THERMOANALYTICAL INVESTIGATIONS ON THE DECOMPOSITION OF DOUBLE SALTS
III. The decomposition of double salts MBr · MgBr2 · 6H2O

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The melting and decomposition behaviour of the double salts MBr·MgBr2·6H2O (M = K, NH4, Rb, Cs) has been investigated in a closed system under dynamic and quasi-isothermal and quasi-isobaric conditions between 20°C and 300°C or 600°C, respectively. DTA heating and cooling cycles illustrate the melting behaviour of the double salts and give information on the melting point of these substances.

The thermal decomposition of double salts under quasi-isothermal and quasi-isobaric conditions takes place in the melt (with the exception of RbBr·MgBr2·6H2O) and under reduced pressure in the solid phase. A double salt of the type MBr·MgBr2·6H2O is formed as a stable intermediate. The final product of all types of thermal decomposition are basic products with different hydroxide or oxide contents, respectively.

In recent years we have investigated the melting behaviour and thermal decomposition behaviour of double salts of the type MCl·MgCl2·6H2O (M = K, NH4, Rb, Cs) [1-4]. In the present paper the results of our investigations on the corresponding bromidic double salts of the same type will be described with special attention being paid to correlations with the corresponding chloride double salts.

From investigations of the solid-liquid phase equilibria both KBr·MgBr2·6H2O and NH4Br·MgBr2·6H2O are certain to exist in the corresponding ternary systems [5–8], whereas there is an empirical method of preparation for CsBr·MgBr2·6H2O [9] and no information whatsoever in literature for RbBr·MgBr2·6H2O [10].

No information concerning the thermal decomposition of these double salts was found in the literature.

Some information about the decomposition of $MgBr_2 \cdot 6H_2O$ and mixtures of $MgBr_2 \cdot 6H_2O$ and MBr (M = Na, K, Cs) has been given by Shoval et al. [11–13].

Experimental

The method of preparation of $CsBr \cdot MgBr_2 \cdot 6H_2O$ cited in literature [9] proved useless so that new methods of preparation had to be developed for both this substance and $RbBr \cdot MgBr_2 \cdot 6H_2O$.

The preparation of the double salts at 25° was achieved by isothermal crystallization with simultaneous elimination of the water from solutions lying in the range of existence of the double salts in the ternary system MBr–$MgBr_2$–H_2O (for composition see Table 1).

Table 1 Composition of solutions to the preparation of double salts $MBr \cdot MgBr_2 \cdot 6H_2O$

Double salt	Mass in g			Temperature, °C
	MBr	$MgBr_2 \cdot 6H_2O$	$6H_2O$	
$KBr \cdot MgBr_2 \cdot 6H_2O$	2.0	69	50	25/50
$NH_4Br \cdot MgBr_2 \cdot 6H_2O$	8.2	69	50	25
$RbBr \cdot MgBr_2 \cdot 6H_2O$	6.5	31.4	20	25
$CsBr \cdot MgBr_2 \cdot 6H_2O$	10.0	82	40	25

The chemical analysis showed all double salts to have theoretical composition, with the exception of $KBr \cdot MgBr_2 \cdot 6H_2O$ which was contaminated with about 4% of $MgBr_2 \cdot 6H_2O$, determined by X-ray technique. The uncertainty in the hydrate water content of the investigated samples was below ±1.5%.

The crystals of about 500 μm size were taken from the solution, washed with hexane and subsequently briefly dried at about 50°; they were then ground to a grain size below 100 μm. DTA curves of the samples (mass $\approx$ 20...50 mg; heating rate ±2 deg/min) were measured at constant gross composition in closed glass ampoules with the low temperature DTA apparatus of SETERAM, France.

The thermal decomposition of the double salts was investigated under quasi-isothermal and quasi-isobaric conditions in the labyrinth crucible using the Derivatograph, Type Q, MOM Hungary. Further experimental details are presented in [1] and the figures.

The error of the temperature indicated for the DTA measurements is $\pm 1°$, that of the thermogravimetric investigation under quasi-isothermal and quasi-isobaric conditions is $\pm 5°$. The temperatures indicated on the DTA curves are extrapolated onset temperatures T_{on} [16].

Results and discussion

Melting and solidification behaviour in a closed system

Figure 1 shows the melting and solidification behaviour of the double salts.

$KBr \cdot MgBr_2 \cdot 6H_2O$

melts incongruently at 219°. Due to some degree of contamination of the double salt by $MgBr_2 \cdot 6H_2O$ and KBr a peak attributed to free $Mg \cdot Br_2 \cdot 6H_2O$ was observed at 162° already in the first heating cycle. KBr does not show any thermal effect in this temperature range. If the system is cooled, the crystallization of the double salt takes place with some super-cooling at 214° and at 199° in the first and second cycle, respectively.

The differences in the degree of supercooling between the first and second cycle can be explained as a consequence of inhibited nucleation due to the small amounts of material. The exothermic peak at 139° is assigned to the solidification of the magnesium bromide hexahydrate taking place with considerable supercooling; the melting of this compound is observed in the second cycle at 158° (Fig. 1). The peaks measured in the cooling run at 164°, 143° and 132° as well as the effects taking place at 136° in the heating run of the second cycle are interpreted as solidification and melting effects of non-equilibrium phases due to the incongruent melting of the double salt formed in the course of the cooling run.

$NH_4Br \cdot MgBr_2 \cdot 6H_2O$

melts at 231°, with the corresponding crystallization peak in the cooling run being observed at 219°. Further exothermic effects occur in the cooling run in the temperature range 138°...134°, as well as in the first cycle at 134° and second heating cycles at 134° and 152°. To clarify these effects the DTA cur-ves of NH_4Br, $MgBr_2 \cdot 6H_2O$, and a mixture of NH_4Br and $NH_4Br \cdot MgBr_2 \cdot 6H_2O$ were recorded under identical conditions. The cor-responding DTA cycle of the mixture is shown in Fig. 2. A comparison of the two experimental peaks with all available data reveals that the peak at 147°

in the heating phase and that at 125.5° in the cooling run can be assigned to the $\alpha \leftarrow \rightarrow \beta$ transformation of NH_4Br.

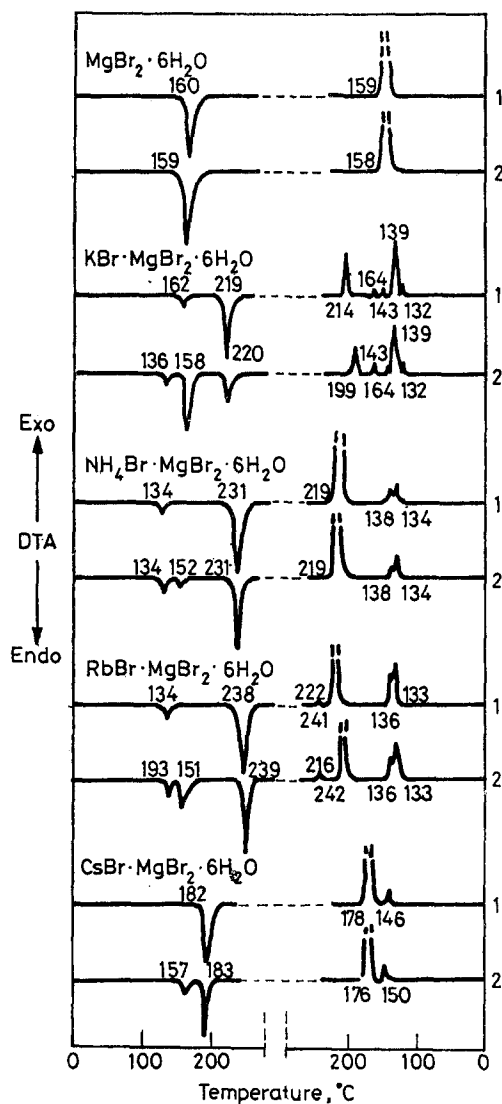The effects at 135° indicate a structural transformation in the double salt.

Fig. 1 DTA curves of the melting and solidification behaviour of $MgBr_2 \cdot 6H_2O$, $KBr \cdot MgBr_2 \cdot 6H_2O$, $NH_4Br \cdot MgBr_2 \cdot 6H_2O$, $RbBr \cdot MgBr_2 \cdot 6H_2O$ and $CsBr \cdot MgBr_2 \cdot 6H_2O$ in closed crucibles; 1, 2 number of cycle; heating rate $q = \pm 2 \deg \min^{-1}$

$RbBr \cdot MgBr_2 \cdot 6H_2O$

also melts incongruently at 238.5° (Fig. 1). The corresponding crystallization peak is observed at 222° and 216° in the first and second cycles, respectively. The relatively small exothermic effect at 133° in the cooling run is interpreted as lattice transformation. The endothermal peak occurring at 151° in the second heating cycle is the melting peak of the $MgBr_2 \cdot 6H_2O$ formed during the incongruent melting of the double salt.
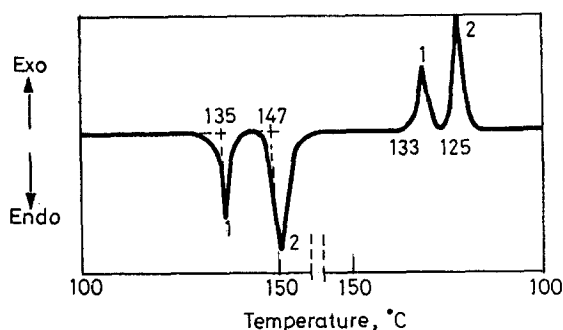

Fig. 2 DTA curve of a mixture from NH_4Br and $NH_4Br \cdot MgBr_2 \cdot 6H_2O$
1) Phase transition of $NH_4Br \cdot MgBr_2 \cdot 6H_2O$, 2) $\beta \rightarrow \alpha$ transition or $\alpha \rightarrow \beta$ transition, respectively, of NH_4Br

There are no data available on the solid-liquid phase equilibria at high temperatures of the ternary system $RbBr–MgBr_2–6H_2O$, and therefore the exothermic peak occurring at about 241° in the cooling phase cannot be assigned.

$CsBr \cdot MgBr_2 \cdot 6H_2O$

melts incongruently at 182°. The exothermic peaks recorded in the ranges 178°–176° and 150°–146° are assigned to the crystallization of the double salt. In the second cycle the melting of the newly formed $MgBr_2 \cdot 6H_2O$ is observed at 157°.

Thermals decomposition behaviour

$KBr \cdot MgBr_2 \cdot 6H_2O$

The results obtained under quasi-isothermal conditions at different partial pressures of the decomposition gases (using labyrinth crucible at about 115 kPa, and multiplate crucible at about 5 kPa [17] are represented in Fig. 3.
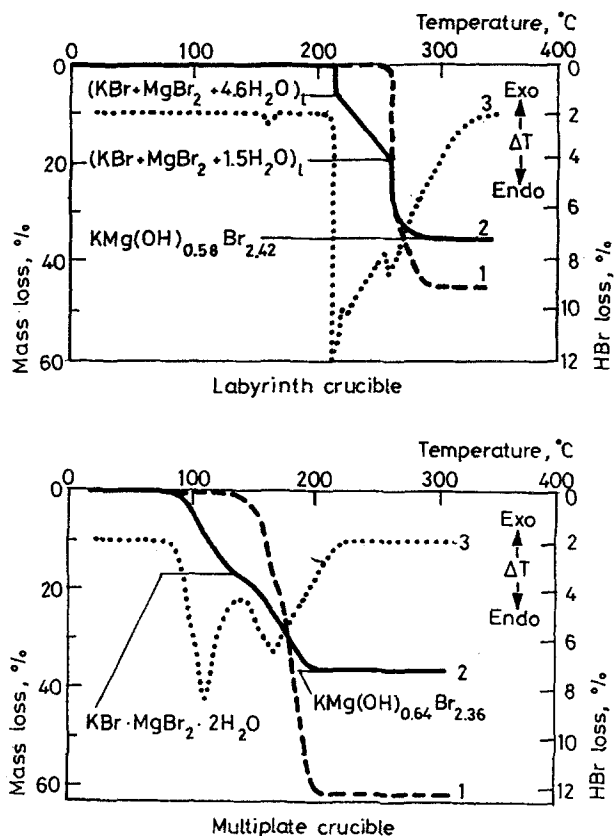
Fig. 3 KBr·MgBr₂·6H₂O decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible

1) gas titration curve, 2) thermogravimetric curve, 3) temperature difference curve (ΔT)

Decomposition starts near the melting temperature at 215° under normal pressure with KBr·MgBr₂·6H₂O and takes place isothermally involving a loss of 1.4 mol H₂O/mol double salt. After the subsequent non-isothermal stage the residue has the gross composition KBr·MgBr₂·1.5H₂O. The observed decomposition behaviour is in analogy with the curve of KCl·MgCl₂·6H₂O [3].

Beginning with a temperature of 265° both H₂O and HBr are released simultaneously in the subsequent stage leading to a basic product with the gross composition KMg(OH)$_{0.58}$Br$_{2.42}$. In the case of decomposition in the multiplate crucible under strongly reduced pressure the dihydrate is formed between 85° and 140° and a more strongly hydrolyzed final product of the

gross composition $KMg(OH)_{0.64}Br_{2.36}$ is formed between 140° and 200°. The decomposition scheme is represented in Fig. 4.

$NH_4Br \cdot MgBr_2 \cdot 6H_2O$

$NH_4Br \cdot MgBr_2 \cdot 6H_2O$ melts at 227° under normal pressure of the decomposition gases being simultaneously and isothermally dehydrated, resulting in the dihydrate formation (Fig. 5). This is followed by an isothermal stage of decomposition at 265° coming to an end (non-isothermally) up to 290°. In a further non-isothermal stage extended over the temperature range between 340° and 550° NH_4Br is sublimed and a product consisting of 0.96 mol $MgBr_2$ and 0.04 mol MgO is obtained. No reactions of the same type as those accompanying the decomposition of $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ were observed [3].
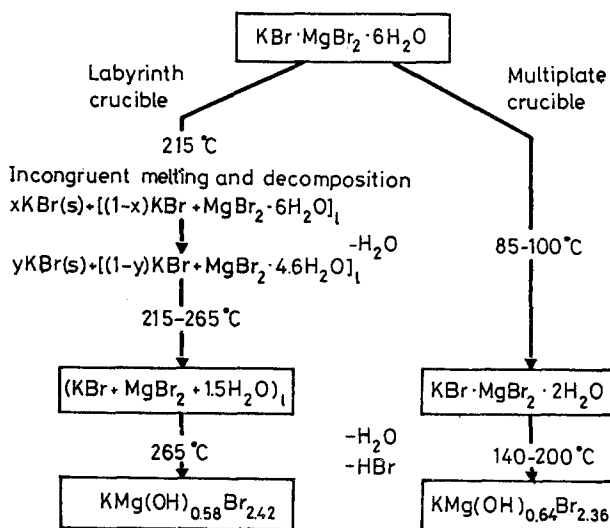

Fig. 4 Decomposition scheme of $KBr \cdot MgBr_2 \cdot 6H_2O$ under quasi-isothermal and quasi-isothermal and quasi-isobaric conditions

Under reduced partial pressure of the decomposition gases the dihydrate of the double salt is formed at 95°–150°. Dehydration takes place between 150° and 180° accompanied by hydrolysis into a basic product of the composition $NH_4Mg(OH)_{0.48}Br_{2.52}$. If the temperature is further increased a product of the composition $Mg(OH)_{0.28}Br_{1.74}$ is formed non-isothermally, i.e. reactions of the type described by us in [3] should occur. However, no water-free $MgBr_2$ is obtained. Results are shown schematically in Figs 5 and 6.

$RbBr \cdot MgBr_2 \cdot 6H_2O$

As with the corresponding chloride double salt, the thermal decomposition of $RbBr \cdot MgBr_2 \cdot 6H_2O$ (Fig. 7) in the pressure range under investigation starts from the solid phase. The corresponding dihydrate $RbBr \cdot MgBr_2 \cdot 2H_2O$ is formed at $220°$; it is decomposed to $RbMg(OH)_{0.21}Br_{2.79}$ in another isothermal stage at $255°$. The final product $RbMg(OH)_{0.32}Br_{2.68}$ is formed in a non-isothermal stage between $255°$ and $265°$.
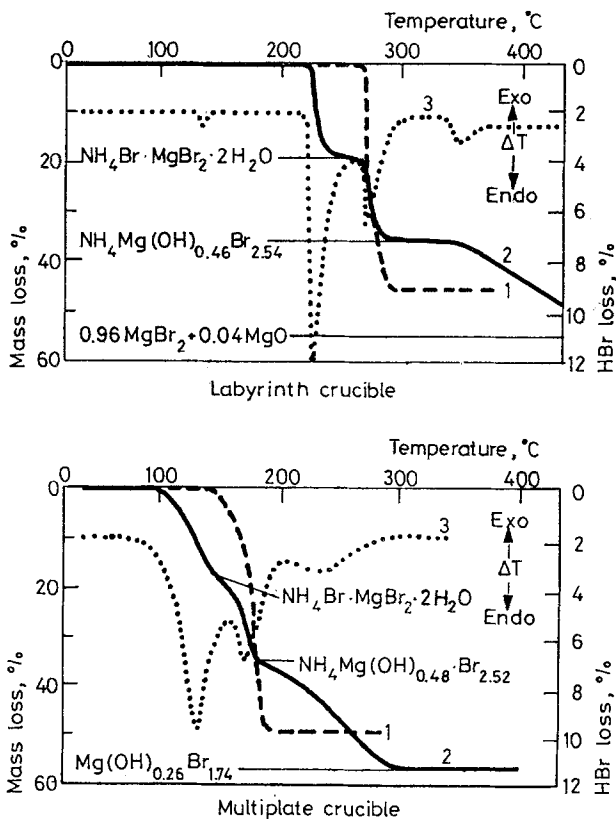

Fig. 5 $NH_4Br \cdot MgBr_2 \cdot 6H_2O$ decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible
1) gas titration curve, 2) thermogravimetric curve, 3) temperature difference curve (ΔT)

Decomposition takes place in two stages in the multiplate crucible, the dihydrate being formed between $100°$ and $150°$ and followed by its thermal

hydrolysis to $RbMg(OH)_{0.20}Br_{2.80}$ between 150°–170°. The decomposition scheme is shown in Fig. 8.

$CsBr \cdot MgBr_2 \cdot 6H_2O$

$CsBr \cdot MgBr_2 \cdot 6H_2O$ melts with decomposition under normal pressure at about 180°. First 0.3 mol of water is evolved. Water continues to be separated in a non-isothermal stage up to 255° when a melt of the gross composition $(CsMgBr_3 + 2.5\ H_2O)_l$ is achieved. A continuous separation of H_2O and HBr first leads to a stable intermediate $CsMg(OH)_{0.06}Br_{2.94} \cdot 0.2H_2O$ which subsequently is decomposed to $CsMg(OH)_{0.08}Br_{2.92}$ in another stage at 265°–268°.
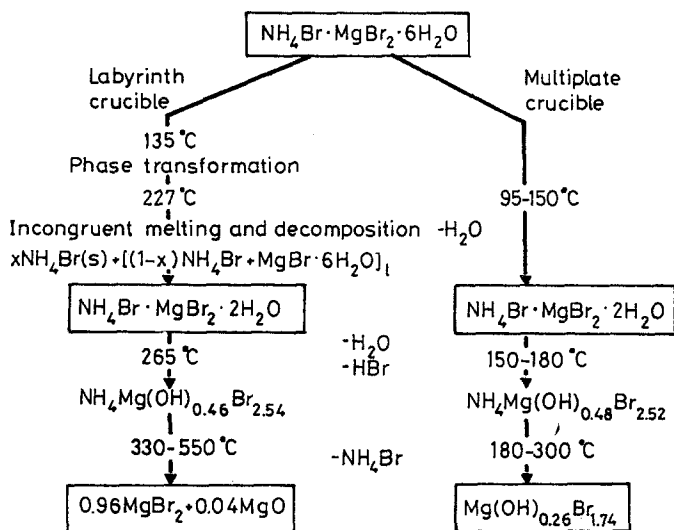

Fig. 6 Decomposition scheme of $NH_4Br \cdot MgBr_2 \cdot 6H_2O$ under quasi-isothermal and quasi-isothermal and quasi-isobaric conditions

A three-stage scheme is observed under reduced pressure. The dihydrate is formed in the temperature range 75°–135°. Decomposition continues under simultaneous evolution of H_2O and HBr between 135° and 155° and separation on the residual water at 183° reaching the composition $CsMg(OH)_{0.04}Br_{2.96}$. The results are shown schematically in Figs 9 and 10.
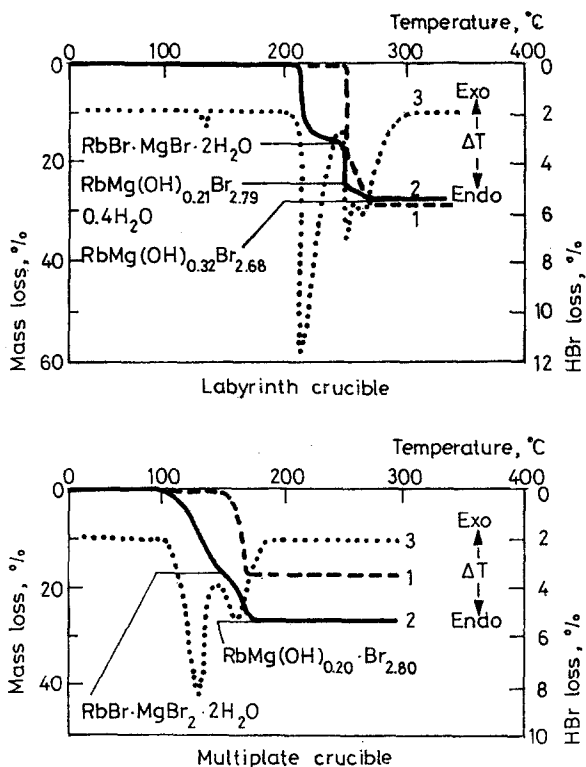
Fig. 7 RbBr·MgBr2·6H2O decomposition under quasi-isothermal conditions in a labyrinth crucible and a multiplate crucible; 1) gas titration curve, 2) thermogravimetric curve, 3) temperature difference curve (ΔT)

Conclusions

An incongruent melting behaviour was observed for all the investigated bromide double salts. This statement is confirmed by the occurrence of several solidification peaks in the DTA cycles (Fig. 1) on the one hand and the occurrence of solid phases of tempered melts somewhat above the melting temperature on the other hand. In Fig. 11 the measured melting points of chloride and bromide double salts are compared as a function of the radii of the monovalent cations.

The melting temperatures increase with growing cation radii from K^+ over NH_4^+ groups to Rb^+ and assume their lowest value for Cs^+. The melting temperatures of the bromide compounds are higher those of the corresponding chloride double salts. Solid-phase transformations can be taken

for certain in the cases of $NH_4Br \cdot MgBr_2 \cdot 6H_2O$ and $RbBr \cdot MgBr_2 \cdot 6H_2O$. Further investigations are planned in the future.
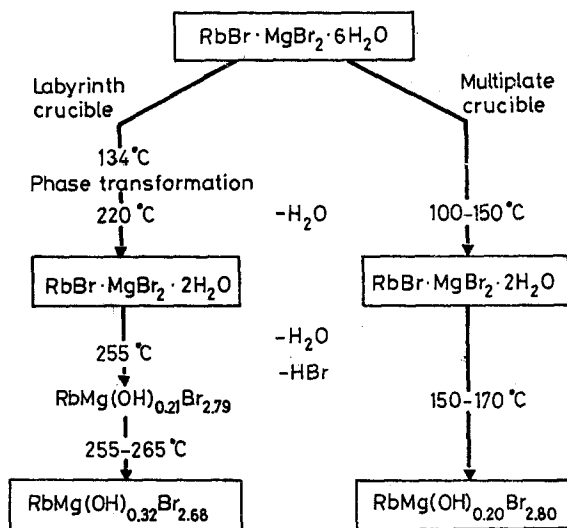
Fig. 8 Decomposition scheme of $RbBr \cdot MgBr_2 \cdot 6H_2O$ under quasi-isothermal and quasi-isothermal and quasi-isobaric conditions

The decomposition of bromide double salts takes place under quasi-equilibrium conditions and a proper vapour pressure of ≈ 0.11 MPa, accompanied by melting in all cases except $RbBr \cdot MgBr_2 \cdot 6H_2O$, which behaves similarly to the chloride double salts [3]. Unlike the decomposition of the chloride double salts the process is realized via the molten salts and not via the dihydrates of the double salts.

Decomposition under a reduced pressure of the decomposition gases takes place always right from the solid phase and is realized via the dihydrate stage for all the investigated double salts. Decomposition takes place at a low temperature. The influence of the monovalent cation on the degree of hydrolysis of the newly formed water-free products under the conditions prevailing in labyrinth crucibles or multiplate crucibles is very interesting (Fig. 12). The degree of hydrolysis α is defined as

$$\alpha = \frac{n_{OH^-,pract}}{n_{OH^-,theor}}$$
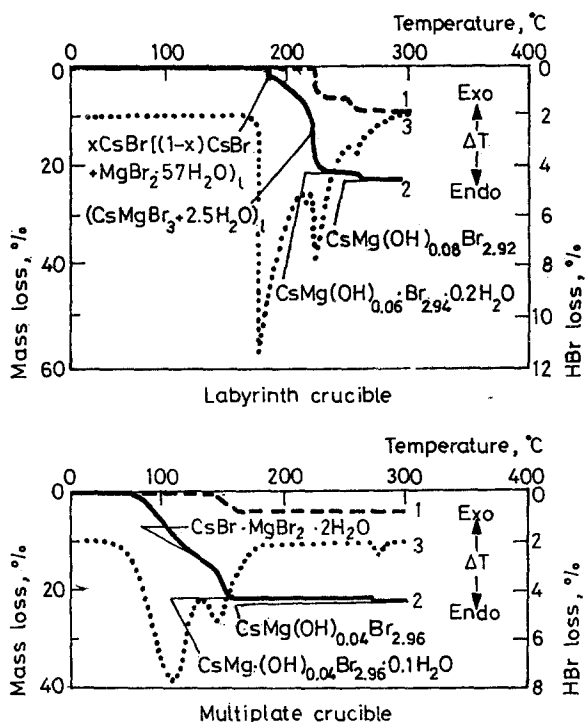
$n_{OH^-,theor} = 3$

Fig. 9 CsBr·MgBr₂·6H₂O decomposition under quasi-isothermal conditions in a labyrinth
crucible and a multiplate crucible
1) gas titration curve, 2) thermogravimetric curve, 3) temperature difference curve (ΔT)

An approximately linear decrease of the degree of thermal hydrolysis is
observed within one series with increasing radius of the monovalent cation.
The anion influence proves to be even greater. The degree of hydrolysis in-
creases considerably from Cl^- to Br^-. Thus, an even higher degree of
hydrolysis is expected for the analogous iodide double salts.

X-ray investigations of powder preparates of double salts [14] have
shown that the structure consists of $(M^+)(X^-)_6$-octahedra combined into
perovskite-type units through their common angles, with the $[Mg(H_2O)_6]^{2+}$-
octahedra arranged in the interstices.

During thermal decomposition Cl^- or Br^- are inserted into the first coor-
dination sphere of Mg^{2+}; this can be formulated as follows:

$$[Mg(H_2O)_6]^{2+} + 4X^- \rightarrow [Mg(H_2O)_2X_4]^{2-} + 4H_2O$$
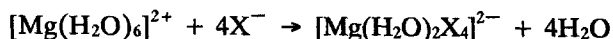
The equation is equivalent to dehydration up to the dihydrate which
takes place without hydrolysis in all cases.

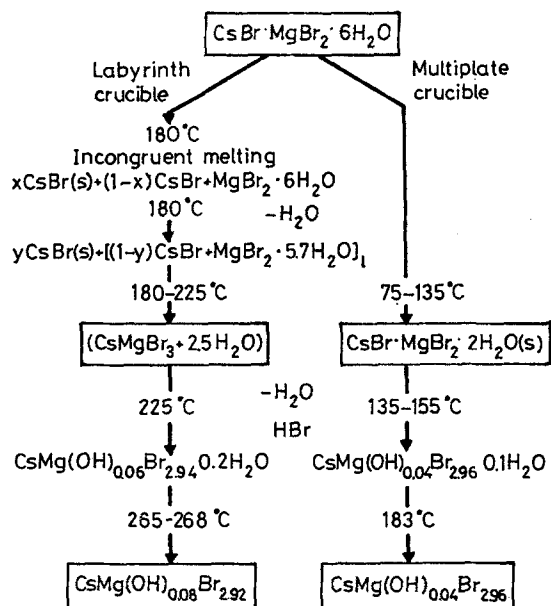**Fig. 10** Decomposition scheme of $CsBr \cdot MgBr_2 \cdot 6H_2O$ under quasi-isothermal and quasi-isothermal and quasi-isobaric conditions

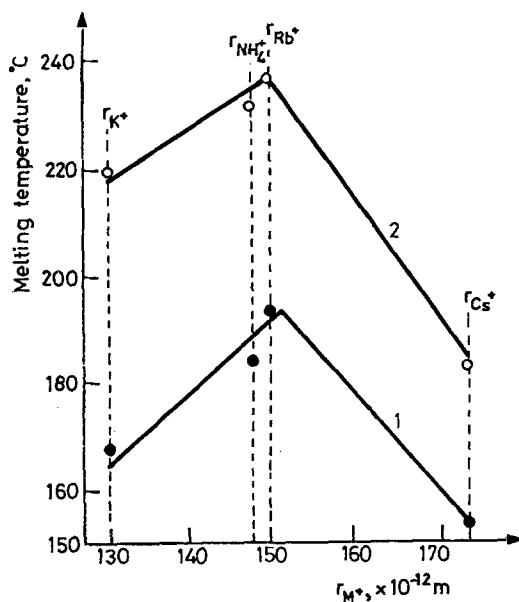**Fig. 11** Melting temperature of double salts depending on the radii of the cations
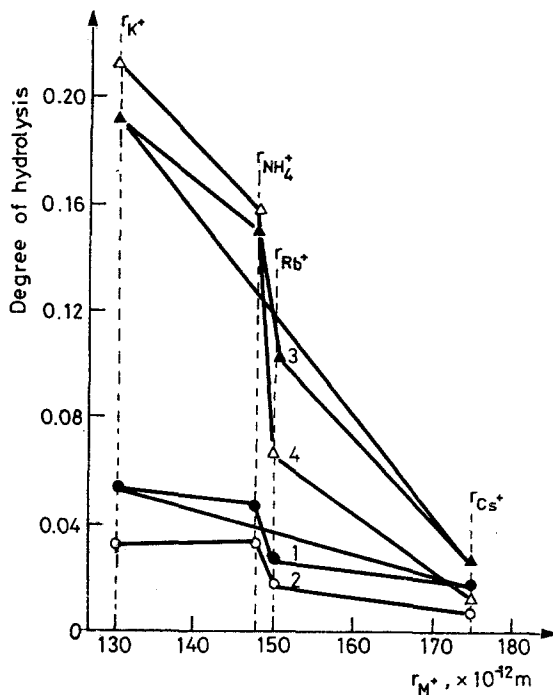1) $X^- = Cl^-$, 2) $X^- = Br^-$

Fig. 12 Degree of hydrolysis depending on the radii of cations; 1) $MCl \cdot MgCl_2 \cdot 6H_2O$; labyrinth crucible, 2) $MCl \cdot MgCl_2 \cdot 6H_2O$; multiplate crucible, 3) $MBr \cdot MgBr_2 \cdot 6H_2O$; labyrinth crucible, 4) $MBr \cdot MgBr_2 \cdot 6H_2O$; multiplate crucible

More accurate measurements of the distances between the water molecules and the magnesium ion by Nakayasu et al. [15] revealed two $Mg-O$-bonds that were shorter by about 5%. Therefore it must be assumed that these bonds are stronger: they are stronger the greater the anion is. This means that the destruction of the $O-H$-bond is more probable in the case of bromide double salts than that of the $Mg-O$-bond. The latter circumstance is equivalent to an increasing degree of hydrolysis of the final products.

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Zusammenfassung — In einem abgeschlossenem System wurde unter dynamischen und quasiisothermen und quasiisobaren Bedingungen im Temperaturbereich zwischen 20°C und 300°C oder 600°C das Schmelz- und Zersetzungsverhalten der Doppel-salze $MBrMgBr_2 \cdot 6H_2O$ (mit M = K, NH_4, Rb, Cs) untersucht. DTA-Heiz- und Kühlzyklen zeigen das Schmelzverhalten der Doppelsalze und geben gleichzeitig Auskunft über den Schmelzpunkt dieser Verbindungen.

Die thermische Zersetzung der Doppelsalze unter quasiisothermen und quasiisobaren Bedingungen erfolgt ausgehend von der Schmelze (mit Ausnahme von $RbBrMgBr_2 \cdot 6H_2O$) und unter vermindertem Druck ausgehend vom Feststoff. Ein Doppelsalz des Typs $MBrMgBr_2 \cdot 2H_2O$ wird als Zwischenprodukt gebildet. Das Endprodukt bei allen Zersetzungstypen sind basische Produkte mit unterschiedlichem Hydroxid- oder Oxidgehalt.