Thermodynamic Modeling of $AlCl_3$-based Molten Chlorides Systems

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SUMMARY

Chloroaluminate melts may be used as electrolytes for the production of aluminum and they are also involved in high energy density batteries ("Zebra" battery) : Na/β-Al_2O_3/$NaAlCl_4$, $FeCl_2$, Fe.

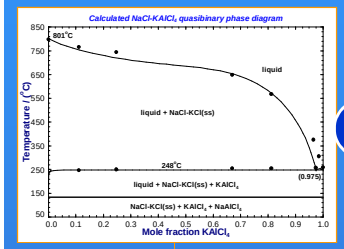
Recently, the thermodynamic database previously developed **[1,2a,2b]** for the LiCl-NaCl-KCl-$MgCl_2$-$CaCl_2$-$MnCl_2$-$FeCl_2$-$CoCl_2$-$NiCl_2$ system was extended with the addition of $AlCl_3$, and the thermodynamic "optimization" of the NaCl-KCl-$AlCl_3$ system was published **[3]**. In a thermodynamic "optimization" of a system, all available phase diagram and thermodynamic data (enthalpy of mixing, emf, vapor pressure measurements,...) are critically evaluated **simultaneously** in order to obtain one set of model equations for the Gibbs free energies of all phases (liquid, solid solutions, stoichiometric compounds) as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated using Gibbs free energy minimization software. In this way, the data are rendered self-consistent, discrepancies among the data are identified, and extrapolations and interpolations are performed. The model parameters are stored in a computer database and the calculation of thermodynamic properties and phase diagram sections can be made over extended ranges of temperature and pressure.

In this work, all binary subsystems of the LiCl-NaCl-KCl-$MgCl_2$-$CaCl_2$-$MnCl_2$-$FeCl_2$-$FeCl_3$-$CoCl_2$-$NiCl_2$-**$AlCl_3$** system (except $AlCl_3$-$FeCl_2$, for which 2 terminal solid solutions remain to be optimized) as well as all higher order (mostly ternary) subsystems for which experimental data were available have been considered. In particular, a thermodynamic modeling of the binary systems ACl-$AlCl_3$ (where A = Li, Na and K) is a real challenge as these systems show strong negative deviations from ideality at the equimolar composition (due to short-range ordering in the liquid phase). This is illustrated for instance by the very steep NaCl liquidus in the calculated NaCl-$AlCl_3$ phase diagram (**Figure 1**) and by the rapid change in activity of $AlCl_3$ in the NaCl-$AlCl_3$ liquid (**Figure 4**).

[1] P. Chartrand and A.D. Pelton, *Metall. Mater. Trans.*, 2001, vol. 32A, pp. 1361-83.
[2a,2b] C. Robelin, P. Chartrand and A.D. Pelton, *J. Chem. Thermodyn.* (in press).
[3] C. Robelin, P. Chartrand and A.D. Pelton, *J. Chem. Thermodyn.*, 2004, vol. 36(8), pp. 683-99.

In ALL figures :
- the LINES are CALCULATED from the models
- the POINTS are EXPERIMENTAL from the literature

NaCl-"$AlCl_3$" System (NO ternary parameters)



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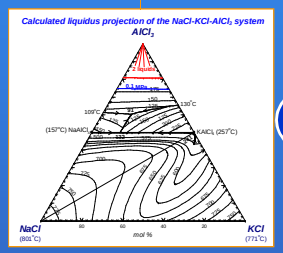

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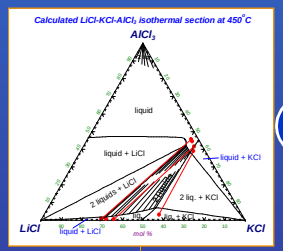
LiCl-KCl-"$AlCl_3$" System (2 ternary parameters)



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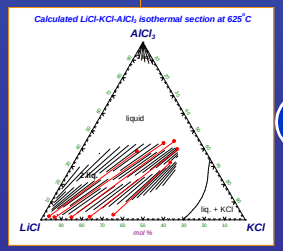

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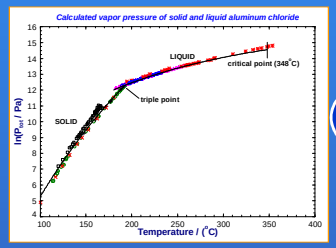
Pure Aluminum Chloride



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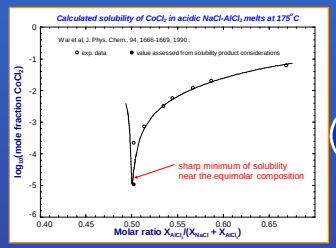
NaCl-$CoCl_2$-"$AlCl_3$" System (NO ternary parameters)



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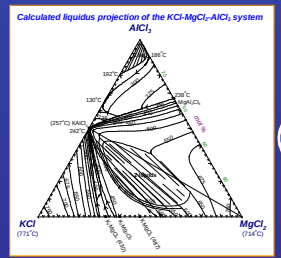
KCl-$MgCl_2$-"$AlCl_3$" System (NO ternary parameters)



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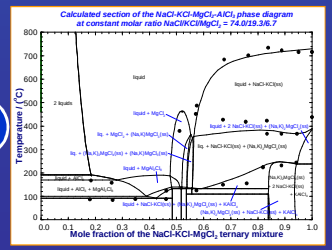
NaCl-KCl-$MgCl_2$-"$AlCl_3$" System



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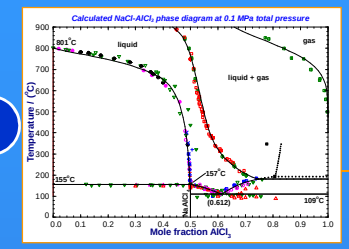
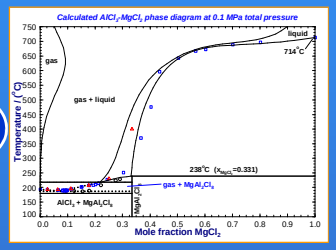
NaCl-"$AlCl_3$" System



1

"$AlCl_3$"-$MgCl_2$ System



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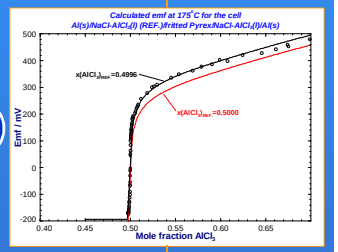

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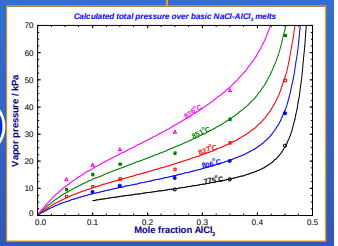

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MODEL FOR THE LIQUID PHASE

The liquid solution was modeled using the Modified Quasichemical Model **[4,5]** which takes into account short-range ordering between second-nearest-neighbor cations (the anionic sublattice is occupied only by Cl⁻ ions). The parameters of the model are the Gibbs free energy changes Δg_{ABCl} for the following pair exchange reactions :

$$(A\text{-}Cl\text{-}A)_{pair} + (B\text{-}Cl\text{-}B)_{pair} = 2\ (A\text{-}Cl\text{-}B)_{pair} \qquad (1)$$

where A and B are two different cations. As Δg_{ABCl} becomes progressively more negative, reaction (1) is shifted to the right, (A-Cl-B) pairs predominate, and the solution becomes progressively more ordered. The Gibbs free energy of the liquid solution is given by :

$$G = \sum_i n_i \cdot g_i^o - T \cdot \Delta S^{config} + \sum_i \sum_{j>i} n_{ij} (\Delta g_{ij}/2) \qquad (2)$$

where n_i and g_i are the number of moles and molar Gibbs free energy of pure component i, ΔS^{config} is an approximate expression for the configurational entropy of mixing, given by randomly mixing the (i-j) pairs, and n_{ij} is the number of moles of (i-j) pairs.

The binary systems ACl-"$AlCl_3$" (where A = Li, Na and K) show strong negative deviations from ideality at the equimolar composition (due to short-range ordering in the liquid phase), and the binary mixtures exhibit a region of liquid-liquid immiscibility at high "$AlCl_3$" content (see the calculated NaCl-"$AlCl_3$" phase diagram in **Figure 1**). The existence in ACl-"$AlCl_3$" melts of $AlCl_4^-$ and $Al_2Cl_7^-$ species has been observed by Raman spectroscopy **[6,7]**. The Modified Quasichemical Model does not explicitly introduce complex anions. However, short-range ordering through reaction (1) when Δg_{ABCl} is very negative is conceptually identical to the explicit assumption of complex anions and yields a very similar configurational entropy expression. In order to introduce two different compositions of maximum short-range-ordering near the $AlCl_4^-$ and $Al_2Cl_7^-$ compositions, pure liquid aluminum chloride was modeled as a mixture of $AlCl_3$ and Al_2Cl_6 (with paired aluminum cations) with the constraint that the experimental solid-liquid and liquid-gas equilibria be satisfactorily reproduced (**Figure 2**). The "ACl-MCl_3" systems (where M = Mg, Mn, Fe, Co and Ni) were modeled by introducing two different compositions of maximum short-range-ordering near the $M(AlCl_4)_2$ and $M(Al_2Cl_7)_2$ compositions (see the calculated "$MgCl_2$-$AlCl_3$" phase diagram in **Figure 3**). Other results for the NaCl-"$AlCl_3$" system are shown in **Figures 4 & 5**. Results for various multicomponent systems are shown in **Figures 6, 7, 8, 9, 10, 11 & 12**.

[4] A.D. Pelton, S.A. Degterov, G. Eriksson, C. Robelin and Y. Dessureault, *Metall. Mater. Trans.*, 2000, vol. 31B, pp. 651-9.
[5] A.D. Pelton and P. Chartrand, *Metall. Mater. Trans.*, 2001, vol. 32A, pp. 1355-60.
[6] S.J. Cyvin, P. Klaeboe, E. Rytter and H.A. Øye, *J. Chem. Phys.*, 1970, vol. 52, pp. 2776-8.
[7] H.A. Øye, E. Rytter, P. Klaeboe and S.J. Cyvin, *Acta Chem. Scand.*, 1971, vol. 25, pp. 559-76.

Optimization of the thermodynamic properties of the gaseous species **$NaAlCl_4$(g)** and **$Na_2Al_2Cl_6$(g)**.