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DTA ANALYSIS OF THE SYSTEM $CuCl_2$–KCl

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Mixtures of $CuCl_2$ and KCl in molar ratios of Cu to K of from 0.5 to 1.0 were heated at 473 K in an air atmosphere, and then subjected to DTA analysis in the temperature range 293–773 K. A number of endothermic processes were observed, the extents of these depending on the molar ratio of Cu to K in the mixture.

In the presence of potassium chloride, $CuCl_2$ forms complex compounds K_2CuCl_4 and $KCuCl_3$ [1, 2]. Phase diagrams of $CuCl_2$–CuCl for specified contents of KCl have been reported [3]. Similar data on the system $CuCl_2$–KCl where copper(I) chloride is absent are not available. In the system $CuCl_2$–KCl, the transition of K_2CuCl_4 into $KCuCl_3$ [4, 5] has been found to be possible within the temperature range 365–390 K.

The present work involved thermogravimetric investigations of the system $CuCl_2$–KCl in which the molar ratio of $CuCl_2$ to KCl was varied from 0.5 to 1.0 within the temperature range 293–773 K. Thermogravimetric investigations were supplemented by X-ray analysis.

Experimental

To obtain the system $CuCl_2$–KCl, dihydrous copper(II) chloride and potassium chloride (POCh Gliwice) were used. Weighed quantities of the two salts, in appropriate proportions, were dissolved in 100 cm^3 of distilled water and the solution was next evaporated to dryness at 343 K. The dry residue was crushed and ground. Powdered samples were roasted at 473 K for 2 h in an air atmosphere. After cooling down to room temperature, the samples were subjected to thermogravimetric and X-ray analyses.

Mixtures with molar ratios of $CuCl_2$ to KCl of 0.5, 0.614, 0.692, 0.768, 0.845, 0.922 and 1.0 were prepared as described above. Thermogravimetric analyses were made with a derivatograph (MOM, Budapest, Hungary) within the temperature

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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, sensitivity DTA 1/5, sensitivity DTG 1/3, sensitivity TG 200 mg. X-ray investigations were made with a DRON–2 X-ray apparatus (USSR) within the range of angles 11–41° in the scale 2θ, using Cu–K_α radiation. The working conditions of the apparatus were as follows: lamp voltage 36 kV, lamp current intensity 20 mA, turning rate of the goniometer 0.5°/min, measurement interval 4 × 1000 imp/s, time constant 2 s.

Results

Figure 1 shows the endothermic effects in the DTA curves of the investigated samples.

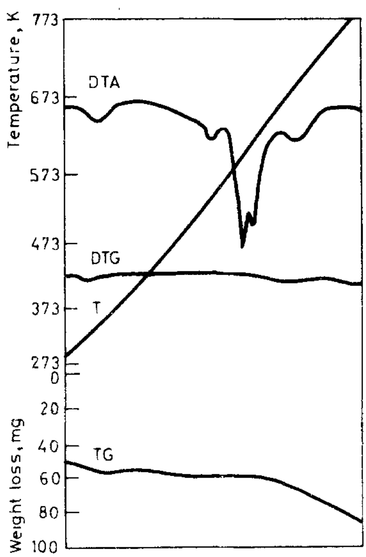

Fig. 1 TG, DTG and DTA curves of a mixture of $CuCl_2$ and KCl heated at 473 K for 2 h. Molar ratio of Cu to K = 0.768

The curves reveal changes in the areas of the individual endothermic effects, or their disappearance, as the molar ratio of $CuCl_2$ to KCl in the investigated samples is varied.

Figure 2 demonstrates that the area of the endothermic effect with peak at 533–543 K is the largest at a molar ratio of Cu to K of 0.614; on increase of the ratio, the area gradually decreases to zero. A similar phenomenon is observed for

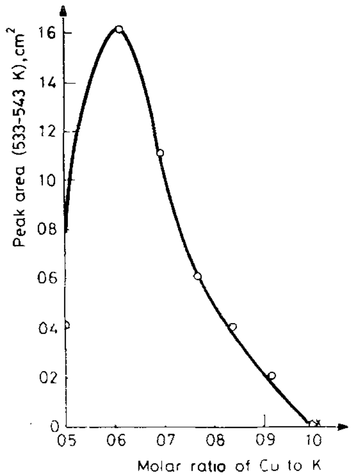

Fig. 2 Variation of the area of the endothermic effect with peak at 533–543 K as a function of the molar ratio of Cu to K in the mixture

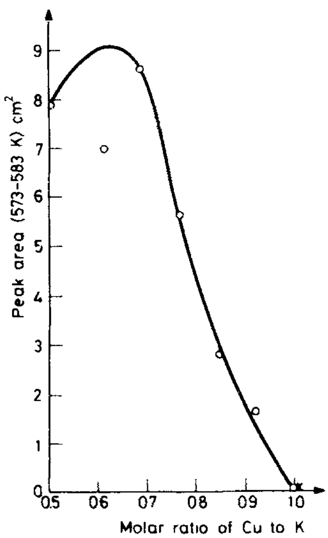

Fig. 3 Variation of the area of the endothermic effect with peak at 573–583 K as a function of the molar ratio of Cu to K in the mixture

the endothermic effect with peak at 573–583 K (Fig. 3). The maximum area is found at a molar ratio of Cu to K of 0.692; the area then gradually decreases to zero at a molar ratio of Cu to K of 1.0. The area of the endothermic effect with peak at 603–618 K increases as the area of the endothermic effect with peak at 573–583 K decreases (Fig. 4).

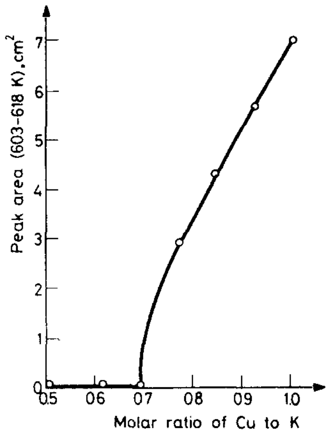

Fig. 4 Variation of the area of the endothermic effect with peak at 603–618 K as a function of the molar ratio of Cu to K in the mixture

The endothermic effect with peak at 603–618 K is not observed until the molar ratio of Cu to K is 0.692.

There are two small endothermic effects in the DTA curves, one with peak at 333 K and the other with peak at 673–693 K. The areas of these endothermic effects do not display regularities as functions of the molar ratio of Cu to K. The mass loss of the samples under analysis takes place stepwise at 333 K, which corresponds to the first endothermic peak, whereas it takes place continually above 533–543 K. It is interesting to note that the diffractograms of the mixture with a molar ratio of Cu to K of 1.0 do not contain reflections from K_2CuCl_4, whereas in the diffractograms of the mixture with a molar ratio of Cu to K of 0.5 there are reflections from K_2CuCl_4, as well as a number of reflections from $KCuCL_3$. The diffractograms also contain a number of unidentified reflections.

Discussion

The DTA curves of the system $CuCl_2$–KCl–H_2O with molar ratios of Cu to K of from 0.5 to 1.0 reveal five endothermic effects, with the peak temperatures of 333 K, 533–543 K, 573–583 K, 603–618 K and 673–693 K. The first effect is attributed to dehydration of the system [6].

Additional X-ray analysis of samples has shown the presence of the following combinations: $KCuCl_3$, K_2CuCl_4, $K_2CuCl_4 \cdot 2H_2O$, Cu_2Cl_2 and Cu_2OCl_2. At the same time, a number of unidentified reflections have also been detected, which may originate from more complicated complexes of $CuCl_2$ and KCl, e.g. $K_2Cu_2Cl_6$. The experimental X-ray data confirm that the diffractograms of the mixture with a molar ratio of Cu to K of 0.5 contains reflections from K_2CuCl_4 and also from $KCuCl_3$. The experimental data and observations during heating, as well as the changes in the areas of individual effects (Figs 2–4), suggest that the processes at 533–543 K, 573–583 K and 603–618 K are connected with melting and with the decomposition of complicated complexes into more simple ones. In the above processes, KCl plays the controlling role. At the same time, from 533–543 K upwards, the TG curves of the samples demonstrate a continuous mass loss, due to the volatilization of chlorine [7]. This process can not influence our interpretation of the data, for it takes place to approximately the same degree for all the samples under analysis, independently of the molar ratio of Cu to K.

Conclusions

Within the range of molar ratios studied here, mixtures of $CuCl_2$ and KCl are subject to endothermic processes at 333 K, 533–543 K, 573–583 K, 603–618 K and 673–693 K. These processes are connected with dehydration of the salts, their melting and the transition of some complexes into others. The individual salts $CuCl_2$ and KCl are practically not subject to these processes.

The amount of the complex (it may be $K_2Cu_2Cl_6$) formed during the roasting of the samples at 473 K is a function of the molar ratio of Cu to K in the mixtures under investigation, but it is the same complex, regardless of the value of this ratio.

The changes at 533–543 K and 573–583 K reach their maximum values when the molar ratio of Cu to K is 0.6–0.7. It may be presumed that they are connected with the decomposition of a complex which is a multiple of the complex $KCuCl_3$, e.g. the complex $K_2Cu_2Cl_6$, from which the unidentified X-ray reflections may originate. In [8] it was shown that active complexes in the catalytic system of the type support—$CuCl_2$, KCl have the structure Cu_mCl_n.

The change at 603–618 K, not occurring for molar ratios of Cu to K of 0.5–0.7, is probably connected with the decomposition of the originally formed combination.

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Zusammenfassung — DTA-Untersuchungen haben ergeben, daß in Mischungen von $CuCl_2$ und KCl mit molaren Cu/K-Verhältnissen von 0,5–1,0 nach Erhitzen in Luft bei 473 K im Temperaturbereich von 293 bis 773 K eine Reihe von endothermen Prozessen verlaufen. Das Ausmaß dieser Prozesse hängt vom Cu/K-Verhältnis der Gemische ab.

Резюме — ДТА анализ смесей хлористой меди и хлористого калия (при молярном соотношении меди и калия от 0,5 до 1,0) в пределах температурного интервала 293–773 К, показал несколько эндотермических процессов, большинство которых зависит от молярного соотношения меди и калия в смесях.