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# THERMOANALYTICAL INVESTIGATIONS ON THE DECOMPOSITION OF DOUBLE SALTS

## I. The decomposition of carnallite

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The melting and decomposition behaviour of carnallite was investigated in the closed system under dynamic heating conditions and in the open system under dynamic and quasi-isothermal and quasi-isobaric conditions in the temperature range between 20 and 300°. DTA heating and cooling cycles in the closed system illustrate the incongruent melting of carnallite and the occurrence of different magnesium chloride hydrate phases. The thermal decomposition under quasi-isothermal and quasi-isobaric conditions begins at a pressure of at least 100 kPa from the melt and under reduced pressure from the solid. In any case $KCl \cdot MgCl_2 \cdot 2\,H_2O$ is formed which is decomposed to a basic product $KMgCl_{2.84-2.90}(OH)_{0.10-0.16}$.

The thermal decomposition of carnallite ($KCl \cdot MgCl_2 \cdot 6\,H_2O$) has often been the subject of thermoanalytical investigations. However, due to highly different methods the known results do not allow any uniform statements concerning the dehydration mechanism of this double salt. Some authors [1–5] give a two-stage decomposition scheme

$$KCl \cdot MgCl_2 \cdot 6\,H_2O \rightarrow KCl \cdot MgCl_2 \cdot 2\,H_2O + 4\,H_2O \qquad (1)$$

$$KCl \cdot MgCl_2 \cdot 2\,H_2O \rightarrow KCl \cdot MgCl_2 + 2\,H_2O \qquad (2)$$

where the elimination of water from the solid occurs without formation of a melt. According to Van't Hoff and Meyerhofer [6] carnallite melts incongruently at 167,5°.

The position of the decomposition steps is especially influenced by the conditions of investigation. In this way, Grube and Bräuning [7] observe the reaction according to Eq. 1 as early as at 80° with a pressure of 0.9 kPa. For the end of the dehydration (Eq. 2) Laskievich [8] gives a temperature of 330° at $q = 10$ K/min and of 270° at $q = 2.5$ K/min. In some cases a partial elimination of HCl with formation of basic products is also described in the course of the second step [2–5].

The dehydration of carnallite with elimination of 4 Mol $H_2O$ according to Eq. 1 is also observed as a two-stage process [9–12]. In this case first of all a partial dehydration of the $KCl \cdot MgCl_2 \cdot 6\,H_2O$ occurs with simultaneous formation of a melt at 167.5°.

Within the scope of our complex investigations on chloridic double salts the aim of the present paper was to characterize the melting and decomposition behaviour of the carnallite taking into account the gas atmosphere during the decomposition. For this purpose the methods of dynamic and quasi-isothermal thermogravimetry, DTA and thermooptical analysis were applied.

## Experimental

### *Sample material*

For the investigations natural carnallite from the deposit in the Werra region (GDR) was used, because artificial material prepared in the laboratory always continued to contain approximately 2% $MgCl_2 \cdot 6\,H_2O$ the presence of which was identified by the occurrence of a melting peak at 116° during DTA investigations.

The chemical characterization of the natural carnallite showed the following components (the theoretical values are given in brackets):

$H_2O$ = 38.92% (38.90%); $K^+$ = 13.20% (14.07%);

$Mg^{2+}$ = 8.82% (8.75%); $Cl^-$ = 38.60% (38.27%).

The contamination of the material with NaCl amounts to maximally 1%. Free KCl and $MgCl_2 \cdot 6\,H_2O$ could not be detected. The carnallite was crushed in agate mortar and classified to a size range between 0 and 100 $\mu$m.

### *DTA investigations*

To characterize the melting behaviour with constant gross composition of the carnallite, DTA measurements were carried out in a closed system using gas-tight crucibles (material EMO Ti–Pd 0.2). The investigations were performed on the Setaram equipment (France) in a cryostat using crucible holder suspensions with platinel thermocouples.

### *Thermogravimetry*

The thermogravimetric investigations were performed under dynamic and quasi-isothermal conditions.

The dynamic measurements were carried out by means of a derivatograph (MOM, Budapest) of the type 1500 °C using the standard crucible set and different heating rates at $q = 2; 5; 10$ deg/min.

The quasi-isothermal measurements were carried out by means of the derivatograph (Q-type) with coupled gas titration device (MOM, Budapest) [13]. A continuous determination of the hydrogen chloride eliminated from the carnallite could be carried out by means of a gas titration device. The automatic potentiometric titration was carried out at pH = 6 by addition of 0.1 *N* NaOH.

In the case of the quasi-isothermal principle of measurement a coupling exists between DTG signal and temperature controller so as to limit the rate of mass decomposition. A maximum velocity of weight loss of 0.6 mg/min as compared with the weighing range of 100 mg was chosen for the present investigations. In the periods of constant weight the heating rate was $q = 2.5$ K/min. The difference between the weight loss of the investigated sample (Q-TG curve) and the amount of HCl (EGA curve) simultaneously determined by titration results in the formation of $H_2O$ which was eliminated from the carnallite. Additionally the difference temperature signal $\Delta T$ of the sample was recorded compared to the $\alpha$-$Al_2O_3$ used as an inert substance during investigations in the labyrinth crucible.

In all thermogravimetric investigations the mass of the sample amounted to approximately 250 mg.

### *Optical investigations*

For the purpose of studying the phase changes during melting and dehydration of the carnallite optical investigations were performed in the temperature range of 20 to 300° ($q = 2-3$ K/min) in polarized or unpolarized transmitted light by means of the microscope heating stage "Boetius" with viewing system PHMV 05, VEB Analytik Dresden, combined with the camera Pentacon super, VEB Pentacon Dresden. The investigations were carried out in fused glass cells or using slides with cover glass.

## Results and discussion

Figure 1 shows the DTA curves of three heating and cooling cycles of the carnallite in the closed system. In agreement with results given in the literature [6] the melt is formed at 167° during the first heating. In the course of this incongruent melting process the double salt is decomposed to a $MgCl_2 \cdot 6\,H_2O$ melt saturated with KCl and to the solid phase KCl. This statement is supported by results of the thermooptical investigations. The characteristic polarization colours of the carnallite disappear at the melting point. At 168° the material is completely molten. The octahedra of the solid phase KCl are clearly visible in the melt (Fig. 2). On cooling the system the crystallization of carnallite takes place with a slight overcooling, beginning at 152° up to 162° (curves 1 to 3 in Fig. 1). The following exothermic effects at 103° and 76° can be explained by the crystallization of $MgCl_2$ hydrate phases which on reheating the substance result in the formation of $MgCl_2 \cdot 6\,H_2O$. This process is shown by the melting peak at 116° ($T_{ON} = 110°$). The occurrence of $MgCl_2 \cdot 6\,H_2O$ which is not bonded in the double salt, shows that during crystallization the carnallite is only partly reformed according to the amount of KCl dissolved in the melt.

The $MgCl_2 \cdot 6\,H_2O$ melt which was formed at 116° contains KCl and carnallite as solid phase. During further heating up the two substances are dissolved in the $MgCl_2 \cdot 6\,H_2O$ melt, the value of fusion enthalpy of the carnallite is being consumed for the endothermic process in the temperature range between the $MgCl_2 \cdot 6\,H_2O$

peak at 116° and the melting of the carnallite residue at $T_{ON}$ = 169°, 168° (curves 2 and 3). The gross composition of $KCl \cdot MgCl_2 \cdot 6\,H_2O$ remains always constant during the investigations in the closed system.

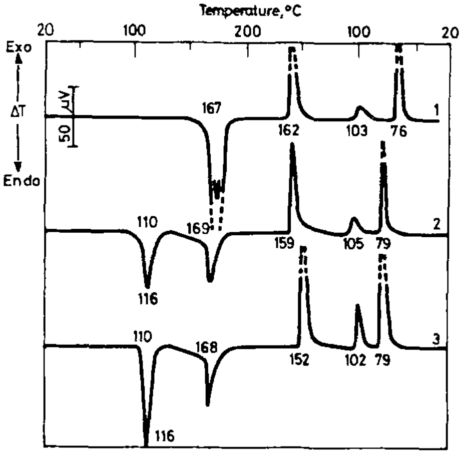

**Fig. 1** DTA curves of the melting and solidification behaviour of carnallite in the closed crucible; 1; 2; 3 number of cycle; $m$ = 42.36 mg; $q$ = ± 1 deg/min

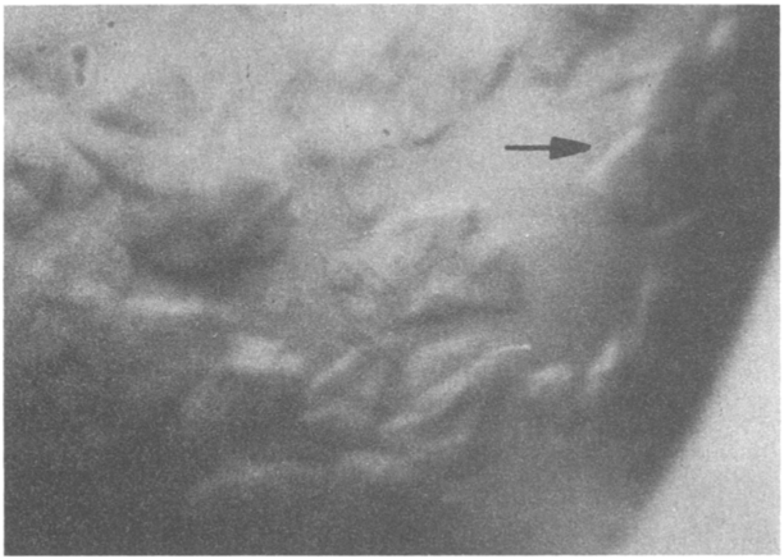

**Fig. 2** Melt of carnallite at 170°

As opposed to this the measurements in the open system give information on the occurring stable phases and mixed phases with a lower water content as compared with the carnallite. Within the scope of these investigations we paid special attention to the variation of the partial pressure of the gases $H_2O$ and HCl which occur during the decomposition of carnallite. In this connection it is known that the partial pressure of the gaseous components above the samples can be changed by variation of the crucible form. The partial pressure rises in the sequence disk crucible (1 kPa), standard crucible – open (5 kPa), standard crucible – with cover (20 kPa) and labyrinth crucible (100 kPa) [13].

Figure 3 shows the TG curves which are obtained in the mentioned crucibles with constant heating rate. From the results it can be seen that with rising partial pressure of the gaseous components the decomposition of $KCl \cdot MgCl_2 \cdot 6\,H_2O$ is shifted to higher temperatures. Irrespective of the crucible form all curves show an inflection point at a value of approximately 26% loss of weight corresponding to 4 Mol $H_2O$/Mol $KCl \cdot MgCl_2 \cdot 6\,H_2O$. From the observed total loss of weight of more than 39% follows that already up to temperatures of 300° HCl is eliminated from the carnallite. An increase of the heating rate results in the decomposition of the carnallite at higher temperatures (Fig. 4). However, under these conditions the decomposition steps are less clearly marked.

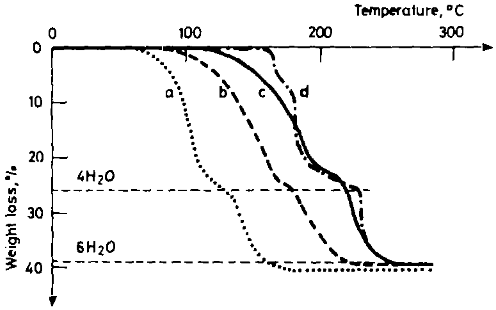

**Fig. 3** Thermogravimetric curves of the carnallite decomposition with variation of the crucibles (a = disk crucible, b = standard crucible – open, c = standard crucible with cover, d = labyrinth crucible). Heating rate 2 deg/min

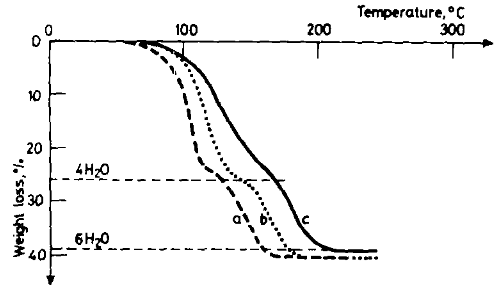

**Fig. 4** Thermogravimetric curves of the carnallite decomposition at different heating rates (a – 2 deg/min, b – 5 deg/min, c – 10 deg/min) – disk crucible

The results shown in Figs 3 and 4 verify the known intermediate stage of the carnallite decomposition, composed of $KCl \cdot MgCl_2 \cdot 2\,H_2O$. The shown experimental effects of the partial pressure of the gaseous components and of the heating rate illustrate the variety of the possible investigation results. Meaningful and reproducible results could be obtained under quasi-isothermal and quasi-isobaric conditions.

Figure 5 shows the decomposition curve of carnallite with a low partial pressure of the gaseous components (approximately 1 kPa) which occur during the decomposition. Under these conditions the decomposition takes place from the solid without formation of a melt. In the first step at 90–105° an elimination of 4 Mol $H_2O$/Mol $KCl \cdot MgCl_2 \cdot 6\,H_2O$ can be stated, in the second step between 130 and 145° 2 Mol $H_2O$/Mol $KCl \cdot MgCl_2 \cdot 6\,H_2O$ are eliminated. The decomposition of the dihydrate which is formed in the first step is accompanied by a slight elimination of HCl resulting in a weakly basic product composed of $KMgCl_{2.90}(OH)_{0.10}$.

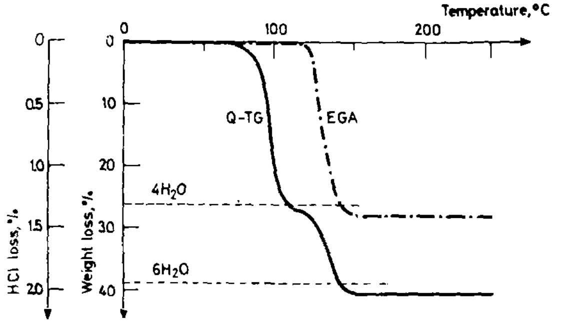

**Fig. 5** Thermogravimetric (Q-TG) and gas titration curve (EGA) of carnallite in the disk crucible under quasi-isothermal and quasi-isobaric conditions ($p \cong 1$ kPa)

The decomposition of carnallite is verified by results of the optical investigations. The polarization colours of carnallite fully disappear at 106°.

Figure 6 shows the dehydration behaviour of carnallite in the equilibrium atmosphere of formed $H_2O$ and HCl at a pressure of $p \cong 100$ kPa. The temperature difference curve shows a five-stage decomposition of carnallite. In the first step the carnallite melts at 167.5° with a beginning dehydration. This behaviour is understandable as the vapour pressure of the solid carnallite in the range of the melting temperature reaches a value of nearly 100 kPa. The extrapolation of the known vapour pressure values in the temperature range between 146° and 160° [7] resulted in a value of 115 kPa for the melting temperature of 167.5°. The thermogravimetric results of the first step show that an isothermal partial step is followed by the anisothermal dehydration. According to the phase rule during the process of the incongruent melting there is an invariant system with the phases melt ($MgCl_2 \cdot 6\,H_2O$, saturated with KCl). KCl (s), $KCl \cdot MgCl_2 \cdot 6\,H_2O$ (s) and $H_2O$ (g) of the three-component system $MgCl_2$–KCl–$H_2O$. $KCl \cdot MgCl_2 \cdot 6\,H_2O$ being completely molten, the system becomes divariant and water evaporates from the melt and the boiling temperature rises with increasing concentration of $MgCl_2$ and KCl in the melt. The solubility of KCl in the melt increases in this concentration range [14].

During the process of thermal decomposition 1.8 Mol $H_2O$/Mol KCl • $MgCl_2$ • • 6 $H_2O$ are evaporated from the melt up to a temperature of 180°. At this temperature further decomposition begins in two steps with the formation of dihydrate KCl • $MgCl_2$ • 2 $H_2O$. Exact statements concerning the transition to the dihydrate cannot be deduced from the present thermoanalytical results, but the known solubility curve according to D'Ans [14] allows the following discussion.

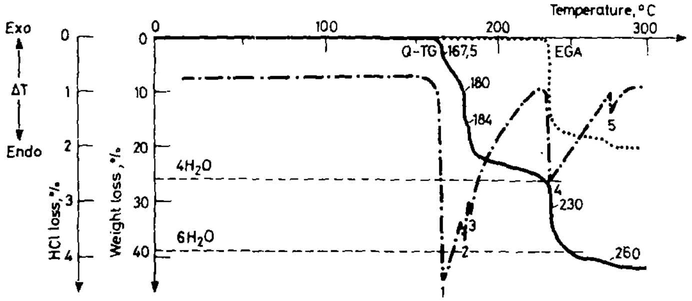

**Fig. 6** Results of the carnallite decomposition under quasi-isothermal and quasi-isobaric conditions ($p \cong 100$ kPa) in the labyrinth crucible. Q-TG = thermogravimetric curve, EGA = gas titration curve, $\Delta T$ = temperature difference curve

At 180° a concentration of 238 Mol $MgCl_2$/1000 Mol $H_2O$ can be calculated from the water quantity which was eliminated during the first step. With this concentration the double salt lines with the solid phases $MgCl_2$ • 2 $H_2O$ (s) and KCl (s) lie in the vicinity of the 180° isotherm so that it is possible to reach a double salt point at the beginning of the second step at 180° taking into account the error of the thermoanalytical methodics. With the formation of a second solid phase $MgCl_2$ • 2 $H_2O$ (s) in addition to the already existing KCl (s) there is again an invariant system. In this way the isothermal course of the second step in Fig. 6 is explained. The transition to $MgCl_2$ • 2 $H_2O$ (s) does not proceed in a complete way. After the elimination of approximately 2.5 Mol $H_2O$/Mol KCl • $MgCl_2$ • 2 $H_2O$ the anisothermal formation of the dihydrate KCl • $MgCl_2$ • 2 $H_2O$ (3. step) is beginning at 184°.

At the end of the third step there are no appreciable components of free $MgCl_2$ • • 2 $H_2O$ (s) and KCl (s). This statement follows from quasi-isothermal investigations on equimolar mixtures of $MgCl_2$ • 2 $H_2O$ and KCl, as a result of which the decomposition steps of the pure $MgCl_2$ • 2 $H_2O$ [15] were obtained at 230 and 290°. By way of contrast, at 235° the dihydrate KCl • $MgCl_2$ • 2 $H_2O$ is almost completely decomposed to a weakly basic product of the gross composition $KMgCl_{2.86}(OH)_{0.14}$ • • 0.15 $H_2O$ (4. step). The residual elimination of small amounts of $H_2O$ and HCl occurs at 260° (5. step). The gross composition $KMgCl_{2.84}(OH)_{0.16}$ obtained from the thermoanalytical results could also be confirmed by chemical analysis.

The results of the decomposition of carnallite under quasi-isothermal conditions at $p \cong 100$ kPa and $p \cong 1$ kPa allow a specification of the decomposition scheme according to Eqs 1 and 2. Figure 7 shows the decomposition scheme. It can be seen that the decomposition of carnallite from the melt takes place at a partial pressure of the decomposition gases of at least 100 kPa. The step of the dihydrate $KCl \cdot MgCl_2 \cdot 2\,H_2O$ is passed in any case. The final product of the thermal decomposition is no pure $KCl \cdot MgCl_2$, but a basic product of the gross composition $KMgCl_x(OH)_y$ ($x = 2.84$–$2.90$, $y = 0.10$–$0.16$). The position of the decomposition temperatures is determined by the partial pressures of $H_2O$ and HCl. With increasing partial pressure the decomposition is shifted to higher temperatures.

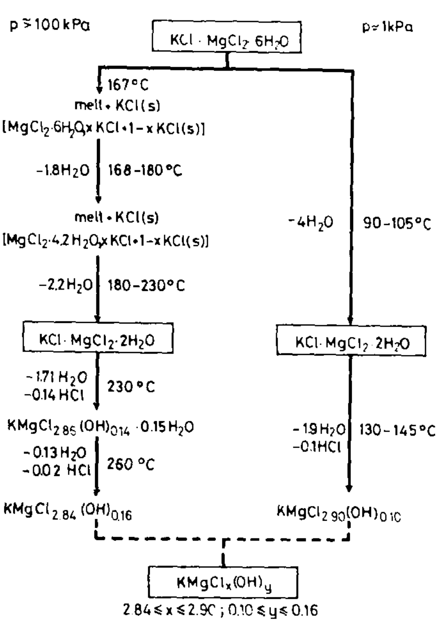

**Fig. 7** Decomposition scheme of carnallite under quasi-isothermal and quasi-isobaric conditions

In the literature [16] the complete dehydration of $KCl \cdot MgCl_2 \cdot 2\,H_2O$ as compared with the dehydration of $MgCl_2 \cdot 2\,H_2O$ at lower temperatures was explained by the fact that due to the metastable character of $KCl \cdot MgCl_2 \cdot 2\,H_2O$ this substance must have a higher vapour pressure. However, the present investigations show that the decomposition of the two compounds begins at approximately 230° in the labyrinth crucible. Under these conditions the beginning of the decomposition is in accordance with the increase in vapour pressure of the investigated compounds to $p \cong 100$ kPa. However, in the case of the decomposition of $MgCl_2 \cdot 2\,H_2O$ the complicated formation of waterfree final products results from the occurrence of a stable weakly basic monohydrate in the temperature range between 235 and 290° [15].

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**Zusammenfassung** — Die Schmelz- und Zersetzungseigenschaften des Carnallits wurden im geschlossenen System unter dynamischen Heizbedingungen und im offenen System under dynamischen und quasi-isothermen und quasi-isobaren Bedingungen im Temperaturbereich von 20 bis 300°C untersucht. DTA Heiz- und Kühlzyklen im geschlossenen System verdeutlichen das inkongruente Schmelzen des Carnallits und das Auftreten verschiedener Magnesiumchlorid-Hydratphasen. Die thermische Zersetzung beginnt unter quasi-isothermen und quasi-isobaren Bedingungen bei einem Druck von mindestens 100 kPa aus der Schmelze und unter verminderten Druck aus der festen Phase. Die Zersetung verläuft stets über $KCl \cdot MgCl_2 \cdot 2\,H_2O$ zu einem basischen Produkt $KMgCl_{2.84-2.90}(OH)_{0.10-0.16}$.

**Резюме** — Плавление и разложение карналлита исследовано в закрытой системе в режиме динамического нагрева и в открытой системе - в динамических и квази-изотермических, квази-изобарных условиях в области температур 20–300°. ДТА измерения циклов нагрева и охлаждения в закрытой системе показали инконгруэнтное плавление и случаи образования различных гидратов хлорида магния. В квази-изотермическом и квази-изобарном режимах термическое разложение начинается при давлении около 100 кПа из расплава, а при пониженном давлении — из твердого состояния. В любом случае образуется соединение $KCl \cdot MgCl_2 \cdot 2\,H_2O$, которое разлагается с образованием основной соли $KMgCl_{2.84-2.90}(OH)_{0.10-0.16}$.