

SOME ASPECTS OF THE PHASE CHANGES OF THE CuCl₂-KCl SYSTEM

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Abstract

The mixtures of CuCl₂ and KCl with Cu to K molar ratios from 0.2 to 2.0 were analysed by thermogravimetry in air and argon atmosphere under different conditions. The samples differed in the temperature of their preparation. Conclusions were drawn concerning the phase changes and the constitution of the CuCl₂-KCl system.

Keywords: CuCl₂-KCl system

Introduction

The phase changes of the CuCl₂-KCl system [1] have not been described unequivocally, especially in respect of the ion constitution. The question arises whether the phase changes of the CuCl₂-KCl system are influenced by the temperature of the preparation of the solid phase, whether the atmosphere has an effect on the reaction. It is important to estimate the character (i.e. single, double) of the DTA peaks presented in [1]. This can be done by varying the experimental conditions during the thermogravimetric analyses. In this work thermogravimetric investigations of the system CuCl₂-KCl obtained at room temperature, at 363 and at 423 K are described. In the experiments inert and air atmosphere, different rate of heating and different DTA sensitivity were used. The Cu to K molar ratios in the samples was varied from 0.2 to 2.0. Therefore there was excess of the KCl and CuCl₂ over the stoichiometry of K₂CuCl₄ and KCuCl₃.

Experimental

To obtain the system CuCl₂-KCl, copper(II) chloride dihydrate and potassium chloride (POCh Gliwice) were used. Weighed quantities of the two salts were dissolved in distilled water and the solutions were evaporated to dryness at

room temperature. The dry residue was crushed and ground. A part of the solution was rapidly evaporated to dryness at 363 and another part at 423 K for 4 h in air atmosphere. After cooling down to room temperature, the samples were subjected to thermogravimetric analysis using a Derivatograph (MOM Budapest, Hungary) within the temperature range 293–773 K. Argon was used as an inert gas.

Results

Table 1 shows the areas of the endothermic peaks in the DTA curves of the samples investigated in which the molar ratios of Cu to K changed from 0.5 to 1.0. The peak areas were obtained for the mixtures of CuCl_2 and KCl obtained at 363 K (air and argon atmosphere) and 423 K.

Table 1 The areas of the endothermic peaks at 573–583 K and at 603–618 K depending on the temperature of preparing the samples and on the atmosphere of analyses

Atmosphere		Air				Argon	
T of preparation / K		363		423		363	
T of peak / K		573–583	603–618	573–583	603–618	573–583	603–618
Molar ratio	Cu/K	Area / cm^2					
0.5		7.2	0	7.5	0	7.0	0
0.622		6.8	0	7.0	0	7.0	0
0.691		7.6	0	7.2	0	7.3	0
0.768		5.5	2.2	5.7	1.5	5.2	1.5
0.845		3.8	4.0	3.5	4.5	3.2	4.2
0.922		1.2	6.5	1.1	7.0	1.0	6.2
1.0		0	9.0	0	9.2	0	9.0

The area of the endothermic peaks at 573–583 K and at 603–618 K was almost the same for the mixtures obtained at 363 and 423 K, independently of the atmosphere used in the DTA analyses. The variations of the peak areas measured were identical to those described in [1], when the mixtures of CuCl_2 and KCl were obtained at 473 K. It is worth mentioning that the small endothermic DTA peak at 533–543 K described in [1] was not observed in the present study. It may be assumed, that the mixtures investigated undergo an energetically very small phase change between 423 and 473 K or exactly at 473 K. To prove this phase change, DTA curves of the mixtures of CuCl_2 and KCl obtained at 423 K were recorded at a small rate of heating ($2.5 \text{ deg}\cdot\text{min}^{-1}$) and very high DTA sensitivity (1/1.5). As an example, the thermoanalytical curves of the mixture with a Cu to K molar ratio of 0.622 is shown in Fig. 1. Up to 523 K, no

phase change was registered in the DTA curves of the mixtures with Cu to K molar ratios from 0.5 to 1.0.

It was interesting to find out whether the phase changes at 573–583 K and at 603–618 K are accompanied by a reaction between ions. The DTA curves of the system $\text{CuCl}_2\text{-KCl}$ with molar ratios from 0.5 to 1.0 were obtained using very slow heating ($1.25 \text{ deg}\cdot\text{min}^{-1}$). Although the mixtures were prepared at room temperature, the same phenomenon of disappearance and growing of the peaks at 573–583 K and at 603–618 K as it was seen in Table 1 and in [1], was observed. A double peak was obtained at 573–583 K for the mixture with a Cu to

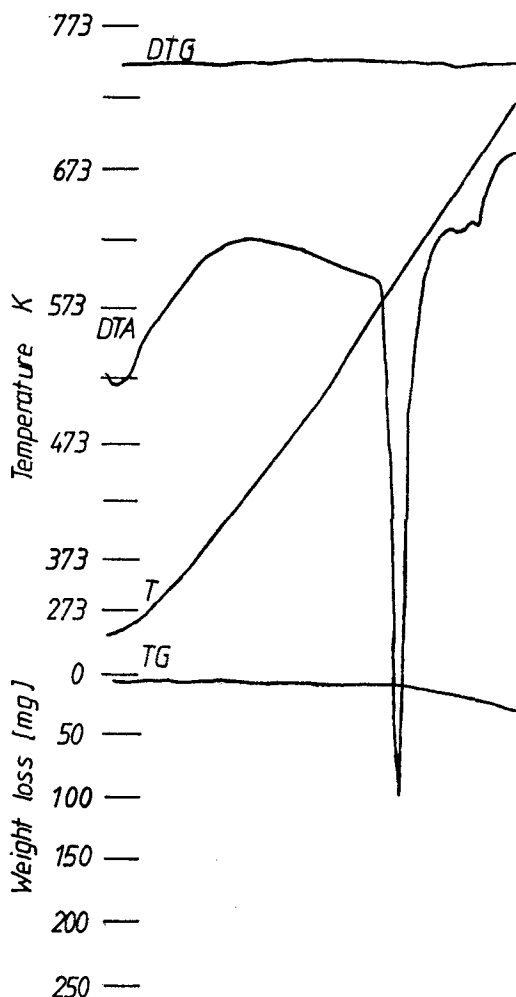


Fig. 1 DTA, TG and DTG curves of a mixture of CuCl_2 and KCl . Molar ratio of Cu to K = 0.622. Rate of heating $2.5 \text{ deg}\cdot\text{min}^{-1}$, DTA sensitivity $1/1.5$, $m = 0.600 \text{ g}$

K molar ratio of 0.5. Both effects, with minima at 583 and at 593 K, were well shaped.

The peak at 603–618 K was also expected to consist of two peaks but this was not observed and its minimum was shifted to 623 K. It is interesting that the separation of the two peaks at 573–583 K was observed only for the mixture of CuCl_2 and KCl with a Cu to K molar ratio of 0.5 and did not appear in the DTA curves of the samples with Cu to K molar ratio higher than 0.5. The area of the endothermic peaks at 583 and at 593 K decreases linearly with the decrease of the Cu to K molar ratio below 0.5 (Fig. 2). The two curves which are presented in Fig. 2 are parallel. The area of the peak at 623 K shows a slight linear decrease as the Cu to K molar ratio increases over 1.0 (Fig. 3). No sepa-

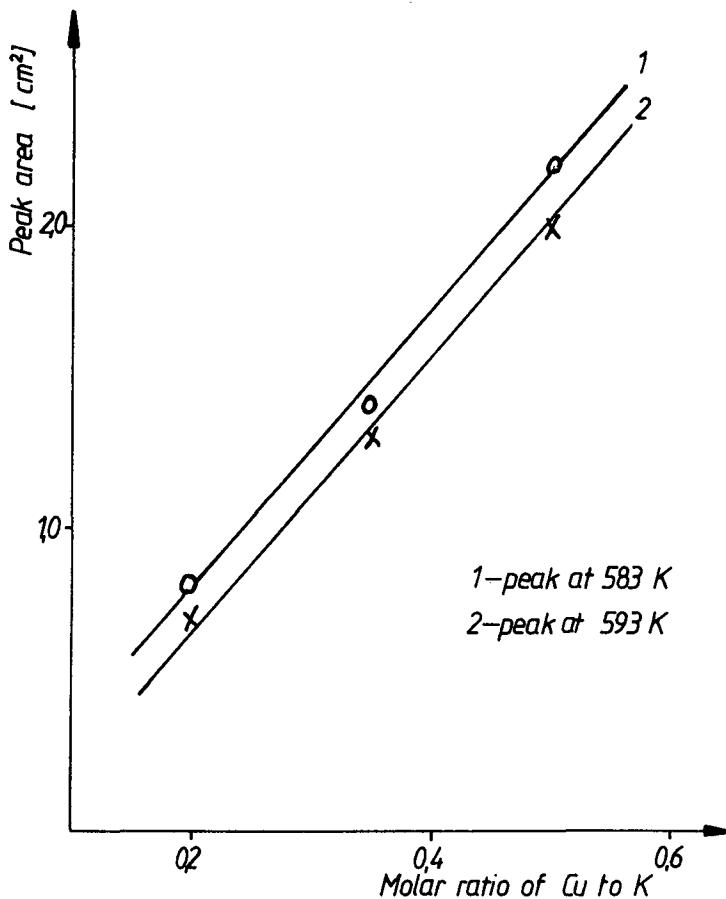


Fig. 2 Variation of the areas of the endothermic effects represented by peaks at 583 and 593 K as function of the molar ratio of Cu to K below 0.5 in the mixtures. Rate of heating $1.25 \text{ deg}\cdot\text{min}^{-1}$, DTA sensitivity $1/3$, $m = 0.760 \text{ g}$

ration of the peak at 623 K was observed for mixtures with Cu to K molar ratio higher than 1.0.

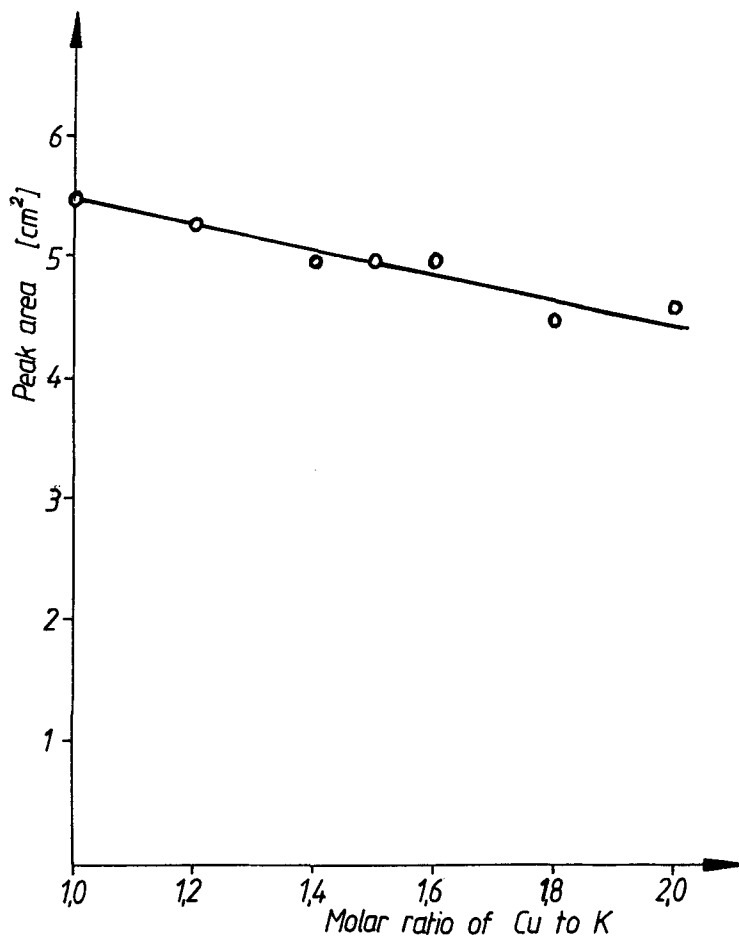


Fig. 3 Variation of the area of the endothermic effect represented by a peak at 623 K as function of the molar ratio of Cu to K higher than 1.0 in the mixtures. Rate of heating $2.5 \text{ deg}\cdot\text{min}^{-1}$, DTA sensitivity $1/5$, $m = 0.600 \text{ g}$

Discussion

The data presented in Table 1 indicate a very good repeatability of the measurements. Similar values and variations were obtained for the areas of the endothermic peaks at 573–583 K and at 603–618 K, independently of the atmosphere used in the analysis. Hence, the above phase changes are not accompanied by any oxidation process. The results presented in Table 1 and the results of the DTA analyses with very small rate of heating ($1.25 \text{ deg}\cdot\text{min}^{-1}$)

show also that phase changes at 573–583 K and at 603–618 K are not dependent on the temperature used during the preparation of the $\text{CuCl}_2\text{-KCl}$ solid system. It may be suggested that the phase change:



which takes place at 365–397 K [2], has any importance in creating the ion constitution of the $\text{CuCl}_2\text{-KCl}$ melt. Moreover, reaction (1) is the last phase change before the melting of the $\text{CuCl}_2\text{-KCl}$ system at 573–583 K and at 603–618 K, because no phase change was observed here between 397 and 573 K. Therefore, the small phase change at 533–543 K exhibited by the DTA curves of the $\text{CuCl}_2\text{-KCl}$ samples heated at 473 K [1], probably results from the decomposition process of the samples during their heating before the DTA analyses. The existence of the peak at 533–543 K in the DTA curves of samples heated at 473 K [1] indicates the unstable character of the $\text{CuCl}_2\text{-KCl}$ system in the solid state, too.

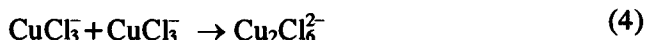
It is very interesting that a double peak was obtained at 573–583 K only for the mixture of CuCl_2 and KCl with a molar ratio of 0.5. The parallel character of the curves presented in Fig. 2 indicates that the phase changes at 583 and at 593 K are consecutive. The last observations suggest that after melting at 583 K the mixture of CuCl_2 and KCl with a Cu to K molar ratio of 0.5 undergoes a reaction between the ions at 593 K. No such reaction between the ions was observed after melting the mixtures with Cu to K molar ratios between 0.622 and 0.691. According to [3], this may be the result of the formation of Cu^{2+} and CuCl_4^{2-} ions at 593 K or the establishment of the equilibrium of the reaction:



It should be noted that according to these results and reaction (1) the $\text{KCuCl}_3 + \text{KCl}$ system melts in the mixtures investigated therefore, unstable [3] CuCl_3^- ions may react as follows:



or



A linear decrease of the curves in Fig. 2 together with the decrease of the Cu to K molar ratio below 0.5 suggests that KCl , over stoichiometry of K_2CuCl_4 combination (reaction 1), does not participate in the phase changes at 583 K and 593 K. It may be only supposed that KCl formed in reaction (1) does not

participate either. These results support that KCl exists in the melt as a solid crystal [4]. Analogously, it may be stated that CuCl_2 over stoichiometry of KCuCl_3 combination does not participate in the phase change at 623 K, and in this phase change ions are released immediately into the melt, as no separation of the peak at 623 K is observed and the curve in Fig. 3 decreases. The phase change with a peak at 623 K may yield stable $\text{Cu}_2\text{Cl}_6^{2-}$ ions [3] in the melt.

Together with the results connected with the solid phase constitution of the investigated mixtures and their melting process [4, 5], it may be supposed that the melting of mixtures with a Cu to K molar ratio of 0.622 and 0.691 produces all the ions existing in the equilibrium of the reaction (2). That is why probably, the separation of the peak at 573–583 K was observed only in the DTA curves of the mixture with a Cu to K molar ratio of 0.5. The above conclusion of course, should be supported by other methods.

Conclusions

The phase changes of the $\text{CuCl}_2\text{-KCl}$ system at 573–583 K and at 603–618 K are not dependent on the temperature of the preparation of the system.

The above phase changes take place without gas atmosphere, therefore no oxidation process of the solid phase and ions accompany them.

Transformation of K_2CuCl_4 into KCuCl_3 [2] at 365–397 K is the last phase change of the mixtures investigated before melting. The phase change at 533–543 K [1] results from the decomposition of the mixtures investigated during heating at 473 K.

The melting of the mixture with a Cu to K molar ratio of 0.5 at 573–583 K is accompanied by reactions between ions at 593 K.

The reactions between ions at 593 K may be connected with the formation of Cu^{2+} , CuCl_4^{2-} and $\text{Cu}_2\text{Cl}_6^{2-}$ ions from CuCl_3^- ions or simply with the establishment of an equilibrium between them.

KCl , probably, does not participate in the phase changes at 573–583 K and at 603–623 K.

CuCl_2 over stoichiometry of the KCuCl_3 combination probably does not participate in the phase change at 603–623 K.

The phase change at 603–623 K produces stable ions in the melt maybe $\text{Cu}_2\text{Cl}_6^{2-}$ ions.

References

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Zusammenfassung — Mittels TG wurden in Luft und in Argonatmosphäre unter verschiedenen Bedingungen Gemische aus CuCl_2 und KCl mit einem Cu zu K Molverhältnis von 0,2 bis 2,0 untersucht. Die Proben unterschieden sich in der Temperatur ihrer Darstellung. Es wurden Schlußfolgerungen bezüglich der Phasenänderungen und des Aufbaues des CuCl_2 -KCl-Systemes gezogen.