Journal of Thermal Analysis, Vol. 47 (1996) 775-790

CHANGES IN ION COMPOSITION IN THE LIQUID SYSTEM $CuCl_2$–KCl, INVESTIGATED BY THERMOGRAVIMETRY

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Abstract

$CuCl_2$–KCl mixtures were annealed at 603 K and thermogravimetrically analysed after cooling to room temperature. The mixtures differed in the molar ratio Cu/K and in the duration of heating at 603 K. The constitutions of the ions, the reactions between them and the mechanisms of their decomposition in the melt are proposed, as are the constitutions of the active centres in the oxychlorination process.

Keywords: $CuCl_2$–KCl system, ion constitution

Introduction

Fontana *et al.* investigated liquid melts in the system $CuCl_2$–KCl–Cu_2Cl_2 [1] by measuring the equilibrium chloride pressure over the melt. They proposed the compositions of the ions in the liquid melt, and the equilibrium between them. Similar results for the liquid system $CuCl_2$–KCl without Cu_2Cl_2 have not been published. Direct investigation of the system is very difficult on account of the unstable [2], corrosive [3] character of the melt, and there are no standard data which may be used for direct instrumental techniques. In paper [1], assumptions were made to describe the results. At a molar ratio Cu/K from 0.5 to 1.0, the solid system $CuCl_2$–KCl undergoes a phase change at 533–543 K, and melts at 573–593 K or 603–623 K [4, 5]. A crystal lattice constitution which undergoes the melting process has been established [6–8]. Probable reactions of the ions, or their decomposition after melting, have been suggested [8, 9]. The present work supplements results proposed in [8, 9]. It involves thermogravimetric investigations of the system $CuCl_2$–KCl, in which Cu/K was varied from 0.5 to 1.0. The system $CuCl_2$–KCl was heated at 603 K for different times. Changes in the ion composition in the $CuCl_2$–KCl melt were investigated by thermogravimetric analysis of the mixtures, which were rapidly crystallized and cooled to room temperature.

0368–4466/96/ $ 5.00

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Experimental

To obtain the system $CuCl_2$–KCl, dihydrous copper(II) chloride and potassium chloride (PoCh, Gliwice) were used. Weighed quantities of these two salts, in appropriate proportions, were dissolved in distilled water and the solution was evaporated to dryness at 343 K. The dry residue was crushed and ground. Powdered samples were roasted at 603 K for 1, 3, 6 or 72 h in an air atmosphere. After heating, the samples were rapidly cooled down to room temperature and subjected to thermogravimetric analyses. Mixtures with molar ratios Cu/K of 0.5, 0.622, 0.691, 0.768, 0.922 and 1.0 were prepared and heated at 603 K.

Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293–773 K. The measurement conditions were as follows: constant sample mass 0.600 mg, corundum crucible, air atmosphere, Al_2O_3 as reference material, heating rate 5°C min^{-1}, sensitivity DTA 1/5, sensitivity DTG 1/5, sensitivity TG 200 mg.

Results

Figure 1 shows the thermal curves of the system $CuCl_2$–KCl at Cu/K= 0.845, after heating of the mixture for 1 h at 603 K.

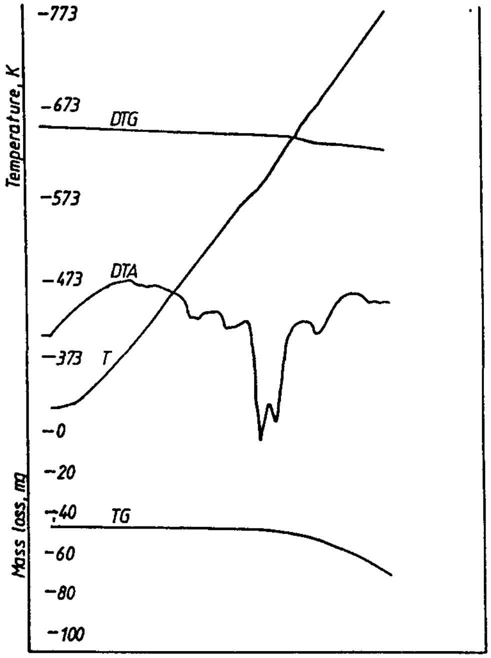


Fig. 1 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 603 K for 1 h. Molar ratio of Cu to K=0.845

In the DTA curves of the mixtures heated for 1 h at 603 K, the analyses revealed intense endothermic effects with minima at 573–593 K and 603–623 K, small and well-shaped endothermic effects with minima at 483–513 K, 533–543 K and 663–706 K, and a very small endothermic effect with minimum at 418–428 K. The endothermic effect with minimum at 483–513 K has a double character. Figure 2 shows the thermal curves for an identical sample to that presented in Fig. 1, but after heating for 3 h.

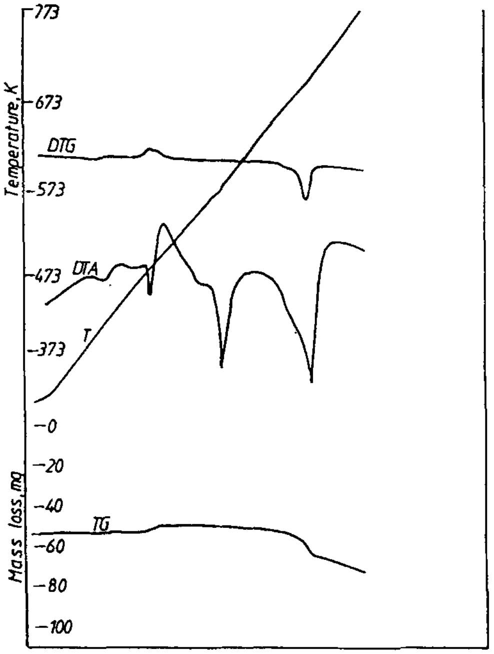


Fig. 2 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 603 K for 3 h. Molar ratio of Cu to K=0.845

In the DTA curves of the mixtures of $CuCl_2$ and KCl heated at 603 K for 3 or 6 h, an exothermic effect appears with maximum at 508–553 K. It is clear that this exothermic effect makes it impossible to detect the peak at 533–543 K in the DTA curves. The peak at 603–623 K is not present in the DTA curves of the mixtures heated for 3 or 6 h. The 573–593 K peak is considerably decreased in the DTA curves of the mixtures heated for 3 h, and is absent in the DTA curves of the mixtures heated for 6 h. In the TG curves of the mixtures heated for 3 or 6 h, an increase in sample mass is observed. This mass increase begins from the peak at 418–428 K (Fig. 2), and is much more considerable after the endothermic effect at 483–513 K. Thermal curves for the mixture of $CuCl_2$ and KCl with Cu/K=0.845 after heating for 72 h at 603 K are presented in Fig. 3.

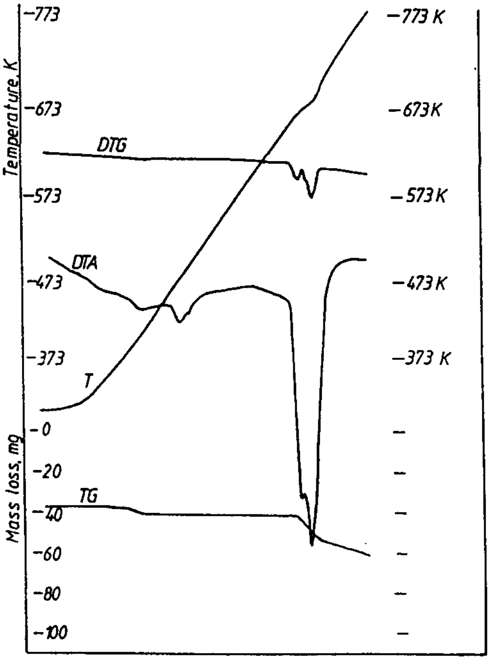


Fig. 3 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 603 K for 72 h. Molar ratio of Cu to K=0.845

An increase in sample mass is to be seen in the TG curve in Fig. 3. The exothermic effect and endothermic effects at 533–543 K, 573–593 K and 603–623 K were not presented in the DTA curve. In the DTA curve in Fig. 3, there are endothermic effects with minima at 418–428 K and 483–513 K, and a very large endothermic effect at 663–706 K. The peak at 663–706 K has three minima: at 678 K, 688 K and 697 K. these three minima in the endothermic effect at 663–706 K were also seen in the DTA curves of the mixtures heated for 3 or 6 h. Ideal separation of these three peaks was not attained, even after change of the DTA sensitivity or variation of the temperature increase rate. The most intensive minimum of the peak at 663–706 K shifts to higher temperature as the duration of heating or Cu/K is increased. For the mixture with Cu/K=1.0 heated for 3 h, five minima were recorded for the 663–706 K peak: at 663 K, 678 K, 688 K, 697 K and 706 K. Similarly as observed in [8, 9], the DTA picture of the samples differed as Cu/K and the duration of heating increased. Figure 4 shows the variation in area of the peaks at 603–623 K and at 533–543 K, as a function of Cu/K in the mixtures, when the mixtures were heated at 603 K for 1 h. The curves obtained after the same mixtures were heated at 473 K [9] for 2 h are also presented in Fig. 4, for comparison.

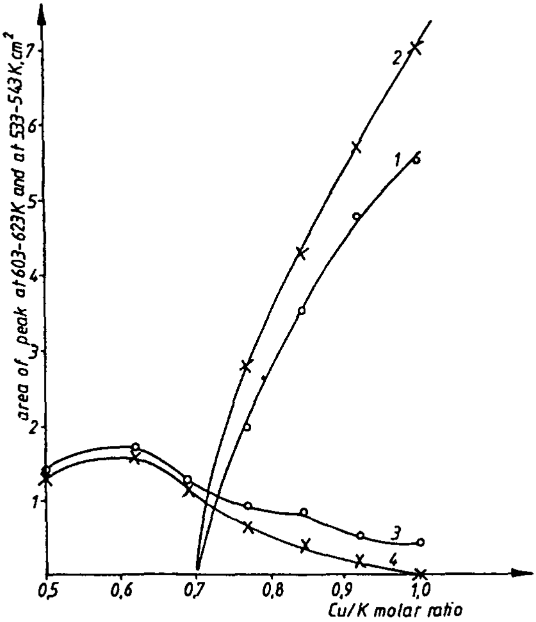


Fig. 4 Variation of the area of the endothermic effects with peak at 603–623 K (curve 1 and 2) and with peak at 533–543 K (curve 3 and 4) as a function of the molar ratio of Cu to K in the mixture. Curve 1 and 3 – the mixtures heated at 603 K, curve 2 and 4 – the mixtures heated at 473 K

It is seen that the run of curve 1 is almost identical to that of curve 2 obtained for the mixtures heated at 473 K for 2 h. Curve 1 is located a little below curve 2. The area of the 533–543 K peak (curve 3) is practically the same as that of this peak for the identical mixture but after heating for 2 h at 473 K (curve 4), when Cu/K is increased from 0.5 to 0.7. The area of the 533–543 K peak in curve 3 is larger that of in curve 4, as Cu/K in the mixtures is increased from 0.75 to 1.0. The endothermic effects with minima at 533–543 K and 603–623 K were not observed in the DTA curves for the $CuCl_2$–KCl mixtures heated at 603 K for 3 h or more. The peak at 533–543 K may be masked by the exothermic effect in the DTA curves. Figure 5 shows the variation in area of the 573–593 K peak as a function of the mixture composition, after heating at 603 K for 1 h (curve 1) or for 3 h (curve 2). The curves after heating at 473 K [9] for 12 h (curve 3), and after a third heating during investigation of the phase change reproducibility [8] (curve 4), are also presented in Fig. 5.

Curve 1 is located below curve 4 for Cu/K values from 0.5 to about 0.78. Curves 1, 2 and 3 are located above curve 4 for a Cu/K from about 0.8 to 1.0. It is seen that the shapes of curves 1, 3 and 4 are similar. Curve 1 markedly exceeds curve 3 for a Cu/K from 0.5 to about 0.85. However, after 3 h of heating

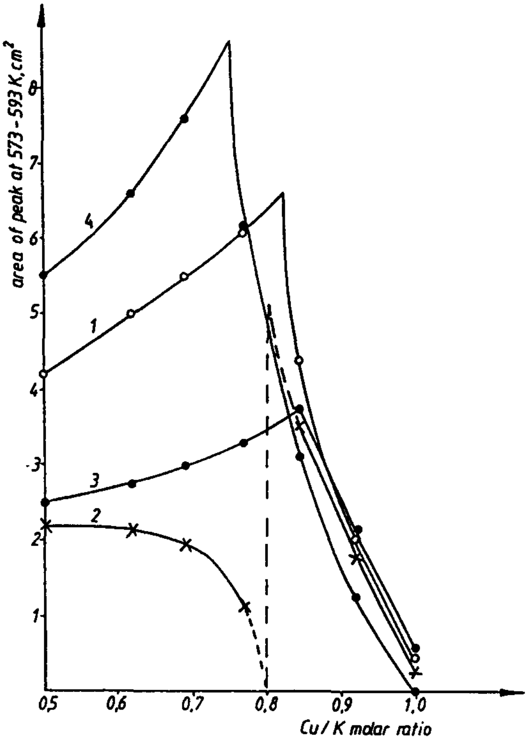


Fig. 5 Variation of the area of the endothermic effect with peak at 573–593 K as a function of the molar ratio of Cu to K in the mixture. Curve 1 – the mixtures heated at 603 K for 1 h, curve 2 – the mixtures heated at 603 K for 3 h, curve 3 – the mixtures heated at 473 K for 12 h, curve 4 – obtained after third heating during investigation of the phase change reproducibility [8]

at 603 K, curve 2 is located below curve 3. Curve 2 has a completely different shape as compared with the shapes of curves 1 and 3, for a Cu/K of from 0.5 to 0.85. Curve 2 is located below curve 3 and decreases, it seems, to zero for a Cu/K about 0.8. It also seems that curve 2 may have two different values for Cu/K about 0.8. Above Cu/K=0.8, curve 2 runs almost identically to curves 1 and 3. The endothermic effect with minimum at 573–593 K does not appear in the DTA curves obtained after 6 h of heating $CuCl_2$–KCl mixtures at 603 K. Figure 6 shows the variation in area of the peak at 418–428 K as a function of Cu/K in the mixtures after heating for different times.

It is seen that the area of the 418–428 K peak increases as Cu/K is increased independently of the duration of heating. The area of this peak becomes larger as the duration of heating the mixtures becomes longer. A considerable decrease in peak area is observed for a Cu/K about 0.8 in curves 2 and 3. Figure

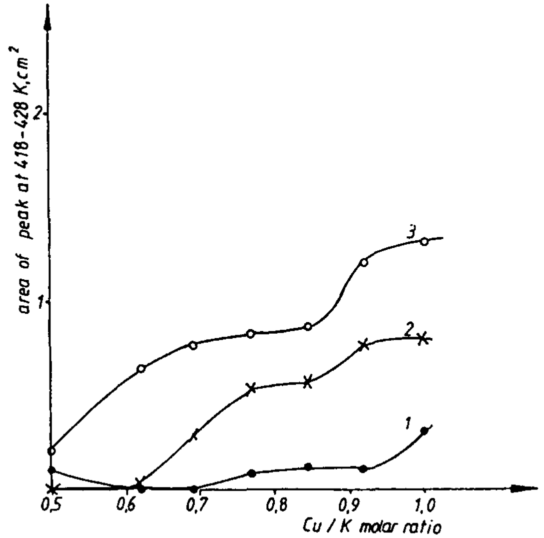


Fig. 6 Variation of the area of the endothermic effect with peak at 418–428 K as a function of the molar ratio of Cu to K in the mixture. Curve 1 – the mixtures heated at 603 K for 1 h, curve 2 – the mixtures heated at 603 K for 3 h, curve 3 – the mixtures heated at 603 K for 6 h

7 shows the variation in area of the 483–513 K peak as a function of Cu/K in the mixtures, and as a function of the duration of heating at 603 K.

Extrapolation of curves 1 and 2 leads to the identification of the extremum for a Cu/K about 0.8. This extremum is equal to those in curve 3 for Cu/K=0.5 and 1.0. In Fig. 7, curve 2 is located above curve 1. However, curve 3 has almost the same values as curves 1 and 2, at a Cu/K about 0.8. Curve 3 increases as Cu/K becomes more different from 0.8. Figure 8 shows the variation in the 663–706 K peak area as a function of Cu/K in the mixtures.

Curve 1 decreases as Cu/K in the mixtures increases from 0.5 to about 0.85, and next increases until Cu/K becomes equal to 1.0. Curve 2 is located considerably above curve 1. Curve 2 increases as Cu/K increases. It has a deep minimum for Cu/K=0.845.

Discussion

The oxidation of the $CuCl_2$–KCl melt to be observed in Fig. 2 will not be discussed in this work. It may be said that the phase changes at 533–543 K and 573–593 K indicate the existence of $CuCl_4^{2-}$ in the $CuCl_2$–KCl mixtures [8, 9]. After the results presented in [9], the phase change at 573–593 K indicates the existence of the complexes $CuCl_4^{2-}$ and $CuCuCl_4$ in the melt. The phase change

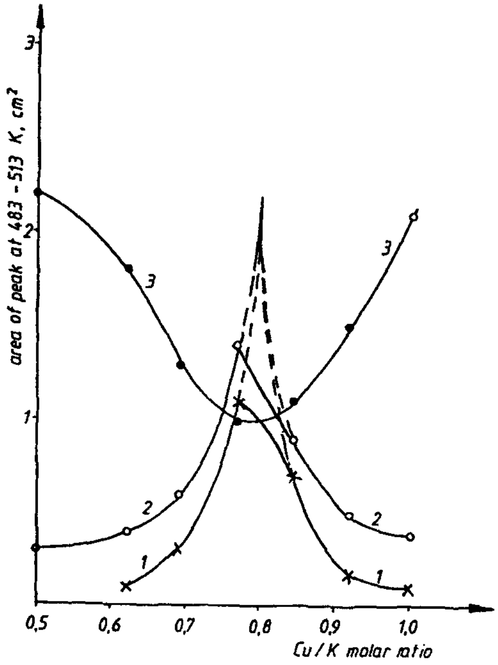


Fig. 7 Variation of the area of the endothermic effect with peak at 483–513 K as a function of the molar ratio of Cu to K in the mixture. Curve 1 – the mixtures heated at 603 K for 1 h, curve 2 – the mixtures heated at 603 K for 3 h, curve 3 – the mixtures heated at 603 K for 6 h

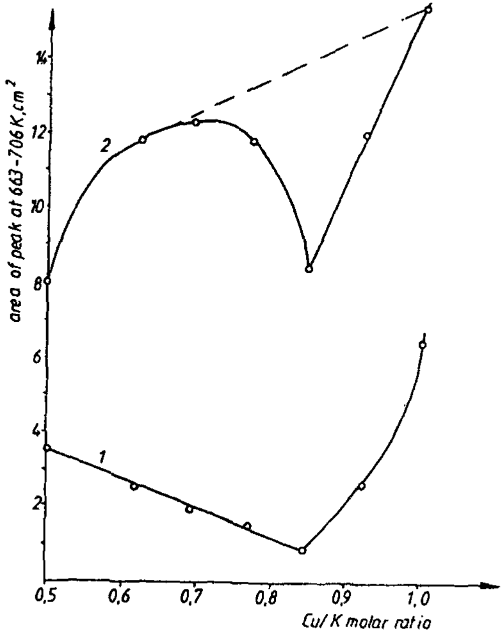
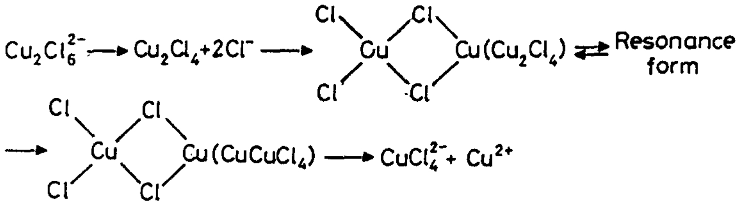


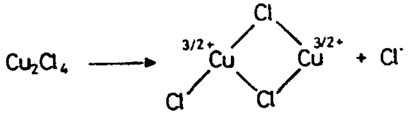
Fig. 8 Variation of the area of the endothermic effect with peak at 663–706 K as a function of the molar ratio of Cu to K in the mixture. Curve 1 – the mixtures heated at 603 K for 1 h, curve 2 – the mixtures heated at 603 K for 3 h

at 603–623 K indicates the existence of the complexes $Cu_2Cl_6^{2-}$ and Cu_2Cl_4, obtained by the elimination of two Cl^- [8, 9]. The origin of the peak at 663–706 K is not yet explained. The results presented in Fig. 4 (curve 1 below curve 2) and the disappearance of curve 1 after heating at 603 K for 3 h indicate that $Cu_2Cl_6^{2-}$ decomposes readily to Cu_2Cl_4 ($CuCuCl_4$) and $2Cl^-$ [8, 9]. The location of curve 3 above curve 4 in Fig. 4 indicates the decomposition of Cu_2Cl_4 in the melt to form $CuCuCl_4$ and $CuCl_4^{2-}$:



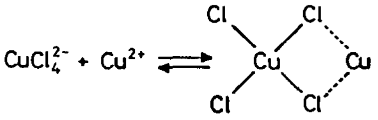
(1)

It is probable Cu^{2+} in Cu_2Cl_4 compete for the negative charge. Thus, a resonance form may be formed in the $CuCl_2$–KCl melt, with a balanced contribution of the covalent bond, as already proposed in [9]. This rivalry may lead to the creation of stable $CuCl_4^{2-}$ and Cu^{2+}. On the other hand, increase of the covalent bond, above the resonance form, may lead to the transfer of about $1/2e^-$ negative charge to both Cu^{2+} in the complex Cu_2Cl_3:



(2)

The location of curve 1 below curve 4 in Fig. 5 for a Cu/K from 0.5 to 0.75 may indicate the occurrence of the following reaction of $CuCl_4^{2-}$ and Cu^{2+} [9] in the melt:



(3)

The similar shapes of curves 1, 3 and 4 in Fig. 5 support the existence of a similar ion composition in the solid state [9] and in the liquid melt of $CuCl_2$–KCl mixtures. Curves 1, 2 and 3 slightly exceed curve 4 in Fig. 5 for a Cu/K from about 0.8 to 1.0. This would support the proposals in (1) of the decomposition of Cu_2Cl_4 and the increases in the amounts of $CuCl_4^{2-}$ and $CuCuCl_4$ in the melt. Long heating of solid mixtures at 473 K [9] (curve 3 in Fig. 5 is considerably below curve 1) would convert Cu^{2+} and $CuCl_4^{2-}$ into complex (3) more efficiently in the solid, on account of the more rigid immediate neighbourhood of the ions. Meanwhile, curve 2 is located below curve 3 in Fig. 5. This is a result of further decomposition of $CuCl_4^{2-}$ in the melt. This decomposition

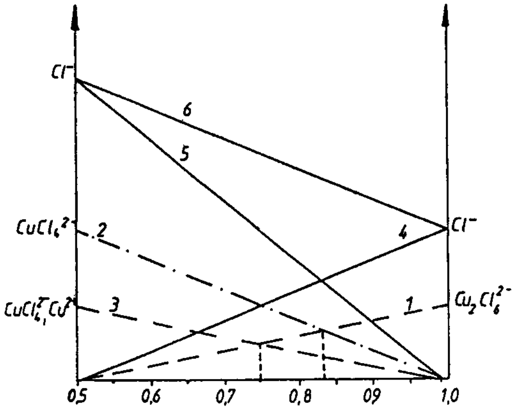
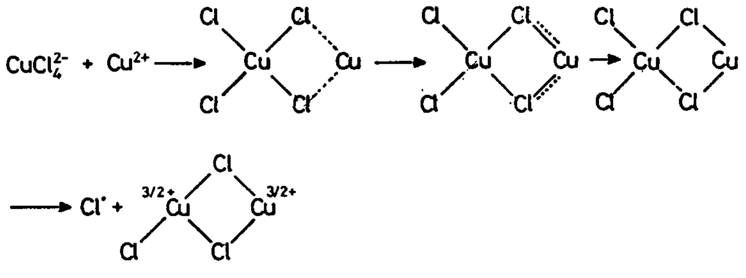


Fig. 9 Theoretical variation of ions obtained after melting $CuCl_2$–KCl solid phase with the molar ratio of Cu to K from 0.5 to 1.0. Curve 1 – amount of $Cu_2Cl_6^{2-}$ existed in the $Cu_2Cl_6^{2-}$ solid phase, Curve 2 – amount of $CuCl_4^{2-}$ existed in the $CuCl_4^{2-}$ solid phase, curve 3 – amounts of $CuCl_4^{2-}$ and Cu^{2+} ions obtained after melting of $CuCl_4^{2-}$ solid phase, curves 4 and 5 – amount of Cl^- ions obtained in the melt after decomposition of $Cu_2Cl_6^{2-}$ and $CuCl_4^{2-}$ solid phases adequately, curve 6 – resultant amount of Cl^- ions in the melt

increases as Cu/K is increased up to about 0.8. It should be noted that the amount of Cu_2Cl_6 in the solid phase increases and that of $CuCl_4^{2-}$ in the solid phase decreases as Cu/K in the mixtures is raised from 0.5 to 1.0 [7]. When Cu/K is about 0.8, the solid system $CuCl_2$–KCl theoretically gives to the melt at 603 K comparable amounts of $CuCl_4^{2-}$ and the complex $CuCuCl_4$ (1) [9] from the $CuCl_4^{2-}$ and the $Cu_2Cl_6^{2-}$ in the solid phase adequately[7] (Fig. 9). Thus, the decrease of $CuCl_4^{2-}$ in the melt in the reaction



(4)

should be the most effective and visible for the above Cu/K, on account of the probable equilibrium in (3). This may be due to the comparable amounts of $CuCl_4^{2-}$ (Cu^{2+}) and $Cu_2Cl_6^{2-}$ from the solid phases (Fig. 9), which pass into the melt at 573–593 K and 603–623 K, respectively. This would suggest that equivalent amounts of Cu^{2+} and $CuCl_4^{2-}$ prevent the complex $CuCuCl_4$ from further decomposition in Eq. (1). This would explain the role of Cu^{2+} in the decomposition of $Cu_2Cl_6^{2-}$ [1], but it may now be written that the complex Cu_2Cl_4 undergoes this decomposition process:

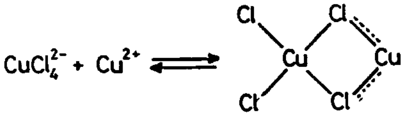
$$Cu^{2+} + Cu_2Cl_4 \longrightarrow Cu_2Cl_3(2) + 1/2\ Cl_2 + Cu^{2+} \qquad (5)$$

For the above reasons, decomposition of $CuCuCl_4$ *via* Cu_2Cl_4 at 603 K, to form Cu_2Cl_3 in reaction (4), would be visible mostly for mixtures with a Cu/K about 0.8. Accordingly, the value estimated by extrapolation in Fig. 5, which is twice the theoretical value for Cu/K=0.8 supports the existence of equilibrium (3). When Cu/K becomes higher than about 0.8, excess of $CuCuCl_4$ above the amount for equilibrium (3) is presumed to exist in the melt, due to reaction (1). The location of curves 1, 2 and 3 slightly above curve 4 in Fig. 5 indicates the existence of the complex $CuCuCl_4$ in the melt [9]. Practically the same values for curves 1 and 2 as that for curve 3 in the range of Cu/K above about 0.88 suggests that it is the same $CuCuCl_4$ complex as proposed in the solid phase [9]. The same values for curves 1 and 2 in this range of Cu/K indicates the high stability of the complex $CuCuCl_4$ in the melt, probably on account of the existence of the resonance form proposed in [9]:

$$CuCuCl_4 \rightleftarrows \begin{matrix}\text{Resonance}\\ \text{form}\end{matrix} \rightleftarrows Cu_2Cl_4 \qquad (6)$$

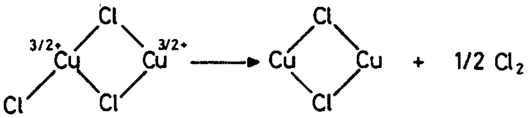
The existence of the flex points in the curves presented in Fig. 6 may result from 'the most effective' decomposition of $CuCuCl_4$ *via* Cu_2Cl_4 in reaction (4). This would suggest that the resonance form (6) in the solid phase undergoes a phase change at 418–428 K, but it is different from the solid phase which melts at 573–593 K or at 603–618 K [8, 9] (it may be a solid phase obtained by rapid non-ordered crystallization). The increase in the curves presented in Fig. 6 as Cu/K increases suggests the formation of $CuCuCl_4$ at 603 K, generally from $Cu_2Cl_6^{2-}$ in the solid phase [7] in reaction (1). The disappearance of the 603–623 K peak in the DTA curves obtained after 3 or 6 h of heating at 603 K indicates the decomposition of $Cu_2Cl_6^{2-}$, but also supports the existence of the above 'non-ordered' crystallization. After heating for 6 h, the peak at 573–593 K also disappears from the DTA curves. At the same time, the area of the 418–428 K peak increases as the duration of heating becomes longer. The 418–428 K peak is again observed for the mixture with Cu/K=0.5 (Fig. 6). This would indicate that the resonance form (6) exists in the melt because of reaction (3), and supports the reversibility of this reaction (3). The flex points in the curves in Fig. 6 correspond to the extrapolated maximum in Fig. 7 for Cu/K about 0.8. It should be concluded that the product of decomposition of the resonance complex (6) undergoes a phase change at 483 –513 K. It is probably Cu_2Cl_3 obtained at 603 K in reaction (2). The 'extrapolated' amount of Cu_2Cl_3 (2) may be obtained at 603 K after long heating of mixtures with Cu/K=1.0 or

0.5 (Fig. 7). It arises as a result of reaction (1), but also of reaction (4). Thus, equilibrium of reaction (3) may be obtained in the melt after long heating:



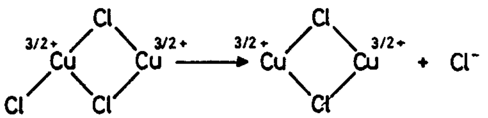
(7)

with simultaneous decomposition of the resonance form (6) in reaction (5). The decrease of curve 3 below the extrapolated values of curves 1 and 2 in Fig. 7 for Cu/K about 0.8 indicates that Cu_2Cl_3 (2) undergoes further reaction. After the results presented in [1], this may be as follows:



(8)

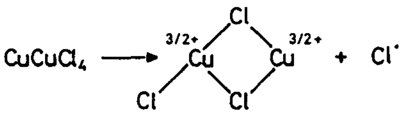
but Cu_2Cl_3 (2) may also dissociate in the following way:



(9)

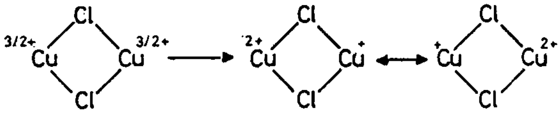
Dissociation (9) should be dependent on the Cl^- environment of the complex Cu_2Cl_3. After heating for 6 h at 603 K, the amount of the resonance form in equilibrium (7) should be theoretically comparable (Fig. 9) in the melts with Cu/K=0.5 and about 0.8. However, the amount of Cl^- in the melt at Cu/K=0.5 is considerably higher (Fig. 9). The amount of the complex Cu_2Cl_3 is also about twice as high in the melt at Cu/K=0.8 (Fig. 7, curve 3). Hence, the deep decrease in curve 3 in Fig. 7 at Cu/K about 0.8 may indicate the decomposition of Cu_2Cl_3 in reaction (9). It is interesting that the values for curves 1, 2 and 3 in Fig. 7 for the mixtures with Cu/K about 0.8 are almost the same. This indicates the high stability of the Cu_2Cl_3 (2) in these mixtures on account of the probable chemical equilibrium of reaction (9). This would suggest that reaction (8) makes an especially considerable contribution in the melt at Cu/K=0.5 and 1.0. The shift in the most intensive minimum of the 663–706 K peak to higher temperature as Cu/K is increased, singling out the 697 K minimum for the mixture with Cu/K=1.0, would indicate the melting of Cu_2Cl_2 at 697 K [10]. Melting of the Cu_2Cl_2 solid phase should make a considerable contribution to the 663–706 K phase change energy, since its crystal lattice is destroyed. The location of curve 2 in Fig. 8 considerably above curve 1, especially for Cu/K=0.8, and the shift in the most intensive minimum of the 663–706 K peak to higher temperature as the duration of heating at 603 K is increased, would indicate melting of the Cu_2Cl_2 obtained in the melt at 603 K in reaction (8). The extrapolated increase in curve 2 as Cu/K is increased supports the existence of reaction (2) and then reaction (8), when Cu_2Cl_4 originates from $Cu_2Cl_6^{2-}$ in the solid phase [7]. The deep decrease in curve 2 in Fig. 8 for Cu/K about 0.8 indicates the considerable contribution of dissociation (9) in these mixtures at 603 K. The shift in the most intensive minimum of the 663–706 K peak to lower temperature (663 K) as Cu/K is decreased supports the early finding [9] that $CuCuCl_4$ undergoes a phase change at 663 K. Accordingly, the following reaction sequence may be proposed, probably occurring at 663–706 K as endothermic phase changes:

at 663 K:



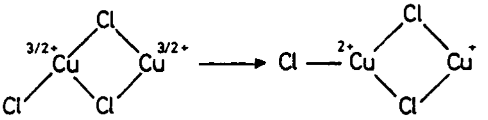
(10)

at 678 K:



(11)

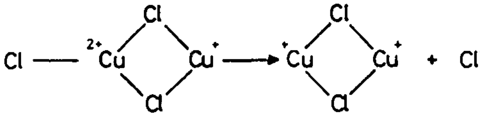
at 688 K:



(12)

at 697 K: Melting of Cu_2Cl_2 (13)

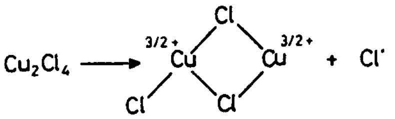
at 706 K:



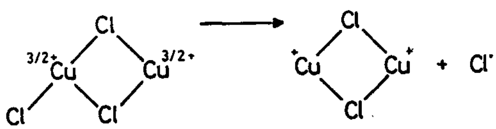
(14)

For this reason, five minima were observed in the 663–706 K phase change of in the $CuCl_2$–KCl melt with Cu/K = 1.0. To summarize all the above results, the following changes in ion composition may be proposed as probably occurring in the melt up to about 663 K:

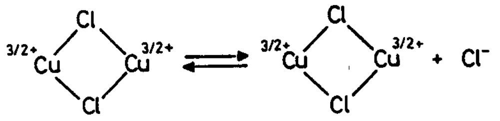
$$Cu^{2+} + CuCl_4^{2-} \rightleftarrows CuCuCl_4 \rightleftarrows \text{Resonance form} \rightleftarrows Cu_2Cl_4 \qquad (15)$$



(16)

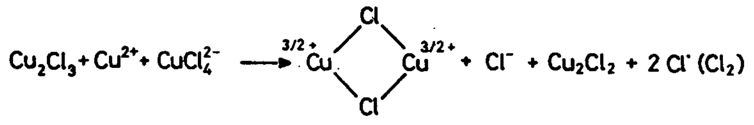


(17)



(18)

After very long heating of $CuCl_2$–KCl mixtures at 603–663 K, the overall reaction may be written:

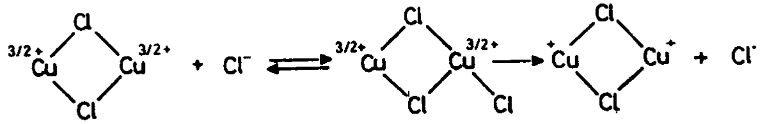


(19)

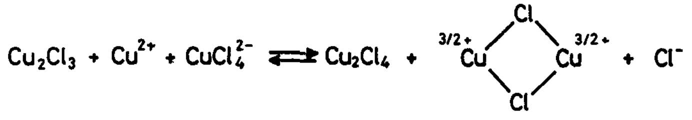
when the Cu_2Cl_2 crystal lattice may grow in the melt and Cu^{2+} and $CuCl_4^{2-}$ may disappear completely:

$$Cu^{2+} + CuCl_4^{2-} \longrightarrow Cu_2Cl_3 + Cl^- \longrightarrow Cu_2Cl_2 + Cl^- \qquad (20)$$

until equilibrium (18) is exhausted:



For this reason, three minima originating from $Cu_2Cl_2^+$ (reaction (11)), Cu_2Cl_3 (reaction (12)) and Cu_2Cl_2 (phase change (13)) were registered for the 663–706 K phase change in the DTA curve in Fig. 3. Hence, the equilibrium of thermal dissociation (18) supports the stability of the system $CuCl_2$–KCl. After the results presented here, the most stable phase should be the melt with the molar ratio Cu/K about 0.8, when thermal dissociation (18) and additionally resonance form (15) have considerable meaning:



(21)

The arrows in Eq. (21) are of no importance from a chemical kinetic point of view. They merely underline the reversibility of reactions (15) and (18). It is seen that Cu_2Cl_4 ($2CuCl_2$) does not compete with Cu_2Cl_2 for Cl^- as described in [1], and Cu_2Cl_2 in (21) does not include monovalent copper ions.

Conclusions

$Cu_2Cl_6^{2-}$ [1] does not exist in the melted system $CuCl_2$–KCl. The resonance form of the complex Cu_2Cl_4 probably exists in the melted system $CuCl_2$–KCl at 603–663 K.

The complexes Cu_2Cl_3 and Cu_2Cl_2 in the $CuCl_2$–KCl melt are proposed as a neutral molecule Cu_2Cl_3 and the ion $Cu_2Cl_2^+$, respectively, which are completely different from that proposed in [1].

The unstable character of the melted system $CuCl_2$–KCl probably results from the secretion $Cl^{\cdot}$ from the melt, possibly as $2Cl^{\cdot} = Cl_2$.

The resonance forms of Cu_2Cl_4 ($CuCuCl_4$) and $Cu_2Cl_2^+$ may exist in the $CuCl_2$–KCl melt due to the tendency of the two Cu^{2+} d^9 electrons to be paired.

The complex Cu_2Cl_4 decomposes in the $CuCl_2$–KCl melt at 603–663 K, giving the neutral molecule Cu_2Cl_3, and next copper(I) chloride, Cu_2Cl_2.

Cu_2Cl_2 may crystallize from the $CuCl_2$–KCl melt at 603–663 K.

Chemical equilibrium between Cu^{2+}, $CuCl_4^{2-}$ and $CuCuCl_4$ is proposed in the $CuCl_2$–KCl melt at 603–663 K.

Chemical equilibrium between $Cu_2Cl_2^+$, Cl^- and Cu_2Cl_3 is proposed in the $CuCl_2$–KCl melt at 603–663 K.

The above two chemical equilibria support the stability of the melted system $CuCl_2$–KCl.

The most unstable should be the melted system $CuCl_2$–KCl with Cu/K about 0.8; probably because of the comparability of the above two chemical equilibria, in agreement with the stoichiometry of the equation:

$$Cu_2Cl_3 + Cu^{2+} + CuCl_4^{2-} \rightleftharpoons Cu_2Cl_4 + Cu_2Cl_4 + Cu_2Cl^{+_2} + Cl^-$$

The unstable character of the melted system CuCl2–KCl with Cu/K=0.5 and 1.0. It probably results from the small contribution of the thermal dissociation of Cu_2Cl_3 and the high degree of Cu_2Cl_3 decomposition with secretion of $Cl^{\cdot}$ and copper(I) chloride, Cu_2Cl_2.

The endothermic phase change at 663–706 K results from the melting of copper(I) chloride, Cu_2Cl_2, the decomposition of Cu_2Cl_4 and Cu_2Cl_3, and the transfer of negative charge from one Cu ion to another. The resonance forms of Cu_2Cl_4 ($CuCuCl_4$) and $Cu_2Cl_2^+$ are probably active centres in oxychlorination process [11].

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