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THERMAL DECOMPOSITION OF THE MAGNESIUM SULPHATE HYDRATES UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS

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In the course of thermal decomposition of the magnesium sulphate hydrates $MgSO_4.nH_2O$ (n = 7; 6; 5; 4; 3; 2; 5/4; 1) the intermediate steps $MgSO_4.3H_2O$, $MgSO_4.2H_2O$, $MgSO_4.H_2O$ and β - $MgSO_4$ are observed under quasi-isothermal and quasi-isobaric conditions at $p \cong 0.1$ MPa dependent on the water contents. The structure of the obtained monohydrate phase is identical with that of kieserite. Thermal decomposition of the magnesium sulphate hydrates is essentially influenced by the water vapour partial pressure.

The system $MgSO_4.H_2O$ is characterized by the occurrence of a great number of hydrates; however, above 25° only $MgSO_4.7H_2O$ (epsomite), $MgSO_4.6H_2O$ (hexahydrite) and $MgSO_4.H_2O$ (kieserite) are contained in the form of stable solid phases in aqueous solution [1]. The compounds $MgSO_4.5H_2O$ (allenite), $MgSO_4.4H_2O$ (leonhardite), $MgSO_4.3H_2O$, $MgSO_4.2H_2O$, and different non-stoichiometric hydrates [2] are considered to be metastable [1, 3]; only Polo [4] reports $MgSO_4.4H_2O$ to be a stable solid phase in the temperature range of 70 - 78°.

Thermal decomposition, especially of $MgSO_4.7H_2O$ into $MgSO_4$ has been repeatedly investigated, however mainly under dynamic conditions. A great number of partly quite different hydrate intermediate stages had been found [5-8]. Heide [9] has found the intermediate stages $MgSO_4.6H_2O$, $MgSO_4.3H_2O$, $MgSO_4.2H_2O$, $MgSO_4.1.4\ H_2O$ and $MgSO_4.0.5H_2O$ in the course of the decomposition in the open crucible under dynamic conditions. The hydrate steps which occur on thermal decomposition without controlled external pressure are highly influenced by the experimental conditions, especially by the pressure of the releasing water.

Lallemant [10, 11] gives two sequences of decomposition as a function of the external pressure. The formation of $MgSO_4.6H_2O$, $MgSO_4.4H_2O$, $MgSO_4.2H_2O$, $MgSO_4.H_2O$ takes place at pressures of $p < 5.33$ kPa. $MgSO_4.2.5H_2O$ is additionally formed at pressures of $p > 6.67$ kPa.

In the course of thermogravimetric measurements of $MgSO_4.7H_2O$ under quasi-isothermal and quasi-isobaric conditions in the labyrinth crucible ($p_{H_2O} \approx 0,1$ MPa) Paulik [12] finds $MgSO_4.3H_2O$ and a mixture of

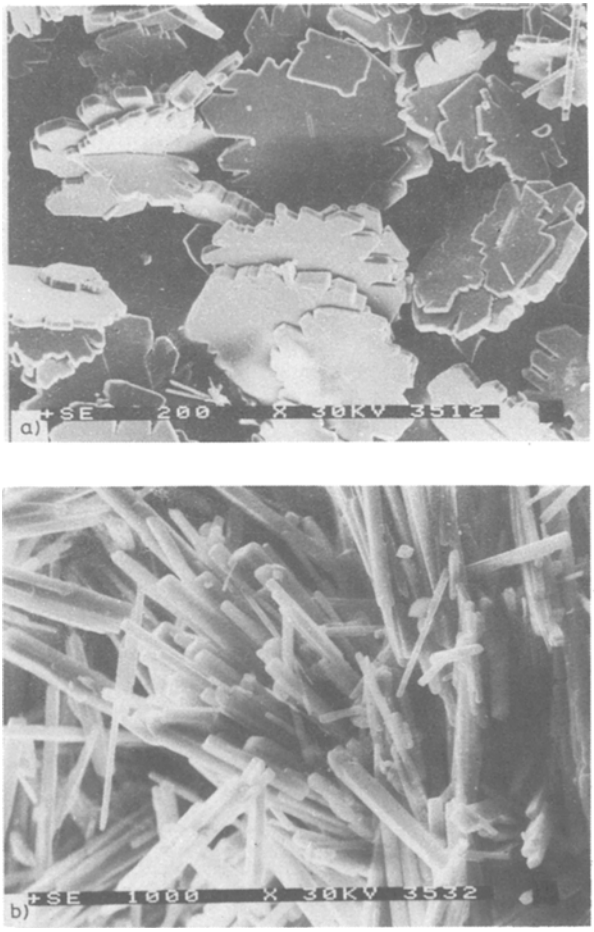

Fig. 1 a) Scanning electronmicrophotograph of $MgSO_4.3H_2O$ magnification 200:1
b) Scanning electronmicrophotograph of $MgSO_4.2H_2O$ magnification 1000:1

$MgSO_4.2H_2O$ and $MgSO_4.H_2O$. Samples which have been predecomposed partly under thermoanalytical control do not form $MgSO_4.3H_2O$. Other mass ratios of the formed hydrates having a low water content can be observed.

In the present work comparative investigations of the thermal decomposition of all stable and metastable stoichiometric $MgSO_4$ hydrates above room temperature and of $MgSO_4.5/4H_2O$ are given. The results which have been obtained by means of the quasi-equilibrium thermoanalysis also allow definite statements on the thermal decomposition of $MgSO_4.7H_2O$.

Fig. 1 c) Scanning electronmicrophotograph of $MgSO_4.5/4H_2O$ magnification 1000:1

Experimental

The preparation of the $MgSO_4$ hydrates was performed by crystallization from solutions in accordance with the literature. The prepared compounds are characterized by means of chemical analysis, X-ray investigations and microscopic methods. The used preparation methods are summarized in Table 1, the X-ray results are given in Table 2. It can be seen that the compounds which have been prepared for the thermoanalytical investigations show a good agreement with the literature concerning their characterization. Maximum deviation from the formulated water content amounts to ±0.15 mol H_2O/mol $MgSO_4$. By repeated careful washing with different mixtures of ethanol and water an absence of chloride in the solid phases could be obtained. The results given in the following figures have been obtained under quasi-isothermal and quasi-isobaric conditions [13] in the labyrinth crucible (p ≈ 0,115 ±0.010 MPa) [15] by means of the Q-type derivatograph (MOM, Hungary).

Table 1 Preparation of the hydrates

$MgSO_4.7H_2O$	Crystallization from a saturated $MgSO_4$ solution at room temperature [3]
$MgSO_4.6H_2O$	Slow isothermal evaporation of a saturated $MgSO_4$ solution at 60°C [1]
$MgSO_4.5H_2O$	Crystallization from an oversaturated methanolic $MgSO_4$ solution (75 g CH_3OH + 25 g H_2O) at 40°C [14]
$MgSO_4.4H_2O$	Crystallization from a methanolic solution at 25°C (220 g CH_3OH + 100 g H_2O + 52 g $MgSO_4$) [14]
$MgSO_4.3H_2O$	Crystallization from a solution of 90 mol $MgCl_2$ and 9 mol $MgSO_4$/1000 mol H_2O at 60°C [2]
$MgSO_4.2H_2O$	Mixing of a saturated $MgCl_2$ solution and a saturated $MgSO_4$ solution at boiling heat and slow evaporation with permanent agitation [2]
$MgSO_4.5/4H_2O$	Mixing of a saturated $MgCl_2$ solution and a saturated $MgSO_4$ solution at boiling heat and evaporation to the initial volume of the $MgCl_2$ solution [2]
$MgSO_4.H_2O$	Natural product; obtained from kieseritic hard salt and purified by repeated agitation with mixtures of glycerol and ethanol [17]

Standard measuring conditions: sample weight: 200 - 300 mg; TG = 100 mg, program II, Q - DTG =0.6 mg/min, flushing by N_2. In addition to the TG signal a ΔT signal (E =250 μV) has been registrated. The inert labyrinth crucible was filled with α - Al_2O_3. The X-ray diffraction investigations have been performed by means of a vertical goniometer PW 1050/70 (manufactured by Philips) with graphite monochromator (Co - K_α radiation; 1000 pulses/s; goniometer rate 1/2 deg/min).

Results

$MgSO_4.H_2O$ (natural kieserite), $MgSO_4.5/4H_2O$ (Fig. 2).

Natural kieserite shows a single-step thermal decomposition with formation of β - $MgSO_4$ in the temperature range of 360 - 380°.

$MgSO_4.5/4H_2O$, frequently called synthetic kieserite, continuously releases 1/4 mol H_2O/mol $MgSO_4$ in the temperature range of 100 - 330°. Decomposition of the formed monohydrate phase is already initiated at 330°

in contrast with that of kieserite and also leads to the anhydrite in a single-step process.

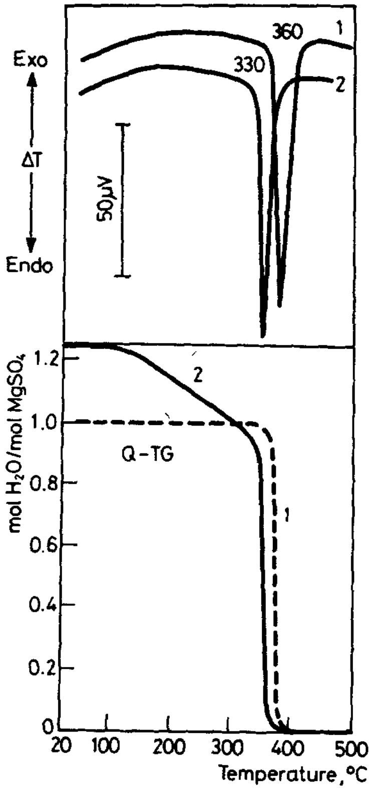

Fig. 2 Thermal decomposition of Kieserite (curves 1) and $MgSO_4.5/4H_2O$ (curves 2). The onset-temperatures are indicated on DTA curves

$MgSO_4.2H_2O$, $MgSO_4.3H_2O$ (Fig. 3)

$MgSO_4.2H_2O$ releases 1 mol H_2O/mol $MgSO_4$ in the range of 150 - 200° in a non-isothermal process and is converted to the anhydrite phase, beginning at 340°. The release of 0.15 mol H_2O/mol $MgSO_4$ in the temperature range of 100 - 150° can be attributed to the adhering and enclosed solution, respectively. $MgSO_4.3H_2O$ shows a three-stage thermal decomposition which results in the formation of the dihydrate in an isothermal process at 120°. The decomposition temperature of this dihydrate and the monohydrate phase being formed later on show a good agreement with that of the pure synthetic $MgSO_4.2H_2O$.

Table 2 Chracteristics of the $MgSO_4$-hydrates

Hydrate	Chemical analysis	Crystal shape	X-ray results			
			Literature [2]		Measured	
			I/I_o, %	d, nm	I/I_o, %	d, nm
$MgSO_4.7H_2O$	$MgSO_4.7.01H_2O$	longprismatic	100	0.42	100	0.42
			50	0.534	50	0.534
			50	0.599	50	0.599
			45	0.266	20	0.266
			25	0.448	30	0.447
$MgSO_4.6H_2O$	$MgSO_4.5.95H_2O$	tabular	100	0.442	100	0.442
			40	0.406	50	0.404
			35	0.2909	60	0.2904
			30	0.2952	80	0.2952
			30	0.3629	10	0.362
			30	0.549	60	0.549
$MgSO_4.5H_2O$	$MgSO_4.5.08H_2O$	prismatic	100	0.493	100	0.498
			40	0.326	40	0.327
			35	0.515	36	0.515
			30	0.365	36	0.369
			25	0.268	70	0.268
			20	0.300	60	0.300
			20	0.584	72	0.590
$MgSO_4.4H_2O$	$MgSO_4.4H_2O$	prismatic	100	0.446	100	0.446
			100	0.2947	30	0.295
			50	0.549	75	0.549
			40	0.3972	75	0.397
			35	0.687	30	0.684
$MgSO_4.3H_2O$	$MgSO_4.3.1H_2O$	lamellar	100	0.3172	15	0.3170
		(Fig. 1a)	90	0.3060	20	0.3070
			60	0.4279	40	0.4300
			60	0.2537	50	0.2540
			45	0.3102	8	0.3106
			25	0.5030	35	0.5030
			10	0.5510	100	0.5530

Table 2 continued

Hydrate	Chemical analysis	Crystal shape	X-ray results			
			Literature [2]		Measured	
			I/I_0, %	d, nm	I/I_0, %	d, nm
$MgSO_4.2H_2O$	$MgSO_4.2.15H_2O$	needlelike	100	0.3100	5	0.309
		(Fig. 1b)	90	0.4250	100	0.430
			80	0.4420	10	0.442
			50	0.2725	50	0.265
			40	0.3920	5	0.396
			40	0.3740	10	0.370
$MgSO_4.5/4H_2O$	$MgSO_4.2.15H_2O$	spindleshaped	100	0.337	100	0.339
		(Fig. 1c)	60	0.343	90	0.344
			50	0.323	75	0.323
			40	0.485	90	0.484
			40	0.317	75	0.318
$MgSO_4.H_2O$	$MgSO_4.H_2O$	natural product	100	0.342	100	0.342
		only crushed	95	0.334	90	0.334
			75	0.484	80	0.484
			60	0.305	50	0.305
			45	0.337	50	0.337

$MgSO_4.4H_2O$; $MgSO_4.5H_2O$ (Fig. 4)

In a solid-state decomposition reaction $MgSO_4.4H_2O$ releases 1 mol H_2O/mol $MgSO_4$ at 110°. This process results in the formation of $MgSO_4.3H_2O$.

Thermal curves of $MgSO_4.5H_2O$ shows an endothermic effect without any loss in weight at 100°. At 105° there is a release of 2 mol H_2O/mol $MgSO_4$ with formation of $MgSO_4.3H_2O$. The trihydrate phases which have been formed from $MgSO_4.4H_2O$ and from $MgSO_4.5H_2O$ are decomposed by analogy with the synthetic $MgSO_4.3H_2O$ (curve 2 in Fig. 3).

$MgSO_4.6H_2O$ (Fig. 5)

The thermal curves of $MgSO_4.6H_2O$ show an endothermic effect at 95° prior to the dehydration. At 105° there is a release of 3 mol H_2O/mol $MgSO_4$ with formation of $MgSO_4.3H_2O$ which is further decomposed as has been described.

$MgSO_4.7H_2O$ (Fig. 6)

After the occurrence of 2 endothermic ΔT signals at 50 and 95°, respectively, the formation of $MgSO_4.3H_2O$ takes place at 105° with release of 4 mol H_2O/mol $MgSO_4$. Its further decomposition again proceeds with formation of $MgSO_4.2H_2O$ and $MgSO_4.H_2O$ to the water free compound.

In most cases the thermal decomposition of $MgSO_4.7H_2O$ takes place as demonstrated in Fig. 6. However, in certain cases it occurs that the decomposition process takes a different path. In Fig. 7 five Q-TG curves of such irregular courses can be seen. These curves were traced by using the conic crucible under the application of various transformation rates (0.1, 0.15, 0.2, 0.3, 0.4 mg min^{-1}).

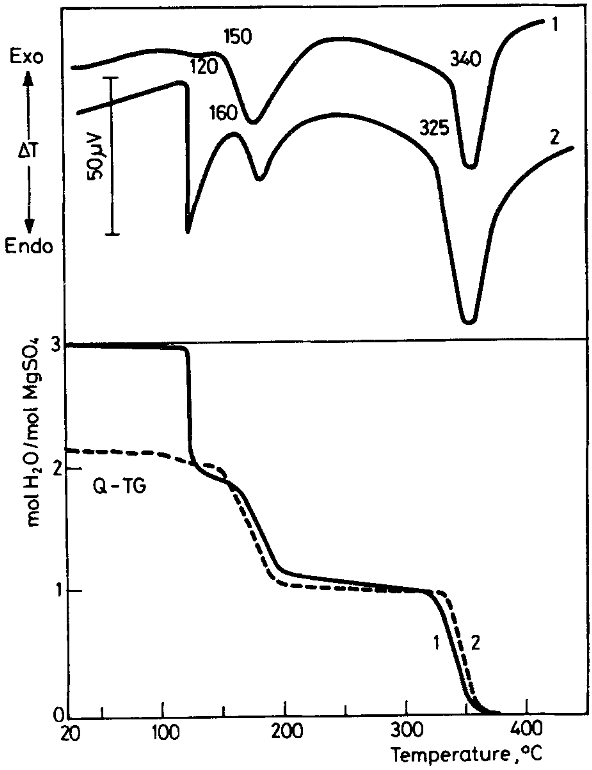

Fig. 3 Thermal decomposition of $MgSO_4.2H_2O$ (curves 1) and $MgSO_4.3H_2O$ (curves 2)

$MgSO_4.7H_2O$ (Fig. 8 original diagram)

In this figure the simultaneous, T, Q-TG, Q-DTG and Q-DTA curves can be seen plotted in function of time at a transformation rate of 0.15 mg min^{-1}. Curve 2 of this figure is identical with curve 2 in Fig. 7 with the difference that the weight changes of the latter one was plotted as function of temperature.

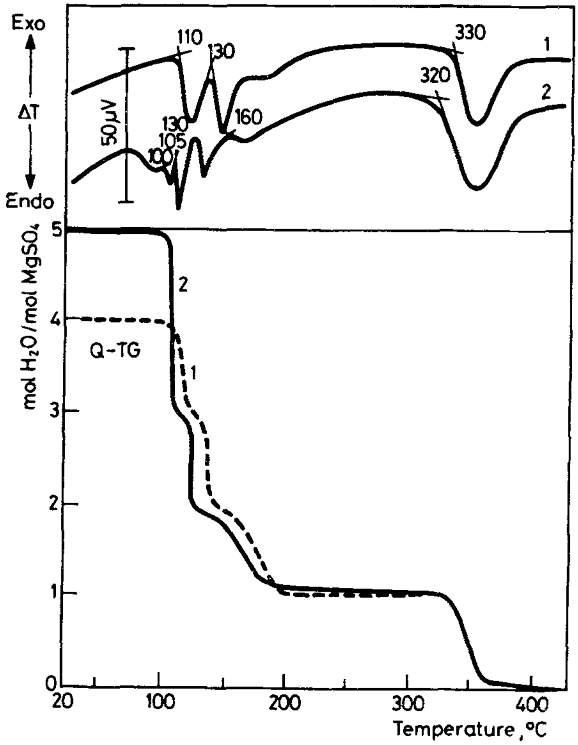

Fig. 4 Thermal decomposition of $MgSO_4.4H_2O$ (curves 1) and $MgSO_4.5H_2O$ (curves 2)

X-ray diagram of $MgSO_4.H_2O$ and kieserite (Fig. 9)

As shown in X-ray diffraction investigations of the formed monohydrate phase (*A*) it can be considered to be identical with natural kieserite (*B*).

Mixture of $MgSO_4.H_2O$ and natural kieserite (Fig. 10)

The Q-TG curve in this figure illustrates the thermal decomposition process of $MgSO_4.6H_2O$ and natural kieserite mixed in a ratio of 70 and 30 weight % respectively. It is to be noted that above 200^0 the mixture of the formed artificial kieserite and the natural kieserite was present.

Discussion

Comparison of the individual decomposition schemes (Figs 2-6) shows that the thermal decomposition of the stable and metastable $MgSO_4$ hydrates proceeds in a well reproducible manner under near-equilibrium conditions (see also Fig. 8 up to 250 min) at an approximately constant pressure of the water vapour being formed. The results of the hydrates with low water content compared with $MgSO_4.7H_2O$ fit well into its decomposition behaviour. The compounds $MgSO_4.3H_2O$, $MgSO_4.2H_2O$ and $MgSO_4.H_2O$ are characteristic intermediate steps in the formation of waterfree $MgSO_4$. The transition of $MgSO_4.2H_2O$ to $MgSO_4.H_2O$ proceeds in a nonisothermal process as a solid-state decomposition reaction. Two melting processes at about 50° and 95° (endothermic ΔT signals in Fig. 6) take place prior to the dehydration from $MgSO_4.7H_2O$. While the first melting process clearly

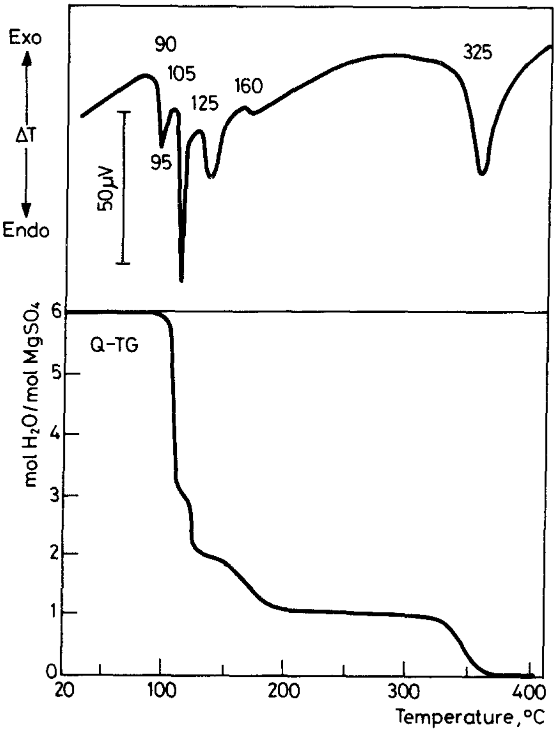

Fig. 5 Thermal decomposition of $MgSO_4.6H_2O$

shows the transition to $MgSO_4.6H_2O$ (literature: 48.1° [3]), the ΔT curve of $MgSO_4.6H_2O$ in Fig. 5 showing the effect at 90-95° and the subsequent decomposition to $MgSO_4.3H_2O$ illustrates a melting process with formation of the same solid phase and a saturated solution which boils at 105° in a good agreement with vapour pressure data [3]. While incongruent melting of $MgSO_4.7H_2O$ is known from the solid-liquid equilibria, such a transition point for $MgSO_4.6H_2O$ cannot be found in the stable system. This transition must therefore be considered to be metastable. The ΔT signal occurring in the thermogram of $MgSO_4.5H_2O$ at 100° can be explained by the incongruent melting with formation of $MgSO_4.3H_2O$ (curve 2, Fig. 4).

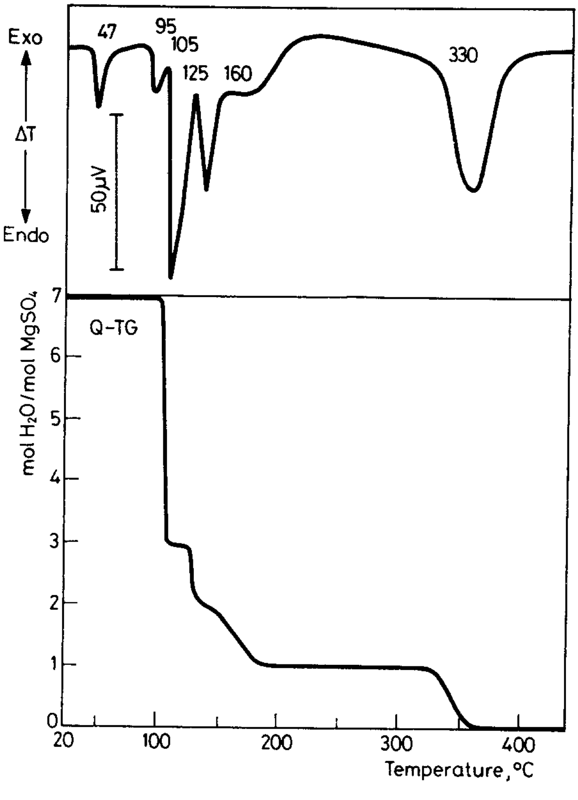

Fig. 6 Thermal decomposition of $MgSO_4.7H_2O$

On the transition of $MgSO_4.3H_2O$ to the metastable $MgSO_4.2H_2O$ partly varying water contents of the dihydrate phase are observed due to inhibi-

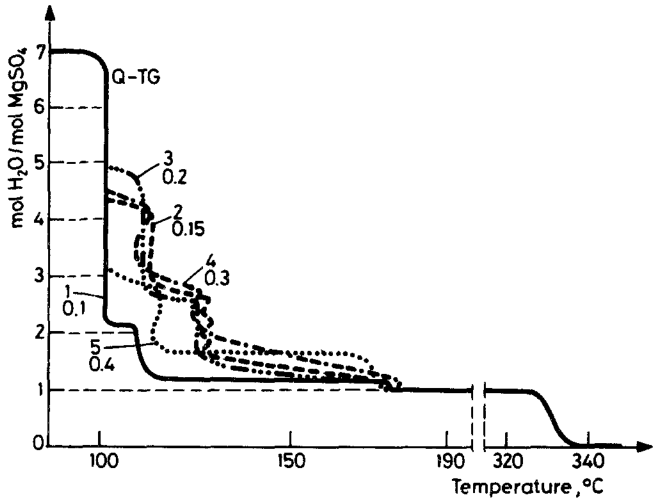

Fig. 7 Thermal decomposition of $MgSO_4.7H_2O$ in conic crucible; transformation rate 0.1, 0.15, 0.2, 0.3, 0.5 mg min^{-1}

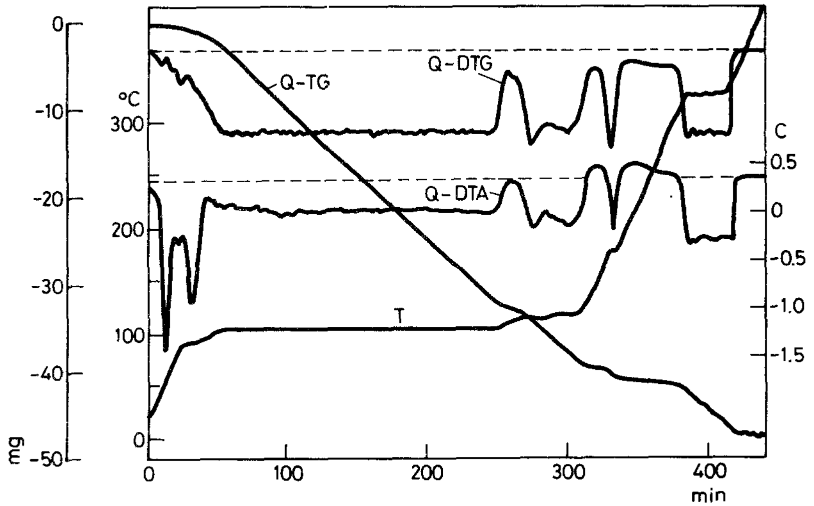

Fig. 8 Simultaneous Q-TG, Q-DTG, Q-DTA and T curves plotted in function of time. Sample holder: conic crucible, transformation rate: 0.15 mg min^{-1}. Original chart

tions such as crust formation which are induced by kinetics. (Fig 8, beginning at 250 min). The variation amounts to ±0.2 mol/mol $MgSO_4$.

The different course of the curves in Fig. 7 indicates that the progress of the transformation took place in an accidental way. With the changes of the transformation rate namely no interpretable correspondence can be found in the course of the curves. The repetition of the experiment under the very same conditions of transformation rate led usually to changes in the form of the curves. Other experimental conditions did not cause a uniequivocal effect upon the course of the curves either. All these indicate that beside or instead of the formation of stable $MgSO_4.3H_2O$ and $MgSO_4.H_2O$ there exist also a possibility for the formation of metastable $MgSO_4.6H_2O$ $MgSO_4.4H_2O$ or $MgSO_4.2H_2O$. The probability of the formation of the various metastable phases is nearly identical. The direction of these transformations is defined by chance. However, the results of many experiments shows, that the probability of the regular course of the transformation (Fig. 6) is statistically far greater than that of the anomaleous ones (Fig. 7).

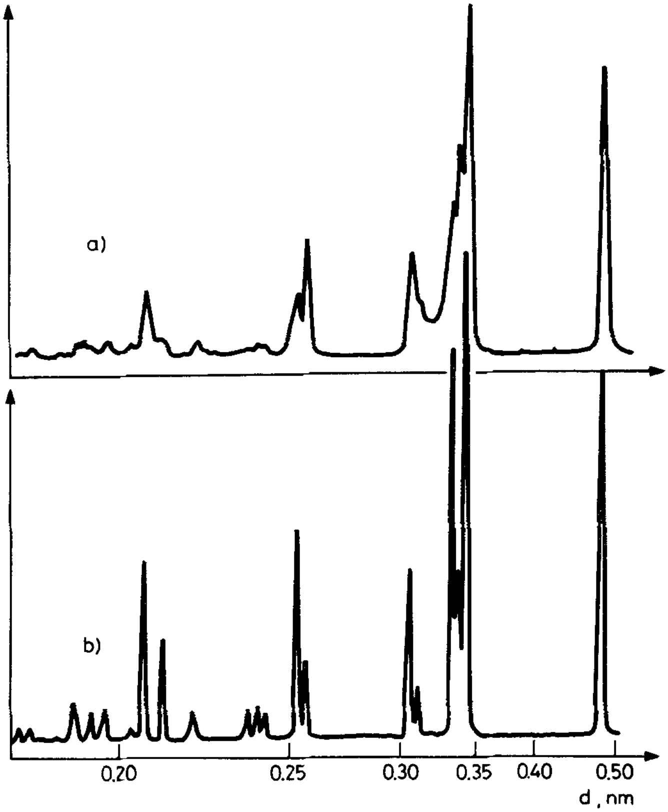

Fig. 9 Results of the X-ray powder diffraction. a: $MgSO_4.H_2O$, prepared in the course of the dehydration of $MgSO_4.7H_2O$ in the labyrinth crucible (p_{H_2O} 0.1 MPa); b: natural Kieserite

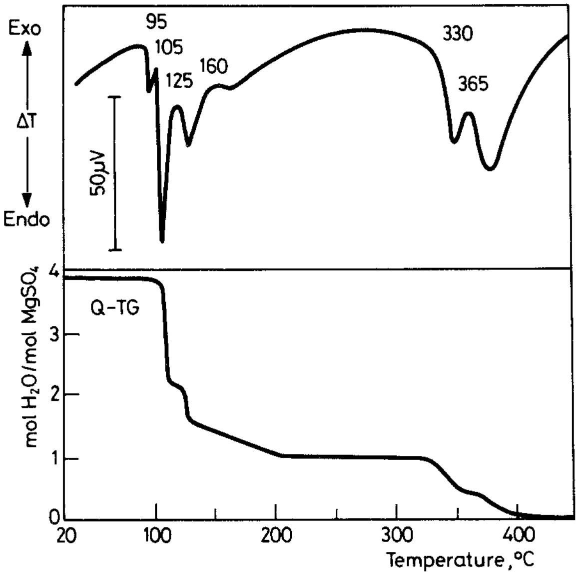

Fig. 10 Thermal decomposition of a mixture of Kieserite and $MgSO_4.6H_2O$ (mass ratio 30:70) with the formal water content of 3.9 mol H_2O/mol $MgSO_4$

$MgSO_4.H_2O$ which has been formed by thermal decomposition of hydrates with a high water content has a decomposition temperature being lower by about 20 - 30° in spite of the structural identity with the natural kieserite. We suppose a low order and higher structural defects due to widening of the X-ray interferences of the artificial monohydrate (Fig. 9) compared with the natural product. This can be explained by a very quick crystallization in the course of the decomposition process. This process results in a lower thermal stability. The different decomposition temperatures of the natural monohydrate phase of kieserite and of a synthetic phase which has been obtained by thermal decomposition of $MgSO_4.6H_2O$, for example, become clearly visible in the investigation of a mixture of them (Fig. 10).

At the same time it can be seen that the presence of kieserite does not change the fundamental course of the decomposition, that means a seed crystal effect which gives rise to the formation of a decomposition corresponding to the stable solid-liquid phase equilibria cannot be found.

On thermal decomposition with controlled external pressure a monohydrate phase similar to kieserite is also formed as an intermediate step at 330° (curve 2, Fig. 2) from the $MgSO_4.5/4H_2O$. As a result of the continuous release of 0.25 mol H_2O/mol $MgSO_4$ it can be supposed that it is bonded as excess water on interstitial sites. The results show that $MgSO_4.5/4H_2O$ cannot be considered as a defined hydrate phase.

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Zusammenfassung — Beim thermischen Abbau der Magnesiumsulfathydrate $MgSO_4.nH_2O$ (n = 7; 6; 5; 4; 3; 2; 5/4; 1) unter quasiisothermen- und quasiisobaren Bedingungen werden bei p ≈ 0.1 MPa, in Abhängigkeit von den Wassergehalten, die Zwischenstufen $MgSO_4.3H_2O$; $MgSO_4.2H_2O$; $MgSO_4.H_2O$ sowie β-$MgSO_4$ beobachtet. Die erhaltene Monohydratphase ist strukturell mit Kieserit identisch. Der thermische Abbau der Magnesiumsulfathydrate wird wesentlich vom Wasserdampfpartialdruck beeinflußt.