}] \} / \\ [\Delta H_f(\text{BX}_{q_B}) / T^\circ(\text{BX}_{q_B}) - R \ln X_B] \quad (7)$$

$$T(\text{CX}_{q_C}) = \{ \Delta H_f(\text{CX}_{q_C}) + q_C [-X'_A X'_B \lambda_{AB} \\ + (X'_A + X'_B) X'_B \lambda_{BC} + (X'_A + X'_B) X'_A \lambda_{AC}] \} / \\ [\Delta H_f(\text{CX}_{q_C}) / T^\circ(\text{CX}_{q_C}) - R \ln X_C]$$

A congruently melting compound

$\text{B}_m \text{C}_n \text{X}_{(mq_B + nq_C)}^*$, which dissociates completely on melting, is assumed to be formed in the binary system $\text{BX}_{q_B} - \text{CX}_{q_C}$. The standard state for the binary compound is chosen to be the melt with the composition corresponding to this compound. The mol fractions of B and C are X_B^0 and X_C^0 .

To calculate the activity coefficient of the compound, the excess Gibbs energy of mixing must be related to the standard state for the binary compound. The excess Gibbs energy of mixing for a melt with the composition corresponding to the compound is:

$$\Delta G_m^E(0) = X_B^0 X_C^0 \lambda_{BC}$$

For a melt with any other composition, the excess Gibbs energy of mixing is given by eqn. (1).

When related to the new standard state, the excess Gibbs energy of mixing for the binary system $\text{BX}_{q_B} - \text{CX}_{q_C}$ will be:

$$\Delta G_m^E = [X'_B X'_C - X_B^0 X_C^0] \lambda_{BC}$$

When mol fractions are introduced:

$$\Delta G_m^E = [X'_B X'_C - X_B^0 X_C^0 q_B q_C (mq_B + nq_C) / \\ (q_B X_B^0 + q_C X_C^0)^2] \lambda_{BC} \quad (8)$$

The activity coefficient of B-C-X in the binary system is calculated by partial differentiation of the expression for the total excess Gibbs energy of mixing:

* The compound is denoted B-C-X in the following text and formulas.

$$\begin{aligned}
 RT \ln \gamma(\text{B}-\text{C}-\text{X}) &= \frac{\partial(n_{\text{tot}} \Delta G_m^E)}{\partial n(\text{B}-\text{C}-\text{X})} \\
 &= m \frac{\partial(n_{\text{tot}} \Delta G_m^E)}{\partial n_B} + n \frac{\partial(n_{\text{tot}} \Delta G_m^E)}{\partial n_C} \\
 RT \ln \gamma(\text{B}-\text{C}-\text{X}) &= [mq_B X_C'^2 + nq_C X_B'^2 \\
 - X_B^0 X_C^0 q_B q_C (mq_B + nq_C) / (q_B X_B^0 + q_C X_C^0)^2] \lambda_{BC} \quad (9)
 \end{aligned}$$

The activity of the binary compound is expressed by:

$$a(\text{B}-\text{C}-\text{X}) = k X_B^m X_C^n \gamma(\text{B}-\text{C}-\text{X}) \quad (10)$$

k is a factor which normalizes the activity of the molten compound to unity. Combination of eqns. (9) and (10) with eqn. (3) gives an equation for the liquidus temperatures for the compound in equilibrium with the binary melt:

$$\begin{aligned}
 T[\Delta H_f(\text{B}-\text{C}-\text{X})/T^0(\text{B}-\text{C}-\text{X}) - R \ln(k X_B^m X_C^n)] \\
 - \Delta H_f(\text{B}-\text{C}-\text{X}) = [mq_B X_C'^2 + nq_C X_B'^2 - \\
 X_B^0 X_C^0 q_B q_C (mq_B + nq_C) / (q_B X_B^0 + q_C X_C^0)^2] \lambda_{BC} \quad (11)
 \end{aligned}$$

An equation for the liquidus curve for binary systems with a congruently melting compound also has been derived by methods of statistical mechanics in terms of nearest-neighbour interactions.¹¹ For a compound with 1:1 composition, the equation may be shown to be identical to eqn. (11).

When a compound is formed in one of the binary systems, the equations for the ternary activity coefficients of AX_{q_A} , BX_{q_B} and CX_{q_C} are unchanged from the previous case where no compound was formed. The equations for the liquidus temperatures in the phase fields of these components are thus the same as before. The excess Gibbs energy of mixing for the ternary system when a binary compound B-C-X is formed, is obtained by combining eqns. (5) and (8):

$$\begin{aligned}
 \Delta G_m^E = X'_A X'_B \lambda_{AB} + [X'_B X'_C - X_B^0 X_C^0 q_B q_C (mq_B \\
 + nq_C) / (q_B X_B^0 + q_C X_C^0)^2] \lambda_{BC} + X'_A X'_C \lambda_{AC} \quad (12)
 \end{aligned}$$

By partial differentiation of eqn. (12) the activity coefficient of B-C-X in the ternary system is found:

$$\begin{aligned}
 RT \ln \gamma(\text{B}-\text{C}-\text{X}) = A = mq_B (X'_A + X'_C) [X'_A \lambda_{AB} \\
 + X'_C \lambda_{BC}] + nq_C (X'_A + X'_B) [X'_A \lambda_{AC} + X'_B \lambda_{BC}] \\
 - X'_A [mq_B X'_C \lambda_{AC} + nq_C X'_B \lambda_{AB}] \\
 - X_B^0 X_C^0 q_B q_C \lambda_{BC} (mq_B + nq_C) / (q_B X_B^0 + q_C X_C^0)^2 \quad (13)
 \end{aligned}$$

The liquidus temperatures in the primary phase field of B-C-X then may be calculated:

$$\begin{aligned}
 T(\text{B}-\text{C}-\text{X}) = [\Delta H_f(\text{B}-\text{C}-\text{X}) + A] / \\
 [\Delta H_f(\text{B}-\text{C}-\text{X}) / T^0(\text{B}-\text{C}-\text{X}) - R \ln(k X_B^m X_C^n)] \quad (14)
 \end{aligned}$$

III. CALCULATION OF PHASE DIAGRAMS FOR TERNARY ADDITIVE SYSTEMS

The calculation of the phase diagrams was performed by a UNIVAC 1108 computer. Thermodynamic input data were the heats of fusion and the melting points of the pure salts, and the binary eutectic temperatures.

In the ternary additive systems with no compound formation, the melt composition was used as a variable to calculate both the interaction parameters and the melt compositions in the binary eutectics, according to eqn. (4). In systems with a binary compound, eqn. (11) was used to calculate the interaction parameter. To perform this calculation, the data needed were the temperatures and melt compositions of the two eutectic points, and the heat of fusion and the melting point of the compound.

The isotherms of the ternary system and the phase field boundaries were calculated using eqn. (7), and eqns. (7) and (14) when a congruently melting binary compound was formed. The mol fraction of each component was changed in steps of 0.005 throughout the entire concentration range, and the liquidus temperatures were calculated for each composition. The phase field boundaries were assigned to compositions at which the liquidus temperatures in two phase fields differed by less than ± 0.5 K. The ternary eutectic was assigned to the composition where the three calculated liquidus temperatures agreed within ± 2.5 K.

IV. RESULTS

The enthalpies of fusion and the melting points of the salts are given in Table 1. Structural transitions are not taken into account in the calculations. The eutectic temperatures given by the investigators of the particular ternary system have been used in the calculation, and reported phase diagrams are shown in Figs. 1-14.

Table 1. Melting points and enthalpies of fusion for the salts selected in this work.

Salt	M.p. (°C)	ΔH_f kJ/mol	Ref.
LiF	848	27.087	12
NaF	996	32.593	12
KF	858	27.196	12
CaF ₂	1418	41.171	38
SrF ₂	1400	43.514	39
LiCl	606	19.920	14
NaCl	801	28.158	12
KCl	770	26.531	14
CsCl	645	20.250	16
CaCl ₂	772	28.543	12
FeCl ₂	677	43.095	12
CuCl ₂	598	44.493 ^a	15
SnCl ₂	247	12.761	13
LaCl ₃	855	54.392	13
CeCl ₃	822	53.555	16
NdCl ₃	760	50.208	17
KCuCl ₃	365	24.895 ^a	15
CsCaCl ₃	910	82.467	18
NaBr	747	26.108	12
Na ₂ CO ₃	850	29.665	12
Na ₂ SO ₄	884	23.012	13
LiNO ₃	254	25.606	16
NaNO ₃	306	14.602	13
TlNO ₃	206	8.201	16
Ca(NO ₃) ₂	561	21.338	13
Cd(NO ₃) ₂	300	18.200	13

^aThe ΔH_f -values are calculated from the phase diagram given in Ref. 15.

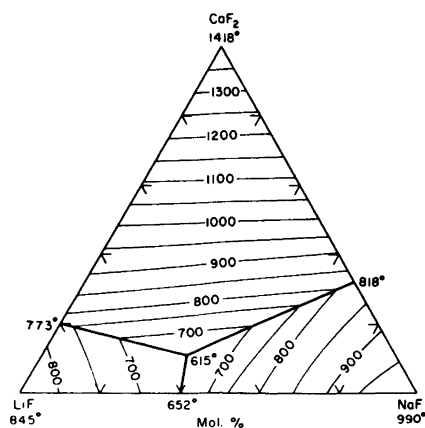
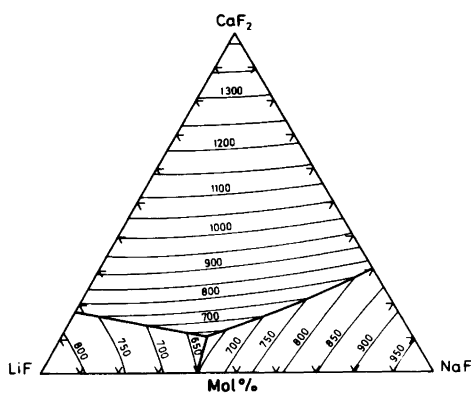


Fig. 1544.—System LiF–NaF–CaF₂.

Fig. 1. Phase diagram of the (Li,Na,Ca)F system. Calc. (left) and measured³¹ (right).

Reported and calculated eutectic compositions and temperatures for binaries are given in Table 2 and for ternary systems in Table 3.

V. DISCUSSION

V.1. Ternary additive systems without a binary compound

In spite of the simple equations used to describe the binary systems, experimental and calculated values for the eutectic compositions show a reasonable agreement for most systems (Table 2). The interaction parameters calculated from the binaries have the same sign as the reported data,^{16,28,29,36} except from the binaries NaF–KF, NaF–NaBr and NaCl–Na₂CO₃. The values, however, may deviate from those reported.

The shape of the calculated isotherms of the ternary systems are compared with that found experimentally in Table 4. The calculated binary interaction parameters also are given. At first, the difference between calculated and reported diagrams might seem considerable. However, the difference between the classifications +, 0 and – is small in most cases. In three of the systems, some of the phase fields are small, and no isotherms were reported or calculated.

The activity of a component along a liquidus isotherm will be constant. When the isotherms in a phase field are convex, as viewed from the corner representing the component AX_{4A}, i.e. they bend

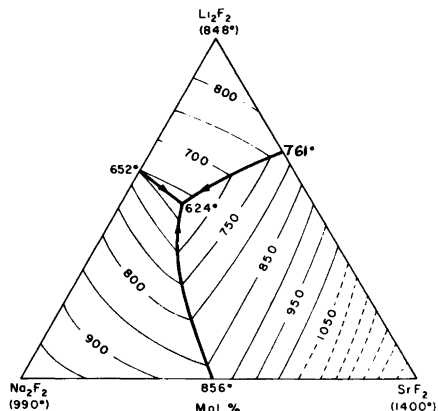
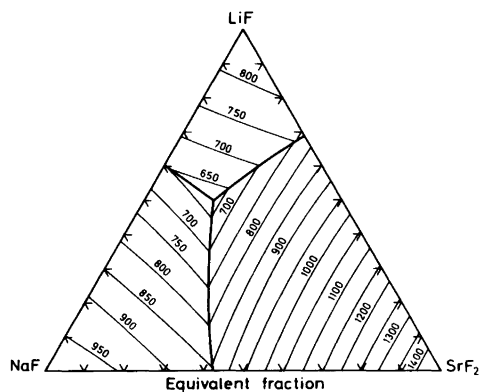


FIG. 3438.—System LiF–NaF–SrF₂.

Fig. 2. Phase diagram of the (Na,Sr,Li)F system. Calc. (left) and measured²¹ (right).

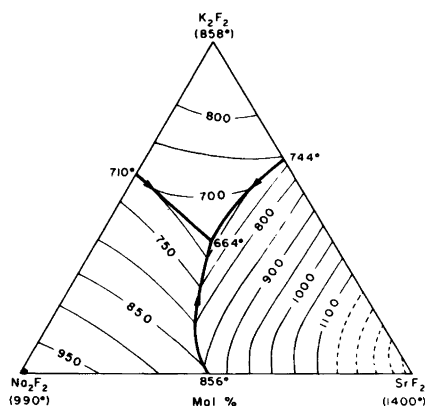
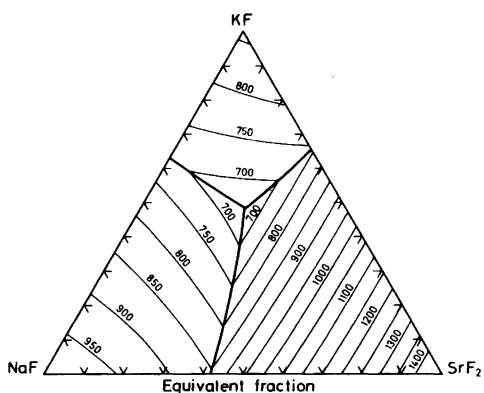


FIG. 3422.—System KF–NaF–SrF₂.

Fig. 3. Phase diagram of the (Na,Sr,K)F system. Calc. (left) and measured²¹ (right).

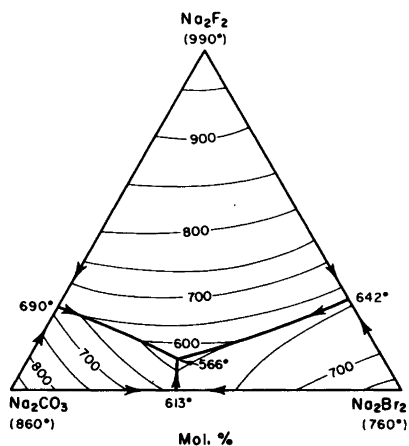
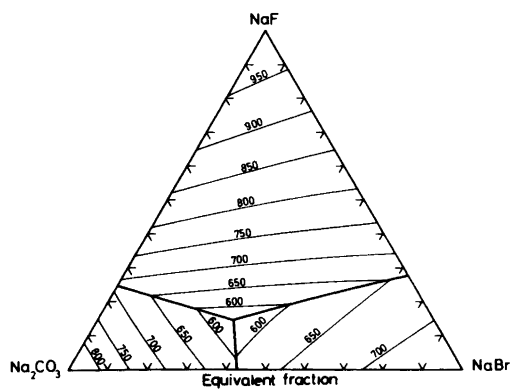


FIG. 3745.—System NaBr–NaF–Na₂CO₃.

Fig. 4. Phase diagram of the Na(CO₃,Br,F) system. Calc. (left) and measured³² (right).

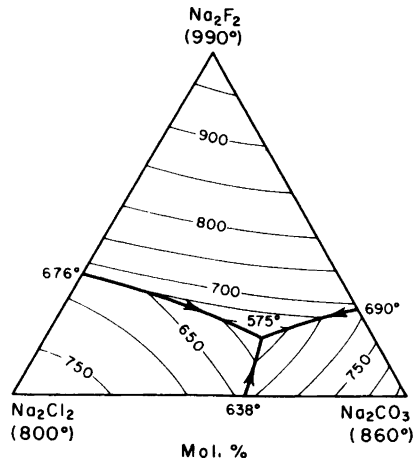
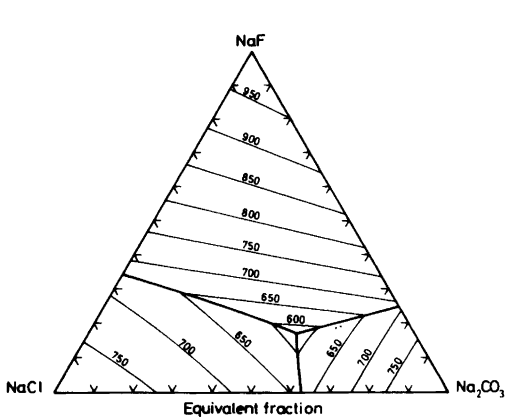


FIG. 3750.—System Na_2Cl_2 - Na_2F_2 - Na_2CO_3 .

Fig. 5. Phase diagram of the $\text{Na}(\text{Cl},\text{CO}_3,\text{F})$ system. Calc. (left) and measured¹⁹ (right).

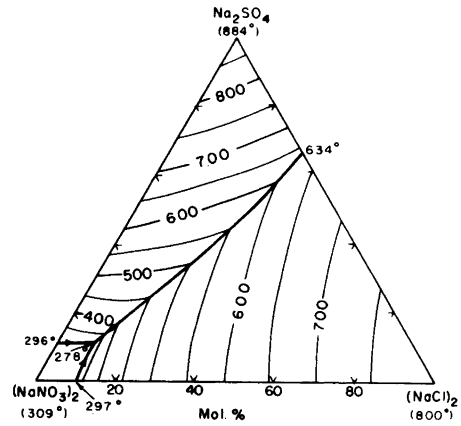
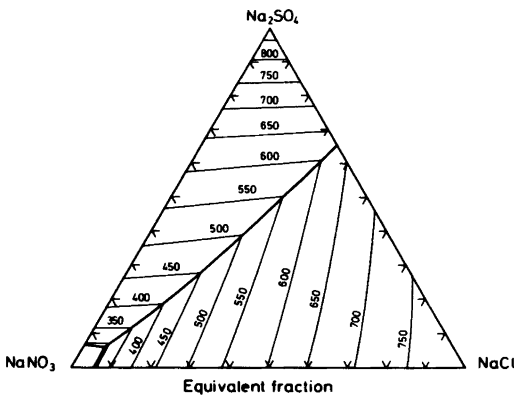


FIG. 3913.—System $(\text{NaCl})_2$ - $(\text{NaNO}_3)_2$ - Na_2SO_4 .

Fig. 6. Phase diagram of the $\text{Na}(\text{NO}_3,\text{Cl},\text{SO}_4)$ system. Calc. (left) and measured¹⁹ (right).

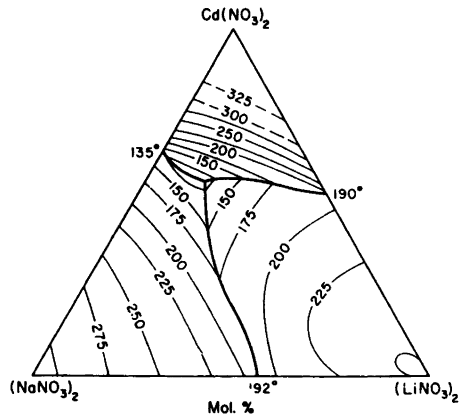
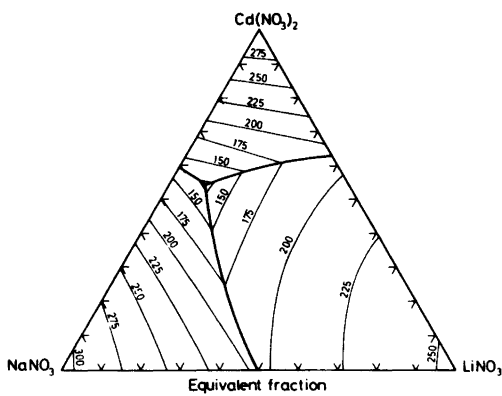


FIG. 1076.—System LiNO_3 - NaNO_3 - $\text{Cd}(\text{NO}_3)_2$.

Fig. 7. Phase diagram of the $(\text{Na},\text{Li},\text{Cd})\text{NO}_3$ system. Calc. (left) and measured³³ (right).

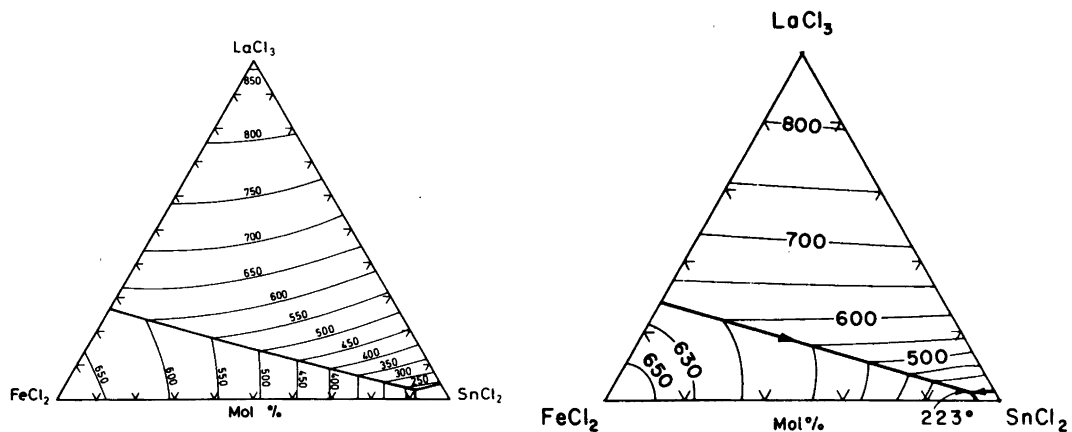


Fig. 8. Phase diagram of the (Fe,Sn,La)Cl system. Calc. (left) and measured²⁴ (right).

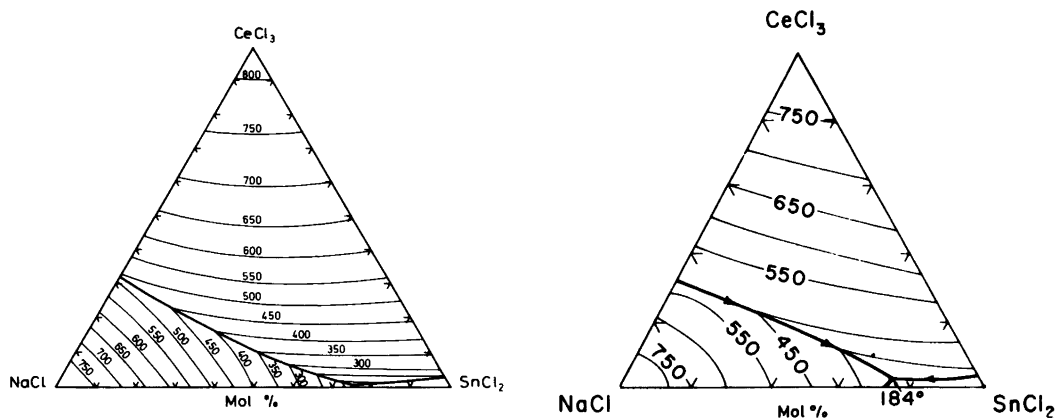


Fig. 9. Phase diagram of the (Na,Sn,Ce)Cl system. Calc. (left) and measured²⁴ (right).

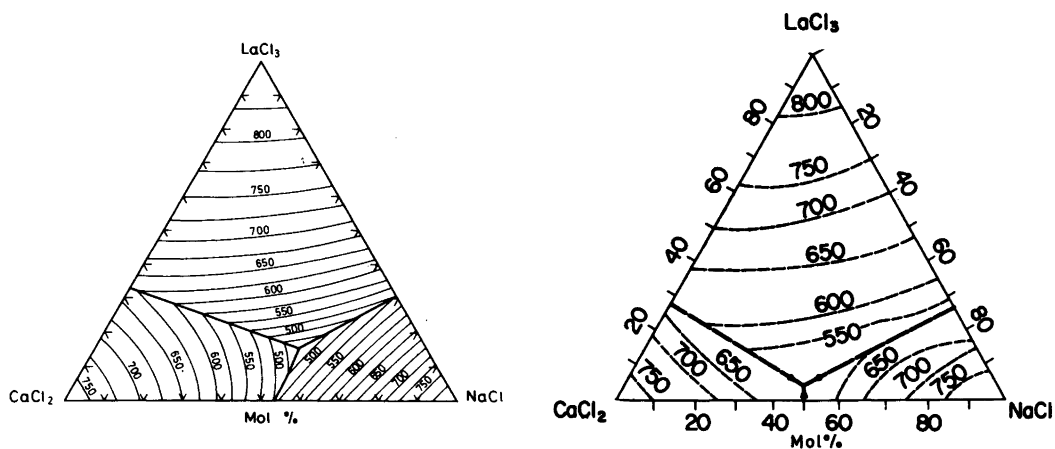


Fig. 10. Phase diagram of the (Ca,Na,La)Cl system. Calc. (left) and measured¹⁹ (right).

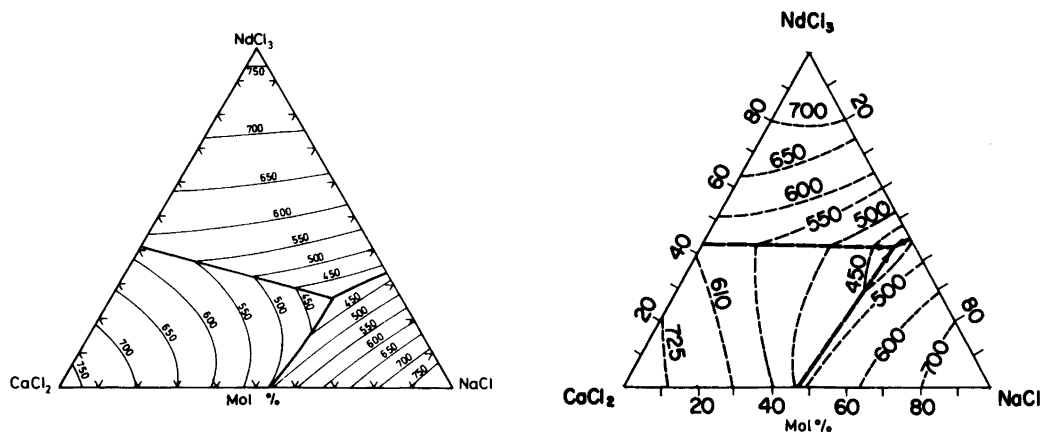


Fig. 11. Phase diagram of the (Ca,Na,Nd)Cl system. Calc. (left) and measured²⁵ (right).

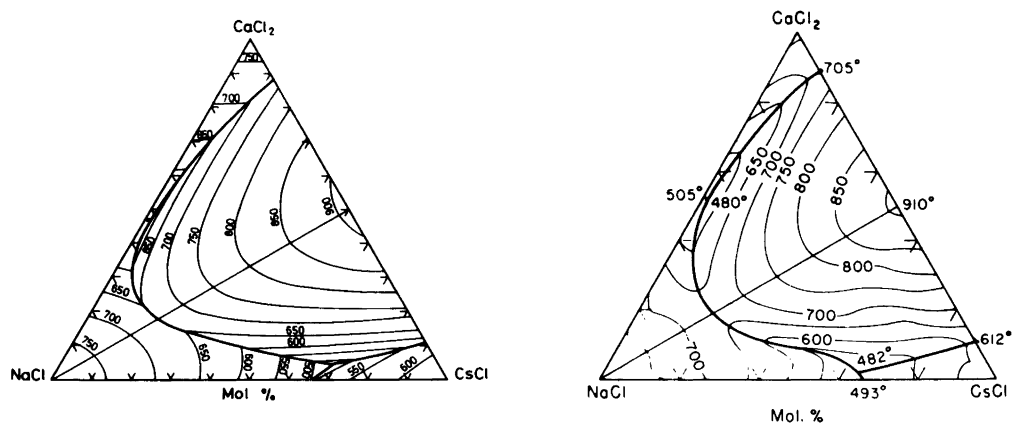


FIG. 1405.—System CsCl–NaCl–CaCl₂.

Fig. 12. Phase diagram of the (Na,Cs,Ca)Cl system. Calc. (left) and measured²⁶ (right).

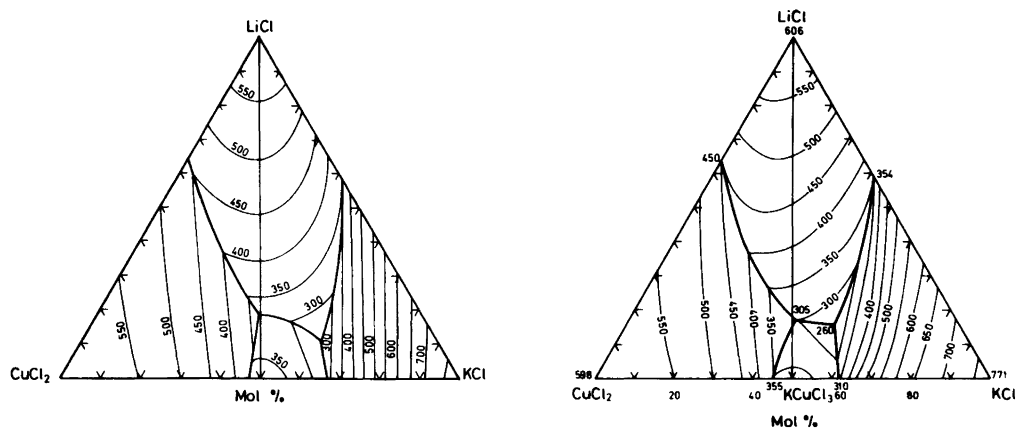


Fig. 13. Phase diagram of the (K,Cu,Li)Cl system. Calc. (left) and measured²⁷ (right).

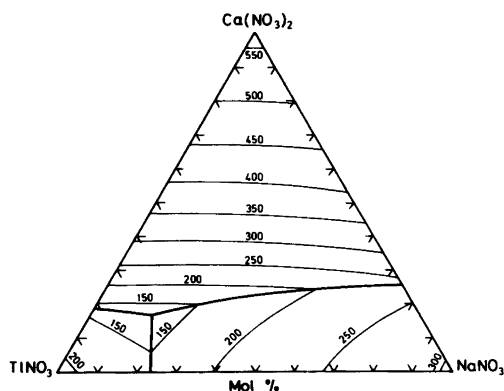


Fig. 14. Calculated phase diagram of the (Ti,Na,Ca)-NO₃ system.

towards the corner, the activity of the component is the same as in the binaries $AX_{qA}-BX_{qB}$ and $AX_{qB}-CX_{qC}$, but at a higher concentration of AX_{qA} than in the two binaries. The compound AX_{qA} exhibits negative deviation from the values in the binaries in this case. When the isotherms of a phase field are concave, the component thus exhibits positive deviations. A ternary additive ideal system will have linear isotherms in all phase fields, as may be seen from eqn. (7).

When the signs of the binary interaction parameters are equal, one can see how the shape of the isotherms will depend on the magnitude of the interaction parameters from eqn. (7). The equation for the liquidus temperatures in the AX_{qA} phase field reduces to the binary expression, eqn. (4), when X_B or X_C is zero.

When the sign of the interaction parameters is changed, while the magnitude is kept equal, four different cases must be considered.

Case a. In this case all binary interaction parameters are positive. For a constant value of X_A , all calculated liquidus temperatures in the phase field of AX_{qA} will be lower than calculated at the same composition in the binaries $AX_{qA}-BX_{qB}$ and $AX_{qA}-CX_{qC}$, eqn. (4). Thus, the isotherms in the phase field will be convex.

Case b. When all binary interaction parameters are negative, the same kind of reasoning leads to the AX_{qA} phase field isotherms being concave.

Case c. $\lambda(AX_{qA}-BX_{qB})$, $\lambda(AX_{qA}-CX_{qC}) > 0$; $\lambda(BX_{qB}-CX_{qC}) < 0$. The isotherms in the phase field will be concave in the AX_{qA} corner. Their symmetry around the line connecting the AX_{qA}

corner and the composition of $X_B=0.50$ in the binary system $BX_{qB}-CX_{qC}$, is dependent on the charges of the cations and the magnitude of the interaction parameters.

Case c. 1. $\lambda(AX_{qA}-BX_{qB})$, $\lambda(BX_{qB}-CX_{qC}) > 0$; $\lambda(AX_{qA}-CX_{qC}) < 0$. This case may be obtained from *case c* by a rotation of the diagram. However, if the discussion is restricted to one phase field only, this situation must be considered. For a constant value of X_A , eqn. (7) now gives lower temperatures in the ternary than in the $AX_{qA}-BX_{qB}$ binary system, and higher temperatures than in the $AX_{qA}-CX_{qC}$ binary. Hence, the isotherms in the phase field of AX_{qA} are asymmetric around the line connecting the AX_{qA} corner and the composition of $X_B=0.50$ in the $BX_{qB}-CX_{qC}$ binary. At the binary ends of an isotherm, X_A in the $AX_{qA}-CX_{qC}$ binary will be higher than the corresponding value in the $AX_{qA}-BX_{qB}$ binary.

Case d. $\lambda(AX_{qA}-BX_{qB})$, $\lambda(AX_{qA}-CX_{qC}) < 0$; $\lambda(BX_{qB}-CX_{qC}) > 0$. Eqn. (7) now gives lower temperatures in the ternary than in the $AX_{qA}-BX_{qB}$ and $AX_{qA}-CX_{qC}$ binaries at a constant X_A . The isotherms are convex in the AX_{qA} corner.

From eqn. (7) it may be seen that when two of the calculated binary interaction parameters have the same sign, the shape of the isotherms in a phase field may be related to the sign of the interaction parameter in the binary, which in the ternary diagram is opposite the phase field in question. This also may be observed in Table 4. If $\lambda(BX_{qB}-CX_{qC})$ is negative, the contribution from this term to the liquidus temperature in the AX_{qA} phase field, eqn. (7), is positive, and *vice versa*. Provided the magnitudes of the binary interaction parameters are not too different, the isotherms in a phase field will be concave when the interaction parameter in the opposite binary is negative and convex when the parameter is positive.

By changing the sign of the interaction parameters cases which are equivalent to *c* and *d* will be obtained.

In the phase diagram calculations by Fellner *et al.*⁸ the excess Gibbs energy of mixing is given by a two-parameter equation, which corresponds to the equation given by Saboungi and Blander⁶ up to third order. The difference between a one- and two-parameter representation of the excess Gibbs energy of mixing is found to have little effect on the topology of the phase diagram for the system LiF-NaF-CaF₂. Both representations reproduce the reported diagram satisfactorily. In the measured

Table 2. Experimental and calculated values for eutectic compositions and interaction parameters.

Binary system Comp. 1 – Comp. 2	Eutectic temp. (°C)	Eutectic composition		Interaction parameters ^a		Ref. ^b
		Rep. ($X_{\text{comp. 1}}$)	Calc. ($X_{\text{comp. 1}}$)	Rep. (J/mol)	Calc. (J/mol)	
LiF – NaF	652	0.61	0.603	– 5440, – 5858	– 5322	19, 20
CaF ₂ – NaF	818	0.325	0.302	– 19665	– 6581	19, 38
LiF – CaF ₂	773	0.79	0.819	– 5440	– 874	19, 20, 38
NaF – SrF ₂	856	0.734	0.734	– 12134	– 4481	21, 39
LiF – SrF ₂	761	0.802	0.815	– 10460	– 3485	21, 39
KF – SrF ₂	744	0.78	0.789	– 23430	– 5975	21, 39
NaF – KF	710	0.40	0.370	1046, – 377	1586	19, 21
NaF – Na ₂ CO ₃	690	0.39	0.399	– 837	– 1209	19
NaBr – Na ₂ CO ₃	613	0.62	0.596		1153	19
NaF – NaBr	656	0.28	0.275	– 2092	2042	20
NaCl – Na ₂ CO ₃	638	0.55	0.540	– 837	1028	19
NaF – NaCl	676	0.34	0.341	0	111	19
NaCl – Na ₂ SO ₄	628	0.52	0.511	0	1133	20
NaCl – NaNO ₃	296	0.065	0.052	0	153	19
NaNO ₃ – Na ₂ SO ₄	300	0.95	0.967	0	2644	20
NaNO ₃ – Ca(NO ₃) ₂	232	0.73	0.745		– 3804	22
NaNO ₃ – TiNO ₃	162	0.23	0.234		2723	20
TiNO ₃ – Ca(NO ₃) ₂	137	0.78	0.814		– 5429	23
LiNO ₃ – Cd(NO ₃) ₂	135	0.54	0.540		– 1858	19
NaNO ₃ – Cd(NO ₃) ₂	190	0.53	0.578		– 7004	19
LiNO ₃ – NaNO ₃	194 ^c		0.495	– 2259	– 703	20
NaCl – LaCl ₃	525		0.692		– 14724	19
CaCl ₂ – LaCl ₃	630		0.672		– 2481	19
NaCl – CaCl ₂	494	0.48	0.536	– 9414	– 9656	19
NaCl – SnCl ₂	184	0.28	0.237		– 14342	19, 24
NaCl – CeCl ₃	488	0.675	0.680		– 16761	19, 24
SnCl ₂ – CeCl ₃	240	0.975	0.966		– 4823	19, 24
NaCl – NdCl ₃	430	0.588	0.660		– 21024	25
CaCl ₂ – NdCl ₃	585	0.57	0.590		– 2984	25
FeCl ₂ – LaCl ₃	620	0.723	0.734		– 1192	24
SnCl ₂ – LaCl ₃	237	0.977	0.956		– 6307	24
FeCl ₂ – SnCl ₂	228	0.06	0.086		– 6201	24
CsCl – CaCl ₂	612	0.89			– 25096	26
	705	0.11				
KCl – CuCl ₂	310	0.54			– 44576	15
	355	0.45				
LiCl – KCl	354	0.58	0.59		– 17142	19
LiCl – CuCl ₂	454	0.64			– 2665	27
NaCl – CsCl	493	0.34			– 2821	20

^a Taken from Refs. 16, 28 and 39. The lowest values for the binaries LiF–NaF and NaF–KF are from Ref. 29. ^b References for the binary systems. ^c Several values for the eutectic composition are given in Ref. 20.

Table 3. Experimental and calculated eutectic temperatures and compositions.

Ternary system	Eutectic composition		Eutectic temp.		Ref.
	Rep. (mol fraction)	Calc. (mol fraction)	Rep. (°C)	Calc. (°C)	
LiF	0.517; 0.53	0.525	615; 607	623.1	31, 30
NaF	0.372; 0.36	0.370			
CaF ₂	0.111; 0.11	0.105			
LiF	0.554	0.550	624	625.3	21
NaF	0.359	0.355			
SrF ₂	0.087	0.095			
KF	0.47	0.550	664	656.7	21
NaF	0.36	0.295			
SrF ₂	0.17	0.155			
NaF	0.124	0.200	566	564.2	32
NaBr	0.532	0.460			
Na ₂ CO ₃	0.344	0.340			
NaF		0.233		578.4	19
NaCl		0.409			
Na ₂ CO ₃		0.358			
NaCl		0.058	278	288.7	19
NaNO ₃		0.912			
Na ₂ SO ₄		0.030			
NaNO ₃		0.150		116.2	33
TiNO ₃		0.680			
Ca(NO ₃) ₂		0.170			
NaNO ₃	0.560	0.500		121.3	
LiNO ₃	0.145	0.130			
Cd(NO ₃) ₂	0.295	0.370			
FeCl ₂	0.06	0.075	223	223.5	24
SnCl ₂	0.92	0.900			
LaCl ₃	0.02	0.025			
NaCl	0.22	0.235	184	181.3	24
SnCl ₂	0.76	0.755			
CeCl ₃	0.02	0.010			
NaCl		0.520		449.5	
CaCl ₂		0.325			
LaCl ₃		0.155			
NaCl	0.45	0.563	428	392	25
CaCl ₂	0.50	0.177			
NdCl ₃	0.05	0.260			
NaCl	0.345; 0.462	0.270; 0.515	482; 480	470; 494	26
CsCl	0.642; 0.017	0.685; 0.015			
CaCl ₂	0.013; 0.521	0.045; 0.470			
KCl	0.532; 0.481 ^a	0.600; 0.410	257; 285	236.3; 316.5	27
LiCl	0.200; 0.139	0.105; 0.180			
CuCl ₂	0.268; 0.380	0.295; 0.410			

^a In the cited work, the composition in the second column corresponds to a peritectic. The calculated phase diagram shows two eutectics.

Table 4. Comparison between calculated and experimentally determined shape of isotherms in the ternary systems.

Ternary system components			Calculated binary interaction parameters (J/mol)			Shape of isotherms ^a					
						Calculated			Reported		
AX _{qA}	BX _{qB}	CX _{qC}	λ _{BC}	λ _{AC}	λ _{AB}	AX _{qA}	BX _{qB}	CX _{qC}	AX _{qA}	BX _{qB}	CX _{qC}
LiF	NaF	CaF ₂	-6581	-874	-5322	-	-	-	-	-	0
NaF	SrF ₂	LiF	-3485	-5322	-4481	-	-	-	+	+	+
NaF	SrF ₂	KF	-5975	1586	-4481	-	+	-	-	-	-
Na ₂ CO ₃	NaBr	NaF	2042	-1209	1153	+	-	+	+	-	-
NaCl	Na ₂ CO ₃	NaF	-1209	111	1028	-	-	0	-	+	-
NaNO ₃	NaCl	Na ₂ SO ₄	1133	2644	153	+	0	-	-	-	-
TiNO ₃	NaNO	Ca(NO ₃) ₂	-3804	-5429	2723	-	-	+	-	-	-
NaNO ₃	LiNO ₃	Cd(NO ₃) ₂	-1858	-7004	-703	-	-	0	-	-	+
FeCl ₂	SnCl ₂	LaCl ₃	-6307	-1192	-6201	-	-	-	-	-	-
NaCl	SnCl ₂	CeCl ₃	-4823	-16761	-14342	-	-	-	-	-	-
CaCl ₂	NaCl	LaCl ₃	-14724	-2481	-9656	-	-	-	+	-	-
CaCl ₂	NaCl	NdCl ₃	-21024	-2984	-9656	-	-	-	-	-	-
NaCl	CsCl	CaCl ₂	-25096	-9656	-2821	-	-	-	-	-	-
KCl	CuCl ₂	LiCl	-2665	-17142	-44576	+	+	-	+	+	-

^a -, Isotherm bends away from the corner (concave); 0, Linear isotherms; +, Isotherm bends towards the corner (convex).

diagram the isotherms in the CaF₂ phase field are straight lines. The calculation of Fellner *et al.*⁸ shows a tendency of the isotherms to be convex in the CaF₂ corner, while the present calculation gives isotherms which are weakly concave. Both the experimental and the calculated values of the interaction parameters are negative. Hence, it would be expected that the isotherms are concave in all phase fields in this system.

In addition to the system discussed above, two other fluoride systems were calculated. In the system LiF–NaF–SrF₂ all calculated binary interaction parameters are negative, and the isotherms are concave. The experimental interaction parameters also are negative in this system. In the experimental diagram all isotherms are slightly convex. This tendency is weak, however, in the LiF and SrF₂ phase fields.

For the system KF–NaF–SrF₂ the calculated interaction parameters are negative for the binaries KF–SrF₂ and NaF–SrF₂, and positive for the NaF–KF binary, as are the experimental values. The calculated shape of the isotherms gives a reasonable reproduction of those experimentally determined in the NaF and KF phase fields, whereas the calculation shows some deviation from the experimental isotherms in the SrF₂ phase field.

In the calculated phase diagram of the system NaCl–NaNO₃–Na₂SO₄, the shapes of the isotherms are slightly different from those of the reported diagram, and the phase field of NaNO₃ is calculated to be smaller than reported. No isotherms are reported or calculated for this phase field. In spite of the positive values of the calculated binary interaction parameters, the isotherms in the Na₂SO₄ phase field are straight lines. This is due to the relatively large values of λ_{NO₃-SO₄} and λ_{Cl-SO₄}.

The phase diagrams of two nitrate systems were calculated. The system NaNO₃–TiNO₃–Ca(NO₃)₂ to our knowledge is not experimentally determined. The calculated ternary eutectic composition for the system LiNO₃–NaNO₃–Cd(NO₃)₂ deviates from the reported value.^{3,3} Calculated isotherms and phase field boundaries exhibit the same shape as those reported, but are more regular.

The phase diagrams of two additive ternary systems containing Na₂CO₃ were calculated. In the system NaF–NaBr–Na₂CO₃ the calculated isotherms of the Na₂CO₃ and NaBr phase fields have the same shape as in the experimental diagram. The isotherms are concave in the NaBr field, and convex in the Na₂CO₃ phase field. In the NaF field, the calculated isotherms are weakly

convex, whereas the experimental isotherms are concave.

In the system $\text{NaCl}-\text{NaF}-\text{Na}_2\text{CO}_3$, the shape of the experimental isotherms in the NaCl phase field is reproduced by the calculated ones. The isotherms in the NaF field are calculated to be straight lines. The experimental isotherms are slightly concave in the same phase field. The calculated shapes of the isotherms in the Na_2CO_3 phase field are the opposite of the experimental.

The phase diagrams of four chloride systems were calculated. For the ternary systems $\text{NaCl}-\text{SnCl}_2-\text{CeCl}_3$ and $\text{FeCl}_2-\text{SnCl}_2-\text{LaCl}_3$ the calculated phase diagrams agree satisfactorily with reported diagrams. Isotherms are neither calculated nor reported for the small phase field of SnCl_2 in these systems. For the systems $\text{NaCl}-\text{CaCl}_2-\text{LaCl}_3$ and $\text{NaCl}-\text{CaCl}_2-\text{NdCl}_3$ the isotherms are calculated to have the same shape as in the reported systems, but there are discrepancies between calculated and reported eutectic compositions.

The discussion given here on the shapes of the isotherms is based on eqn. (7) and calculated values of the binary interaction parameters. This might suggest that the shape of the isotherms in a phase field can be predicted from the sign of the experimental interaction parameters, provided the difference in magnitude is small. As seen from the calculations, the curved shape of the isotherms may be difficult to predict in cases where the interaction parameters are small or when the difference in magnitude is substantial.

V.2. Ternary additive systems with one congruently melting compound

Two additive ternary systems, where a congruently melting compound exists in one of the constituting binaries, were calculated. Complete dissociation of this compound was assumed. Fellner *et al.*⁹ with good results have calculated parts of the phase diagrams containing cryolite, by splitting the ternary systems into a necessary number of partial ternary systems. The authors also assumed a certain number of species present in the melt.

The interaction parameter for the $\text{CsCl}-\text{CaCl}_2$ binary was calculated from eqn. (11), using the heat of fusion for CsCaCl_3 obtained by Markov *et al.*,¹⁸ while the melting point of CsCaCl_3 , and the eutectic compositions and temperatures were taken from Plyushchev *et al.*²⁶ Dergunov and Bergman²⁰

determined the melting point of CsCaCl_3 to be 120°C higher than reported by Plyushchev *et al.* Two values of the binary interaction parameter were found. In the CaCl_2 -rich range of the binary $\lambda_{\text{Cs}-\text{Ca}} = -21\,171$ J/mol, and in the CsCl -rich range $\lambda_{\text{Cs}-\text{Ca}} = -29\,016$ J/mol. The mean value, $\lambda_{\text{Cs}-\text{Ca}} = -25\,094$ J/mol, was used in the calculation of the ternary phase diagram.

Different values were obtained for $\lambda_{\text{Cs}-\text{Na}}$ when the calculation was based on the NaCl - or CsCl rich side of the $\text{NaCl}-\text{CsCl}$ binary. This may be due to a large uncertainty, $\sim 25\%$, in the reported enthalpy of fusion for CsCl .¹² The value of $\lambda_{\text{Cs}-\text{Na}}$ calculated from thermodynamic data for NaCl was used in the calculation of the ternary system.

The topology of the ternary phase diagram is largely reproduced in the calculation. The shifts in the calculated ternary eutectics probably may be related to the crude treatment of $\lambda_{\text{Cs}-\text{Ca}}$, but uncertainties in the heat of fusion and in the melting point of CsCaCl_3 also partly may be responsible. The area of the primary phase field of CsCaCl_3 in the reported diagram is in accordance with a high value for the enthalpy of fusion for the compound.

The phase diagram of the system $\text{LiCl}-\text{KCl}-\text{CuCl}_2$ was measured by Sutakshuto *et al.*²⁷ who also determined the binary $\text{LiCl}-\text{CuCl}_2$. In the binary $\text{KCl}-\text{CuCl}_2$ the compound KCuCl_3 is formed. The heats of fusion of KCuCl_3 and CuCl_2 were not found in the literature, and it was decided to calculate the necessary data from the binary phase diagrams. From the $\text{LiCl}-\text{CuCl}_2$ phase diagram the enthalpy of fusion of CuCl_2 was calculated to be 44.5 kJ/mol.

The binary interaction parameter for the $\text{KCl}-\text{CuCl}_2$ system was obtained from the quasi-binary eutectic compositions and temperatures given by Vorobei and Skiba.¹⁵ In the CuCl_2 -rich range of the binary $\lambda_{\text{K}-\text{Cu}} = -55\,124$ J/mol, and in the KCl -rich range $\lambda_{\text{K}-\text{Cu}} = -34\,024$ J/mol.

Eqn. (11) then was used to derive the heat of fusion of KCuCl_3 . Each of the calculated values of $\lambda_{\text{K}-\text{Cu}}$ gave one value for the heat of fusion. $\lambda_{\text{K}-\text{Cu}}$ on the CuCl_2 -rich side of the binary gave $\Delta H_f(\text{KCuCl}_3) = 22.9$ kJ/mol, and $\lambda_{\text{K}-\text{Cu}}$ on the KCl -rich side gave $\Delta H_f(\text{KCuCl}_3) = 26.9$ kJ/mol. The mean value of the calculated interaction parameters and the mean value of the heat of fusion were used in the calculation of the ternary phase diagram.

In the calculated ternary system, the phase field boundaries between KCl and KCuCl_3 , and CuCl_2

and KCuCl_3 show some inconsistencies, as the boundaries do not pass through the binary eutectic compositions. These deviations are small, however. The calculated ternary phase diagram shows two eutectic points, whereas the experimental diagram has one eutectic and one peritectic point. However, a lower value for the heat of fusion of KCuCl_3 very easily may change the calculated eutectic point at 316°C into a peritectic point. The calculated ternary eutectic point is shifted towards the $\text{KCl}-\text{CuCl}_2$ binary, and a temperature lower than experimentally determined, is calculated.

There is reasonable agreement between the calculated and the experimental phase diagram. The marked concavity of the isotherms in the LiCl phase field may be attributed to the large and negative value of the interaction parameter in the $\text{KCl}-\text{CuCl}_2$ binary.

VI. CONCLUSION

From the present calculation of phase diagrams of ternary systems with binary congruently melting compounds, it appears that such systems may be predicted with a reasonable accuracy even if the predictions are based on relatively crude information on the binaries. A more general way to include compounds in the calculations will probably be to minimize the total Gibbs energy of the system, as proposed in a recent publication by Saboungi and Blander.³⁷ The number of systems which can be calculated then will be larger, as incongruently melting compounds also may be taken into consideration.

The present calculations indicate that a fairly simple representation of the ternary excess Gibbs energy of mixing is sufficient to calculate, with relatively small errors, additive ternary systems with ions of different charge. The equations also may be used in the prediction of phase diagrams with congruently melting binary compounds.

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