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THERMOGRAVIMETRIC ANALYSIS OF THE WAY OF WATER RELEASE FROM THE $CuCl_2$–KCl SYSTEM

K. Żurowski

Institute of Chemistry, Pedagogical University, 25–020 Kielce, Ul. Chęcinska 5, Poland

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Abstract

Mixtures of $CuCl_2$ and KCl with molar ratios of Cu to K from 0.5 to 1.0 were heated at 393 K and then they absorbed water from the surroundings at room temperature. DTA, TG and DTG curves were analyzed for the mixtures with absorbed water in the temperature range between 293 and 473 K. The mechanism of the phase changes and water release from the mixtures in the temperature range from 293 to 473 K is proposed.

Keywords: $CuCl_2$–KCl system, water evolution, TG-DTG-DTA

Introduction

It was reported earlier [1] that mixtures of $CuCl_2$ and KCl, during heating up to 473 K exhibit four endothermic processes. It was concluded that $K_2Cu_2Cl_6$ was formed at 336 K from the $K_2CuCl_4{\cdot}2H_2O+CuCl_2{\cdot}2H_2O$ phase but the crystal lattices of both phases were not defined. Meyerhoffer phase change [2] has not been described unambiguously. It was suggested [3] that the water is released from $K_2CuCl_4{\cdot}2H_2O$ at 365.4 K and dissolves crystals, forming a saturated solution. This water evaporates according to the work of Vriens [4] at about 393 K. Meanwhile, according to Suga and Sorai [3] the water evaporation at 365–393 K is not continuous but takes place in two separate stages at 365.4 K and at 389 K. Thus, the way of water release from the mixtures investigated here within the temperature range 293–473 K is still interesting. It is also interesting to find out whether any change in the crystal lattice of the mixtures accompanies the water evolution process.

The present work includes thermogravimetric investigations of the $CuCl_2$-KCl system, in which the molar ratio of Cu to K was varied from 0.5 to 1.0, within the temperature range 293–473 K. Experimental results which indicated the reversible character of the water evolution process from the $CuCl_2$–KCl

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mixtures [5] were also taken into account. Samples which absorbed water from room atmosphere were analyzed.

Experimental

To obtain the $CuCl_2$–KCl system, dihydrous copper(II) chloride and potassium chloride (POCh Gliwice) were used. The required amounts of the salts were dissolved in distilled water and the solutions were evaporated to dryness at 363 K. Then, the mixtures were heated at 393 K for 2 h. Brown-coloured samples of the mixtures were crushed and ground and then placed into the wet room with the air temperature about 288 K for two weeks. Mixtures with molar ratios of Cu to K of 0.5, 0.622, 0.691, 0.768, 0.845, 0.922 and 1.0 were obtained as described above.

Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293–473 K. The measurement conditions were as follows: constant sample mass 0.700 g, corundum crucible, air atmosphere, Al_2O_3 as reference material, heating rate 2.5 deg·min^{-1}, TG sensitivity 200 mg.

Results

Depending on the molar ratio of Cu to K in the investigated mixtures, the DTA curves demonstrate endothermic effects with the same peak temperatures as in [1]. The curves reveal changes in the areas of the individual endothermic effects as the molar ratio of Cu to K in the investigated samples is varied. Figure 1 demonstrates that the areas of the endothermic effects at 336 K and at 388 K increase as the molar ratio increases from 0.5 to 1.0.

The area of the peak at 336 K increases from zero for the mixture with Cu to K ratio of 0.5, whereas the peak at 388 K does not increases from zero. At the same time, the area of the peak at 366 K decreases to zero and for the sample with a molar ratio of Cu to K 0.5 it is equal to about 6.0 cm^2. Each curve presented in Fig. 1 has a flex point for the molar ratio of Cu to K from about 0.75 to 0.80. Figure 2 demonstrates the TG curves for the mixtures investigated during heating up to 473 K.

The total weight loss of samples increases as the molar ratio of Cu to K increases. Curves 3 and 4 have practically identical shape. Curves 3, 4 and 5 have a flex point for the same time, i.e. at the same temperature. The kinetics of the weight loss of $CuCl_2$–KCl mixtures is presented in Fig. 3, where the DTG curves of all the analyzed samples are shown.

Figure 3 demonstrates that the weight of all samples gradually decreases during heating up to 323 K. For the mixture with a Cu to K molar ratio of 0.5

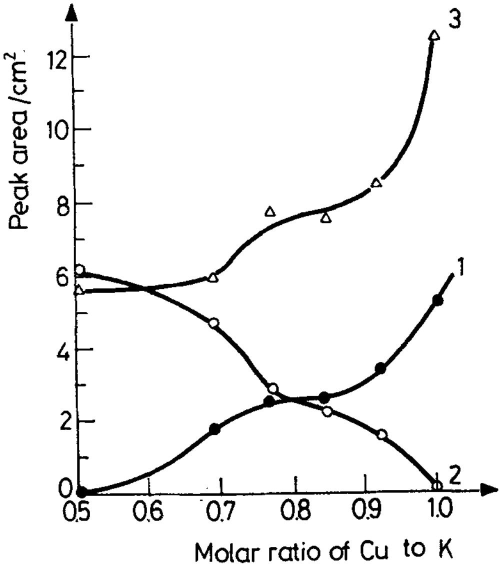


Fig. 1 Variation of the area of the endothermic effects with peak at 336 K - curve 1, at 366 K - curve 2, at 388 K - curve 3

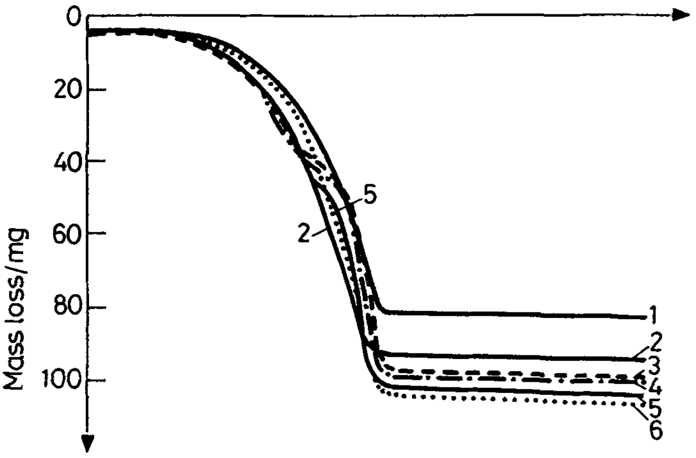


Fig. 2 TG curves obtained in the thermogravimetric analysis of mixtures with Cu to K molar ratio as follows: 0.5 - curve 1, 0.622 - curve 2, 0.768 - curve 3, 0.834 - curve 4, 0.922 - curve 5, 1.0 - curve 6

(Curve 1), this gradual decrease is observed up to about 363 K. Curves 2 to 6 have a 'plateau' between 323 and 335 K which was not observed in curve 1. For the mixtures with Cu to K molar ratios of 0.768, 0.845 and 0.922, a peak with

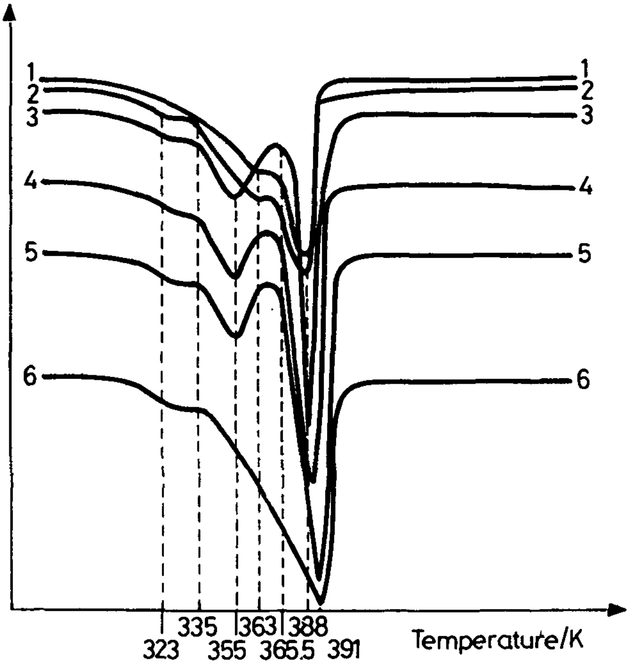
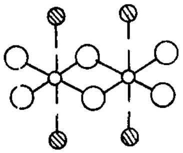


Fig. 3 DTG curves obtained in the thermogravimetric analysis of mixtures with Cu to K molar ratio as follows: 0.5 - curve 1, 0.622 - curve 2, 0.768 - curve 3, 0.845 - curve 4, 0.922 - curve 5, 1.0 - curve 6

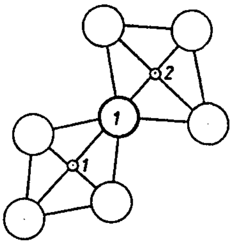
minimum at 355 K is observed which was not observed in curves 1 and 2 and which disappeared in curve 6. A second 'plateau', between 363 and 365.5 K, exists in the DTG curves of the mixtures with molar ratios from 0.5 to 0.768 and disappears as the Cu to K molar ratio of increases in the mixtures. The largest peak with minimum at 388–391 K appears in all the curves presented in Fig. 3. The temperature of its minimum shifts from 388 to 391 K together with the increase of the molar ratio of Cu to K in the mixtures. It seems that for the mixture with Cu to K ratio of 1.0, the peak with minimum at 391 K immediately adheres to the peak with minimum at 355 K. That is why it looks like a single wide peak.

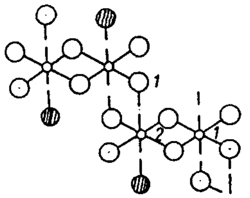
Discussion

The results presented in Fig. 1 support the reversible character of the phase changes at 336, 366 and 388 K [5]. The peak temperatures of the above phase changes are identical with those obtained in [1]. Investigation of the samples with absorbed water gave more contrasting variations of the areas of the DTA peaks. The existence in each curve (Fig. 1) of a flex point for Cu to K molar ratios from 0.75 to 0.80 suggests that two different parts of the mixtures [1] affect the process of water evolution, with different contributions. The nearly parallel character of curves 1 and 3 indicates that the $K_2CuCl_4{\cdot}2H_2O+CuCl_2{\cdot}2H_2O$ phase [1] releases much more water than the $K_2CuCl_4{\cdot}2H_2O$ phase [1]. That is why the combined process of water evolution at 388 K is proportional to the amount of the $K_2Cu_2Cl_6$ phase formed at 336 K [1]. Comparing the area of the peak at 388 K (Fig. 1) for the mixtures with Cu to K molar ratio of 0.5 and 1.0, it is seen that for the second mixture the area is about twice the one for the mixture with a molar ratio of 0.5. According to literature results [3], it should be concluded that $CuCl_4^{2-}$ groups may absorb water due to the tendency of Cu to form 4+2 coordination with two molecules of water. $K_2Cu_2Cl_6$ would absorb twice as much water due to its constitution.



The total weight loss of the samples investigated (Fig. 2) slightly increases (by about 3%) when the molar ratio of Cu to K increases from 0.5 to 1.0. In practice such difference in the total weight loss may be disregarded. The practically comparable weight loss of the samples indicates that all copper atoms in the crystal lattice of the mixtures absorb water, whether they are in $CuCl_4$ or in Cu_2Cl_6 groups. It may also be concluded here that in the Meyerhoffer reaction [3], KCl is not formed as a separate phase. That is why probably the whole mass of sample absorbs water. The nearly identical DTA picture (comparing the same molar ratio of Cu to K) of the mixtures analyzed initially [1] with that analyzed after water absorption, indicates also the reversibility of the phase changes which accompany the evolution and absorption of water. Suga and Sorai [3] and Wells [6] have proposed a constitution of the crystal lattice for $K_2CuCl_4{\cdot}2H_2O$ and $K_2Cu_2Cl_6$ as follows:





Accordingly, a displacement of $CuCl_4$ and Cu_2Cl_6 groups is possible. It may be proposed that after this displacement chloride ion 1 will be placed above copper ion 1 (water release). During water absorption, reversible displacement may occur and water may be located above and under copper 1 and 2. The proposed phase change mechanism is in accordance with the results presented in Fig. 3. Gradual water release from the investigated mixtures below 323 K enables the proposed displacement of Cu_2Cl_6 groups. The displacement of Cu_2Cl_6 groups takes place without mass loss in the phase change at 323–336 K and causes a rapid release of water from the mixtures and a peak at 355 K appears in the DTG curves (Fig. 3). This peak at 355 K is not observed in the DTG curve of the mixture with a Cu to K molar ratio of 1.0, because there is no $K_2CuCl_4 \cdot 2H_2O$ phase in this mixture. The $K_2CuCl_4 \cdot 2H_2O$ phase (Fig. 1, Curve 1) gradually loses water, but up 363 K. The displacement of $CuCl_4$ groups takes place also without mass loss at 363–365.5 K. That is why the peak at 355 K is observed only in the curves of the mixtures which have significant amount of $K_2CuCl_4 \cdot 2H_2O$ and $K_2Cu_2Cl_6$ phase. The existence of a 'plateau' at 363–365.5 K near the peak at 355 K in the DTG curves corresponds to the flex point in Fig. 2. In Fig. 3, in curve 6, rapid water release from the mixture is observed after displacement of Cu_2Cl_6 groups at 323–335 K. This rapid release is also observed in the DTG curves of the other mixtures. Rapid release which may be termed 'explosive' ~~release~~, may also be an explanation. During the displacement of $CuCl_4$ and Cu_2Cl_6 groups, part of the water is trapped in the mixtures and 'explosively' evolves at 388–391 K. The shift of the peak from 388 to 391 K results from the fact that the water leaves from the mixtures with different contribution of the K_2CuCl_4 and $K_2Cu_2Cl_6$ phases.

That is why probably Vriens [4] and Suga [3] showed the phase changes at 365.4 and at 389 K as two separate stages. The results presented here showed that during heating of the $CuCl_2$-KCl mixtures the crystal lattice is completely developed at 391 K. The $K_2Cu_2Cl_6$ crystal lattice is developed at 336 K and the K_2CuCl_4 crystal lattice at 366 K.

Conclusion

All phase changes of the $CuCl_2$–KCl mixtures have a reversible character in the temperature range from 293 to 473 K.

Thermal analysis of $CuCl_2$–KCl mixtures with absorbed water reveals more contrasting DTA pictures than those described in [1].

The $K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O$ phase [1] exchanges much more water than the $K_2CuCl_4 \cdot 2H_2O$ phase.

The $K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O$ phase [1] forms $K_2Cu_2Cl_6$ phase at 336 K, and the $K_2CuCl_4 \cdot 2H_2O$ phase forms $KCuCl_3 + KCl$ phase at 366 K.

The above phase changes are probably realized by displacement of Cu_2Cl_6 and $CuCl_4$ groups due to the tendency of copper to achieve 4+2 coordination.

Cu_2Cl_6 absorbes the water using probably two Cu ions, but additional investigations are needed.

Independently of the molar ratio of Cu to K in the investigated mixtures, the samples absorb the water in the whole mass.

In the Meyerhoffer phase change, KCl is formed probably not as a separate phase, but maybe as a sublattice.

A part of the water is trapped in the crystal lattice of the $CuCl_2$–KCl mixtures during the displacement of $CuCl_4$ and Cu_2Cl_6 groups, and then 'explosively' leaves into the surroundings at 388–391 K.

'Explosive' evolution of the water will be really dependent on the pressure of the surroundings [3].

The crystal lattice, obtained in the Meyerhoffer phase change, is developed at 366 K.

The crystal lattice of the $K_2Cu_2Cl_6$ phase is developed at 336 K.

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Zusammenfassung — Gemische aus $CuCl_2$ und KCl mit einem Molverhältnis von 0,5 bis 1,0 wurden bei 393 K erhitzt und absorbierten dann bei Zimmertemperatur Wasser aus der Umgebung.Für die Gemische mit Wasser wurden die DTA-, TG- und DTG-Kurven für den Temperaturbereich 293 bis 473 K untersucht. Der Mechanismus für den Phasenwechsel und die Abgabe von Wasser aus den Gemischen im Temperaturintervall 293 bis 473 K wird vorgeschlagen.