MECHANISM AND KINETICS OF FORMATION AND DECOMPOSITION OF CARNALLITIC DOUBLE SALTS

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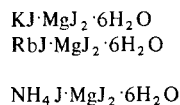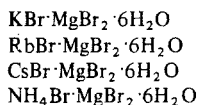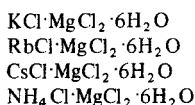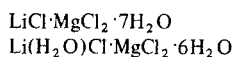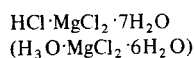
Insufficient thermochemical data are available on the carnallitic double salts $M^I Mg \cdot X_3 \cdot 6H_2O$ ($M = Li (H_2O)$, K, Rb, Cs, NH_4; $X = Cl$, Br, I). In the present work, findings relating to the salt paragenesis are given on the basis of solution-calorimetric measurements. The melting and decomposition behaviour is characterized by means of DTA and thermogravimetric investigations under quasiequilibrium conditons. Except for $Li(H_2O) Cl \cdot MgCl_2 \cdot 6H_2O$, the decomposition of the chloridic carnallitic double salts always proceeds via the intermediate stage of the corresponding dihydrate. For each of the different anions, a linear correlation is found between the degree of hydrolysis of the hydrate water-free final products and the radii of the monovalent cations.

Mineral salts are of considerable importance in inorganic chemistry, and especially in the fertilizer industry. Besides the simple salts, more or less complicated double and triple salts can be found. Among the double salts, those of the carnallitic type are of specific importance to the GDR because more than three-quarters of the explored salt deposits consist, of carnallite rock, the main constituent of which being carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$.

A great variety of compounds of the carnallite type are obtained by isomorphic replacement of individual ions in the salt minerals, such as K^+ by Rb^+, Cs^+, NH_4^+, $Li(H_2O)^+$ or H_3O^+ and Cl^- by Br^- or I^-. A survey is given in Table 1. Special cases are $HCl \cdot MgCl_2 \cdot 7H_2O$ and $LiCl \cdot MgCl_2 \cdot 7H_2O$. In these compounds a water molecule is bonded to the monovalent cation and occupies the cation site together with it [1].

In spite of the great practical importance of these double salts, detailed investigations have been reported on only a few compounds. Frequently, contradictory statements are to be found in the literature. So far, a comprehensive characterization of the double salts of the carnallite type, together with a uniform description of the effects of the monovalent cation and anion on their behaviour, has not been given. In the following, some selected results of thermoanalytical and calorimetric investigations into the formation and decomposition of the carnallitic double salts are given. The crystallization kinetics of carnallite and the mechanism of dissolution determined by tracer measurements have been published elsewhere [2, 3].

Table 1 Carnallite-type double salts

$HCl \cdot MgCl_2 \cdot 7H_2O$
$(H_3O \cdot MgCl_2 \cdot 6H_2O)$

$LiCl \cdot MgCl_2 \cdot 7H_2O$
$Li(H_2O)Cl \cdot MgCl_2 \cdot 6H_2O$

$KCl \cdot MgCl_2 \cdot 6H_2O$	$KBr \cdot MgBr_2 \cdot 6H_2O$	$KJ \cdot MgJ_2 \cdot 6H_2O$
$RbCl \cdot MgCl_2 \cdot 6H_2O$	$RbBr \cdot MgBr_2 \cdot 6H_2O$	$RbJ \cdot MgJ_2 \cdot 6H_2O$
$CsCl \cdot MgCl_2 \cdot 6H_2O$	$CsBr \cdot MgBr_2 \cdot 6H_2O$	
$NH_4Cl \cdot MgCl_2 \cdot 6H_2O$	$NH_4Br \cdot MgBr_2 \cdot 6H_2O$	$NH_4J \cdot MgJ_2 \cdot 6H_2O$

Methods

The double salts were prepared by crystallization from ternary equilibrium solutions at 25° and 50°. The compounds had a purity of at least 99%, except for $KBr \cdot MgBr_2 \cdot 6H_2O$, which was contaminated by starting materials to an extent of about 4%. The solution-calorimetric measurements were performed in an improved LKB calorimeter (type 8700) at 298.15 K. Experimental details and evaluation methods for determination of the crystallization enthalpy have been described in [4, 5].

DTA investigations were carried out by means of the low-temperature equipment (−150 up to +500°) manufactured by Setaram (France), in lockable Ti-Pd crucibles or closed glass ampoules.

Thermal decomposition was performed under near-equilibrium conditions by means of the Q-derivatograph. The simultaneous acquisition of the EGA signal of released hydrogen halide was carried out by means of a gas-titration apparatus. A pressure of the decomposition gases 0.12 ± 0.01 MPa was achieved in the applied labyrinth crucible [6].

Results and discussion

Solution-calorimetric investigations into the determination of the crystallization enthalpy and the calculated partial molar enthalpy of a component allow important findings relating to salt paragenesis. This fact is illustrated by the system $KCl - MgCl_2 - H_2O$.

Figure 1 shows the course of the partial molar enthalpy of KCl, H_{KCl}, vs. the KCl content in the solution. In the absence of $MgCl_2$ (curve I), H_{KCl}
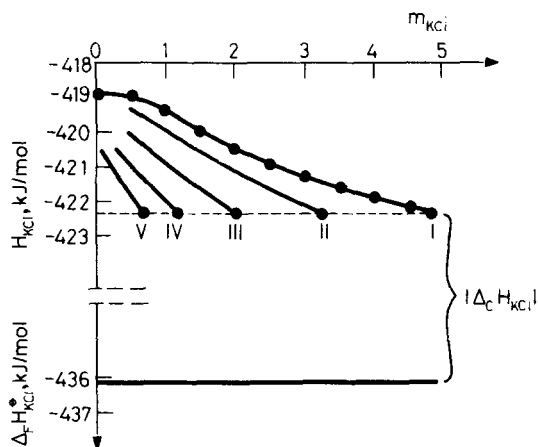

Fig. 1 = Dependence of the partial molar enthalpy of KCl, H_{KCl} (in kJ mol^{-1}), on its concentration m_{KCl} (in mol KCl kg^{-1}H$_2$O) at different contents of MgCl$_2$ in the solution curves II–V (schematic); content of MgCl$_2$ (in mol MgCl$_2$/kg H$_2$O): I = 0; II = 1; III = 2; IV = 3; V = 4

H_{KCl} = partial molar enthalpy of KCl

$\Delta_F H^{\ominus}_{KCl}$ = molar enthalpy of formation of KCl

$\Delta_C H_{KCl}$ = molar enthalpy of crystallization of KCl

falls with increasing KCl concentration, until at saturation concentration a characteristic value is reached where crystallization begins. The enthalpy difference relating to the standard enthalpy of formation, $\Delta_F H^\ominus_{KCl}$, is the enthalpy of crystallization.

In the presence of $MgCl_2$ in the solution (curves II–V), the characteristic value of the partial molar enthalpy of KCl is reached at the saturation concentration with lower KCl concentrations. Decrease of the solubility of KCl with rising $MgCl_2$ content in the solution is in agreement with the course of the saturation isotherm of the $MgCl_2 - KCl - H_2O$ system [7].

By analogy with the precipitation of KCl, correlations with the crystallization of double salts can be derived from the course of the partial molar enthalpy of $MgCl_2$ in the ternary systems. Figure 2 shows the linear rise of the partial molar enthalpy of $[Mg(H_2O)_6]Cl_2$ with increasing $MgCl_2$ content in the solution. This course is not influenced by the KCl content of the solution. The saturation concentration of $MgCl_2$ is reached at the end-point at 5.8 mol $MgCl_2$/kg H_2O [7]. The difference relative to the standard enthalpy of formation of $MgCl_2 \cdot 6H_2O$, $\Delta_F H^\ominus_{MgCl_2 \cdot 6H_2O}$, in curve II is the enthalpy of crystallization of $MgCl_2 \cdot 6H_2O$, with a value of about -12 kJ/mol.
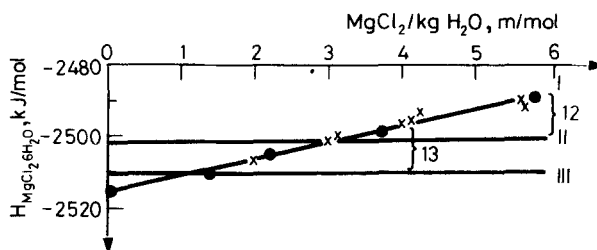

Fig. 2 = Dependence of the partial molar enthalpy of magnesium chloride on the concentration
     ● – $MgCl_2$ solution, pure
     X – in the presence of KCl, saturated
     I – partial molar enthalpy, $H_{[Mg(H_2O)_6]Cl_2}$, solution
     II – molar standard enthalpy of formation, $\Delta_F H^\ominus_{MgCl_2 \cdot 6H_2O}$
     III– partial molar enthalpy, $H_{MgCl_2 \cdot 6H_2O}$, double salt

The double salt point $KCl \cdot MgCl_2 \cdot 6H_2O(s) - KCl(s)$ is at a concentration of about 4 mol $MgCl_2$/kg H_2O [7]. The results in Fig. 2 show that crystallization of $MgCl_2 \cdot 6H_2O$ (bischofite) cannot take place at this concentration. The enthalpy difference between curves II and I, with a value of -4.5 kJ/mol, is far below the crystallization enthalpy of bischofite. On the other

hand, the difference relative to the partial molar enthalpy of $MgCl_2$ $6H_2O$ in the double salt $KCl \cdot MgCl_2 \cdot 6H_2O$ (curves III—I), with a value of -13 kJ/mol, approximately corresponds to its crystallization enthalpy of -12 kJ/mol. Accordingly, precipitation of the double salt $KCl \cdot MgCl_2 \cdot 6H_2O$ in addition to KCl, and not of $MgCl_2 \cdot 6H_2O$, takes place at the double salt point.

Recently, we determined the standard enthalpies of formation of a great number of single and double salts via solution-calorimetric measurements. Consequently, extended studies of the salt paragenesis are possible. The results will be published in the near future [8]. The thermal stabilities of the double salts were studied in the closed system, maintaining the constant gross composition of the system. Furthermore, the mechanism of the thermal decomposition was investigated in the open system.
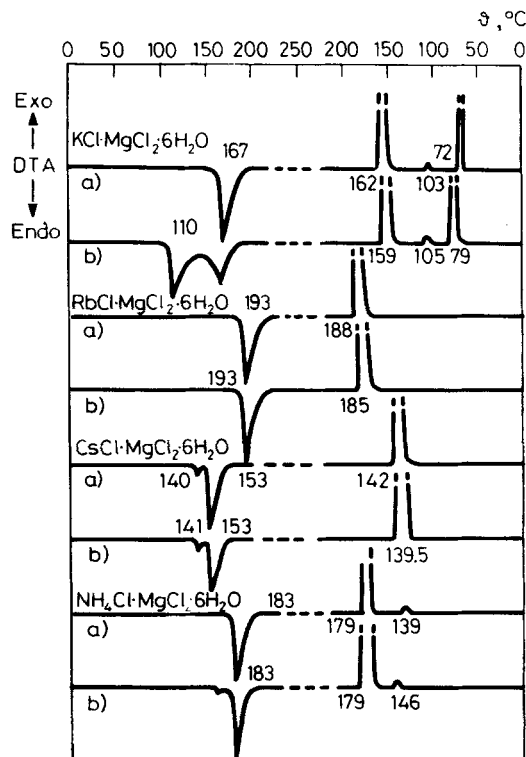

Fig. 3 = DTA curves of chloridic double salts ($q = \pm 2$ deg/min, $m = 10$–50 mg. DTA $= \pm 100$ μV)
a) first heating and cooling,
b) reheating and cooling

A survey of the DTA diagrams of the chloridic double salts obtained in the closed system is given in Fig. 3. The melting points of these compounds are in the range from 153°

$$(CsCl \cdot MgCl_2 \cdot 6H_2O) \text{ to } 193° (RbCl \cdot MgCl_2 \cdot 6H_2O).$$

Incongruent melting of $KCl \cdot MgCl_2 \cdot 6H_2O$ and congruent melting of $RbCl \cdot MgCl_2 \cdot 6H_2O$ are revealed by phase analysis. In the case of carnallite, KCl is formed as a solid phase during melting [9]. Therefore, upon cooling carnallite is only partially re-formed at 162°. During further cooling, $MgCl_2 \cdot 6H_2O$ crystallizes out of the residual melt rich in $MgCl_2$, which melts on reheating (curve b) at an onset temperature of 110°. The formed melt dissolves the crystallized carnallite with rising temperature. Consequently, the melting peak of carnallite at 167° appears to be reduced.

At present, investigations into the solid phases in solid-liquid equilibria are being performed for the phase-analytical characterization of the melting and solidification peaks of

$$CsCl \cdot MgCl_2 \cdot 6H_2O \text{ and } NH_4Cl \cdot MgCl_2 \cdot 6H_2O.$$

The results of the thermal decomposition of the chloridic carnallitic double salts under near-equilibrium quasi-isothermal and quasi-isobaric conditions at a self-generated pressure· of the released gases of the order of 0.12±0.01 MPa are summarized in Table 2. The decomposition reactions begin after melting of the double salts, except for $RbCl \cdot MgCl_2 \cdot 6H_2O$, which is decomposed in the solid state due to its high vapour pressure. Approximately isothermal decomposition stages exist under the chosen experimental conditions. In each case, the dihydrate of the applied compound, $MCl \cdot MgCl_2 \cdot 2H_2O$ ($M = K, Rb, Cs, NH_4$), is the stable intermediate. Under the hydrothermal conditions, the dihydrates are decomposed into basic compounds, the phase compositions of which are not yet known.

The structural characteristics of $LiCl \cdot MgCl_2 \cdot 7H_2O$ (see above) also become apparent through its thermal decomposition behaviour. In contrast to the other chloridic double salts, no dihydrate is formed. After release of water at 310°, a product with the composition $LiMg(OH)_{0.55}Cl_{2.45}$ is obtained.

The degree of hydrolysis of the hydrate water-free final products gives some indications of the influence of the monovalent cation on the thermal decomposition of the double salts. The degree of hydrolysis is defined by the number of OH ions divided by the theoretically possible number of OH ions (=3) according to the gross composition. Figure 4 shows the depen-

Table 2 Decomposition schemes of the chloridic double salts under quasi-isothermal, quasi-isobaric conditions in the labyrinth crucible
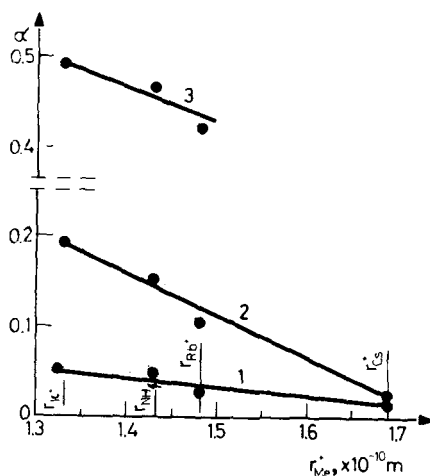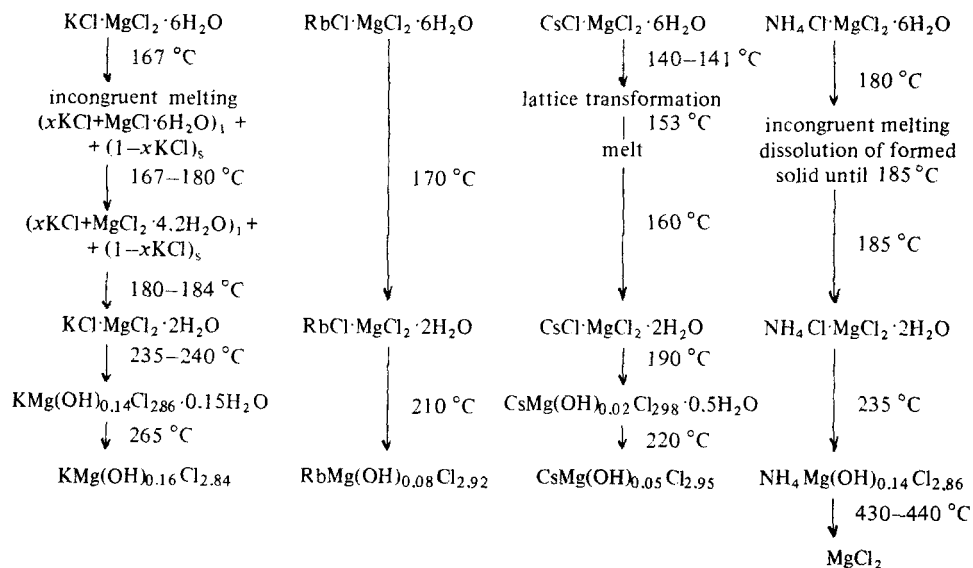(TG = 100 mg, Q–TG = 0.6 mg/min, EGA of HCl with 0.1 N NaOH, pH = 9)

$KCl \cdot MgCl_2 \cdot 6H_2O$ $RbCl \cdot MgCl_2 \cdot 6H_2O$ $CsCl \cdot MgCl_2 \cdot 6H_2O$ $NH_4 Cl \cdot MgCl_2 \cdot 6H_2O$

↓ 167 °C

incongruent melting
$(xKCl + MgCl \cdot 6H_2O)_1 +$
$+ (1-xKCl)_s$

↓ 167–180 °C

$(xKCl + MgCl_2 \cdot 4.2H_2O)_1 +$
$+ (1-xKCl)_s$

↓ 180–184 °C

140–141 °C

lattice transformation
↓ 153 °C
melt

180 °C

incongruent melting
dissolution of formed
solid until 185 °C

170 °C

160 °C

185 °C

$KCl \cdot MgCl_2 \cdot 2H_2O$ $RbCl \cdot MgCl_2 \cdot 2H_2O$ $CsCl \cdot MgCl_2 \cdot 2H_2O$ $NH_4 Cl \cdot MgCl_2 \cdot 2H_2O$

↓ 235–240 °C

190 °C

210 °C

235 °C

$KMg(OH)_{0.14}Cl_{286} \cdot 0.15H_2O$ $CsMg(OH)_{0.02}Cl_{298} \cdot 0.5H_2O$

↓ 265 °C

220 °C

$KMg(OH)_{0.16}Cl_{2.84}$ $RbMg(OH)_{0.08}Cl_{2.92}$ $CsMg(OH)_{0.05}Cl_{2.95}$ $NH_4 Mg(OH)_{0.14}Cl_{2.86}$

↓ 430–440 °C

$MgCl_2$

Fig. 4 = Degree of hydrolysis α of the final products of thermal decomposition of the double salts $MX \cdot MgX_2 \cdot 6H_2O$ until the complete release of hydrate water, as a function of the radius of the monovalent cations M.
1. $X^- = Cl^-$; 2. $X^- = Br^-$; 3. $X^- = I^-$

dence of the degree of hydrolysis of the final products on the (Pauling) radius of the monovalent cations. It becomes evident that under quasi-equilibrium conditions the degree of hydrolysis is lowered with increasing cation radius. This rule is valid for each of the anions (curves 1–3). On the other hand the degree of hydrolysis increases inversely with growing anion radius. It can be seen that the exchange of the anions in the double salt has a greater influence on the degree of hydrolysis than that of the cations. The structure of the carnallitic double salts consists of a network of halide anions, the closest packing being achieved with the $Mg(H_2O)_6^{2+}$ octahedra [10], and contains three times more anions than univalent cations in the unit cell. The exchange of the anions has a greater influence on the lattice, and thus on the properties, than the insertion of another cation into the octahedron vacancies.

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Zusammenfassung — Die Kenntnis thermodynamischer Daten carnallitischer Doppelsalze $M^1MgX_3 \cdot 6H_2O$ (M = $Li(H_2O)$. K, Rb, Cs, NH_4; X = Cl, Br, I) ist bisher nur ungenügend. Die vorliegende Arbeit enthält Angaben zur Salzparagenese auf der Grundlage lösungskalorimetrischer Messungen. Das Schmelz- und Zersetzungsverhalten wird mittels DTA und TG-Untersuchungen unter Quasi-Gleichgewichtsbedingungen verfolgt. Mit Ausnahme von $Li(H_2O)MgCl_3 \cdot 6H_2O$ verläuft die Zersetzung der chloridischen Carnallit-Doppelsalze stets über ein intermediäres Dihydrat. Eine lineare Beziehung wird zwischen dem Hydrolysegrad des Hydratwasser-freien Endprodukts der Zersetzung und den Radien der einwertigen Kationen für jedes der drei möglichen 3 Anionen Cl^-, Br^- und I^- gefunden.

РЕЗЮМЕ — Все еще недостаточним является знание термохимического поведения двойных карналлитных солей. В настоящей работе на основе калориметрических измерений растворов таких солей сделаны заключения относительно их парагенезиса. Плавление в разложение солей охарактеризовано с помощью ДТА и термогравиметрических измерений в квази-равновесных условиях. За исключением соли $Li/H_2O/Cl \cdot MgCl_2 \cdot 6H_2O$, разложение хлоридных карналитных двойных солей всегда протекает через промежуточную стадию образования соответствующего дигидрата. Найдена линейная зависимость между степенью гидролиза конечных продуктов, свободных от гидратированной воды, и радиусом одновалентных катионов для солей с различными анионами.