Journal of Thermal Analysis, Vol. 45 (1995) 437-445

REPRODUCIBILITY OF PHASE CHANGES IN THE SYSTEM $CuCl_2$–KCl

K. Żurowski

Institute of Chemistry, Pedagogical University, 20-020 Kielce, ul. Chęcińska 5, Poland

Abstract

The reproducibility of the phase changes at 533–543, 573–593K and 603–623 K in the system $CuCl_2$–KCl was investigated by DTA analysis, supplemented with röntgenographic analysis. Conclusions were drawn in connection with a liquid melt and the solid state of the system.

Keywords: $CuCl_2$–KCl system, phase changes

Introduction

The reproducibility of the phase changes at 533–543, 573–593 and 603–623 K in the system $CuCl_2$–KCl has been investigated by DTA and thermogravimetric techniques in the present work in order to obtain information on the nature of the ionic species in the liquid melts obtained during fusion in the system at 573–593 and at 603–623 K [1]. These phase changes occur in a range of temperatures of about 20 deg, depending on the Cu/K molar ratio in the mixture and on the temperature of preparation of the mixture. This 20 deg temperature range also results from the occurrences of reactions between the ions obtained immediately after melting of the mixtures. It was earlier discovered [2] that all the above phase changes take place without a special gas atmosphere and that the existence of the phase change at 533–543 K depends on the temperature at which the sample was prepared. It was proposed [2] that the phase change at 533–543 K results from decomposition of the $CuCl_2$–KCl mixtures during their annealing at 473 K. Melting of the (1:2) $CuCl_2$–KCl mixtures at 573–593 K is accompanied by the reactions between the ions at 593 K [2]. It has also been established [1, 2] that KCl crystals probably exist in the melts and do not participate in the above reactions. From the results presented in [2], it is possible to conclude that the phase change at 603–623 K yields stable ions in the melt, probably $Cu_2Cl_6^{2-}$.

Experimental

The reproducibility of the phase changes was investigated with a derivatograph (MOM, Budapest, Hungary). Weighed quantities of $CuCl_2 \cdot 2H_2O$ and

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

KCl (Poch, Gliwice), mixed in appropriate proportions, were evaporated to dryness at 393 K. After cooling down to room temperature, the samples were crushed and ground, and subjected to the first thermogravimetric analysis. Mixtures with $CuCl_2$ to KCl molar ratios of 0.5, 0.622, 0.691, 0.768, 0.845, 0.922 and 1.0 were prepared as described above. Thermogravimetric analyses were performed within different temperature ranges, depending on the number of heating cycles of the system $CuCl_2$–nKCl. The samples with n=2.0, 1.61 and 1.45 were heated three times during the DTA experiments: twice up to 601 K, and the third time up to 663 K. All other samples were heated five times: twice up to 601 K, and the following three times up to 663 K. It should be noted that the first temperature is closely above the melting range of the samples at 573–593 K, and the second one is closely above the melting range of the samples at 603–623 K [2]. After each heating, the heater was rapidly removed and the samples were quickly crystallized in the crucible. After cooling down to room temperature, the samples were heated for measurement in the same crucible. All DTA measurement conditions were identical: a constant sample mass of 0.900 g, a corundum crucible, air atmosphere, Al_2O_3 as reference material, a heating rate of 5 deg/min and sensitivity TG 200 mg.

Additionally, the samples with n=2.0 and 1.0 were rapidly crystallized after melting and were next dissolved in C_2H_5OH of analytical grade purity. The white crystalline residue in the solution was analysed röntgenographically with a DRON-2 diffractometer. The X-ray diffraction spectra of the samples that were rapidly crystallized from the same melts were also analysed.

Results

Figure 1 shows the endothermic effects in the DTA curves of the sample with n=1.084 in the 5th heating experiment.

The DTA curves reveal changes in the areas of the endothermic effects with peaks at 533–543 K, 573–593 K and 603–623 K. The endothermic effect with minimum at 533–543 K appears in the DTA curve obtained in the 2nd heating, but not in the DTA curve obtained during the 1st heating. This effect continues to appear in the subsequent DTA curves (3rd, 4th and 5th heatings). The endothermic effect associated with the peak at 573–593 K is diminished during the 2nd heating, but is constant after each subsequent heating. The endothermic effect with minimum at 603–623 K starts to appear in the 3rd DTA experiment, but its area is reduced in the subsequent runs. Figure 2 demonstrates the variation in area of the 533–543 K peak as a function of the composition of the samples, for each heating experiment.

The Figure clearly shows that the area of the peak with minimum at 533–543 K decreases to zero as the molar ratio of Cu to K in the samples is increased to 1.0. It is also seen that the area of the peak is practically independent

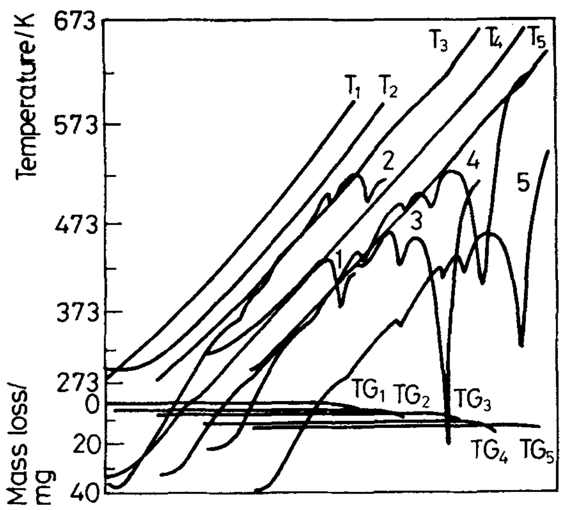


Fig. 1 DTA, DTG and T curves of the system $CuCl_2$–KCl with the molar ratio of Cu to K equal 0.922. Index 1, 2, 3, 4 and 5 is a number of heating

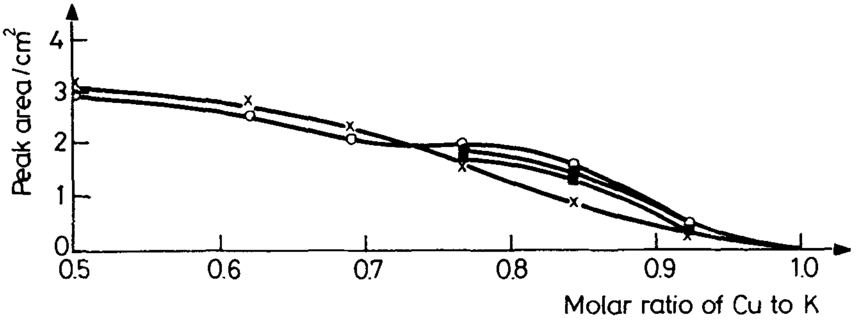


Fig. 2 Variation of the peak areas of the endothermic effects at 533–543 K as a function of the molar ratio of Cu to K in the system $CuCl_2$–KCl. o: 2nd heating; x: 3rd heating; •: 4th heating; ■: 5th heating

of the number of heating cycles. Figure 3 demonstrates the variation in area of the peak with minimum at 573–593 K in the DTA curves as a function of the composition of the sample for each heating experiment.

Figure 3 shows that the area of the peak with minimum at 573–593 K decreases to zero as the molar ratio of Cu to K in the samples is increased to 1.0. It is also seen that the area of the endothermic effect with minimum at 573–593 K is reduced in the 2nd DTA curves and is practically constant after the subsequent heatings. It is worthy of note that the appearance of the 603–623 K peak in the DTA curves does not influence the areas of the 533–543 K peak (Fig. 2) and the 573–593 K peak (Fig. 3). Figure 4 demon-

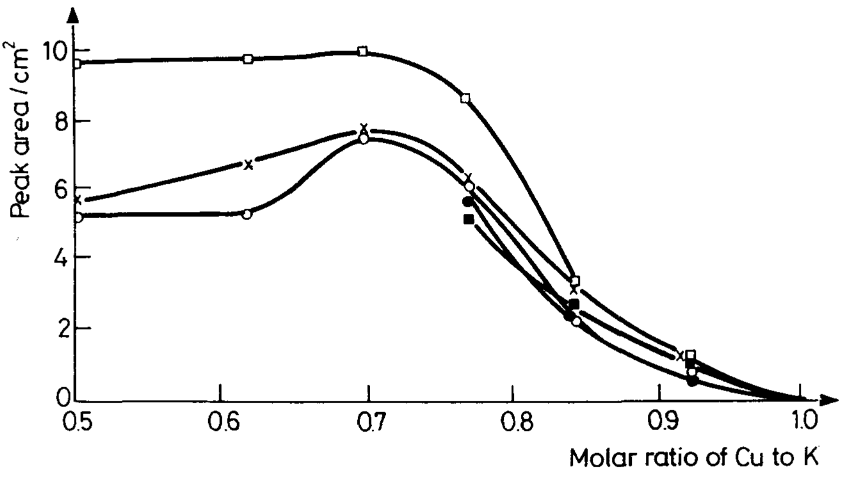


Fig. 3 Variation of the peak areas of the endothermic effects at 573–593 K as a function of the molar ratio of Cu to K in the system $CuCl_2$–KCl. □: 1st heating; o: 2nd heating; x: 3rd heating; •: 4th heating; ■ : 5th heating

strates that the area of the 603–623 K peak increases as the molar ratio of Cu to K in the samples is increased to 1.0.

The area of the peak at 603–623 K is markedly reduced in the DTA curves of the samples obtained after the 4th heating and decreases slightly during the next heating. It is noteworthy that the 603–623 K peak does not appear in the first three DTA curves for the samples with n=2.0, 1.61 and 1.45. Röntgenographic analysis of the white crystals from C_2H_5OH solution led to the residue being identified as KCl. Röntgenographic analyses of the sample of $CuCl_2$–2KCl rapidly crystallized at 573–593 K showed Bragg peaks from K_2CuCl_4 and KCl phases in addition to very weak peaks from $CuCl_2$.

Discussion

The phase change at 533–543 K occurs in the solid state of the system $CuCl_2$–KCl [1, 2]. It was not detected in the 1st DTA curves. Crystallization of the system $CuCl_2$–KCl at 573–593 K gave the solid phase which undergoes the phase change at 533–543 K. After such rapid crystallization, interplanar spacings characteristic of K_2CuCl_4 were identified röntgenographically in the solid samples. This appears to indicate the existence of $CuCl_4^{2-}$ in the liquid melts obtained at 573–593 K. Analogously, lines of very weak intensity in the X-ray spectra of $CuCl_2$ indicate the existence of Cu^{2+} in the liquid melts obtained at 573–593 K. The white crystals of KCl and the diffraction peaks of KCl in the X-ray spectra of the samples obtained by rapid crystallization at 573–593 K indicate the existence of Cl^- in the liquid melts. The area of the 533–543 K peak

(Fig. 2) decreases to zero in a similar manner to that of the peak at 573–593 K [3]. The area of the 533–543 K peak was practically unchanged when the liquid system crystallized at 603–623 K (2nd and 5th heatings, Fig. 2). All the above observations suggest that the peak at 533–543 K is a result of the crystallization of that part of the system $CuCl_2$–KCl which melts at 573–593 K. This means that the peak at 533–543 K in the DTA curves is a result of crystallization of the mixture of $CuCl_4^{2-}$, Cu^{2+} and Cl^- which exist in the melt above 603–623 K.

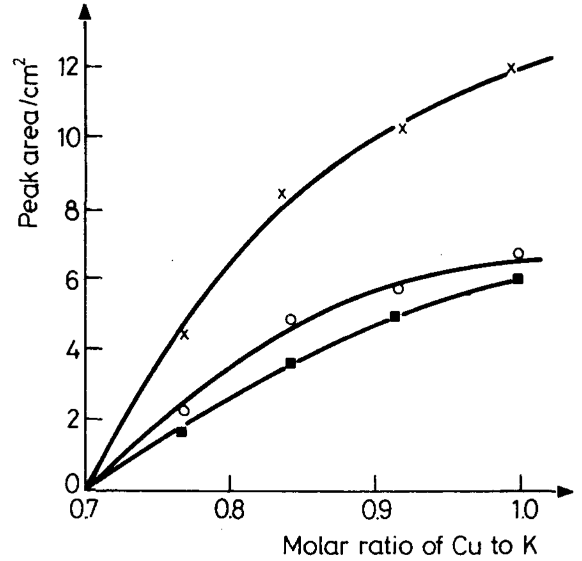


Fig. 4 Variation of the peak areas of the endothermic effects at 603–623 K as a function of the molar ratio of Cu to K in the system $CuCl_2$–KCl. x: 3rd heating; o: 4th heating; ■: 5th heating

If it is assumed that $KCuCl_3$ crystallizes first from the $CuCl_2$–KCl melt [4], together with the results which suggested the possibility of Cu hexacoordination involving $CuCl_4^{2-}$ groups in the solid state [5], it may be stated that $CuCl_4^{2-}$ groups crystallize together with Cu^{2+} and Cl^- to give the system K_2CuCl_4–KCl–$KCuCl_3$ [4], while Cu hexacoordination and deformed $CuCl_4^{2-}$ groups are created similarly as presented in Fig. 5.

Figure 5 shows that the shift of Cl^- towards the creation of Cu hexacoordination in the crystal lattice of the system $CuCl_2$–KCl gives the surface configuration $4K^+ + Cl^-$ [6], which is characteristic of the wall of the KCl unit cell. $K_2Cu_2Cl_6$ in the solid phase melts at 603 K [1, 8]. The phase change at 603–623 K was not detected for the 3rd heating of the samples with $n=2$, 1.61 and 1.45. This indicates that $K_2Cu_2Cl_6$ does not exist in samples of the system $CuCl_2$–KCl crystallized at 573–593 K as a separate phase. Thus, it may be supposed that $Cu_2Cl_6^{2-}$ does not exist in the melt obtained at 573–593 K and that a

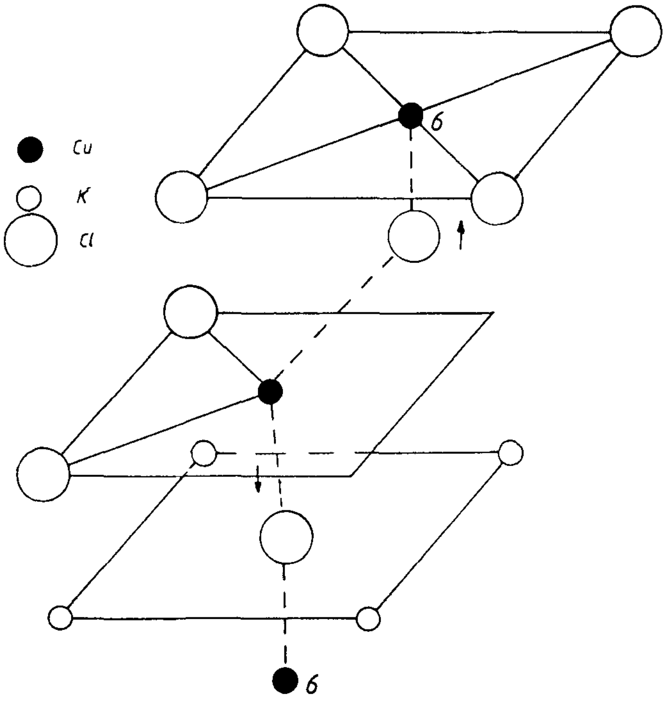


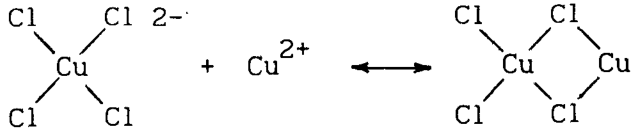
Fig. 5 Probable configuration of the $CuCl_4^{2-}$ ions after crystallization of the system $CuCl_2$–KCl at 573–593 K

posed that $Cu_2Cl_6^{2-}$ does not exist in the melt obtained at 573–593 K and that a space configuration of K_2CuCl_4, KCl and $KCuCl_3$ (Fig. 5) undergoes a phase change at 533–543 K. It was proposed in [4] that K_2CuCl_4–KCl–$KCuCl_3$ undergoes a phase change at 540 K. It may be said that during such a phase change deformed $CuCl_4^{2-}$ groups may become planar at 540 K and pass into the liquid melt at 573–593 K, giving Cu^{2+} and Cl^- from durable deformed $CuCl_4^{2-}$ groups. An equilibrium between the above ions is probably achieved. The shapes of the curves presented in Fig. 3 are the same, independently of the number of heating cycles, and similar to that obtained in [3]. This suggests that only that part of the solid system $CuCl_2$–KCl which was established in [8] as the phase K_2CuCl_4 melts and crystallizes at 573–593 K. The decrease in area of the 573–593 K peak (Fig. 3) in the DTA curves for the 2nd to 5th heatings, as compared with the 1st one, supports the statement that KCl crystallizes from the melts as a separate phase (röntgenographic analysis). However, this reduction in area (Fig. 3) evidently results from crystallization of the system K_2CuCl_4–KCl–$KCuCl_3$ from the melt. The same phenomenon of peak area reduction is observed in Fig. 4, when the phase change at 603–623 K was registered in the

DTA curves during the 3rd to 5th heatings of the system $CuCl_2$–KCl. The 603–623 K phase change does not provide $CuCl_4^{2-}$ and Cu^{2+} in the melt under the DTA conditions, because the curves for the 2nd to 5th heatings in Fig. 3 are practically the same. The decrease in the 603–623 K peak area results from decomposition of $Cu_2Cl_6^{2-}$, as the peak at 603–623 K in the DTA curves was attributed to the solid phase $K_2Cu_2Cl_6$ [1, 8]. This decomposition generally gives Cl^- in the melt, as the KCl phase was found röntgenographically in the sample of composition $CuCl_2 \cdot 1KCl$ after its crystallization. Decomposition of $Cu_2Cl_6^{2-}$ under the present DTA conditions does not lead to a considerable amount of $CuCl_4^{2-}$ and Cu^{2+} because neither of the phase changes at 533–543 K and 573–593 K were registered in the DTA curves obtained during successive heatings of $CuCl_2 \cdot 1KCl$ (Figs 2 and 3). The curves presented in Figs 2 and 3 are also practically the same for the system $CuCl_2$–KCl with molar ratios of Cu to K from 0.768 to 1.0 during successive heatings. Thus, with regard to the proposed constitution of $Cu_2Cl_6^{2-}$ [4, 8], it may be suggested that $Cu_2Cl_6^{2-}$ decomposes in the following way:

(1)

The liquid melt then crystallizes to give $K_2Cu_2Cl_6$ and KCl as solid phases. The complex Cu_2Cl_4 proposed in reaction (1) can be stabilized in the $CuCl_2$–KCl liquid melt by the $CuCl_4^{2-}$ and Cu^{2+} provided in the melt by the 573–593 K phase change:



(2)

The existence of Cu_2Cl_4 in the liquid melt arising from reaction (2) would explain the double character of the peak at 573–593 K [2]. The double character of that peak may also result from reaction (3):

$$CuCl_4^{2-} + Cu^{2+} + 2Cl^- \rightarrow Cu_2Cl_6^{2-} \tag{3}$$

but it is much less probable that the four ionic species participate in the formation of $Cu_2Cl_6^{2-}$ at the same time. The equilibrium constant of reaction (3) is therefore assumed to be very small. No double character of the peak at 573–593 K was observed for the system $CuCl_2$–KCl with a molar ratio of Cu to K higher than 0.5 [2]. This may be due to partial dissolution of the $K_2Cu_2Cl_6$

phase in the liquid melt obtained at 573–593 K and the attainment of equilibrium in reaction (3) or more probably in reaction (2).

Conclusions

The phase change at 533–543 K results from the shift of Cl^- towards the formation of planar $CuCl_4^{2-}$ in the solid state of the system $CuCl_2$–KCl. Under the present DTA conditions, this phase change is not a result of a decomposition process, as suggested in [2].

$CuCl_4^{2-}$, Cu^{2+} and Cl^- generally exist in the liquid melts obtained at 573–593 K. Equilibrium may be achieved among them.

White crystals of KCl crystallize as a separate phase from the liquid melts of the system $CuCl_2$–KCl.

The system $CuCl_2$–KCl crystallizes at 573–593 K a space configuration system K_2CuCl_4–KCl–$KCuCl_3$, which undergoes a phase change at 533–543 K.

The double character of the phase change at 573–593 K probably results from the following reaction, which occurs additionally at 593 K under the DTA conditions:

$$CuCl_4^{2-} + Cu^{2+} \rightarrow Cu_2Cl_4$$

The phase change at 603–623 K gives $Cu_2Cl_6^{2-}$. This is not stable, as mentioned in [2, 4]. After melting of the system $CuCl_2$–KCl at 603–623 K, $Cu_2Cl_6^{2-}$ decomposes, probably as follows:

$$Cu_2Cl_6^{2-} \rightarrow Cu_2Cl_4 + 2Cl^-$$

The complex Cu_2Cl_4 crystallizes from the liquid melt, similarly as the solid phase $K_2Cu_2Cl_6$ [9], and during successive heating it melts, also at 603–623 K.

* * *

The author dedicates this work to the memory of the late Professor Zdzislaw Czarny.

References

1 K. Żurowski, J. Thermal Anal., 38 (1992) 2369.
2 K. Żurowski, J. Thermal Anal., in press.
3 Z. Czarny and K. Żurowski, J. Thermal Anal., 32 (1987) 1387.
4 C. M. Fontana and E. Gorin, Ind. Eng. Chem., 44 (1952) 363.
5 K. Żurowski, Polish J. Chem., 66 (1993) 1.
6 H. Suga and M. Sorai, Bull. Chem. Soc. Japan, 38 (1965) 1007.
7 K. Żurowski, Polish J. Chem., 67 (1993) 1.
8 K. Żurowski, J. Thermal Anal., in press.
9 A. F. Uells, Structural Inorganic Chemistry (in Russian), Mir, Moscow 1987, pp. 274–277.

Zusammenfassung — Mittels DTA, verbunden mit röntgenographischer Analyse wurde im System $CuCl_2$-KCl die Reproduzierbarkeit der Phasenumwandlungen bei 533–543 K, bei 573–593 K und bei 603–623 K untersucht. Schlußfolgerungen in Verbindung mit der flüssigen Schmelze und dem Festzustand des Systemes wurden gezogen.