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Calculation of Phase Diagrams of Ternary Reciprocal Molten Salt Mixtures. The System Li^+—K^+—F^-—Cl^-

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In order to calculate phase diagrams of ternary reciprocal molten salt systems, the conformal ionic solution theory and an earlier developed binary ionic-interaction model has been used to derive the excess chemical potentials of the components. A computer program has been developed which delivers data on phase equilibria in the form of tables of liquidus temperatures against the composition of the system. The method of calculation has been applied to the system $Li^+ — K^+ — F^- — Cl^-$ and the calculated phase diagram is compared with the experimental one.

INTRODUCTION

A reciprocal molten salt system of the type A^+—B^+—C^-—D^- has four possible salt species, AC, AD, BC, BD, but only three components (independent thermodynamic variables) owing to the restriction imposed by the metathetical reaction

$$\mathrm{AC}\,(l) + \mathrm{BD}\,(l) \overset{\Delta G_T^{\circ}}{\rightleftharpoons} \mathrm{AD}\,(l) + \mathrm{BC}\,(l) \tag{1}$$

which is defined in the liquid phase (l) by the standard Gibbs free energy change ΔG_T° at temperature T. The composition of the system can be defined either by the number of moles of the components (three variables), or in terms of mole fractions of the components (two variables) when an additional restriction is imposed by the equation $\sum_i \sum_j x_{ij} = 1$ (x_{ij} is the mole fraction of the component with the cation i and anion j). When dealing with reciprocal systems it is often practical to express the composition in ionic fractions x_i, x_j, so that in the above case, $x_A + x_B = 1$ and $x_C + x_D = 1$, which gives again two independent variables to describe the composition of the system (say, x_A and x_C). If one chooses, for example, AD, BC and BD as components, the following relations are valid: $x_A = x_{AD}$, $x_B = x_{BC} + x_{BD}$, $x_C = x_{BC}$, $x_D = x_{AD} + x_{BD}$.

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In order to calculate the phase diagram of a simple reciprocal system A^+, B^+, C^-, D^- (which does not form compounds of the thype $A_{n+m-k}B_kC_nD_m$ and the mutual solubility of species in the solid phase is negligible) one needs two kinds of data: (1) thermodynamic parameters relevant to the pure salts, such as the enthalpy of melting, the melting point and the heat capacity, and (2) the excess chemical potentials of the salt species in the liquid mixture. The latter data reflect the ionic interactions caused by mixing the liquid components and they cannot be deduced *a priori* unless a suitable non-thermodynamic model is available.

The present paper is an attempt to calculate the phase diagram of the simple reciprocal system Li^+, K^+, F^-, Cl^-, using the conformal ionic solution theory[1] and a recently developed binary ionic—interaction model[2] in order to calculate the chemical potentials.

Data for phase equilibria have been obtained with a computer program and the calculated and experimental phase diagrams are compared and discussed.

CALCULATION OF EXCESS CHEMICAL POTENTIALS

A statistical-mechanical calculation according to the conformal ionic solution theory[2] derives the following expression for the excess Gibbs free energy change of mixing:

$$\Delta G^E = x_i\,(1 - x_j)\,\Delta G_T^{\circ} + x_A\,\Delta G_A^{\,E} + x_B\,\Delta G_B^{\,E} + x_C\,\Delta G_C^{\,E} + \\ + x_D\,\Delta G_D^{\,E} - x_A x_B x_C x_D\,(\Delta G_T^{\circ})^2/2\,ZRT \qquad (2)$$

Here, x_i and x_j are cationic and anionic fractions (i = A, B; j = C, D; $\sum\limits_i x_i = \sum\limits_j x_j = 1$), ΔG_T° is defined by eq. (1), Z is a coordination number, *i. e.* the average number of nearest anions around a cation in the melt. ΔG_i^E and ΔG_j^E are the excess Gibbs free energy changes of mixing for the binary systems having i or j as a common ion. They are defined by

$$\Delta G_i^E = x_j\,(1 - x_j)\,\lambda_i$$

$$\Delta G_j^E = x_i\,(1 - x_i\,\lambda_j \qquad (3)$$

where i = A, B and j = C, D; λ_i and λ_j are unkown binary ionic interaction parameters which cannot be derived by the conformal ionic solution theory.

Taken strictly, eqn. (2) and (3) are only second order approximations which neglect higher terms. Moreover, we have used the excess Gibbs free energy (ΔG^E) instead of the excess Helmholtz free energy ΔA^E, but given the approximate character of these equations, the difference is not significant.

The first term on the right-hand side of eq. (2) shows that the contribution of the metathetical reaction (eq. (1)) depends upon the choice of the component which is the reactant, *i. e.*, $x_i\,(1 - x_j)$. For example, if our choice is the component AC, then $x_i = x_A$, $x_j = x_C$ and the first term is $x_A x_D\,\Delta G_T^{\circ}$, *i. e.* proportional to the product of ionic fractions $x_A x_D$, since AC is converted to AD. If the reactant is the component BC, the first term is $-x_B x_D\,\Delta G_T^{\circ}$. The negative sign indicates that the reverse reaction takes place, *i. e.* BC is converted to BD (see eq. (1)).

Eqn. (2) and (3) have been used to survey the topology[3] and miscibility gap[4] of phase diagrams, but in all cases the λ_i and λ_j values have been obtained from experimental data, usually from corresponding binary phase diagrams. This simply means that instead of investigating experimentally one ternary reciprocal salt system, it is sufficient to know the four constituting binary diagrams. The job is, no doubt, much simpler, but experimental data are still required. However, recently we have developed an ionic interaction model[2] which makes it possible to calculate *a priori* (without resorting to experimental data relevant to the salt mixture) binary[2] and ternary additive[5] phase diagrams of systems with a common anion. Thus, one can use this model in order to calculate the λ_C and λ_D values of eq. (3), so that λ_A and λ_B are the only experimental parameters required. According to the model,[2] for a binary system of 1 : 1 salts with a common anion *j*, the interaction energy parameter is

$$\lambda_j = -\frac{U_A^{\,l} + U_B^{\,l}}{2}\left(\frac{d_{Aj} - d_{Bj}}{d_{Aj} + d_{Bj}}\right)^2 \tag{4}$$

Here d_{ij} is the sum of cation and anion radii of the salt *ij*, whereas $U_i^{\,l}$ is the quasi-lattice energy of the pure molten salt *ij* at the melting point. $U_i^{\,l}$ can be obtained to a good approximation from the standard crystal lattice energy U_i and the enthalpy of fusion of the crystal ($\Delta H_{F(i)}{}^{\circ}$) at the melting point:[2]

$$U_i^{\,l} \simeq 0.95\,(U_i - \Delta H_{F(i)}{}^{\circ}) \tag{5}$$

The calculation of excess chemical potentials of a salt species of the ternary reciprocal system is now straightforward from the thermodynamic view, although the partial differentiation required is somewhat tedious. Thus, the chemical potential of the salt *ij* is:

$$\mu_{ij}^{\,E} = RT\ln\gamma_{ij} = \frac{\partial}{\partial_{nj}}(n\Delta G^E) = \frac{\partial}{\partial_{ni}}(n\Delta G^E) + \frac{\partial}{\partial_{nj}}(n\Delta G^E) \tag{6}$$

Here, *n* is the total number of mols:

$$n = n_{AD} + n_{BC} + n_{BD} = n_A + n_B = n_C + n_D$$

and γ_{ij} is the thermodynamic activity coefficient of the species *ij* (reference state: $\gamma_{ij} = 1$, when $n = n_{ij}$). Also, one must take into account that $x_A = \frac{n_A}{n_A + n_B}$, $x_C = \frac{n_C}{n_C + n_D}$, *etc.* Eqn. (2), (3) and (6), after differentiation and rearrangement give:

$$\begin{aligned} RT\ln\gamma_{AC} = {} & x_B x_D\,\Delta G_T{}^{\circ} + (x_A x_D{}^2 + x_B x_C x_D)\,\lambda_A + \\ & + (x_B x_D{}^2 - x_B x_C x_D)\,\lambda_B + (x_B{}^2 x_C + x_A x_B x_D)\,\lambda_C + \\ & + (x_B{}^2 x_D - x_A x_B x_D)\,\lambda_D - \\ & - (x_B{}^2 x_C x_D + x_A x_B x_D{}^2 - x_A x_B x_C x_D)\,\frac{(\Delta G_T{}^{\circ})^2}{2\,ZRT} \end{aligned} \tag{7}$$

$$\begin{aligned} RT\ln\gamma_{AD} = {} & - x_B x_C\,\Delta G_T{}^{\circ} + (x_A x_C{}^2 + x_B x_C x_D)\,\lambda_A + \\ & + (x_B x_C{}^2 - x_B x_C x_D)\,\lambda_B + (x_B{}^2 x_C - x_A x_B x_D)\,\lambda_C + \\ & + (x_B{}^2 x_D + x_A x_B x_C)\,\lambda_D - (x_B{}^2 x_C x_D + x_A x_B x_C{}^2 - x_A x_B x_C x_D)\,\frac{(\Delta G_T{}^{\circ})^2}{2\,ZRT} \end{aligned} \tag{8}$$

$$\begin{aligned} RT\ln\gamma_{BC} = {} & - x_A x_D\,\Delta G_T{}^{\circ} + (x_A x_D{}^2 - x_A x_C x_D)\,\lambda_A + \\ & + (x_B x_D{}^2 + x_A x_C x_D)\,\lambda_B + (x_A{}^2 x_C + x_A x_B x_D)\,\lambda_C + \\ & + (x_A{}^2 x_D - x_A x_B x_D)\,\lambda_D - (x_A{}^2 x_C x_D + x_A x_B x_D{}^2 - x_A x_B x_C x_D)\,\frac{(\Delta G_T{}^{\circ})^2}{2\,ZRT} \end{aligned} \tag{9}$$

$$RT \ln \gamma_{BD} = x_A x_C \Delta G_T^{\circ} + (x_A x_C^2 - x_A x_C x_D) \lambda_A + (x_B x_C^2 + x_A x_C x_D) \lambda_B + (x_A^2 x_C - x_A x_B x_C) \lambda_C + (x_A^2 x_D + x_A x_B x_C) \lambda_D - (x_A^2 x_C x_D + x_A x_B x_C^2 - x_A x_B x_C x_D) \frac{(\Delta G_T^{\circ})^2}{2\,ZRT} \tag{10}$$

CALCULATION OF THE PHASE DIAGRAM

In order to calculate the liquidus temperature T_{ij} of the phase field of a salt species ij in the ternary reciprocal melt, the well—known freezing—point equation is used in the form:[5]

$$RT_{ij} \ln x_i x_j \gamma_{ij} + \Delta \overset{\circ}{H}_{F(ij)} (1 - T_{ij}/T_{ij}^{\circ}) - \Delta C_{p(ij)} [T_{ij}^{\circ} - T_{ij} + T_{ij} \ln (T_{ij}/T_{ij}^{\circ})] = 0 \tag{11}$$

Here, T_{ij}, T_{ij}° and $\Delta \overset{\circ}{H}_{F(ij)}$ are the liquidus temperature, the melting point and the enthalpy of fusion (latent heat of fusion) at m. p. of the salt ij, respectively, and $\Delta C_{p(ij)} = C^{l}_{p(ij)} - C^{s}_{p(ij)}$ is the difference in the molar heat capacities of the pure liquid and solid salt. This difference is rather small for most salts and we shall assume that it is practically independent of temperature and obtain it from the published values of heat capacities at the melting point.

For the ternary reciprocal system i = A, B and j = C, D, so that four expressions of the type given in eq. (11), for the salts AC, AD, BC and BD are obtained. Each of these equations can be combined with the corresponding expression for the excess chemical potential (eqn. 7—10) so that T_{ij} as a function of melt composition is obtained, which makes it possible to construct the complete phase diagram. We have obtained T_{ij} as a function of composition (x_A, x_C), by solving eq. (11) with an iterative procedure. Calculation of the phase diagram has been done with a computer program with sets of input parameters U_{ij}, $\Delta \overset{\circ}{H}_{F(ij)}$, T_{ij}°, $\Delta C_{p(ij)}$, d_{ij} relevant to the salt species. Additional input parameters are the two λ_i values deduced from experimental data, ΔG_T°, and Z. The input variables are x_A and x_C .The iterative procedure gives T_{ij} values consistent within ± 0.01 K. The intersection lines of two phase fields have been deduced as those melt compositions at which two liquidus temperatures differed by less than 0.05 K, whereas a ternary eutectic point has been obtained at a composition at which three liquidus temperatures agreed within 0.1 K. The increased error margins of ± 0.05 and ± 0.1 K, relative to the basic ± 0.01 K, are well within experimental accuracy, but they reduced considerably the time required for iteration.

The physical parameters for single salts used in the computation are listed in Table I, together with corresponding references. In Table II are listed the values of the binary interaction-energy parameters.

RESULTS AND DISCUSSION

In Figure 1 are reproduced the calculated and experimental[12] phase diagrams for the reciprocal ternary system Li^+—K^+—F^-—Cl^-. As usual, the two diagrams are two-dimensional orthogonal projections with coordinates in an ion-fraction scale. Comparing the two diagrams, one can note that the calculated one reproduce fairly well the magnitude of the four phase-fields and the phase-field intersection lines of the published experimental diagram. Also, the shape and position of the isotherms are fairly well reproduced. A more quantitative insight is presented in Table III, where the composition and temperatures of the four binary and two ternary eutectic points, obtained experimentally and calculated, are compared.

TABLE I

Physical Parameters for Single Salts Used in Computation

Salt	m. p. $T_{ij}{}^{o}$/K (ref. 6)	Fusion enthalpy $\Delta H^{o}_{F(ij)}$/J mol^{-1} (ref. 7)	$\Delta C_{p(ij)}$ /J mol^{-1} K^{-1} (ref. 8)	Lattice energy U_{ij}/kJ mol^{-1} (ref. 9.	Sum of Pauling radii d_{ij}/nm
LiF	1121	27070	3.3	1033.0	0.196
KF	1129	28240	7.1	806.7	0.269
LiCl	878	19920	0.8	849.7	0.241
KCl	1045	26530	9.2	707.1	0.314

TABLE II

Binary Interaction Parameters λ_i, λ_j, and General Parameters for the Reaction $LiF + KCl \rightleftarrows LiCl + KF$

Bin. system.	λ_i or λ_j/J mol^{-1}	ref.	Gen. parameters:	ref.
LiF — KF	—20674	calc. with eq. 4	$\Delta G_T^{\circ} = 68199$ J mol^{-1} $T = 1131$ K	11
LiCl — KCl	—12638		$Z = 6$	7
LiF — LiCl	—837	10		
KF — KCl	—418	3		

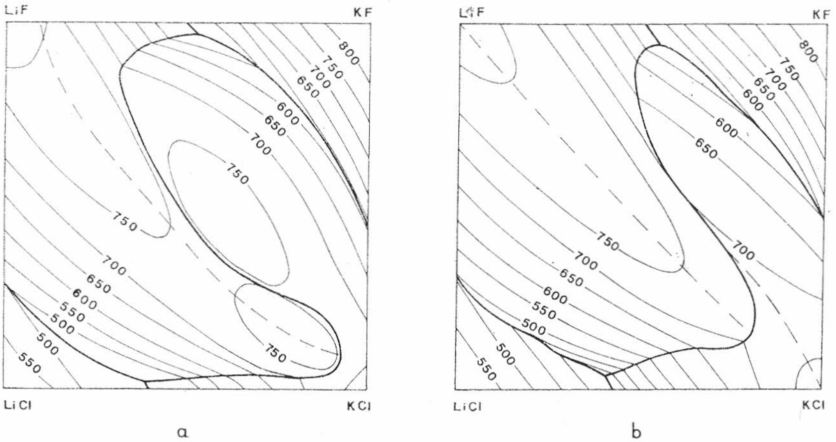

Figure 1. The system $Li^+ — K^+ — F^- — Cl^-$. (A) calculated phase diagram, (B) experimental phase diagram.[12] Temperature units: °C.

Referring first to the binary eutectic points, one can note that there is a good agreement for the KF—KCl and LiF—LiCl systems. This is not surprising since the two λ_i values are of experimental origin (see Table II). The agreement is less good for the LiF—KF and LiCl—KCl system, where the λ_j values are derived with the simple and approximate model of binary ionic interactions (eq. 4). However, it should be mentioned that Janz[8] reports for LiCl—KCl a eutectic temperature of 361 °C at 41.5 mol % KCl. Moreover, if λ_F is calculated with eq. (4) using Johnson-Waddington ionic radii,[9] the eutectic temperature obtained for LiF—KF is 492 °C,[2] in excellent agreement with experimental data. (In spite of this, in the present calculation we have consistently used Pauling radii because by employing them a generally better fit is obtained). Referring now to the ternary eutectic points of Table III, one can note that the calculated and experimental temperatures differ in one case by 21°, in the other by 31°, whereas differences in composition amount to 0.01—0.04 mole

TABLE III

Comparison of Calculated and Experimentally[12] *Obtained Binary and Ternary Eutectic Points of the System* $Li^+—K^+—F^-—Cl^-$

System	Composition/mole fraction								Temp./°C		type of eutectic
$A^+—B^+—C^-—D^-$	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	
	x_{LiF}		x_{LiCl}		x_{KF}		x_{KCl}				
	—	—	0.588	0.575	—	—	0.412	0.425	381	354	binary
A = Li	—	—	—	—	0.436	0.450	0.564	0.550	600	606	binary
B = K	0.503	0.495	—	—	0.497	0.505	—	—	454	492	binary
C = F	0.299	0.300	0.701	0.700	—	—	—	—	501	498	binary
D = Cl	0.480	0.460	—	—	0.497	0.475	0.023	0.065	449	468	ternary
	0.023	0.035	0.591	0.560	—	—	0.386	0.405	377	346	ternary

fraction units. Thus, the calculated phase diagram is, quantitatively, only a fairly good approximation. Generally, one cannot expect much better agreement since the basic equations (*i. e.* eqn. (2)—(4)) used in the computation are approximations. Nevertheless, the proposed method of calculation can be useful since it requires only few experimental data and with modern computers the phase diagram is obtained in a matter of minutes.

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SAŽETAK

Izračunavanje faznih diagrama za trojne recipročne smjese rastaljenih soli. Sustav Li^+—K^+—F^-—Cl^-

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Da bi se izračunali fazni dijagrami ternarnoga recipročnog sustava rastaljenih soli, upotrijebljena je teorija konformalne ionske otopine i ranije razvijeni model binarnih ionskih interakcija za izvod prekomjernih (»excess«) kemijskih potencijala komponenata. Razvijen je kompjuterski program, koji daje podatke o ravnoteži faza u obliku tablica temperatura talina prema sastavu sistema. Računska metoda primijenjena je na sustav Li^+—K^+—F^-—Cl^-, a izračunani fazni dijagram uspoređen je s eksperimentalnim.