Excess Free Energies in Molten CuCl-KCl-LiCl by EMF Measurements

Z. Giazitzoglou, H. Engels, and U. Schiller
Lehrstuhl für Technische Thermodynamik an der RWTH Aachen

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The ternary liquid system CuCl-KCl-LiCl has been investigated by means of emf measurements at about 450 up to 700 °C. Excess free energies and activity coefficients for molten CuCl in the KCl-LiCl eutectic are calculated by a best fit to the obtained data and from literature data for the corresponding binary systems employing the Redlich-Kister equation.

Introduction

In contrast to the investigations presented in [1], emf measurements for a very pure CuCl quality (Ventron Karlsruhe, FRG, No. 400151, 99.999%) in molten KCl-LiCl eutectic (41.5 mol% KCl) have been carried out in the present work using a reversible CuCl formation cell and a technique which has been described previously [1, 2]. Excess free energies for the ternary system, using data for the three corresponding binary systems, have been calculated by a method already reported [2]. The following indication has been chosen here for the components: CuCl = 1, KCl = 2, LiCl = 3.

Results

The emf measurements, corrected according to the relations given in [1], are plotted in Fig. 1 versus temperature for various concentrations of CuCl. Their least squares lines are presented in form of the following equations:

$x_1 = 0.0202$	$(E - E^0)/\text{mV} = -10.7 + 0.4203\ T$
0.0795	$-14.8 + 0.2990\ T$
0.1010	$-6.2 + 0.2682\ T$
0.1407	$1.1 + 0.2247\ T$
0.1761	$-13.7 + 0.2211\ T$
0.2451	$-4.9 + 0.1713\ T$

where x_1: mole fraction of CuCl, E: measured emf, E^0: standard emf of pure liquid CuCl, T/K.

Reprint requests to Z. Giazitzoglou, Lehrstuhl für Technische Thermodynamik an der RWTH Aachen, D-5100 Aachen.

The partial molar excess free energy of CuCl (G_1^E) in the system investigated has been calculated from the present data using the Margules equation $G_1^E = (1 - x_1)^2 [A + 2(B - A)\, x_1]$. The coefficients obtained are $A/J\ \text{mol}^{-1} = 1144 - 8.488\ T$ and $B/J\ \text{mol}^{-1} = 653 - 9.197\ T$ with T/K.

In order to determine the integral molar excess free energy of the ternary system CuCl-KCl-LiCl the integral excess free energies for the corresponding binary systems have to be calculated applying the Redlich-Kister equation. By using the emf measurements for the CuCl-KCl system [3] and for the CuCl-LiCl system [4] the following results have been achieved:

$$\text{CuCl-KCl}\quad G_{12}^E = x_1 x_2 [A_{12} + B_{12}(x_1 - x_2)],$$
$$A_{12} = -6054 - 30.155\ T,$$
$$B_{12} = 5554 - 12.402\ T;$$
$$\text{CuCl-LiCl}\quad G_{13}^E = x_1 x_3 [A_{13} + B_{13}(x_1 - x_3)],$$
$$A_{13} = 13471 - 15.221\ T,$$
$$B_{13} = 1138 - 3.444\ T.$$

For the KCl-LiCl system holds [2]: $G_{23}^E = A_{23} x_2 x_3$, $A_{23} = -17991 + 5.753\ T$, where $G_{ij}^E/\text{J mol}^{-1}$, T/K. Thus the integral excess free energy of the CuCl-KCl-LiCl system (G^E), the partial excess free energy of CuCl (G_1^E) according to the following equation

$$G_1^E = A_{12} x_2 (1 - x_1) + A_{13} x_3 (1 - x_1) - A_{23} x_2 x_3 + 2(B_{12} x_1 x_2 + B_{13} x_1 x_3) - (B_{12} x_2^2 + B_{13} x_3^2) - 2[B_{12} x_1 x_2 (x_1 - x_2) + B_{13} x_1 x_3 (x_1 - x_3)]$$

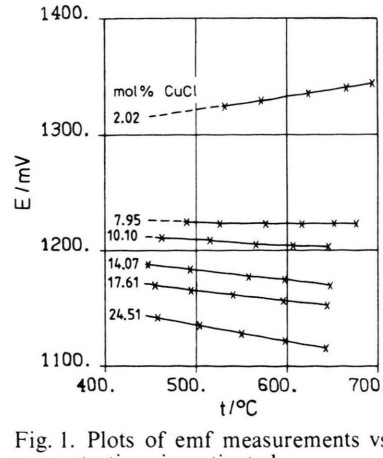

Fig. 1. Plots of emf measurements vs. temperature at the concentrations investigated.

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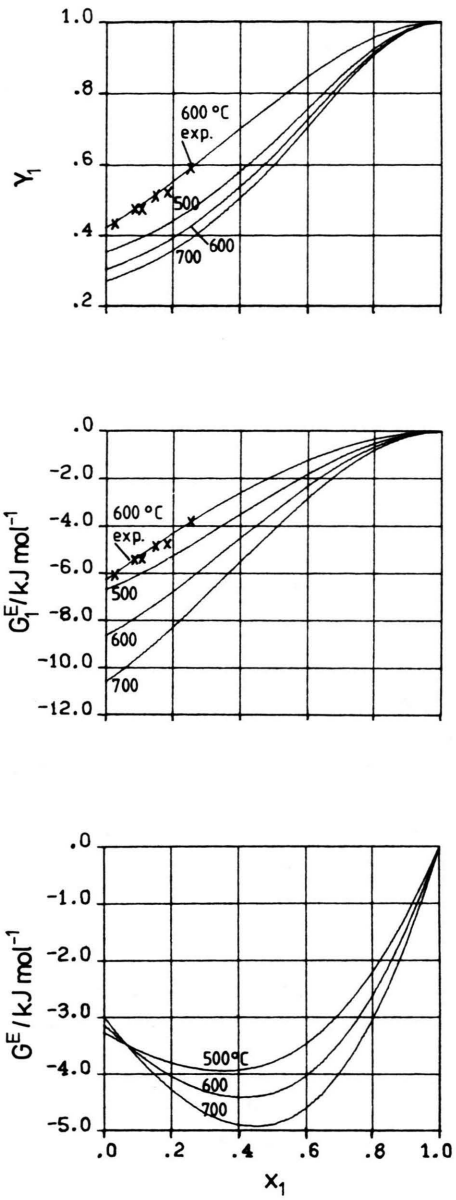

Fig. 2. Plots of the integral (G^E) and partial molar (G_1^E) excess free energies and activity coefficient (γ_1) of CuCl calculated from binary data at three temperatures (——), and the experimental (x) and thereby calculated (——) data at 600 °C in the molten CuCl-KCl-LiCl system.

and its activity coefficient (γ_1) are obtained, being presented in Fig. 2 for three temperatures. There result some deviations from the experimental data, as exemplified by the curves shown for 600 °C.

Discussion

The present emf results lie on the average by about 5 mV higher than the values achieved in [1] with a less pure CuCl quality. Therefore somewhat higher values result in this work for the excess properties of CuCl.

The method for calculating the thermodynamic excess properties of a ternary system from binary data was successfully used in [2, 5] for similar molten chloride mixtures. The probable reason for the deviations appearing here is the different source of the data used. This is also confirmed by the fact that the literature data for the CuCl-KCl and CuCl-LiCl systems [3, 4] used in this work are not in agreement at all with the results published in [6] by the same authors about these mixtures. Especially in the case of the CuCl-LiCl system there appears a sign reversal for the excess free energies [4] not typical for this kind of salts. Because of the uncertainty arising in regard to the quality of the available binary data no ternary interaction terms for the investigated system by correlation of the experimental data obtained in this work were determined.

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