

THERMAL DECOMPOSITION OF CARNALLITE (KCl·MgCl₂·6H₂O)-COMPARISON OF EXPERIMENTAL RESULTS AND PHASE EQUILIBRIA

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The thermogravimetric curve (TG) for the decomposition of carnallite (KCl·MgCl₂·6H₂O) at constant water vapor pressure (1 bar) was calculated from the phase diagram (solid-liquid equilibria) and vapor pressure data, and the calculated and experimental results were compared.

Thermal analysis is a very useful method of surveying the thermal behavior of a compound. However, for the interpretation of the results by means of phase equilibria, one problem often arises: no kinetic data are available on the different phase transitions. Since thermal analysis is a dynamic method, the results are very closely connected with the accompanying experimental conditions and procedures. It is often very problematic to compare the results from different sources.

For the investigation of salt hydrates or double salt hydrates, the quasi-isothermal, quasi-isobaric technique is often used. In the application of this technique, it is assumed that the decomposition process takes place not far from equilibrium. For binary systems, e.g. simple salt hydrates, this assumption can be proved within the temperature range in which liquid phase is present, by comparing the results of thermal decomposition with the solid-liquid-vapor equilibria. For ternary systems, e.g. double salt hydrates, the interpretation of the results of thermal decomposition is much more complicated, due to the higher degree of freedom. In addition, no information is available about the kinetics of the different phase transition processes for most systems.

Many double salts of the type M'X·MgX₂·6H₂O (M' = [Li(H₂O)]⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺; X = Cl⁻, Br⁻, I⁻) have been investigated by DTA and TG [1-4]. However, for the most appropriate ternary salt-water systems, no reliable data exist concerning the solid-liquid-vapor equilibria at temperatures above 100°, except for the system KCl-MgCl₂-H₂O. For this system, the solid-liquid and vapor-liquid equilibria are known for temperatures up to 250°.

The aim of this contribution is to compare the results of the thermal decomposition of carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), as described in [1], with the recent results concerning the solid-liquid-vapor equilibria, to deduce how much information about the phase equilibria of ternary salt-water systems can be derived from the results of thermal analysis of double salt hydrates.

Calculation of the TG curve of thermal decomposition of carnallite

We wish to consider the equilibria in the presence of a liquid phase. Hydrolysis (formation of HCl) is neglected. Hence, the gas phase consists of pure water vapor. Due to the application of the quasi-isothermal, quasi-isobaric technique (labyrinth crucibles) to double salt hydrates, the water vapor pressure during the decomposition process is constant and equal to the ambient (in general, atmospheric) pressure.

From the phase rule, it follows for such a 3-component system (two salts and water) at $p_w = \text{const}$, that

$$ph + f = 4$$

(p_w = water vapor pressure; ph = number of phases; f = degree of freedom).

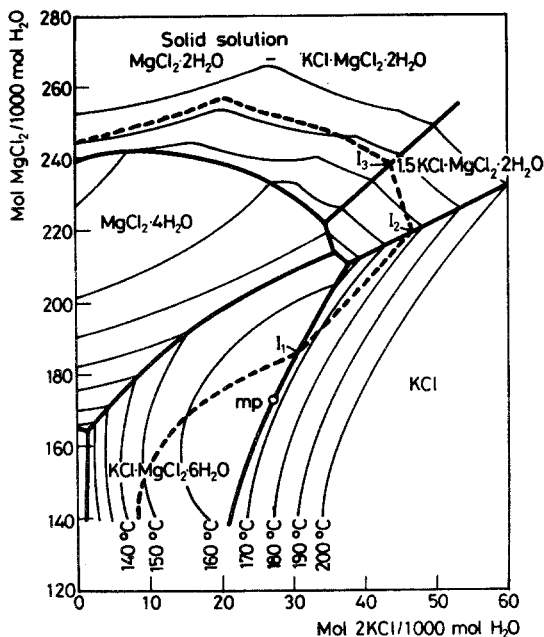


Fig. 1 Projection of the MgCl_2 -rich part of the phase diagram of the system $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$ at 120°C to 200°C . — boundaries between the liquidus surfaces; - - - isotherms; water vapor pressure $p_w = 1$ bar; mp = incongruent melting point of carnallite

In principle, only the following two equilibria are important for the thermal decomposition of a double salt hydrate in the presence of a liquid phase:



s = solid phase; l = liquid phase; g = gas (water vapor); ϑ = temperature.

Reaction (I) represents an isothermal isobaric invariant equilibrium, where the two liquidus surfaces corresponding to s_1 and s_2 and the surface for $p_w = \text{const.}$ cross each other in the phase diagram, while reaction (II) takes place along the intersection curve between one liquidus surface and the surface for $p_w = \text{const.}$ In the TG curve for equilibrium (I), a vertical portion occurs, but equilibrium (II) has a curve which is neither horizontal nor vertical.

A projection of the MgCl_2 -rich part of the phase diagram of the system $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ in the temperature range $120\text{--}200^\circ$ is given in Fig. 1. The results on the determination of the solid-liquid equilibria are described in more detail in [5–8]. The thick lines in Fig. 1 represent the boundaries between the liquidus surfaces, while the thin lines are the isotherms. In the considered temperature and concentration intervals, the following solid phases are stable:

- KCl
- $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- $1.5 \text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
- $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$
- $\text{MgCl}_2 \cdot 2\text{H}_2\text{O-KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ solid solution.

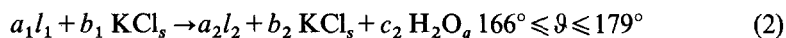
The dashed line represents the intersection curve between the liquidus surface and the surface for $p_w = 1$ bar. To calculate this curve, the vapor pressure data on the system $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ [9] were extrapolated to saturation by application of a modified BET equation as described in [10].

During the decomposition process, the composition of the liquid phase has to follow the dashed line, if we assume that all decomposition steps take place under equilibrium. From Fig. 1, we can deduce 5 steps for the decomposition of carnallite:

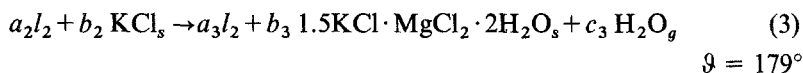
1. Carnallite melts incongruently at 167° . The resulting liquid phase already has a vapor pressure higher than 1 bar (1.3 bar). Hence, the loss of water starts during and partly even before the melting process. The resulting liquid phase composition is represented by point l_1 at a temperature of 166° in the phase diagram (Fig. 1). During this step, solid KCl is formed:



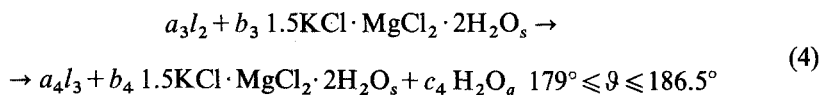
2. A portion of the solid KCl is dissolved. The liquid phase composition moves from l_1 to l_2 , and the temperature increases from 166° to 179° :



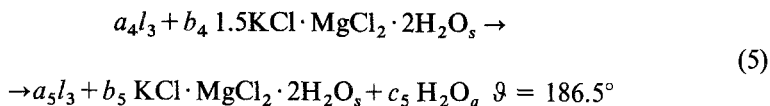
3. At constant temperature, the double salt $1.5\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ is formed. All the solid KCl is consumed in this process, while the liquid phase composition remains constant at l_2 :



4. Further, $1.5\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ precipitates in the temperature interval $179^\circ \leq \vartheta \leq 186.5^\circ$. The liquid phase composition changes to l_3 :



5. At constant temperature, the double salt $\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ (end-member of the solid solution series) is formed through the consumption of all the solid $1.5\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. The liquid phase composition remains constant at l_3 :



(a_i, b_i, c_i = stoichiometric coefficients).

Through introduction of the vector $\begin{bmatrix} \text{mol KCl} \\ \text{mol MgCl}_2 \\ \text{mol H}_2\text{O} \end{bmatrix}$ for the

composition of the different phases with

$$l_1 = \begin{bmatrix} 60 \\ 185 \\ 1000 \end{bmatrix}, \quad l_2 = \begin{bmatrix} 94 \\ 220 \\ 1000 \end{bmatrix} \quad \text{and} \quad l_3 = \begin{bmatrix} 87 \\ 238 \\ 1000 \end{bmatrix},$$

Equations (1) to (5) can be solved. The values of the coefficients are listed in Table 1. Because of $a_5 = 0$, in the last step all the liquid phase is consumed and the remaining phase is only $\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$.

Table 1 Coefficients of Equations (1)–(5)

$i =$	1	2	3	4	5
a_i	0.00541	0.00455	0.00212	0.00185	0
b_i	0.676	0.573	0.534	0.559	1
c_i	0.595	0.860	1.358	0.216	0.971

Discussion

In Fig. 2, the experimental results of the decomposition of carnallite, taken from [1], are compared with the results calculated above.

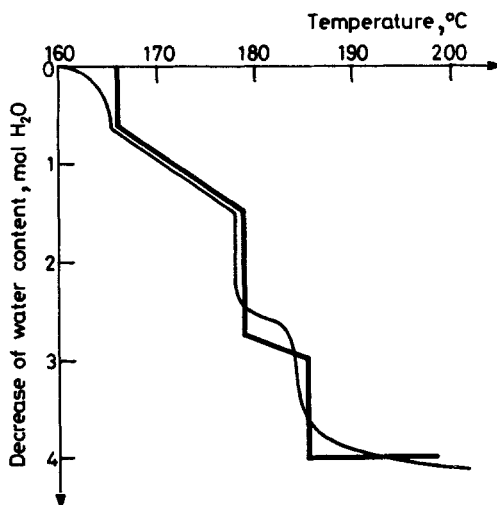


Fig. 2 Decomposition of $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ under quasi-isothermal, quasi-isobaric conditions. $p = 1$ bar; — experimental [1]; — calculated on the assumption that all steps take place under equilibrium

The two curves are very similar. The main differences between them are the different lengths of the vertical portions at 179° and 186.5° . (Small differences in temperature of about 1–2 deg are within the limits of accuracy of the thermal analysis.) These two vertical portions represent the isothermal, isobaric invariant equilibria. At these temperatures, one solid phase has to transform into another one, while both the liquid phase composition and the temperature have to remain constant. These reactions take place only to a certain degree. A portion of the former solid phase does not react with the liquid phase, probably because it is covered during the reaction by a layer of the newly formed solid phase.

Similar behaviour could be observed during the investigation of the solid-liquid equilibria of the $\text{KCl}-\text{MgCl}_2-\text{H}_2\text{O}$ system by applying an "analytical" method. Even on equilibration of the solid-liquid system for more than one week (at constant temperature), the equilibrium was not completely established, if such a reaction as mentioned above had to take place. The liquid phase was in equilibrium only with a surface layer of the solid particles [7, 8].

The simple assumption that the reactions which represent the isothermal, isobaric invariant equilibria take place only to about 60–70%, while the remaining unstable phase is considered to be inert, leads to the result shown in Fig. 3. Under these conditions, the liquid phase is not completely consumed in step 5. Further reactions for the formation of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} - \text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ mixed crystals have to be formulated. In a 6th step, almost pure $\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ is formed, after which solid phases with even lower KCl contents are precipitated. As we can see from Fig. 3, this assumption fits the experimental results very well.

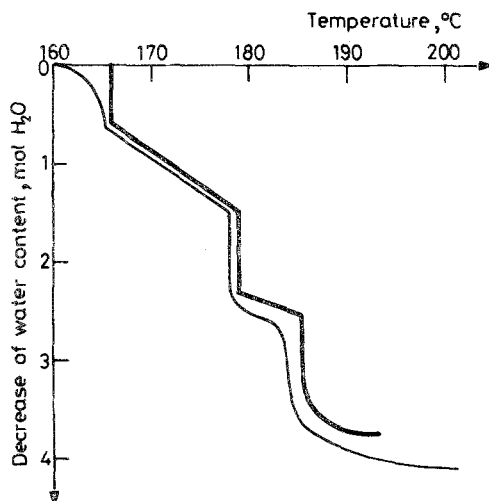


Fig. 3 Decomposition of $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ under quasi-isothermal, quasi-isobaric conditions. $p = 1$ bar; — experimental [1]; - - - calculated on the assumption that the reactions at constant temperatures take place to 66%

If the thermal decomposition of 1 mol carnallite were interrupted at 195° , the following solid phases would be present according to this model:

- 0.21 mol KCl
- 0.09 mol $1.5\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
- 0.55 mol $\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
- 0.36 mol $x \text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$; $x < 1$

The conclusion can be drawn that all steps of decomposition which are monovariant, e.g. $\vartheta \neq \text{const.}$, take place in accordance with the phase equilibria, even the dissolution of KCl in step 2. The reactions at $\vartheta = \text{const.}$, e.g. at invariant points, take place to approximately 60–70%. During the whole decomposition process, the liquid phase composition follows the intersection curve between the surface for $p_w = 1$ bar and the liquidus surfaces of the different solid phases. In

addition, the consistency of the three different sets of data (solid-liquid equilibria, vapor pressure data, and thermal analysis) is proved.

References

- 1 H.-H. Emons, R. Naumann, T. Pohl and H. Voigt, *J. Thermal Anal.*, 29 (1984) 571.
- 2 H.-H. Emons, H. Voigt, T. Pohl and R. Naumann, *Thermochim. Acta*, 121 (1987) 151.
- 3 S. Shoval and S. Yariv, *Thermochim. Acta*, 92 (1985) 819.
- 4 S. Shoval, S. Yariv, Y. Kirsh and H. Peled, *Thermochim. Acta*, 109 (1986) 207.
- 5 W. Voigt, Th. Fanghänel and H.-H. Emons, *Z. Phys. Chem. (Leipzig)*, 266 (1985) 522.
- 6 Th. Fanghänel, K. Kravchuk, W. Voigt and H.-H. Emons, *Z. anorg. allg. Chem.*, 547 (1987) 21.
- 7 Th. Fanghänel and H.-H. Emons, *Z. anorg. allg. Chem.*, 562 (1988) 165.
- 8 Th. Fanghänel, K. Köhnke and H.-H. Emons, *Z. anorg. allg. Chem.*, 576 (1989) 99.
- 9 H.-H. Emons, A. Dittrich and W. Voigt, *Proceedings of the Joint International Symposium on Molten Salts 87-7* (1987) 111.
- 10 A. Dittrich, *Dissertation, Bergakademie Freiberg*, 1986.

Zusammenfassung — Die thermogravimetrische Kurve TG der Zersetzung von Carnallit ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) bei konstantem Wasserdampfdruck (1 bar) wurde basierend auf dem Phasendiagramm (fest-flüssig-Gleichgewichte) und auf Dampfdruckdaten berechnet und mit experimentellen Ergebnissen verglichen.

Резюме — На основе фазовой диаграммы (равновесие типа твердое тело-жидкость) и давления паров, была вычислена кривая ТГ разложения карналлита ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) при постоянном давлении паров воды (1 бар) и которая была сопоставлена с экспериментально найденной.