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DTA INVESTIGATION OF THERMAL DISSOCIATION OF THE SOLID SYSTEM $CuCl_2$-KCl

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Abstract

Solid mixtures of $CuCl_2$ and KCl were annealed at 473 K for different times, then cooled down to room temperature and thermogravimetrically analysed. The differences in the DTA pictures of the samples were analysed. Conclusions were drawn as concerns the solid and liquid states of the mixtures.

Keywords: $CuCl_2$–KCl solid system, thermal dissociation

Introduction

In paper [1], the oxidation of hydrogen chloride over a melt of copper, potassium and lanthanium chlorides was interpreted in terms of ionic reactions involving the reduction and the reoxidation of the copper. The equilibrium state between the melt and the gaseous phase was described by an equation including the thermal dissociation of $CuCl_2$. In the case of $CuCl_2$ alone (on a support), the Deacon reaction was considered to take place on the surface of the solid state [2]. According to the results presented in [3], ions similar to those assumed in [4] exist in the solid system $CuCl_2$–KCl. Investigation of their thermal dissociation and the influence of this process on the phase changes in the system $CuCl_2$–KCl is therefore expected to yield new information on the properties of the nature of the ions in the solid state and in the liquid melt. The DTA picture of the system $CuCl_2$–KCl is dependent on the temperature of sample preparation. A peak at 533–543 K was not observed in the DTA curves for the samples obtained at 363 and 423 K [5]. It appeared only in the DTA curves of the sample obtained at 473 K [6]. The present work involved thermogravimetric investigations of the system $CuCl_2$–KCl heated at 473 K. This temperature is about 25 deg below the temperature of the phase change in which the phase ($KCuCl_3$+KCl) is obtained [4, Fig. 6].

Experimental

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. To obtain the system $CuCl_2$–KCl, dihy-

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drous copper(II) chloride and potassium chloride (POCh, Gliwice) were used. Weighed quantities of these two salts were dissolved in distilled water. After drying, the system CuCl2–KCl was crushed and ground. Powdered samples were roasted at 473 K for 2, 6, 12 or 72 h. After annealing, the samples were cooled to room temperature and subjected to thermogravimetric analysis with a derivatograph (MOM, Budapest, Hungary) in the temperature range 293–773 K. The measurement conditions were as follows: constant sample mass 0.600 g, corundum crucible, air atmosphere, Al_2O_3 as reference material, heating rate 5 deg·min^{-1}, sensitivity TG 200 mg.

Results

Figure 1 shows the variation in area of the endothermic peak at 533–543 K as a function of the molar ratio of Cu to K in the system $CuCl_2$–KCl for samples kept at 473 K for 2, 6 and 12 h.

It is seen that annealing of the sample at 473 K causes a considerable reduction in area of the peak at 533–543 K for the mixtures with Cu to K molar ratios of from 0.5 to about 0.7. Curve 2 exceeds curve 1 for a Cu to K molar ratio higher

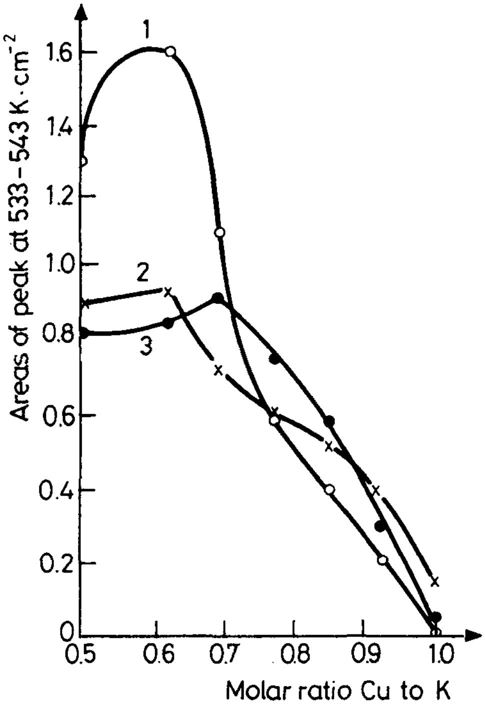


Fig. 1 Variation of the 533–543 K peak area as a function of the molar ratio of Cu to K in the mixtures annealed at 473 K. 2 h of heating – curve 1; 6 h of heating – curve 2; 12 h of heating – curve 3

than 0.75. Curve 3 exceeds curve 2 in the Cu to K molar ratio region from 0.64 to 0.88, and is then situated below curve 2 and above curve 1 as the molar ratio is increased up to 1.0. The annealing has a considerable influence on the peak area at 533–543 K for Cu to K molar ratios of from 0.5 to about 0.65, as compared with the higher molar ratios (about 0.75–1.0).

Figure 2 demonstrates the variation in area of the peak at 573–593 K in the DTA curves obtained after 2, 6 and 12 h of annealing.

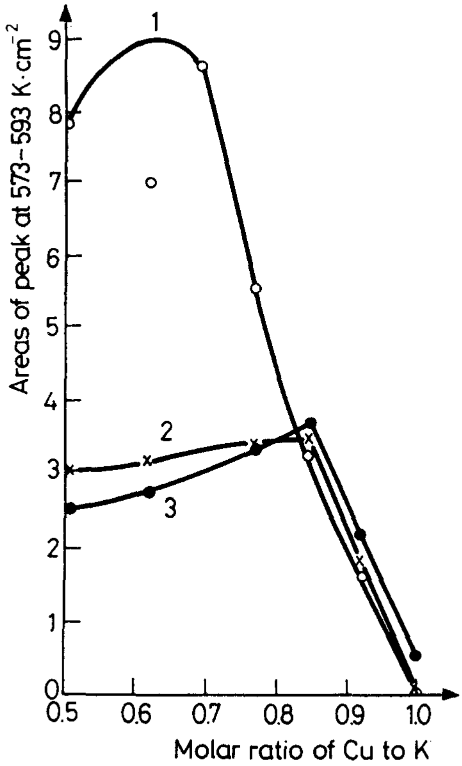


Fig. 2 Variation of the 573–593 K peak area as a function of the molar ratio of Cu to K in the mixtures annealed at 473 K. 2 h of heating – curve 1; 6 h of heating – curve 2; 12 h of heating – curve 3

The annealing appreciably changes the 573–593 K peak area for Cu to K molar ratios of from 0.5 to about 0.85, as compared with higher molar ratios. Curves 2 and 3 increase as the molar ratio is increased from 0.5 to about 0.85. The run of curves 2 and 3 is slightly above that of curve 1 as the Cu to K molar ratio of the mixtures is increased from 0.85 to 1.0.

Figure 3 demonstrates the variation in area of the 603–623 K peak in the DTA curves obtained after 2, 6 and 12 h of annealing.

After 6 h of annealing, a considerable reduction in area of the 603–623 K peak is observed. After 12 h of annealing, there is a further reduction in peak

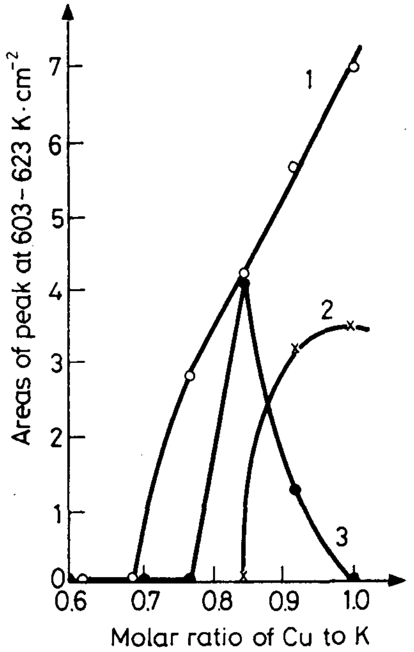


Fig. 3 Variation of the 603–623 K peak area as a function of the molar ratio of Cu to K in the mixtures annealed at 473 K. 2 h of heating – curve 1; 6 h of heating – curve 2; 12 h of heating – curve 3

area. It should be pointed out that the 603–623 K peak was not observed in the DTA curve of the sample with a Cu to K molar ratio of 0.845 after 6 h of annealing. However, after 12 h of annealing, this peak had the same area as that of the identical sample heated for 2 h. Curve 3 is located between curves 1 and 2 in the range of Cu to K molar ratios of from 0.768 to 0.845. The sample with a Cu to K molar ratio of 0.845 was also annealed at 473 K for 72 h and then thermogravimetrically analysed. After such a long annealing, the areas of the peaks at 573–593 K and at 603–623 K were almost identical to those for the same sample but heated at 473 K for 2 h.

Additionally, there were two other endothermic effects, with minima at 663–683 K and at 693–703 K, in the DTA curves of the mixtures heated at 473 K. During thermogravimetric analyses, ideal separation of the two effects in the DTA curves was not attained. Figure 4 demonstrates the variation in area of these peaks as a function of the composition of the mixture.

The area of the peak at 663–683 K increases as the Cu to K molar ratio is increased up to 0.845, and next decreases to almost zero. The shape of curve 1 is almost identical to that of curves 2 and 3 in Fig. 2. The area of the peak at

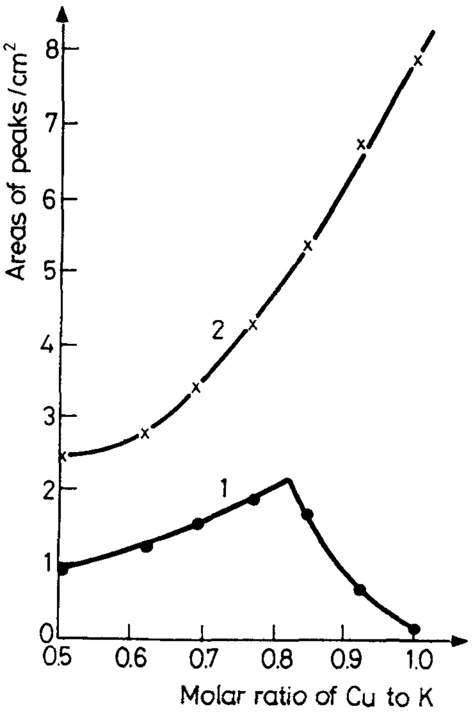
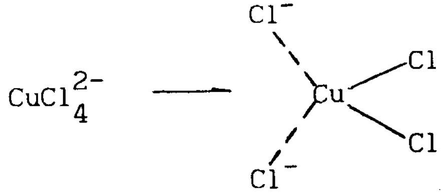


Fig. 4 Variation of the peak areas of the endothermic effects at 663–683 K (curve – 1) and at 693–703 K (curve – 2) as a function of the molar ratio of Cu to K in the mixtures annealed at 473 K for 6 h

693–703 K (curve 2, Fig. 4) rapidly increases as the Cu to K molar ratio in the mixtures of $CuCl_2$ and KCl is increased.

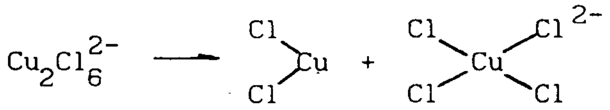
Discussion

It was established earlier [3] that the solid system $CuCl_2$–KCl with Cu to K molar ratios of from 0.5 to 1.0 involves a mixture of two phases: the first is built up from $CuCl_4^{2-}$ elements [7] and the second from $Cu_2Cl_6^{2-}$ elements. It has also been proposed [8] that the phase change at 533–543 K is a result of the formation of planar $CuCl_4^{2-}$ from deformed $CuCl_4^{2-}$ groups in the solid state. The deformation of $CuCl_4^{2-}$ groups [8] results from the location of Cl^- so as to yield a planar configuration of $4K^+ + Cl^-$. Thus, the rapid reduction of the peak at 533–543 K (Fig. 1) for the mixture with a Cu to K molar ratio of 0.5 may result from the fact that not all the Cl^- is able to return to the $CuCl_4^{2-}$ plane. Some of it probably forms the configuration $4K^+ + Cl^-$ [8] or simply exists as Cl^-. During the annealing of the samples at 473 K, such a deformation probably leads to the following thermal dissociation of $CuCl_4^{2-}$:



(1)

The $Cu_2Cl_6^{2-}$ solid phase may dissociate thermally to yield $CuCl_4^{2-}$ groups, and may next form a tiny "excess" of $CuCl_4^{2-}$ solid phase [3] during cooling of the samples to room temperature. The existence of this process would explain the tiny increases in curves 2 and 3 in Fig. 1. Curve 2 (Fig. 1) exceeds curve 1 in the region of Cu to K molar ratios in which the phase $Cu_2Cl_6^{2-}$ should decide [3] the behaviour of the sample during its thermogravimetric analysis. This would support the finding that the $Cu_2Cl_6^{2-}$ groups decompose to $CuCl_4^{2-}$ groups at 473 K:

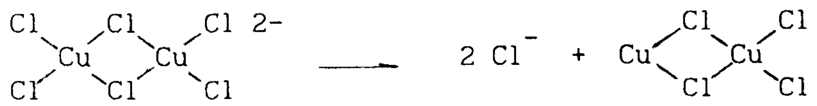


(2)

The latter next undergo deformation (1). Curve 3 (Fig. 1) exceeds curve 2, obviously because a longer time of annealing would give more $CuCl_4^{2-}$ groups in reaction (2). It is interesting that curve 2 exceeds curve 3 (Fig. 1) for the samples with a Cu to K molar ratio near 1.0. This would suggest that $CuCl_4^{2-}$ groups undergo further reaction during annealing or cooling down of the samples. On account of the strong tendency of copper(II) chloride to form Cu^{2+} and stable $CuCl_4^{2-}$ even in the melt [4], the decomposition of $CuCl_4^{2-}$ at 473 K probably does not occur. However, a reversible reaction of Cu^{2+} and $CuCl_4^{2-}$ is possible, giving the combination $CuCuCl_4$, because of the tendency of the Cu^{2+} d^9 electron to undergo pairing:

(3)

The differences in influence of the time of annealing of the samples at 473 K on the area of the 533–543 K peak in two regions of sample composition (molar ratios of from 0.5 to 0.65 and of from 0.75 to 1.0) (Fig. 1) indicate that Cu^{2+} from $Cu_2Cl_6^{2-}$ groups effectively prevents $CuCl_4^{2-}$ from taking part in the deformation process (reaction 3). This would suggest that the thermal dissociation of $Cu_2Cl_6^{2-}$ may also occur at 473 K as follows:



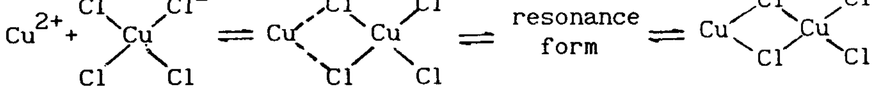
(4)

The $CuCl_4^{2-}$ solid phase melts at 573–593 K [3]. The considerable reduction in area of the 573–593 K peak in Fig. 2 (curves 2 and 3 as compared with curve 1) for the samples with Cu to K molar ratios of from 0.5 to about 0.85 results from deformation of $CuCl_4^{2-}$ (1) at 473 K and from partial decomposition of $CuCl_4^{2-}$ solid phase. The increases in curves 2 and 3 and the shifts in their maxima a Cu to K molar ratio of from 0.6–0.7 (Fig. 1) to 0.85 (Fig. 2) may result only from the thermal decomposition of some $Cu_2Cl_6^{2-}$ (reactions 2 and 4) at 473 K. This increase may result from the following reactions, which occur immediately after melting of the mixtures at 573–593 K, making an additional energy contribution to this phase change:


(5)


(6)

Disproportionation reaction (5) was assumed by Fontana *et al.* [4]. Reaction (6) and the existence of $CuCuCl_4$ in the melt was proposed in [5, 8]. $CuCuCl_4$ in the solid phase is energetically similar to the system of Cu^{2+} and $CuCl_4^{2-}$ in the melt (reactions 5 and 6), so it will pass into the melt even at 573–593 K, making a very small contribution to the energy of this phase change. Curves 2 and 3 are located slightly above curve 1 in Fig. 2 for a Cu to K molar ratio above 0.85, which therefore indicates the thermal dissociation of $Cu_2Cl_6^{2-}$ at 473 K, as in reaction (4). According to the results presented in [8], $Cu_2Cl_6^{2-}$ and Cu_2Cl_4 take part in the phase change at 603–623 K. It should be suspected that Cu_2Cl_4 and $CuCuCl_4$ in the solid phase have different constitutions, despite the same stoichiometry. The location of curve 2 relative to curve 1 in Fig. 3 lends support to the statement about decomposition of the $Cu_2Cl_6^{2-}$ groups during the thermal dissociation of the samples at 473 K. This thermal dissociation at 473 K probably gives both the $CuCuCl_4$ and the Cu_2Cl_4 combination. The different locations of the points in curves 2 and 3 in Fig. 3 for samples with the same Cu to K molar ratio of 0.845 indicates the possibility of transformation of these two combinations into each other at 473 K. In the solid phase at 473 K, a resonance form is probably present:

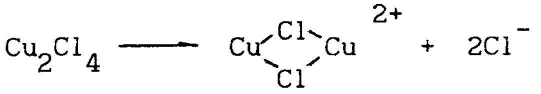


(7)

Thus such a resonance form may undergo the phase change at 603–623 K as the right form, or the phase change at 573–593 K as the left one. Curve 3 in Fig. 3 may therefore be located between curves 1 and 2 for the mixtures with

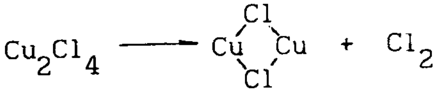
Cu to K molar ratios of from 0.768 to 0.845. For the same reason, the sample with a molar ratio of 0.845 which was annealed for 72 h may give a DTA picture identical to that obtained for the same sample but annealed at 473 K for 2 h.

The appearance of the 663–683 K and 693–703 K peaks in the DTA curves of the samples annealed at 473 K, and the very rapid increase in curve 2 in Fig. 4, indicate another pathway of $Cu_2Cl_6^{2-}$ decomposition during the thermal dissociation. Analogously to the process of liberation of Cl^- in reaction (4), the following thermal dissociation may be suspected:



(8)

This does not seem probable on account of the stabilization role of resonance form (7). However, the liberation of Cl_2 from the $CuCl_2$–KCl solid phase at 473 K [9] is possible in the following way:



(9)

Cu_2Cl_2 undergoes a phase change at 695 K, melting [10]. The formation of Cu_2Cl_2 in reaction (9) at 473 K may be the reason for the 693–703 K peak in the DTA curves (Fig. 4).

It may be suspected that the same ions and combinations as the products of thermal dissociation exist in the liquid melts after melting of the samples at 573–593 K and 603–623 K. The identical shape of curve 1 in Fig. 4 to that of curves 2 and 3 in Fig. 2 suggests that the $CuCuCl_4$ combination undergoes a phase change at 663–683 K. To support this origin of the peaks at 663–683 K and 693–703 K, direct investigations of the liquid melts are necessary.

Conclusions

Not all $CuCl_4^{2-}$ groups deformed at 473 K become planar again in the solid state at 533–543 K. Some of them dissociate in the solid state.

Some Cl^- from deformed $CuCl_4^{2-}$ groups may give the planar configuration $4K^+ + Cl^-$ in the solid state, which is characteristic for the KCl unit cell.

The $Cu_2Cl_6^{2-}$ solid phase dissociates at 473 K, giving primarily the $CuCuCl_4$ combination and $2Cl^-$.

In the solid state, an equilibrium between Cu^{2+}, $CuCl_4^{2-}$ and $CuCuCl_4$ is possible, as follows:

$$Cu^{2+} + CuCl_4^{2-} \rightleftharpoons CuCuCl_4$$

In the solid state, $CuCuCl_4$ may undergo decomposition, producing Cu^{2+} and $CuCl_4^{2-}$, or may produce a complex due to the tendency of the Cu^{2+} d^9 electron to undergo pairing. A resonance form of both combinations probably exists in the $Cu_2Cl_6^{2-}$ solid phase at 473 K.

This resonance form may pass into the liquid melt at 573–593 K as the combination $CuCuCl_4$, or at 603–623 K as the complex Cu_2Cl_4.

The combination $CuCuCl_4$ probably exists in the liquid melt and probably undergoes a phase change at 663–683 K.

Copper(I) chloride Cu_2Cl_2 may be formed in the solid phase of the system $CuCl_2$–KCl at 473 K, and probably undergoes a phase change at 693–703 K.

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Zusammenfassung — Feststoffgemische aus $CuCl_2$ und KCl wurden bei 473 K für verschiedene Zeit getempert, dann auf Raumtemperatur abgekühlt und thermogravimetrisch analysiert. Die Unterschiede in den DTA-Kurven der Proben wurden untersucht. Schlußfolgerungen bezüglich der festen und flüssigen Phase der Gemische wurden gezogen.