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THERMOANALYTICAL INVESTIGATIONS ON THE DECOMPOSITION OF DOUBLE SALTS. PART II. THE DECOMPOSITION OF DOUBLE SALTS $MeCl \cdot MgCl_2 \cdot 6H_2O$ ($Me = NH_4$, Rb, Cs) *

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ABSTRACT

The melting and decomposition behaviour of double salts $MeCl \cdot MgCl_2 \cdot 6H_2O$ ($Me = NH_4$, Rb, Cs) has been investigated in a closed system under dynamic heating conditions and in open systems under dynamic and quasi-isothermal and quasi-isobaric conditions in the temperature range 20–300 ° C. DTA heating and cooling cycles in the closed system illustrate the melting behaviour of the double salts.

Thermal decomposition of the salts under quasi-isothermal and quasi-isobaric conditions occurs at pressures of 115 kPa from the melt (with the exception of rubidium carnallite) and under reduced pressure (~ 5 kPa) from the solid. In all cases dihydrates are stable intermediate products. Further thermal decomposition is accompanied by hydrolysis and basic products are formed.

INTRODUCTION

The behaviour of the carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ has already been described in connection with thermoanalytical investigations on double-salt hydrates of the type $MeCl \cdot MgCl_2 \cdot 6H_2O$ [1,2]. Continuing these studies, we investigated the thermal behaviour of the corresponding compounds with $Me = NH_4$, Rb, Cs.

Extensive, but not comparable results on the thermal decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ are available from different measuring methods and investigation conditions; the double salt $RbCl \cdot MgCl_2 \cdot 6H_2O$ was only briefly investigated and $CsCl \cdot MgCl_2 \cdot 6H_2O$ not investigated.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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Most authors give two steps for the thermal decomposition of ammonium carnallite

$$\text{I}: NH_4Cl \cdot MgCl_2 \cdot 6H_2O \rightarrow NH_4Cl \cdot MgCl_2 \cdot 2H_2O + 4H_2O$$

$$\text{II}: NH_4Cl \cdot MgCl_2 \cdot 2H_2O \rightarrow NH_4Cl \cdot MgCl_2 + 2H_2O$$

In a following third step, decomposition occurs

$$\text{III}: NH_4Cl \cdot MgCl_2 \rightarrow NH_3 + HCl + MgCl_2$$

however, the statements are contradictory, relating to parallel hydrolysis processes.

Table 1 gives a survey of results on the thermal behaviour of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ taken from the literature. During thermal decomposition of $RbCl \cdot MgCl_2 \cdot 6H_2O$ Baimuradov [16] obtained five endothermic peaks. He

TABLE 1

Summary of bibliography of thermal decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$

Author(s)	Decomposition reaction	Temperature (°C)	Remarks
Ball and Ladner [3]	I [a] II [b] III [c]	90–140 140–180 180–340	Kinetics and mechanism of dehydration; existence conditions of stable intermediate products; measurement of temperature and vapour pressure; determination of heats of activation and heats of vaporization
Klementev and Shestakova [4]	I [a] II [b] III [c]	90–140 140–180 180–340	Investigtation of mechanism of decomposition; no hydrolysis was found
Hauer [5]	I [a] II [b]	115 135	Without hydrolysis
Maurits and coworkers [6–9]	I [a] II [b] III [c]	– – –	Kinetics and mechanism of thermal decomposition; heats of solution; heats of dehydration I = +60.5 kcal II = +30.6 kcal III = +46.08 kcal
Mishchenko et al. [10]	I [a] II [b] $NH_4Cl \cdot MgCl_2 \cdot 6H_2O \rightarrow NH_4Cl \cdot MgCl_2 + 6H_2O$ (IV)	– –	Heats of dehydration I = 273.0 J mol^{-1} II = 164.1 J mol^{-1} IV = 437.1 J mol^{-1}
Hautz [11]	I [a] II [b]	115 135	–

Author(s)	Decomposition reaction	Temperature (°C)	Remarks
Suzukawa et al. [12]	$NH_4Cl \cdot MgCl_2 \cdot 6H_2O \rightarrow NH_4Cl \cdot MgCl_2 \cdot 3.5H_2O + 2.5H_2O$	150	Patented
	$NH_4Cl \cdot MgCl_2 \cdot 3.5H_2O \rightarrow NH_4Cl \cdot MgCl_2 \cdot 0.5H_2O + 3H_2O$	300	
	$NH_4Cl \cdot MgCl_2 \cdot 0.5H_2O \rightarrow NH_4Cl + MgCl_2 + 0.5H_2O$	800	
Maeda et al. [13]	I [a] II [b] III [c]	130 165 845	Patented
Nakayasu et al. [14]	I [a] II [b] III[c]	138 176 314	Differential scanning calorimetry in nitrogen atmosphere; partial hydrolysis in stage III
Suvorov and Posoelov [15]	I [a] II [b] III [c]		Dissociation pressure of decomposition stages in relation to temperature; variation of HCl-pressure; or hydrolysis observed

I [a] $NH_4Cl \cdot MgCl_2 \cdot 6H_2O \rightarrow NH_4Cl \cdot MgCl_2 \cdot 2H_2O + 4H_2O$.
II [b] $NH_4Cl \cdot MgCl_2 \cdot 2H_2O \rightarrow NH_4Cl \cdot MgCl_2 + 2H_2O$.
III [c] $NH_4Cl \cdot MgCl_2 \rightarrow NH_3 + HCl + MgCl_2$.

assigned the removal of crystal water in steps of three, one and two molecules of H_2O to the thermal effects at 185, 195 and 225 °C. Pure $RbCl \cdot MgCl_2$ melted at 525 °C. The small endothermic effect at 440 °C represents melting of a eutectic mixture of $RbCl \cdot MgCl_2$ and $MgCl_2$.

For the double-stage mechanism

$$RbCl \cdot MgCl_2 \cdot 6H_2O \rightarrow RbCl \cdot MgCl_2 \cdot 2H_2O + 4H_2O$$

$$RbCl \cdot MgCl_2 \cdot 2H_2O \rightarrow RbCl \cdot MgCl_2 + 2H_2O$$

decomposition temperatures of 179 and 214 °C are obtained by extrapolation of the vapour pressure data according to Busch [17]. Apart from the vapour pressure data of Busch [17] which indicate a single-stage dehydration mechanism at about 173 °C, no further relevant data could be found for $CsCl \cdot MgCl_2 \cdot 6H_2O$.

These contradictory literature data and incomplete results led to characterization of the above mentioned three compounds by thermal decomposition, within the scope of investigations on double salts of the carnallite type. Quasi-isothermal and quasi-isobaric thermogravimetry as well as DTA were applied. Additionally investigations on the melting behaviour were performed by thermomicroscopic methods.

EXPERIMENTAL

The double salts were prepared from solutions of the ternary system $MeCl-MgCl_2-H_2O$ by slow isothermal evaporation of the solvent (several weeks). Before beginning any measurements, the crystals were crushed in an agate mortar to a grain size of 100 μm. Further experimental details can be found in previous work [1].

Chemical analysis showed a stoichiometric ratio of Me : Mg. No magnesium chloride hexahydrate, alkali metal chloride or ammonium chloride could be detected. Because the absolute error of the water determination is ± 0.05 mol H_2O, the theoretical composition can be assumed.

RESULTS AND DISCUSSION

Melting and solidification

Figure 1 shows the DTA curves of two heating and cooling cycles in a closed system. For comparison, the results of the investigations on carnallite [1] are shown and briefly discussed.

Carnallite melts incongruently at 167 °C with formation of a KCl-saturated magnesium chloride hydrate melt and solid KCl. On cooling, crystallization of the carnallite begins at 162–159 °C with slight supercooling. Detailed discussion of the DTA curves [1] shows that carnallite is reformed only in the same degree as KCl is dissolved in the $MgCl_2 \cdot 6H_2O$ melt. As a result of the density differences between solid KCl ($\rho = 1.9$ kg m^{-3}) and the KCl-saturated magnesium chloride hexahydrate melt ($\rho =$ 1.5–1.6 kg m^{-3}), stratification occurs within the sample so that solid KCl is present, carnallite is precipitated and magnesium chloride hydrates finally crystallize.

$NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ melts at 182.5 °C (cooling peak at 179 °C). An incongruent melting analogous to $KCl \cdot MgCl_2 \cdot 6H_2O$ was not observed. An explanation for the exothermic effect at 139–146 °C and of the small endothermic peaks in the next heating cycle at 159 °C cannot yet be given because no comparable investigations were performed on the solid–liquid phase equilibria in the system $NH_4Cl-MgCl_2-H_2O$ including the solid-phase compositions at temperatures above 115 °C. A congruent melting at 193 °C was determined for $RbCl \cdot MgCl_2 \cdot 6H_2O$. On cooling the melt solidifies with supercooling at 188–185 °C.

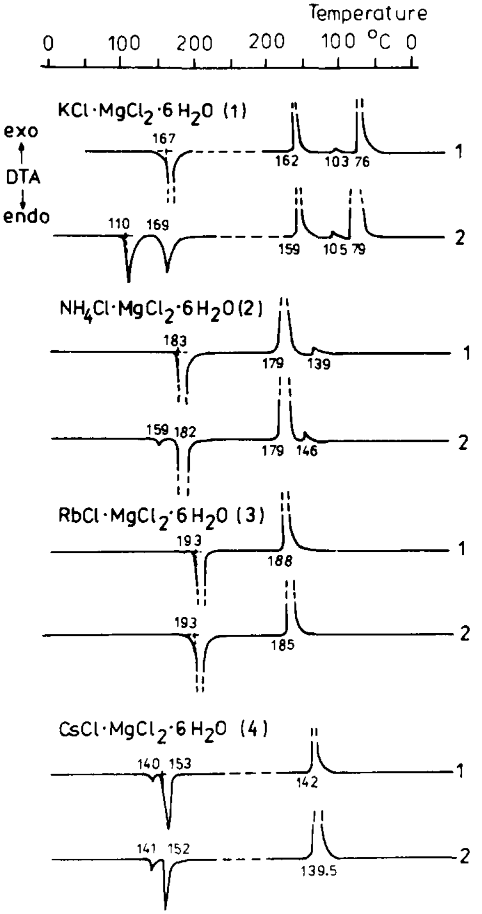
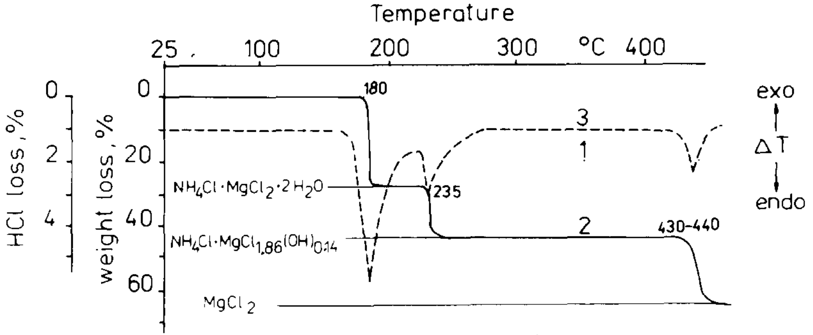


Fig. 1. DTA curves of the melting and solidification behaviour of carnallite, ammonium carnallite, rubidium carnallite and caesium carnallite in closed crucibles. 1, 2, number of cycle; heating rate q = ±1 deg $\min^{-1}$; mass of the sample m(1), 42.36 mg; m(2), 10.70 mg; m(3) 14.25 mg; m(4) 14.25 mg.

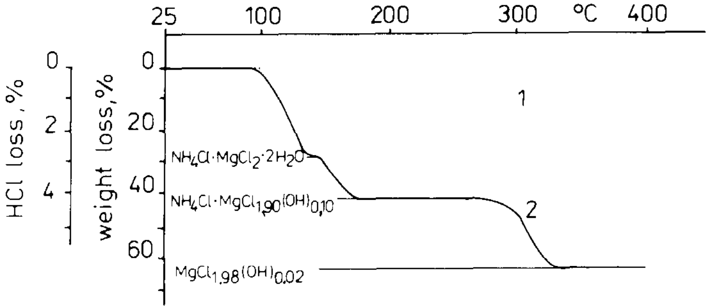
$CsCl \cdot MgCl_2 \cdot 6H_2O$ melts congruently at 152.5 °C. On cooling a single crystallization peak is observed at 142–140 °C. Optical investigations in polarized light were performed in closed microampoules parallel to the thermoanalytical investigations. These studies show that the endothermic effect at 141 °C represents a phase transition of the caesium double salt.

Thermal decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$

The results obtained under quasi-isothermal conditions at different partial pressures of the decomposition gases (labyrinth crucible ~ 115 kPa; multiplate crucible ~ 5 kPa) are shown in Fig. 2.



Labyrinth crucible



Multiplate crucible

Fig. 2. $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible. 1, = gas titration curve; 2, = thermogravimetric curve; 3, ΔT = temperature difference curve.

Decomposition takes place in the labyrinth crucible in three isothermal steps with the formation of defined decomposition products. Melting of the double salt at 182.5 °C is directly associated with the initial evaporation of water, so that only one ΔT signal is recorded for both processes. After removal of four molecules of H_2O per molecule of starting substance the dihydrate of the double salt is obtained as a solid phase. This was confirmed by X-ray diffractometry. The double-salt dihydrate is subject to partial hydrolysis which leads to formation of the basic compound $NH_4Cl \cdot MgCl_{1.86}(OH)_{0.14}$. This process takes place during removal of two further molecules of H_2O at a temperature of 235 °C. In a further isothermal step at 430 °C the thermal decomposition of the basic product with removal of NH_4Cl (NH_3 + HCl) can be detected. As the sublimation temperature of NH_4Cl is 345 °C under analogous experimental conditions, the results confirm the existence of dehydrated, but slightly hydrolyzed $NH_4Cl \cdot MgCl_2$ up to a temperature of 430 °C. In this way the three-stage thermal decomposition is confirmed.

The following equations are formulated including hydrolysis

182.5 °C:

$$NH_4Cl \cdot MgCl_2 \cdot 6H_2O \rightarrow NH_4Cl \cdot MgCl_2 \cdot 2H_2O + 4H_2O \tag{1}$$

235 °C:

$$NH_4Cl \cdot MgCl_2 \cdot 2H_2O \rightarrow NH_4Cl \cdot MgCl_{1.86}(OH)_{0.14} + 0.14HCl + 1.86H_2O \tag{2}$$

430 °C:

$$NH_4Cl \cdot MgCl_{1.86}(OH)_{0.14} \rightarrow NH_4Cl + MgCl_{1.86}(OH)_{0.14} \tag{3}$$

$$NH_4Cl \rightarrow NH_3 + HCl \tag{4}$$

$$MgCl_{1.86}(OH)_{0.14} + 0.14HCl \rightarrow MgCl_2 + 0.14H_2O \tag{5}$$

Thermal decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ in the multiplate crucible begins at temperatures as low as 70 °C. Four molecules of H_2O are removed from the solid double-salt hydrate (compare reaction (1)).

In a further step, beginning at 135 °C, the remaining two molecules of water are removed with simultaneous hydrolysis. A product results according to the composition of reaction (2). In the third step (250 °C) NH_4Cl is removed with formation of the basic magnesium chloride $MgCl_{1.98}(OH)_{0.02}$. In summary, the decomposition diagram shown in Fig. 3 can be plotted for the thermal decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ with different partial pressures of the decomposition gases.

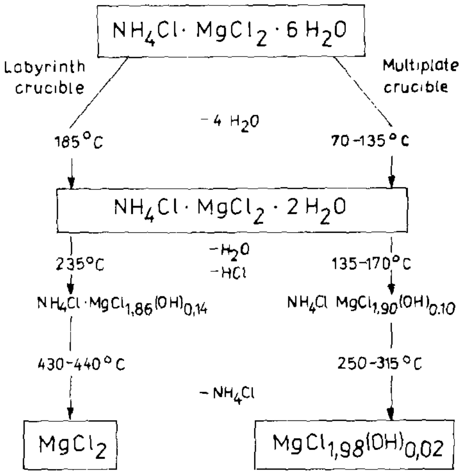


Fig. 3. Decomposition scheme of ammonium carnallite under quasi-isothermal and quasi-isobaric conditions.

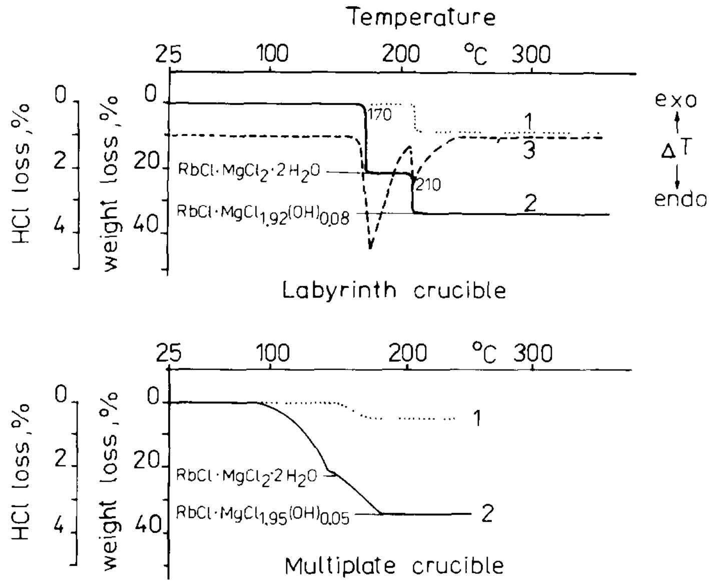


Fig. 4. $RbCl \cdot MgCl_2 \cdot 6H_2O$ decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible. 1, = gas titration curve; 2, = thermogravimetric curve; 3, ΔT = temperature difference curve.

Thermal decomposition of $RbCl \cdot MgCl_2 \cdot 6H_2O$

The results of the thermal decomposition of rubidium carnallite are shown in Fig. 4. Decomposition of $RbCl \cdot MgCl_2 \cdot 6H_2O$ proceeds in two steps, independent of the partial pressures of the decomposition gases. Removal of four molecules of water and formation of the dihydrate take place in the labyrinth crucible at an isothermal temperature step at 170 °C. At the beginning of the second isothermal step at 210 °C, hydrolysis occurs in addition to the removal of water. A basic final product is formed. No RbCl, $MgCl_2$ and basic magnesium chlorides could be detected in this product by X-ray methods.

Two endothermic decomposition peaks are clearly visible in the ΔT curve which was plotted simultaneously. Moreover, during subsequent heating to 550 °C (not shown) a further endothermic peak is detected which must be related to melting of the dehydrated compound $RbCl \cdot MgCl_2$ [18]. In this way, the double-stage decomposition mechanism assumed by Busch [17] and the decomposition temperatures extrapolated from the vapour pressure data under quasi-isothermal and quasi-isobaric conditions are confirmed. Analogous reactions, shifted to lower temperatures, result under reduced partial pressure (~ 5 kPa)
170 °C:

$$RbCl \cdot MgCl_2 \cdot 6H_2O \rightarrow RbCl \cdot MgCl_2 \cdot 2H_2O + 4H_2O \qquad (6)$$

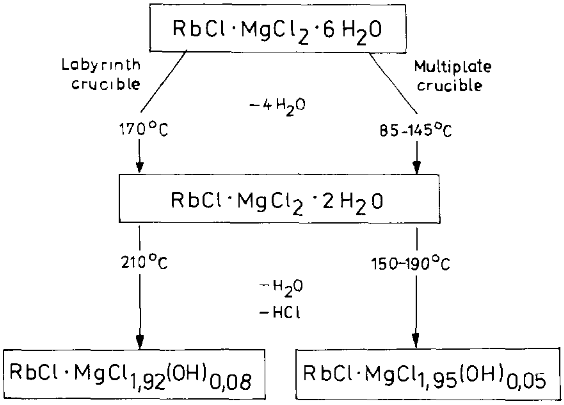


Fig. 5. Decomposition scheme of rubidium carnallite under quasi-isothermal and quasi-isobaric conditions.

210 °C:

$$RbCl \cdot MgCl_2 \cdot 2H_2O \rightarrow RbCl \cdot MgCl_{1.95}(OH)_{0.05} + 1.95H_2O + 0.05HCl \tag{7}$$

The final product is the anhydrous compound $RbCl \cdot MgCl_2$ contaminated by hydrolysis products. The general decomposition diagram is shown in Fig. 5.

Thermal decomposition of $CsCl \cdot MgCl_2 \cdot 6H_2O$

We find a three-stage mechanism (Fig. 6) for thermal decomposition of $CsCl \cdot MgCl_2 \cdot 6H_2O$. Evaporation of four molecules of H_2O from the melt (melting point 152.5 °C) and formation of the solid dihydrate take place in the labyrinth crucible at a temperature of 160 °C. Another 1.5 molecules of H_2O are removed in a further step at 190 °C. A hydrolysis product, $CsCl \cdot MgCl_{1.98}(OH)_{0.02} \cdot 0.5H_2O$ is also formed. With simultaneous hydrolysis the remaining water of crystallization is removed in a third step at 220 °C. The composition of the final product is $CsCl \cdot MgCl_{1.95}(OH)_{0.05}$. These three steps are also indicated in the ΔT curve. Two further endothermic peaks must be related to the phase transition at about 145 °C which has already been discussed for the DTA curves, and to the melting process at 152.5 °C, respectively.

A two-step mechanism was found under multiplate crucible conditions. In the first step four molecules of water are released and the dihydrate is formed (temperature range 60–125 °C). In the second step the anhydrous double salt is formed. At the same time initial hydrolysis is observed.

The results are summarized in Fig. 7. They do not support the single-stage dehydration mechanism assumed by Busch [17].

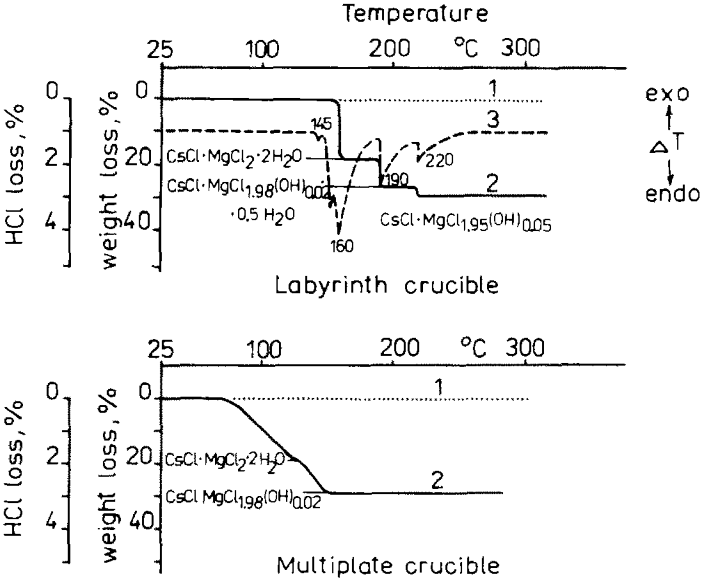


Fig. 6. $CsCl \cdot MgCl_2 \cdot 6H_2O$ decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible. 1. = gas titration curve; 2. = thermogravimetric curve; 3. ΔT = temperature difference curve.

Comparison of our results of the thermal investigations on the double salts $MeCl \cdot MgCl_2 \cdot 6H_2O$ (Me = K, NH_4, Rb, Cs) leads to the following statements: the tendency to incongruent melting decreases with increasing

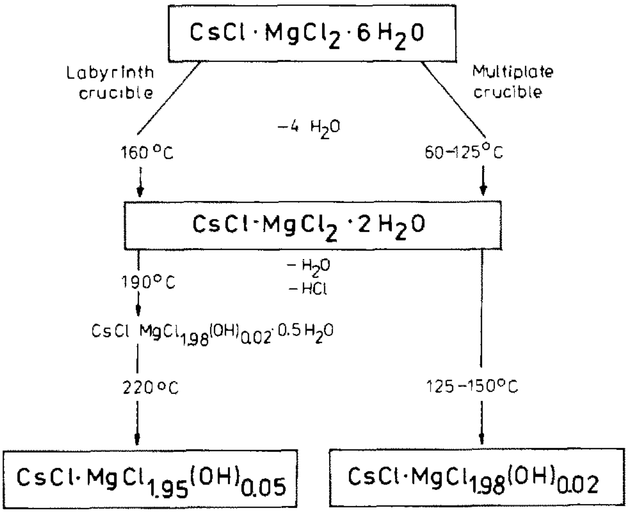


Fig. 7. Decomposition scheme of caesium carnallite under quasi-isothermal and quasi-isobaric conditions.

ionic radius of the alkali metal ion (K < NH_4 < Rb < Cs), $KCl \cdot MgCl_2 \cdot 6H_2O$ melts with a high incongruence, and the KCl crystals which are formed in the magnesium chloride hydrate melt can be observed by microscopic investigations [1].

In the case of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ the character of the melting process cannot be definitely clarified by thermoanalytical and microscopic investigations. The DTA curves indicate congruent melting. If a low incongruent melting of ammonium carnallite should be observed, the deficiency of appropriate thermal effects can be explained if supersaturation of the formed melt with NH_4Cl is very low and nucleation and growth do not take place. The double salt is reversibly reconverted and further ΔT signals cannot be recorded. Crystals of NH_4Cl are not visible even under the microscope. In this case more exact investigations on the solid–liquid phase equilibria in an appropriate temperature range should give further information.

$RbCl \cdot MgCl_2 \cdot 6H_2O$ and $CsCl \cdot MgCl_2 \cdot 6H_2O$ melt congruently. The melting points increase in the following order: 167.5 °C ($KCl \cdot MgCl_2 \cdot 6H_2O$) < 182.5 °C ($NH_4Cl \cdot MgCl_2 \cdot 6H_2O$) < 193 °C ($RbCl \cdot MgCl_2 \cdot 6H_2O$). An exception is $CsCl \cdot MgCl_2 \cdot 6H_2O$ with a melting point of 152.5 °C.

Thermal decomposition of the double salts with increased partial pressure of the decomposition gases occurs from the melt with the exception of $RbCl \cdot MgCl_2 \cdot 6H_2O$. In all cases, the dihydrate of the double salt is obtained as a stable intermediate product. Its further thermal decomposition is accompanied by hydrolysis.

Decomposition with reduced pressure of the decomposition gases (multiplate crucible conditions) occurs from the solid at lower temperatures. The dihydrates of the double salts also form as stable intermediates. The degree of hydrolysis of the products obtained during further thermal treatment is less than that of the decomposition products resulting under a higher partial pressure.

With increased partial pressure, the temperature and pressure dependence of the decomposition equilibria shift to higher temperatures, a fact which also causes an increase in the degree of hydrolysis of the decomposition products.

Therefore, preparation of $MeCl \cdot MgCl_2$ compounds which are free from water and hydroxides is only possible by restricting hydrolysis, i.e. in an HCl atmosphere.

An indication of the reason for the differential release of the six water molecules can be inferred from the study of Nakayasu [19] on the structure of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$. In this study different lengths are given for the Mg–O bonds, two Mg–O bonds being shorter than the other four.

CONCLUSIONS

The melting and decomposition behaviour of double salts of the carnallite type $MeCl \cdot MgCl_2 \cdot 6H_2O$ with Me = NH_4, Rb, Cs has been investigated in a closed system under dynamic heating conditions and in an open system under dynamic and quasi-isothermal and quasi-isobaric conditions in the temperature range 20–300 °C. Investigation of specific processes was also performed by thermo-optical methods.

The melting points of the double salts and character of the melting process have been ascertained: $KCl \cdot MgCl_2 \cdot 6H_2O$, 167.5 °C, incongruent [1]; $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$, 182.5 °C; $RbCl \cdot MgCl_2 \cdot 6H_2O$, 193 °C, congruent; $CsCl \cdot MgCl_2 \cdot 6H_2O$, 152.5 °C, congruent.

Decomposition of the double salts proceeds independently through the dihydrate. Further dehydration to the water-free salt is accompanied by hydrolysis. By reducing the partial pressure of the decomposition gases under multiplate crucible conditions the decomposition is shifted to lower temperatures. Therefore, decomposition takes place from the solid, whereas decomposition in the labyrinth crucible occurs from the melt (an exception is $RbCl \cdot MgCl_2 \cdot 6H_2O$).

In addition, the results show that water-free magnesium chloride from $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ and double salts free from water and hydroxide cannot be prepared by thermal decomposition under a self-generated gas atmosphere. The process of hydrolysis must be restricted by an increased HCl partial pressure.

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