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DEVELOPMENT OF MEDIA FOR DYNAMIC LATENT
HEAT STORAGE FOR THE LOW-TEMPERATURE RANGE.
PART I: THERMAL ANALYSES OF SELECTED SALT
HYDRATE SYSTEMS

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PART I: THERMAL ANALYSES OF SELECTED SALT
HYDRATE SYSTEMS

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Development of Media for Dynamic Latent Heat Storage in the Low-Temperature Range

Part I: Thermal Analyses of Selected Salt Hydrate Systems

Summary

The results obtained during the development of storage media for thermal storages measured by differential thermal analysis, of phase change temperatures and phase change enthalpies of seventeen salt hydrates, three double salts, and four eutectics are reported. Good results were obtained especially for congruently melting salt hydrates. Incongruently melting salt hydrates appear less suitable for heat storage applications. The influence of additives - water, acid, and hydroxide - on the phase change heat is described. From the results basic values for the working temperatures and storage capacities of various media composition may be derived.

* Numbers in margin indicate pagination of original foreign text.

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Numerous research activities in the area of thermal energy storage deal with the development of latent heat storages, which compared to conventional heat storages excel by their considerably higher storage capacity and a constant working temperature. The functional principle of the latent heat storage system is based on the utilization of the thermal energy, which during a reversibly proceeding phase change of a material is used up (charging process) and is again released (discharging process).

The projects known until now have concentrated essentially on the low-temperature range and on the phase change solid/liquid. As storage medium two very different classes of materials were primarily investigated, for one the fatty acids and paraffins belonging to the hydrocarbons, for another the typical inorganic compounds of the salt hydrates. According to Gawron and Schroeder [1] salt hydrates seem to be particularly suited in the low-temperature range, since they are able to best fulfill the requirements made in large numbers of the storage medium.

The basic investigations in the media development include the determination of the phase change temperature and the phase change enthalpy of the material systems being considered, in order to have available as early as possible theoretical basic values for two important selection criteria, the working temperature and the storage capacity.

The here presented work lists the results of the thermal analyses of selected salt hydrate systems in the low-temperature range. The experimental determination of the interesting data was necessary since the literature values, especially for the phase change enthalpies for numerous salt hydrates, differ greatly from one another and for some systems are not available at all. Only very little information exists concerning the influence of additives

- primarily water, acids, and alkali compounds - on the phase change enthalpies of salt hydrate systems. However, here especially there is great interest, since during the realization of latent heat storage systems for cost reasons only materials with the degree of purity of a technical product can be used as storage media. Compared to extremely pure laboratory chemicals technical products are considerably cheaper and available in sufficient quantities; however, they contain because of their reduced degree of purity various impurities (additives!) depending on production conditions.

2. Experimental

2.1 Problem formulation

Using modern measurement techniques the caloric data are conventionally determined quantitatively with the aid of scanning-calorimetry (DSC) processes [2]. The commercial high performance calorimeters agree with respect to the criteria weighing amounts and sample introduction since basically very small sample amounts (in the range from 1 to 10 mg) are used for the DSC measurements, utilizing flat metal pans or metal crucibles as sample containers. In the standard case the metal pans consist of aluminum, for special applications of platinum or gold; they can be used open or closed.

For the testing of salt hydrate systems the described sample containers can be used only with limitations. Salt hydrates and especially hydrate melts are highly oxidizing so that aluminum is practically eliminated as crucible material and only noble metals with high oxidation potential can be considered. Based on their relatively high partial pressures the salt hydrate systems release considerable amounts of water during heating. In order to avoid faulty test results through the formation of water-poorer phases, the thermal analyses must be carried out in hermetically sealed sample containers. When commercial DSC-equipment is used, the listed requirements can be fulfilled only with use of cold-welded noble metal

crucibles, e.g. gold crucibles as sample containers.

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From this there results a very expensive process, which beyond that produces good results only in individual cases. For, it was shown in orientation tests with a DSC-test cell that, because of the small sample amounts required, only homogeneous substances, i.e. practically only the pure starting compounds can be used. The testing of the increasingly more interesting multi-component systems and heterogeneous samples is not possible if good results are expected, since quantities of ca. 100 mg are required here for weighing. Furthermore it was found that for materials with high partial pressure a deformation of the very thin-walled metal crucibles occurs upon heating so that the thermal contact between sample and test system is disturbed. In these cases the basically very accurate DSC method produces only unsatisfactory results.

In order to be able to investigate all samples to be considered - strongly oxidizing materials with high partial pressure and heterogeneous mixtures - and in order to be able to use at the same time a cost-effective method, which permits the processing of a large number of test tasks, we resorted to a special measurement cell which was developed for aggressive, thermally unstable and air-sensitive substances. Here we are dealing with a method in which the samples are melted into thin-walled glass ampules (5.2 mm outer diameter, 0.2 mm wall thickness) and in which the temperatures of the sample and the reference material are measured with two sheathed thermocouples. The described measurement cell operates according to the method of differential thermal analysis (DTA) and is usually intended only for qualitative measurements. Therefore it became necessary to modify the conduct of the measurement and the evaluation such that quantitative data could be obtained with the required accuracy.

2.2 Conduct of the measurements

The tests were made with the thermal analysis system TA 500 of the Heraeus Company. The test cell was used for special applications. The test values were obtained in on-line operation with an HP 9815A and evaluated by using the software packages of the Heraeus Company. For documentation and control the test values were additionally recorded with an x,y recorder. /10

In order to obtain reproducible results with the DTA measurement cell, which allow a quantitative evaluation, the following criteria were basically taken into account: A sufficient run-in time in order to assure the setting of identical oven- and sample temperatures at the start of the test, a determination of the optimum sample amounts, an installation of the sheathed thermocouples as uniform as possible, a constant heating rate (5 K/min), and the taking into account of the thermal sensitivity of the test cell (for this compare chapter 2.3).

The temperature difference ΔT between sample and reference (Al_2O_3) was measured as a function of sample temperature T at a constant heating rate. The DTA test curve of $CaCl_2 \cdot 6 H_2O$, which showed the typical temperature curve for the phase conversion solid/liquid for salt hydrate, is shown in figure 1. The phase change temperature T_u results from the intersection of the tangents in T_1 and in W , the phase change enthalpy ΔH_u is determined by integration between the limits T_1 and T_2 [2,3].

2.3 Calibration and evaluation

2.3.1 Course of the investigation

In order to be able to make a quantitative evaluation of the DTA diagrams, it was first necessary to determine the optimum test parameters and subsequently to determine the necessary correction factors.

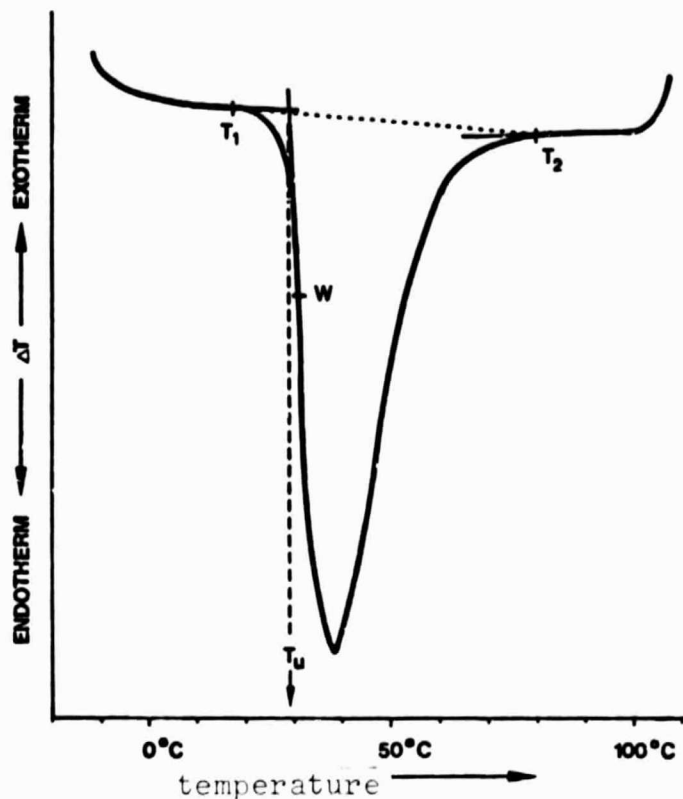


Figure 1: Typical DTA test curve of salt hydrates (here $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$) for the determination of T_u and ΔH_u .

The effect of the test parameters of the test system was tested with naphthalene as basic material and the standard conditions were specified. The literature value for naphthalene as temperature-independent reference quantity was assigned to the thus determined phase change enthalpy. Subsequently the effect of the sample-related parameters was investigated and obtained (compare 2.3.2), and afterward the thermal sensitivity of the test cell and thus a temperature-dependent correction factor were determined (compare 2.3.3). Subsequently the reproducibility and the validity of the method were certified and an error estimation was made (compare 2.3.4). /11

The result of the differential thermal analysis is affected with respect to the sample materials: primarily by its thermal conductivity and the magnitude of the heat transfer. It is furthermore important that the particle size and the packing density of the samples used do not differ too greatly from one another. For the method described in this paper the filling height of the sample ampules additionally has a considerable effect on the test results. Therefore we determined the phase change enthalpies of salt hydrates as compounds with good thermal conductivity and high specific heat transfer as well as those of lauric acid as model substance for compounds with low thermal conductivity and reduced specific heat transfer for different weighing quantities. The results are shown in table 1 whereby for ΔH_u the temperature dependent correction factor K (compare 2.3.3) has already been taken into account.

The graphic representation of the results (figure 2) shows that for salt hydrates maxima of the phase change enthalpies are obtained in the range from 50 to 70 μl for the sample volumes. Thus this range provides the test parameter (weighing) to be set for quantitative measurements. The drop-off observed to lower values can be attributed for volumes, which are too low or also too great, primarily to an unfavorable contact surface ratio between the cylindrical sheathed thermocouple and the sample. For lauric acid an optimum sample volume of ca. 90 μl was determined. Thus the deviation from the salt hydrates emphasizes the differing material properties of the hydrocarbon compounds.

2.3.3 Determination of the temperature-dependent correction factor

For the calibration of the test cell we used selected substances with well known phase change temperature T_u and phase change enthalpy ΔH_u as calibration materials. For the salt-like compounds we used laboratory chemicals with the purity grade p.a. (pro analysi). The

hydrocarbon compounds used were recrystallized several times for purification in the particular prescribed solvent, the caprylic acid was distilled. The deviation of the experimentally determined value $\Delta H_{u,exp.}$ from the literature value $\Delta H_{u,Lit.}$ can be obtained by means of a correction factor K. We have:

$$(1) \quad K = \Delta H_{u,Lit.} / \Delta H_{u,exp.}$$

The results of the calibration measurements as well as the resulting correction factors are listed in table 2.

Table 1 Phase change enthalpy ΔH_u for different weighings

compound	weight mg	sample volume μ l	$\Delta H_u^{*})$ J/g
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	55.70	33	158
	83.42	49	180
	119.19	71	185
	161.76	96	141
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	44.32	30	227
	73.67	51	250
	101.95	70	251
	130.92	90	221
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$	49.14	28	189
	72.95	42	205
	121.17	70	209
	152.27	88	190
lauric acid $\text{C}_{11}\text{H}_{23}\text{COOH}$	42.52	49	135
	60.39	69	166
	80.68	92	182
	102.49	117	158
	121.04	139	141

*) Taking into account the temperature dependent correction factor.

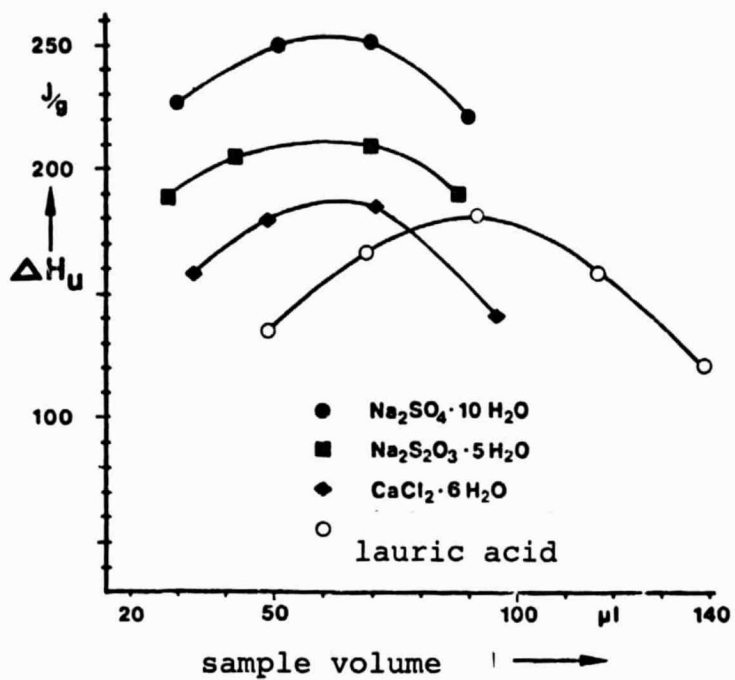


Figure 2: Effect of sample volume on the phase change enthalpy determined.

TABLE 2 RESULTS OF THE CALIBRATION TESTS

Material	$\Delta H_{u,Lit.}$ J/g	$\Delta H_{u,exp.}$ J/g	T_u $^{\circ}C$	K
$Na_2SO_4 \cdot 10 H_2O$	251 [4,5]	295	32.5	0.85
$Na_2S_2O_3 \cdot 5 H_2O$	209 [5,6]	236	47.5	0.89
$Ba(OH)_2 \cdot 8 H_2O$	301* [7,8]	304	78	0.99
KNO_3	50.5 [9,10]	47.4	130	1.07
caprylic acid				
$C_7H_{15}COOH$	148.3 [11,12,13]	172	14	0.86
diphenylmethane				
$C_{13}H_{12}$	109.9* [14,15,16]	124	26	0.89
lauric acid				
$C_{11}H_{23}COOH$	182.9 [12,13]	196	40	0.93
palmitic acid				
$C_{15}H_{31}COOH$	213.7* [14,17,18]	222	60	0.96
naphthalene				
$C_{10}H_8$	147.2* [12,19,20]	147	79	1.00

* average value of the literature values, varying only little

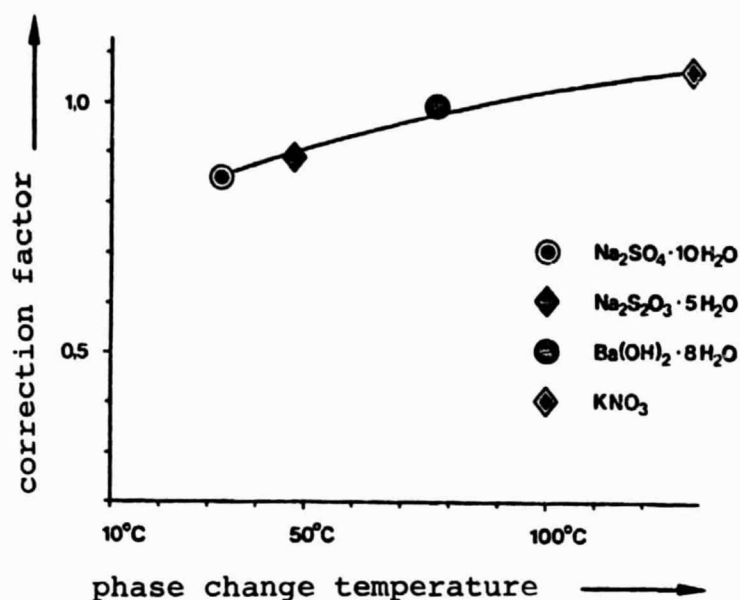


Figure 3 Calibration curve for salt-like compounds

The temperature dependence of the correction factor was shown graphically separately for the two substances. One thus obtains in figure 3 a calibration curve for salt-like samples, i.e., for compounds with good heat conductivity and high heat transfer. This calibration curve was used for the testing of the salt hydrate systems. For samples with low heat conductivity and low heat transfer we obtained the calibration curve shown in figure 4. It applies primarily for hydrocarbon compounds and differs from the calibration curve for salt-like compounds (figure 3) only insignificantly. /15

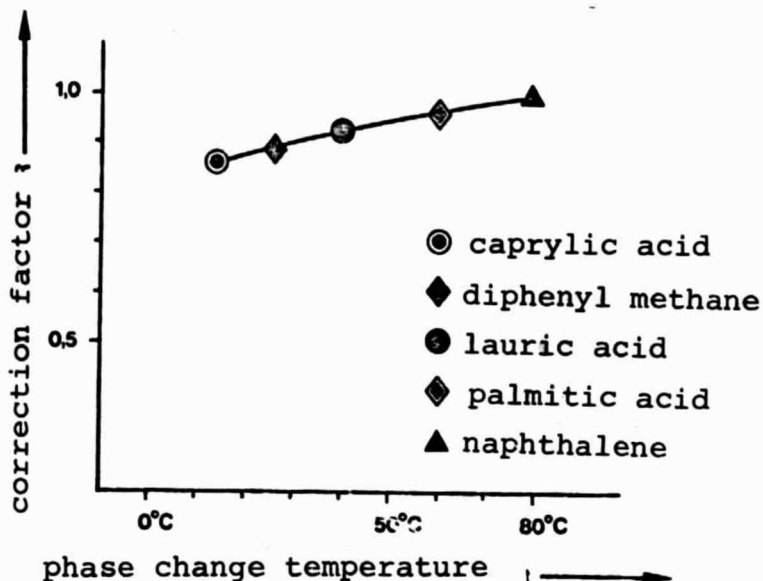


Figure 4: Calibration curve for hydrocarbon compounds

2.3.4 Error determination

Insofar as for the DTA measurements made the optimized test conditions were maintained exactly, the effect of the sample taken into account, and the temperature-dependent correction factor was used, it was possible to make a quantitative evaluation. The reproducibility of a measurement is first affected by the quality of the apparatus itself that was used and was determined by recording several phase change cycles of a single sample. For this we used naphthalene because it melts congruently and also suffers no material changes whatsoever during repeated melting. The results listed in table 3 show that for repeated measurements of identical samples only very minor deviations occurred. As a measure for the accuracy of the measurements we have listed the standard deviation s and the variance V .

Table 3 Repeat measurements of an identical sample

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material	measurement number	T_u °C	ΔH_u J/g	$\overline{\Delta H_u}$ J/g	s J/g	V %
	1	78.5	147.3			
naphthalene	2	78.5	146.9	147.0	± 0.7	± 0.5
57.16 mg	3	78.5	146.1			
	4	78.5	147.6			

As shown by the investigations, the relevant error in the determination of ΔH_u is not brought about by the test instrument, but rather by experimental effects. Here we consider as important factors differences in the attachment of the thermocouples, minor changes in position of the sample- and reference ampules in the test cell, and differing packing densities or different weighings of identical samples. To determine the measurement error we made test series for naphthalene and for sodium thiosulfate and determined the standard deviations and the variance V. The results listed in Table 4 show that for the two differing materials - hydrocarbon and salt hydrate - practically the same error of $\pm 4\%$ occurred; this shows that for this primarily experimental factors and not sample-related effects are controlling. Taking into account the listed problems in the determination of quantitative data it seems that the accuracy in the determination of ΔH_u is very satisfactory for the intended application. The deviations of the observed phase change temperatures T_u from the literature value lie for the case of the heating rate used of 5 K/min at ± 1 K.

However, the listed measurement errors apply only for measurements in which a uniquely evaluable signal results. For samples, which because of additional thermal effects produce multiple peaks

or in which different processes such as melting-, solution-, and decomposition processes superimpose, considerably larger errors for T_u and ΔH_u must be taken into account. In these cases separate statements are presented for the discussion of the particular test results.

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Table 4: Determination of the measurement error for the ΔH_u determination

material	weight mg	T_u °C	ΔH_u J/g	$\overline{\Delta H_u}$ J/g	s J/g	V %
naphthalene	58.57	78.0	152			
$C_{10}H_8$	56.01	78.5	141			
	58.83	78.5	149			
	60.07	78.5	153	147	± 6	± 4.2
	59.17	78.5	137			
	55.96	78.5	147			
	58.75	78.5	150			
$Na_2S_2O_3 \cdot 5 H_2O$	121.17	47.5	222			
	121.12	47.5	215			
	122.65	47.0	204	209	± 9	± 4.3
	120.48	47.5	200			
	122.05	47.5	214			
	120.95	47.5	201			

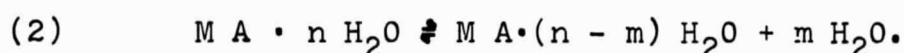
3. Testing of salt hydrates

3.1 The melting behavior as differentiation criterion

Salt hydrates are discrete phases in the system anhydride (water-free salt) and water. They are characterized by a unique

number of water molecules (coordination number) and form typically crystalline solid materials of type $MA \cdot n H_2O$. Here M generally represents a metal as cation and A a nonmetal or an oxo-group as anion.

During heating salt hydrates undergo at a characteristic temperature a transition into a water-poorer compound. Here there develop at least two new phases, a solid with an H_2O coordination number lower than the starting compound and a saturated salt solution. The phase conversion can be described by the following growth formulas:



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Such a phase change includes as characteristic quantity the phase change temperature T_u , the phase change enthalpy ΔH_u as well as knowledge of the phases present during equilibrium.

Since salts and salt hydrates are generally water soluble, there results above T_u not pure H_2O , but rather a part of the new phase $MA \cdot (m-n) H_2O$ is dissolved with the formation of a saturated solution in the separated H_2O molecules. The changes can now be classified into two limiting cases, depending on whether the formed salt dissolves completely because of high solubility or whether it is present, however, primarily as a solid because of low solubility. In the first case - complete solubility - there is formed after T_u is exceeded, only a single phase, a salt solution. This behavior corresponds macroscopically to the melting of a solid and is therefore also termed as a congruent melt. The second case - formation of a solid and a saturated solution - corresponds macroscopically to a partial melting and is therefore also called incongruent melting.

The real melting behavior can often not be described uniquely by these two limiting cases. The case where the formed solid because of a positive solubility is completely dissolved for temperature increases up to ca. $10^\circ C$ above T_u , has been called in this paper a nearly congruent melting.

3.2 Congruently melting salt hydrates

We also tested eight salt hydrates with congruent or nearly congruent melting behavior. The preparations used with their purity grade and the particular significant secondary components are listed in table 5. These are without exception laboratory chemicals with a purity grade, which is completely sufficient for the application case.

Table 5 Preparations used for the investigations

compound	preparation used	degree of purity wt. %	significant secondary component
$\text{KF} \cdot 4 \text{H}_2\text{O}$	from KF; Merck, pure	99	-
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	Fluka, purum	99	H_2O
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$	Merck, p.a.	99.5	-
$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	Merck, purest	97	H_2O
$\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$	Fluka, purum p.a.	98	H_2O
$\text{NaOH} \cdot \text{H}_2\text{O}$	from NaOH; Merck, p.a.	99	Na_2CO_3
$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	Merck, p.a.	98	BaCO_3
$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	Merck, purest	98	KCl, H_2O

The DTA test curves exhibit for the listed salt hydrates - except for $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ - qualitatively nearly identical shapes. They are characterized by a sharp conversion peak and by a practically horizontal base line. As an example we show in figure 5 the test curve of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$.

KF · 4 H₂O

In the system KF/H₂O the existence of two hydrates is assured, KF · 4 H₂O and KF · 2 H₂O [21]. According to Gawron and Schroeder [1] the tetrahydrate has a congruent melting point at 18.5° C with a heat conversion rate of 231 J/g. Our tests essentially confirmed the literature statements. With the DTA we determined for T_u a value of 16° C and for ΔH_u a value of 228 J/g. From cooling tests and in functional tests in a 10-1 storage with direct heat exchange we obtained for the phase change temperature a value of 18° C. The substance used underwent a reversible phase change with a pronounced tendency to subcooling.

CaCl₂ · 6 H₂O

The system CaCl₂/H₂O has been well investigated and has been proposed by several authors as possible storage medium [22,23,24]. Intensive investigations of the kinetics of the phase change and of the influence of additives on the reversibility of the phase change have been conducted by Wettermark and co-workers [25]. The preparation used by us exhibited a congruent melting behavior. For T_u we found in agreement with literature values 29.5° C. For the phase change enthalpy we determined 185 J/g. For this values between 170 J/g and 190.8 J/g were listed in the above-cited works.

Na₂S₂O₃ · 5 H₂O

Na₂S₂O₃ forms hydrates with 12, 10, 6, 5, 4, 3, 2, and 0.5 mols of H₂O. The pentahydrate, which exists in two modifications, is the only stable one and namely at temperatures below 48° C [26].

Na₂S₂O₃ · 5 H₂O was used by us as calibrating substance, whereby for ΔH_u we used the literature value of 209 J/g [5,6]. (Compare table 2 and figure 3).

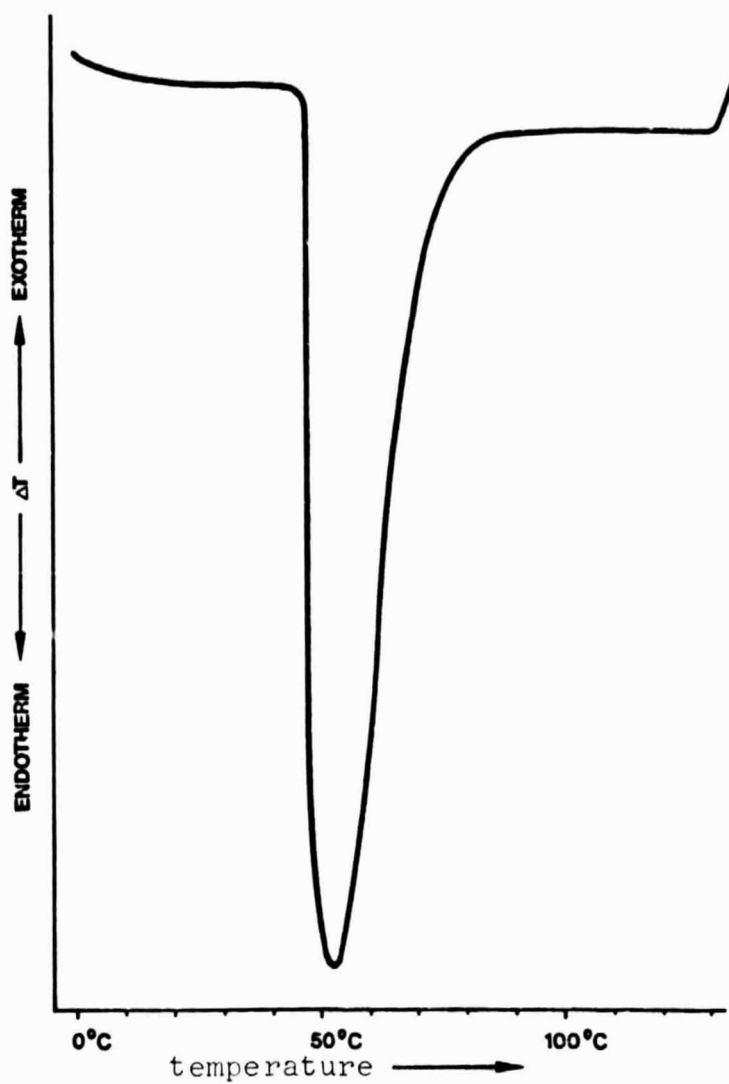
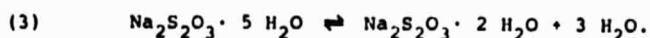


Figure 5 DTA test curve of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ as typical example for a nearly congruently melting salt hydrate

The preparation investigated showed in the range of the observed phase change ($T_u = 47.5^\circ \text{C}$, figure 5) first an incongruent melting behavior. For this the following reaction equation can be formulated:

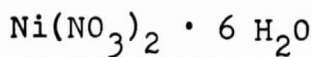


The share of the solid material in the melt is reduced significantly with increasing temperature, in the range from 55 to 60°C the melt was clear. For several phase change cycles the appearance of an opalescent clouding was observed. It suggests the formation of sulfur and seemed to confirm [27, 28] statements concerning the instability of an $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$. It is known that with the addition of acid to the thiosulfide solution sulfur is formed by disproportioning of the $\text{S}_2\text{O}_3^{2-}$ anion:



24

One must still check to see to what extent this reaction is also valid for $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ melt.



From solubility determination we proved for the system $\text{Ni}(\text{NO}_3)_2/\text{H}_2\text{O}$ in the temperature range from -34 to 120°C the existence of $\text{Ni}(\text{NO}_3)_2 \cdot 9 \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ [29, 30]. For the hexahydrate we found a congruent melting course with $T_u = 57^\circ \text{C}$. For ΔH_u the values between 151.6 and 168 J/g were reported [31, 32].

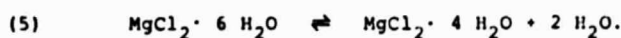
The preparation used for the thermal analytical investigations showed an incongruent phase change point at 53°C when cooling curves were made. The solid material ($\text{Ni}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$) existing in the melt showed a positive solubility with increasing temperature, so that at ca. 65°C a clear melt could be observed. From the

DTA-curve (figure 6) we could not determine T_u and ΔH_u exactly because a polymorphous phase change is preceding the melting process at 26°C and because the two endothermic effects could not be resolved satisfactorily for the prescribed test parameters. References to a phase change at 21 to 22°C can be found in the literature [33]. For the sum of the two phase changes we obtained the value of 186 J/g . For the heat of melting one can assume as a first approximation a value of 176 J/g .



Five different hydrates are known for the system $\text{MgCl}_2/\text{H}_2\text{O}$. The hexahydrate - $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ - separates from aqueous solutions between -3.4°C and 116.7°C upon concentrating [34]. The compound is very hygroscopic, for which reason commercial preparations include a small excess of water. For the melting point a value of 117°C is listed in the literature and for ΔH_u a value of 172.5 J/g [31].

For the preparation used for DTA measurements we observed a phase change temperature of 113°C . It applies for the formation of tetrahydrate: /25



Since upon heating to T_u a large loss of water occurred, melting tests and the recording of cooling curves were carried out in closed apparatuses. The melt was at first noticeably clouded, but upon heating to about 120 to 125°C the solid dissolved. For ΔH_u a value of 164 J/g was determined. /26

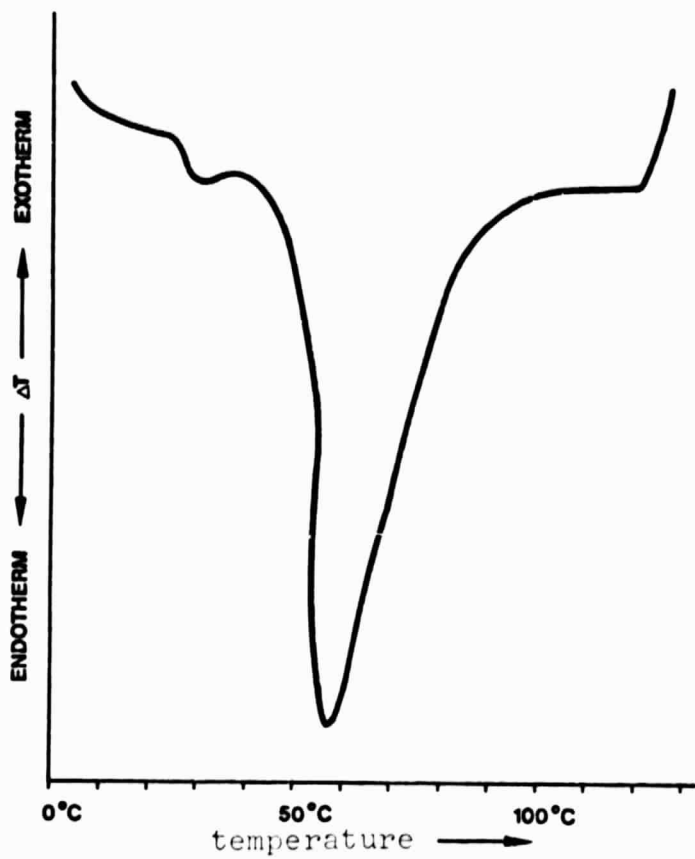


Figure 6 DTA test curve of $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$

The salt hydrates $\text{CH}_3\text{COOH Na} \cdot 3 \text{H}_2\text{O}$, $\text{NaOH} \cdot \text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$, because of their altogether positive thermal behavior, were also tested with varying compositions. The results obtained for the base compounds - the pure salt hydrates - will be described in detail in chapter 4. However, the values for T_u and ΔH_u are also listed in table 6. It presents a summary of the phase change temperatures T_u and phase change enthalpies ΔH_u determined for congruently or nearly congruently melting salt hydrates.

Table 6 T_u and ΔH_u for congruently or nearly congruently melting salt hydrates

salt hydrate	T_u °C	ΔH_u J/g
$\text{KF} \cdot 4 \text{H}_2\text{O}$	16	228
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	29.5	185
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$	47.5	209*
$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	53	(176)**
$\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$	58.5	260
$\text{NaOH} \cdot \text{H}_2\text{O}$	64	259
$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	78	301*
$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	113	164

* used as calibration material (compare chapter 2.3.3)

** approximation value because of preceding polymorphous phase change

3.3 Incongruently melting salt hydrates

Nine different salt hydrates with incongruently melting behavior were investigated. Since for $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ we investigated primarily the effect of additives, the pure $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ will be discussed in detail in chapter 4 where the results obtained for different mixtures are shown. Except for the technical-grade product $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$ we used laboratory chemicals with sufficient purity. The preparations used with their degree of purity and the significant secondary component are listed in Table 7.

/27

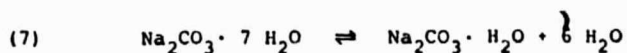
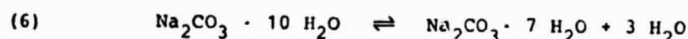
Table 7 Preparations used for the thermal analyses

compound	preparation used	degree of purity	significant secondary component
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	Merck, crystalline purest	99	-
$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$	Fluka, puriss. p.a.	99	-
$\text{Na}_2\text{HPC}_4 \cdot 12 \text{H}_2\text{O}$	Merck, crystalline purest	98	Na_2HPO_4
$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$	Merck, crystalline purest	97	H_2O
$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$	Merck, purest	99	-
$\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$	Van Bearle & Co., techn.	98	SiO_2
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$	Merck, p.a.	99	-
$\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$	Merck, purest	97	NaH_2PO_4
$\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$	Merck, p.a.	98	NaOH

The DTA-test curves of the first six compounds from Table 7 exhibit qualitatively a very similar shape. As an example we list in figure 7 the test curve of $\text{Na}_2\text{CO}_3 \cdot 5 \text{H}_2\text{O}$. The curves observed for $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$, and for $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ are shown during the discussion of the particular salt hydrate.

$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$

Sodium carbonate forms three stable hydrates with 10, with 7, and 1 mol of H_2O . The decahydrate $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ crystallizes below 32°C from saturated Na_2CO_3 solutions. The following transitions



28

proceed within a very narrow temperature interval ($T_{u1} = 32^\circ \text{C}$, $T_{u2} = 35.5^\circ \text{C}$ [35]) and were not recognized by many authors.

In agreement with literature values the preparation used by us showed a clearly incongruent melting behavior. Further heating up to 70°C brought about no increase in precipitation. The DTA measurements produced a value of 33°C for T_u .

Here this could be the case of the formation of the hexahydrate in accordance with equation 6. In the determination of ΔH_u the heat transfer of the total reaction was determined in accordance with equation 8:



29

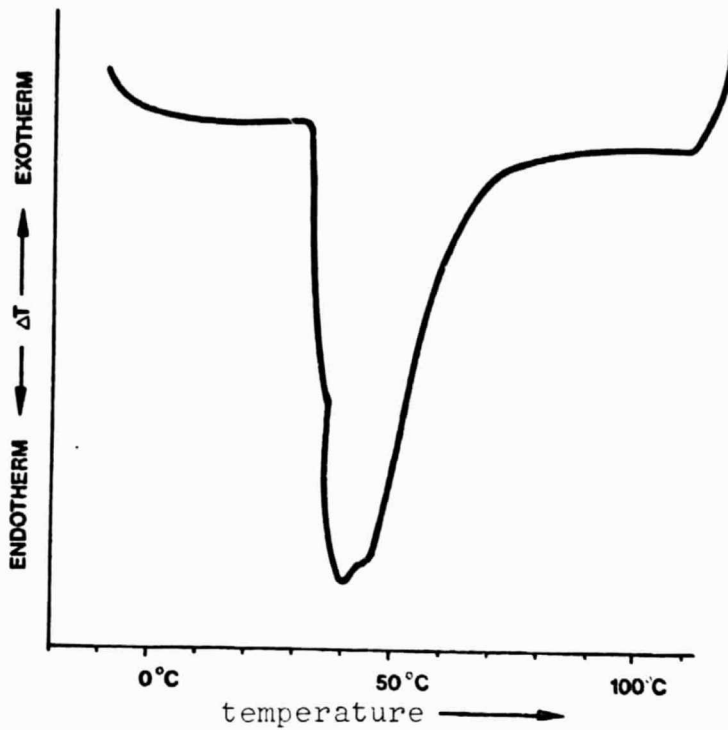


Figure 7 DTA test curve of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ as an example of a salt hydrate with incongruent melting.

With the aid of the DTA-test curve (figure 7) one can recognize the two-step process. For ΔH_u the value of 241 J/g was found. For this values of 251 J/g [4] and 247 J/g [32] are reported in the literature in connection with investigations of storage media.

$\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$

From solubility curves we obtain in the system $\text{Na}_2\text{HPO}_4/\text{H}_2\text{O}$ the existence of three stable hydrates: $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 7 \text{H}_2\text{O}$, and $\text{Na}_2\text{HPO}_4 \cdot 2 \text{H}_2\text{O}$ [36]. The phase change according to equation 9

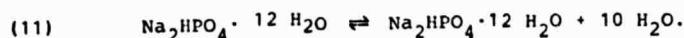


proceeds at 35.4° C and the phase change according to equation 10



proceeds at 48.4° C [36]. The older literature lists for ΔH_u an experimentally determined value of 279.7 J/g and a calculated value of 246 J/g [26]. In conjunction with investigations of storage media values of 265 J/g [6] and 280 J/g [22] are reported. Apparently the listed values apply for the sum of the two partial reactions, since in a subsequent paper [8] a value of 138 J/g was determined for the phase change of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ according to equation 9 and a value of 126 J/g for the phase change of the $\text{Na}_2\text{HPO}_4 \cdot 7 \text{H}_2\text{O}$ according to equation 7.

The preparation used for the thermal analyses exhibited a distinctly incongruent melting behavior. The share of the precipitation decreased noticeably only above 60° C. From cooling tests we observed in agreement with the literature values two stopping points at 46° C and at 35° C. The DTA measurement (fig. 8) /30 carried out under standard conditions gave for T_u a value of 35° C. From the test curve one can recognize the two-step process. For ΔH_u a value of 255 J/g was determined. However, it applies for the total reaction according to equation 11:



An analysis of the test curve is possible in part (fig. 9) /31 for a very low heating rate (0.5 K/min). However, it permits no quantitative evaluation of the two partial reactions. From the shape of the curve in figure 7 one can see that the larger thermal effect is provided by the phase change in accordance with equation 9. The following second step is noticeably smaller which, however, can also be explained by partial solubility of the $\text{Na}_2\text{HPO}_4 \cdot 7 \text{H}_2\text{O}$ formed.

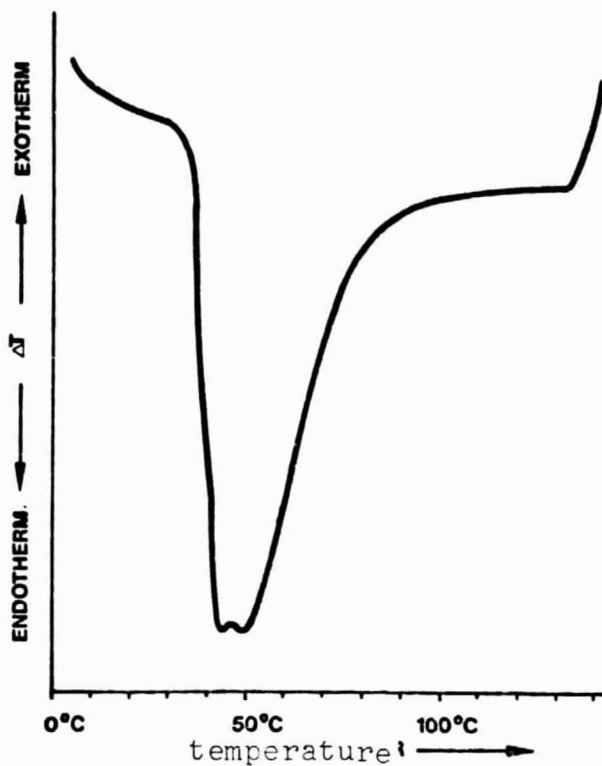


Figure 8: DTA test curve of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ under standard conditions

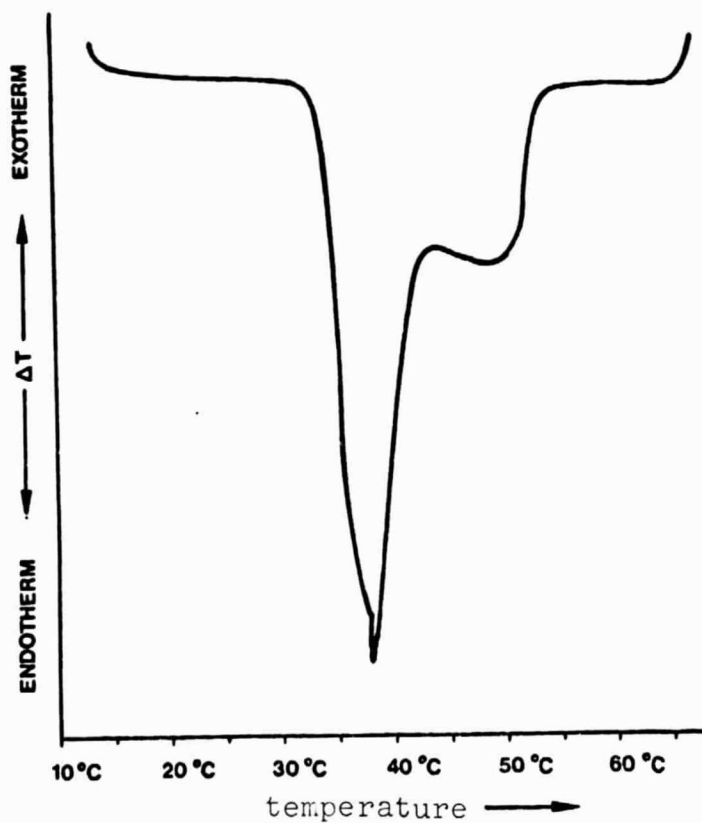


Figure 9: DTA test curve of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$, recorded with a heating rate of 0.5 K/min.

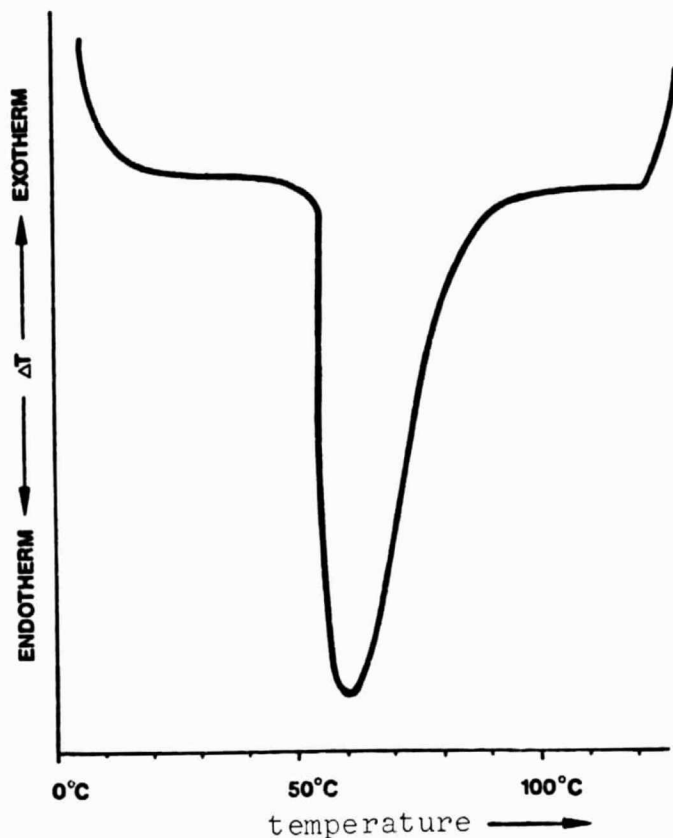
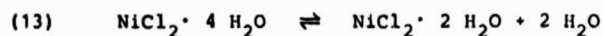


Figure 10: DTA test curve of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$

$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$

From solubility investigations we proved [37, 38] in the system $\text{NiCl}_2/\text{H}_2\text{O}$ above room temperature the existence of the three hydrates $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$, and $\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$. In the low temperature range (below -35°C) we suspect beyond this existence of $\text{NiCl}_2 \cdot 7 \text{H}_2\text{O}$ [37]. Contradictory statements concerning the possible phase changes can be found in part in the literature. Here the transition of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ into the dihydrate is assumed to take place in two reactions (equations 12 and 13),



as well as also in a direct conversion [39]:



As phase change temperatures the value of 29°C was assumed for the first step in accordance with equation 12 and a value of 64°C for the second stage according to equation 13.

The thermal analyses with $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ provided only a single phase change with $T_u = 55^\circ \text{C}$. Based on the test curve (figure 10) one can practically eliminate a two-step process, such as was recognized for $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ (compare figure 7) and for $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ (compare figure 8), since in the test range below T_u (5°C to 50°C) a nearly ideal base line curve exists. For ΔH_u a value of 161 J/g was determined. Thus this value is noticeably smaller than the value of 210 J/g [8] theoretically derived in the more recent literature for the transition hexahydrate/dihydrate.

$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$

The monohydrate $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ exists in the system $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ in the region of high acid- and salt concentrations as a solid phase [40]. Above 60°C it no longer appears. The phase change point is observed [41] at 58.5°C .

The preparation used by us exhibited in melting tests a distinctly incongruent behavior. When cooling curves were made, the stopping point was observed at 58°C . A solubility of the precipitate in the melt did practically not occur for increases in temperature. There exists a parallel to $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. On the thermal analyses we obtained a phase change temperature of 62.5°C , and for the phase change enthalpy there resulted the value of 138 J/g, relatively low for salt hydrates.

/34

Na₂SiO₃ · 5 H₂O

Contradictory values can be found in the literature with respect to the formation of hydrates of the general composition Na₂SiO₃ · nH₂O (or Na₂O · SiO₂ · nH₂O). Unique results are available for the compounds Na₂SiO₃ · nH₂O, Na₂SiO₃ · 6 H₂O, and Na₂SiO₃ · 5 H₂O [42, 43]. The values T_u = 48° C and ΔH_u = 168 J/g (calculated) reported by Furbo and Svendsen [32] during investigations of storage media for Na₂SiO₃ · 5 H₂O must be assigned, based on literature statements [42] and our own test results, to the compound Na₂SiO₃ · 9 H₂O.

The preparation used by us for our thermal analyses showed a clearly pronounced incongruent melting behavior. Cooling tests showed that the pure hydrate does not solidify as crystals, but rather as a gel. An excess of NaOH proved to be positive with respect to crystal formation, but brought about that a unique stopping point no longer occurred. Evaluation of the DTA test curve produced a phase change temperature of 71° C and a phase change enthalpy of 241 J/g. The literature values for Na₂SiO₃ · 5 H₂O agree very well with regard to T_u (72.2° C [44]); however, for ΔH_u a calculated value of 149 J/g is reported [43]. According to our knowledge experimental values for ΔH_u do not exist.

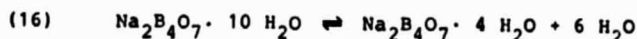
Na₂B₄O₇ · 10 H₂O

Na₂B₄O₇ · 10 H₂O exists in the system Na₂O/B₂O₃/H₂O and in its cut Na₂B₄O₇/H₂O below 60° C as a stable phase. Numerous contradictory statements [26] can be found in the literature concerning the existence of additional hydrates of the type Na₂B₄O₇ · nH₂O and concerning their thermal behavior. Five crystalline and two amorphous hydrates are named, whose existence ranges and phase transitions are not uniquely clarified.

In agreement a phase change is described in the range of 60° C /35 which, however, is interpreted differently. Customarily equation 15 is used here for the reaction:



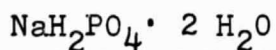
However, there also exist reports according to which the formation of the pentahydrate according to equation 15 is to be considered as a metastable phase change and according to which $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$ is to be considered as thermodynamically stable phase. However, this phase change according to equation 16:



is inhibited kinetically and is therefore often not observed. Which of the two reactions now takes place, is said to depend on the condition of the preparation used and on the test conditions [26].

The thermal investigations conducted by us showed for $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ a very strong incongruent melting behavior. When cooling curves were made, no unique stopping point was found, which points to the fact that the hydrate does not crystallize reversibly. Similar observations were also made by other authors [8].

The DTA measurements (figure 11) produced two endothermic effects. The sharp peak at 65° C corresponds to the phase change of the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ under formation of the penta- or tetrahydrate according to equations 15 and 16. For ΔH_u a value of 190 J/g was determined, but only as an approximation, since the two thermal effects could not be separately exactly. The second, weaker peak above 100° C corresponds to an additional phase change with the formation of $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$. However, there could be superpositions of solution processes.



In the range from - 10° C to 100° C there exists in the system

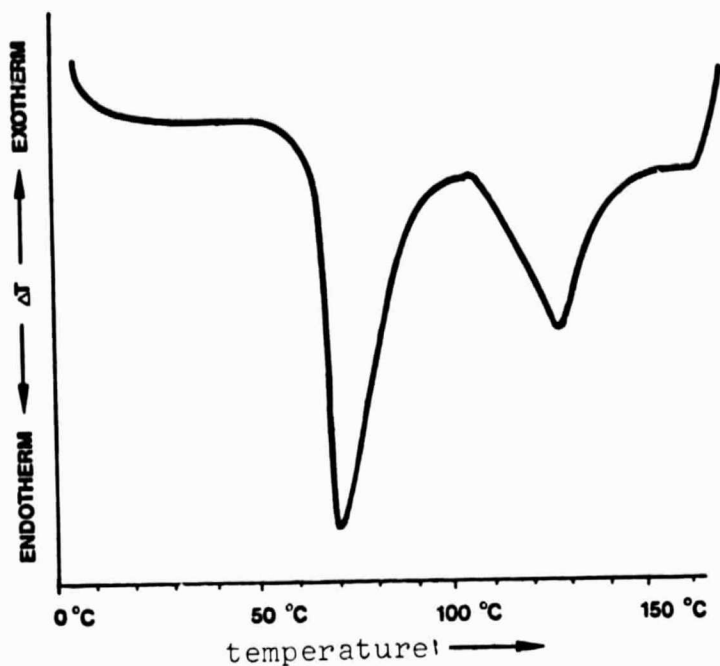
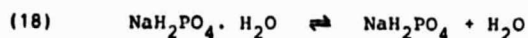


Figure 11: DTA test curve of $\text{NaB}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$

$\text{NaH}_2\text{PO}_4/\text{H}_2\text{O}$ the dihydrate $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$, the monohydrate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and the anhydride NaH_2PO_4 . For the first phase change step in accordance with equation 17 /36



the literature [26] lists values between 41°C and 50°C depending on the methods used for the determination. For the second step in accordance with equation 18



a value of 60°C is predominantly listed as phase change temperature.

The preparation used by us for the melting tests exhibited a pronounced incongruent behavior. Even upon heating to ca. 80°C there still existed a large proportion of solid material. Literature statements also agree with these observations whereby in a mixture, corresponding to the composition of the dihydrates, at 80°C about 30 weight % of the existing NaH_2PO_4 is still undissolved. From the cooling curves we obtain two stopping points at about 65°C and at 47°C . /37

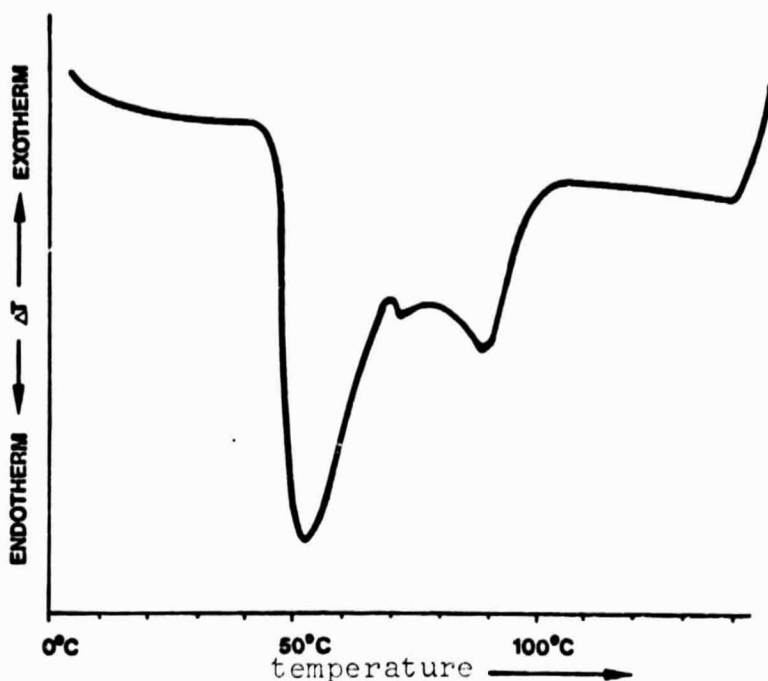
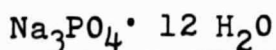


Figure 12: DTA test curve of $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$

The DTA test curve (figure 12) shows no unique shape. There appear altogether three maxima whereby the first, pronounced endothermic effect can unequivocally be assigned to the phase change corresponding to equation 17. For the phase change temperature a value of 47°C was determined. The two additional peaks with their maxima at about 70°C and 90°C can be explained by the formation of NaH_2PO_4 (equation 18) as well as by the subsequent solution process. This is contradicted, however, by the fact that exactly the third peak is unusually sharp for a solution process. For the entire endothermic test effect we determined a heat transfer of 190 J/g . A more exact value for the phase change at 47°C cannot be given.

38



Between 0°C and 100°C there appear in the system $\text{Na}_2\text{O}/\text{P}_2\text{O}_5/\text{H}_2\text{O}$ at normal pressure tertiary, secondary, and primary orthophosphates

as solids; furthermore also some phosphates which can be considered to be double salts. In the range of high Na_2O -concentrations there exist primarily hydrates of the tertiary phosphates [45, 46]. As stable compounds we found hydrates in agreement with the coordination number 12, 8, 6, and 0.5.

From the literature statements it can be seen that one must differentiate between triphosphates of stoichiometric composition with the mol ratio $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ of 3:1 (in the following text called orthophosphate $\text{o-Na}_3\text{PO}_4$) and NaOH-containing triphosphates (in the following text called pseudo-tertiary phosphate $\psi\text{-Na}_3\text{PO}_4$) [45].

Contradictory statements can be found in the literature concerning the possible phase changes. It can be assumed with certainty that from an aqueous solution a ψ -phosphate of composition $\psi\text{-Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O} \cdot 0.25 \text{NaOH}$ is crystallized [45]. According to Bell [46] there results for this at 70 to 74° C the phase change into the $\text{o-Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$; Menzel [45] observed at 69 to 71° C the formation of $\text{o-Na}_3\text{PO}_4 \cdot 6 \text{H}_2\text{O}$. Furthermore Bell describes at 86° C the phase change of the octahydrate to the $\text{o-Na}_3\text{PO}_4 \cdot 6 \text{H}_2\text{O}$.

In more recent works, which treat the media development, statements were made concerning the phase change heats. However, the publications do not allow any differentiation between ortho- and pseudophosphates, and no values are given for the conversion reactions or the water-poorer phases formed. The values for T_u lie in the range from 65 to 70° C [6, 8, 32]. For ΔH_u values of 190.7 J/g [6], 221 J/g [8], and 168 J/g [32] are listed. /39

The preparation used for the thermoanalyses must be classified based on the composition (compare table 7) as $\psi\text{-Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O} \cdot 0.25 \text{NaOH}$. A pronounced stopping point was found at 74° C for cooling curves. For mixtures with differing proportions of NaOH and H_2O the stopping point varied in the range of 70° C, as long as the NaOH content did not exceed 5 weight %. /40

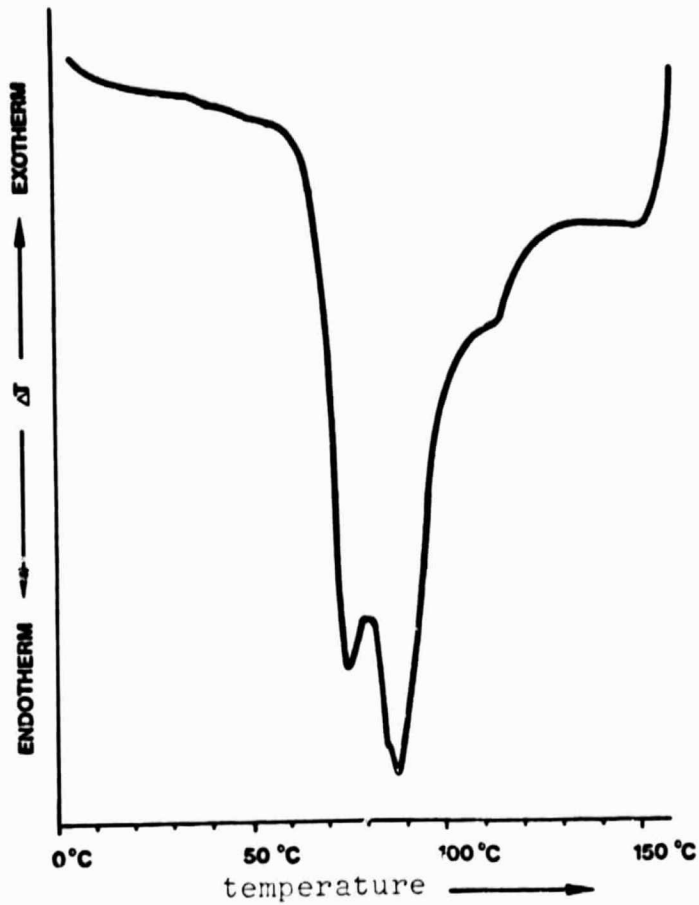
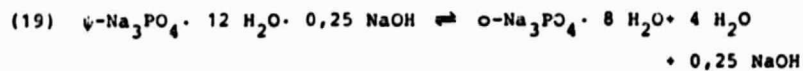


Figure 13: DTA test curve of $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$

The DTA test curve (figure 13) shows an endothermic peak with two pronounced maxima. According to literature statements they can be explained by two phase change reactions, which can be described by equations 19 and 20:



For the reaction according to equation 19 there results for the phase change temperature a value of 69° C. The second phase change temperature cannot be determined exactly because the two thermal effects in the test curve were not resolved. The value for T_u could lie near about 80° C. However, a temperature lowering could be brought about the excess water (compare equation 19). For the total reaction with formation of the $o\text{-Na}_3\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ a phase change enthalpy of 242 J/g was found.

A summary of the results obtained from the thermal analyses of incongruently melting salt hydrates is shown in table 8. The table lists in addition to the phase change temperature T_u and the phase change enthalpy ΔH_u also the water-poorer reaction product newly formed during the phase change.

Table 8: T_u and ΔH_u for incongruently melting salt hydrates

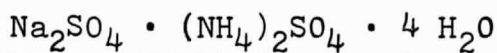
salt hydrate	T_u $^{\circ}\text{C}$	reaction product	ΔH_u J/g
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	32.5	Na_2SO_4	251
$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$	33*	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	241
$\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$	35*	$\text{Na}_2\text{HPO}_4 \cdot 2 \text{H}_2\text{O}$	255
$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$	55	$\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$	161
$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$	62.5	NaHSO_4	138
$\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$	71	not defined	241
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$	65	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5 \text{H}_2\text{O}^{**}$	(190)
$\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$	47	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	not determined
$\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$	69*	$o\text{-Na}_3\text{PO}_4 \cdot 6 \text{H}_2\text{O}$	242

* Applies for first partial reaction. For this the reaction product is not listed.

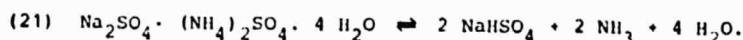
** not certified.

3.4 Double salt and eutectics

For the thermal analyses we used three double salts and four eutectics. The double salts themselves represent hydrates, and the eutectics are formed from salt hydrates as starting compounds. The only exception is the eutectic NaBr/(NH₂)₂CO, which was chosen as an example of a system consisting of salt (NaBr) and hydrocarbon compound ((NH₂)₂CO, urea). The test results for the eutectic MgCl₂ · 6 H₂O/Mg(NO₃)₂ · 6 H₂O are listed in chapter 4 during the representation of the results obtained for mixtures with an excess of water.



In the system Na₂SO₄/(NH₄)₂SO₄/H₂O there appear as solids in addition to the pure starting compounds additionally Na₂SO₄ · 10 H₂O and as double salt Na₂SO₄ · (NH₄)₂ · 4 H₂O. In nature it occurs as the mineral lecontite, from an aqueous solution it can be produced under defined conditions [47]. The double salt is stable in air at room temperature; however, upon heating NH₃ is generated from about 60° C, which with increasing temperature (ca. 100° C) increases noticeably. As final product NaHSO₄ is found [47]. The decomposition reaction can be described by equation 21:



The formation of an anhydride with the composition Na₂SO₄ · (NH₄)₂SO₄ in the range from 50° C to 70° C is reported, but exact thermal and calorimic data are not presented [48]. According to Ricci [49] the double salt melts incongruently at 59.3° C with the formation of a saturated solution and Na₂SO₄ and (NH₄)₂SO₄ as precipitate.

For the production of Na₂SO₄ · (NH₄)₂SO₄ · 4 H₂O 11.36 g of Na₂SO₄ (0.08 mol) and 10.57 g (NH₄)₂SO₄ (0.08 mol) were dissolved in 500 ml of water and concentrated in air at 40° C to 100 ml. Upon

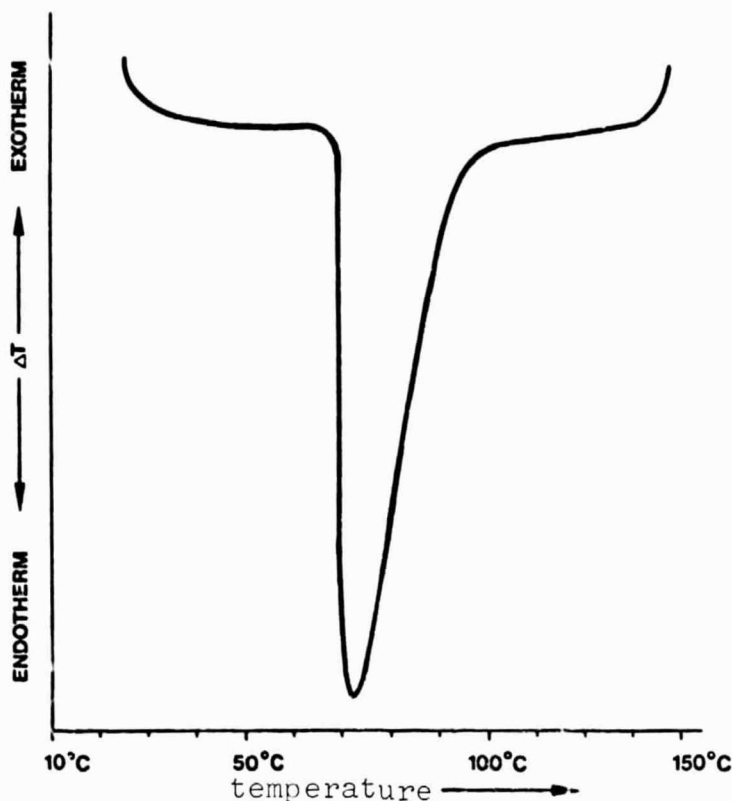
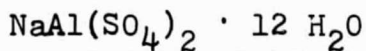


Figure 14: DTA test curve of $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4 \text{H}_2\text{O}$

further concentration at 30° C colorless rod-shaped crystals were formed which were sucked off and dried in air.

The DTA measurements (figure 14) produced a sharp endothermic signal which shows that the substance is very pure and possesses a discrete phase change point. In contrast with literature values a value of 69° C was determined for T_u . ΔH_u was found to be 140 J/g. In the conduct of phase change cycles the DTA test cell behavior typical of incongruently melting salt hydrates was observed, a lowering of the phase change temperature and the phase change enthalpy.



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Alums are double salts containing water of crystallization of the general formula $M^{1+} M^{3+} (A^{2-})_2 \cdot 12 H_2O$. The most common alums are those with aluminum as three-valent metal (M^{3+}) and with sulfate ions as anions (A^{2-}), so that the composition can generally be given by the gross formula $M^+Al(SO_4)_2 \cdot 12 H_2O$. The most well known and technologically most significant ones are the potassium alum and the ammonium alum. The sodium alum $Na Al(SO_4)_2 \cdot 12 H_2O$ has attained no great technological importance since it presents problems during its production and additionally has a pronounced trend toward weathering [50].

/44

Concerning the thermal behavior of the sodium alum one can find contradictory statements in the literature. For the melting point values between 61 and 63° C are listed. However, it is also described that sodium alum undergoes no changes whatsoever at 66° C [51]. The literature also mentions the existence of a hexahydrate and a tetrahydrate, but without many more details. The preparation used for the thermal investigations was prepared from equimolar solutions of Na_2SO_4 and $Al_2(SO_4)_3$. Upon concentration at 40° C there is first formed an amorphous product. After additional standing above 35° C there follows the formation of colorless crystals, which were sucked off and washed with a little alcohol to separate the mother lye.

During the production of cooling curves a noticeably incongruent melting was observed in the range from 65 to 70° C. There still existed a considerable proportion of solid material and a stopping point occurred only if melt and precipitate were well mixed with one another. The DTA test curve (figure 15) exhibits two endothermic effects, whereby the first sharp peak must be assigned to the incongruent melting of the sodium alum. For T_u a value of 67° C is obtained. The second effect, starting at about 110° C, cannot be interpreted exactly. However, it seems that during the phase change

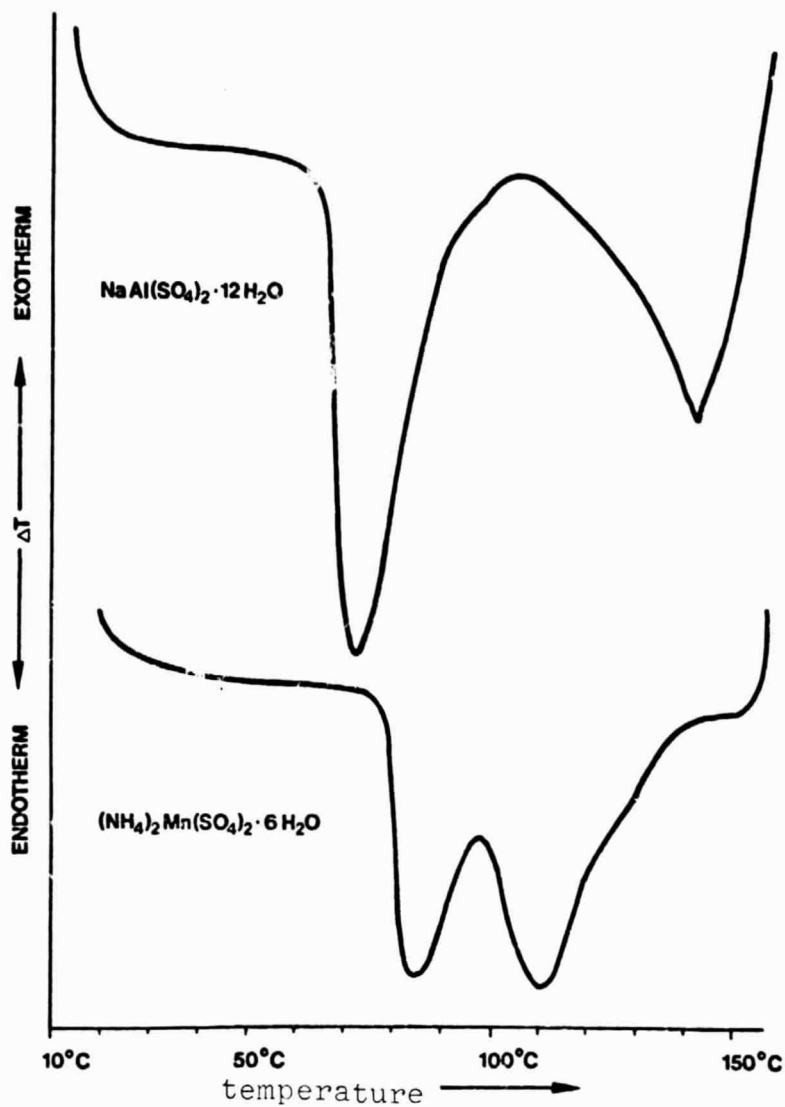


Figure 15: DTA test curves of the double salts $\text{NaAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$

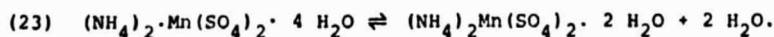
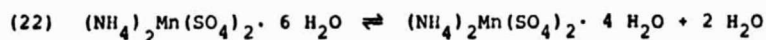
at 67°C a water-poorer hydrate is formed which then is converted at higher temperatures into the anhydride. However, solution processes must also be considered. Since the two test signals are not completely separated, only an approximation value is obtained for ΔH_u of 160 J/g.

From solubility polytherms in addition to three different manganese sulfate hydrates and ammonium sulfites two double salts were also found as a stable phase [52] in the system $(\text{NH}_4)_2\text{SO}_4/\text{MnSO}_4$. The production of the here interesting double salts $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ succeeds only by the evaporation of equimolar solutions of the starting components [53] or by the reaction of finely powdered manganese with an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [54].

Statements contradicting one another exist concerning the thermal behavior of the double salt. Kohler and Franke [53] list an incongruent melting point at 59°C ; older statements report concerning a phase change in the range from 63 to 70°C [55]. During the isobaric decomposition of the hexahydrate $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 2 \text{H}_2\text{O}$ [53] were found as stable phases.

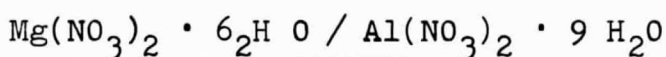
To produce $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ 6.61 g $(\text{NH}_4)_2\text{SO}_4$ (0.05 mol) and 11.15 g $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ (0.05 mol) were dissolved in 50 ml of water. The solution cooled off noticeably with the addition of the salts, upon heating to 30°C brownish flakes appeared to a small degree. The solution was filtered and slowly concentrated at room temperature, whereby transparent crystals were formed.

During the investigations it was found that upon heating in an open apparatus the double salt sintered together with the loss of water. In a closed glass vessel pronounced incongruent melting was observed. The DTA test curve (figure 15) exhibits clearly two endothermic effects which, however, are resolved only with respect to their maxima. The first peak could result from the phase change of the double salt into a water-poorer hydrate whereby the appearance of two stages of the following reaction course can be assumed:



For the phase change according to equation 22 there results a phase change temperature of 74° C. The second reaction according to equation 23 could proceed in the range from 90 to 100° C. For the phase change enthalpy of the total reaction an approximation value of 200 J/g was determined.

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In the system $\text{Mg}(\text{NO}_3)_2 / \text{Al}(\text{NO}_3)_3 / \text{H}_2\text{O}$ there exists a eutectic which is composed of 53 weight % magnesium nitrate hexahydrate and of 47 weight % aluminum nitrate nonahydrate. According to literature statements it melts at 61° C, for ΔH_u a value of 148 J/g is listed [22].

To produce the eutectic the starting components are powdered finely and mixed according to directions. During the recording of cooling curves the appearance of the first crystals is observed at 70° C. The stopping point was indicated only weakly which points to the fact that the latent heat is small. Eutectic mixtures with a small excess of water no longer showed a stopping point, but rather only a kink in the cooling curve at about 65° C.

The DTA test curve (figure 16) shows the expected curve shape. For the phase change temperature T_u there results the value of 66° C, ΔH_u was found to be 171 J/g. During the conduct of cyclic tests in the DTA test cell it was found that during the course of six cycles a lowering of the melting point of about 60° C took place. This observation is unusual for congruently melting systems and is possibly caused by separation processes.

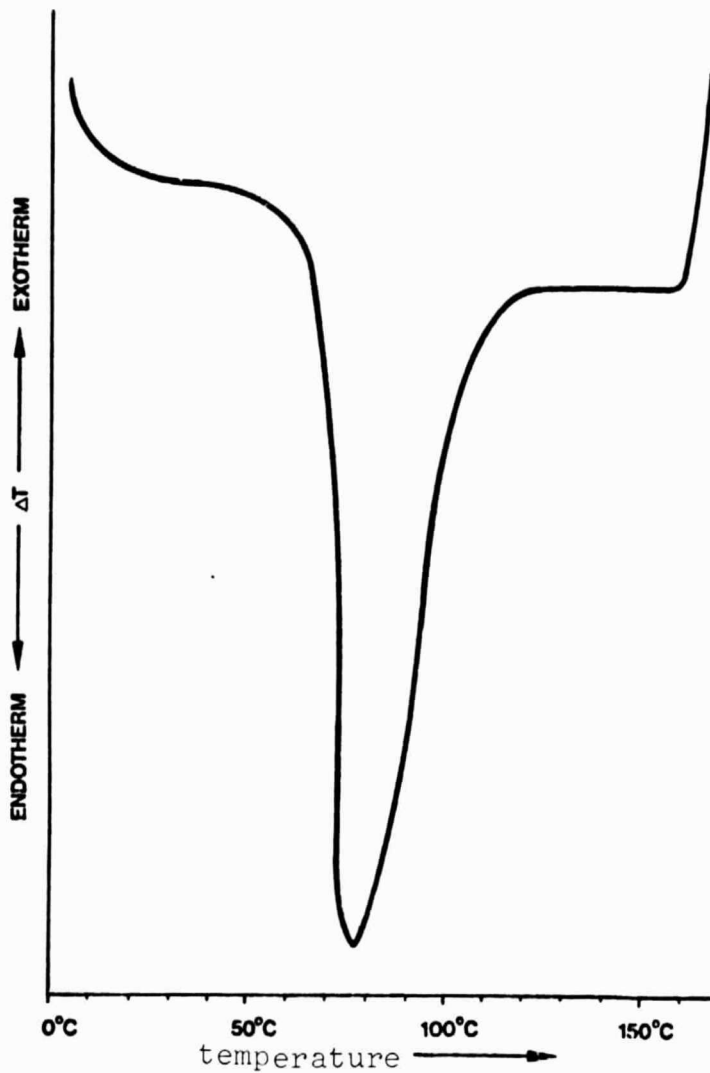


Figure 16: DTA test curve of the eutectic $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O} / \text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$

Mn(NO₃)₂ · 6 H₂O / Mg(NO₃)₂ · 6 H₂O

A Soviet report is available for the system Mn(NO₃)₂ · 6 H₂O / Mg(NO₃)₂ · 6 H₂O, which is reproduced in summary in Gmelin [56]. From the state diagram of the system one can derive the existence of two eutectics and a double salt. The eutectic of interest here is composed of 35 mol % (37.6 weight %) of manganese nitrate hexahydrate and 65 mol % (62.4 weight %) of magnesium nitrate hexahydrate. It has a melting point of 41° C; the heat of melting was not reported. /49

For the thermal analyses we used a preparation which was produced from the starting compounds Mn(NO₃)₂ · 4 H₂O and Mg(NO₃)₂ · 6 H₂O. The DTA test curve of the eutectic mixture shows a very complicated curve shape. It has three maxima which cannot be interpreted based on literature statements. The three thermal effects can be assigned temperatures of about 27° C, 36° C, and ca. 52° C. Additional investigations are necessary to explain the thermal behavior. One must also explain the effect of HNO₃, since in the starting compounds - primarily in Mn(NO₃)₂ · 4 H₂O - nitric acid could be proven to exist. A value of 163 J/g was found for the entire thermal effect.

NaBr / (NH₂)₂CO

As an example for a system consisting of a salt-like compound and a hydrocarbon compound we selected the eutectic NaBr/(NH₂)₂CO. The literature gives for the eutectic mixture a composition of 20.5 mol % sodium bromide and 79.5 mol % urea - (NH₂)₂CO. The melting point is determined [57, 58] from cooling curves at 66° C.

The preparation used for the thermal analyses was produced from sodium bromide and urea in accordance with literature statements. The DTA test curve (figure 17) exhibits a greatly broadened endothermic peak. The broadening is unusual for a eutectic and points to the fact that the composition listed in the literature does not give exactly the eutectic mixture. For T_u a value of 70° C,

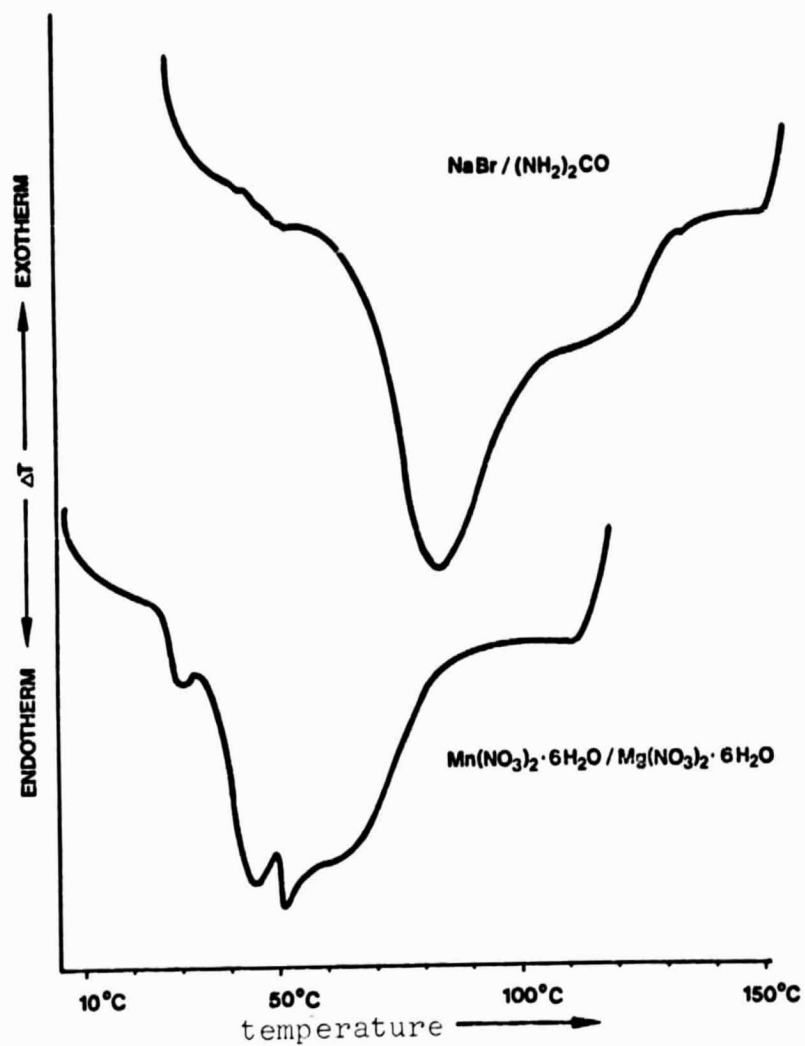


Figure 17: DTA test curve of the eutectics $\text{NaBr} / (\text{NH}_2)_2\text{CO}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

for ΔH_u a value of 139 J/g was determined. In the conduct of cyclic tests in the DTA test cell it was shown that the eutectic crystallizes reversibly and that during cooling reconversion takes place in the range from 49 to 52° C.

Table 9 gives a summary of the results obtained for the double salts and eutectics investigated.

For completeness the results determined for the pure $MgCl_2 \cdot 6 H_2O$ / $Mg(NO_3)_2 \cdot 6 H_2O$ (compare chapter 4.3) are also listed in addition to the eutectics described in detail.

Table 9: T_u and ΔH_u for double salts and eutectics

compound	T_u °C	ΔH_u J/g
$Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4 H_2O$	69	140
$NaAl(SO_4)_2 \cdot 12 H_2O$	67	160*
$(NH_4)_2Mn(SO_4)_2 \cdot 6 H_2O$	74	200
$Mg(NO_3)_2 \cdot 6 H_2O$ / $Al(NO_3)_3 \cdot 9 H_2O$	66	171
$Mn(NO_3)_2 \cdot 6 H_2O$ / $Mg(NO_3)_2 \cdot 6 H_2O$	36*	163*
$NaBr$ / $(NH_2)_2CO$	70	139
$MgCl_2 \cdot 6 H_2O$ / $Mg(NO_3)_2 \cdot 6 H_2O$	58	146

* approximation value

4. Investigations of multi-material systems with salt hydrates as base components

4.1 General

A keypoint of the thermal analyses consisted of the need to obtain quantitative information concerning the effect of additions - generally water, acids and alkali compounds - on the phase change enthalpy of salt hydrates. One must start with the fact that such additives - primarily H_2O - are not present as inert additions in addition to the pure starting components, but rather that they have a direct effect on the hydrate; naturally this effect results primarily from solution processes, but also by complex formation, hydroxide precipitation, or byproduct formation.

For the quantitative determination we measured and evaluated, /52 because of the subcooling tendencies of the salt hydrates, principally the heating process in the DTA. The phase change is affected substantially particularly during heating by a superposition of solution processes, so that the phase change temperature is displaced to lower temperatures. The effect of H_2O as a second component can be seen in figure 18. It represents a repeat of the DTA test curves for pure sodium acetate trihydrate and for mixtures with 5% and 10% of water. A comparison of the curves shows clearly the shift of T_u as well as a decrease in the peak areas - and thus of ΔH_u . From the shape of the base lines of the two water-containing mixtures one can clearly recognize that a solution process has preceded the phase change. After the phase change the base lines exhibit in all three cases a horizontal, i.e., ideal shape.

The phase change temperatures obtained from the thermal analyses by means of DTA do not necessarily agree with the crystallization temperatures occurring during the cooling processes for the case of water-containing mixtures. They must be determined separately by the recording of cooling curves or by measurements in storage installations.

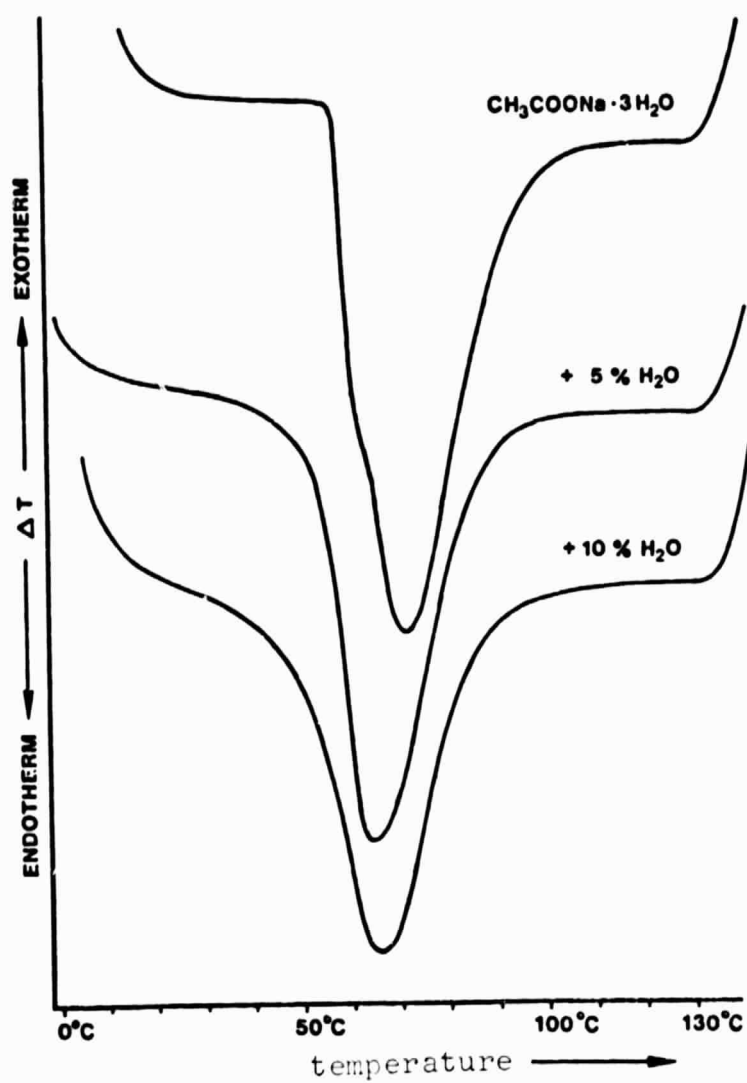
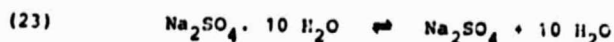


Figure 18: DTA test curve of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ as well as of mixtures with 5% H_2O and with 10% H_2O

4.2 Systems with $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ as base component

In addition to the stable decahydrate (Glauber salt) a metastable heptahydrate $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is also known for the system $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$. $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ was thoroughly investigated and proposed by numerous authors as storage medium [4,5,6,7,8]. The phase change at 32.38°C in accordance with equation 23:



was determined with highest accuracy as a fixed temperature point. For the phase change enthalpy ΔH_u a value of 251 J/g [4,5,6] was listed in the more recent literature. Because of the incongruent melting behavior of the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ (equation 23) and the thus connected problems to achieve a reversible phase change, an Na_2SO_4 solution saturated at 32°C was also used as an alternate storage medium [32, 59, 60].

/54

For the thermal analyses extremely pure crystalline $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ (compare table 7) was used as starting product. Different mixtures with H_2O , with H_2O and H_2SO_4 as well as with H_2O and NaOH were measured quantitatively. The results are listed in table 10 which also contains the standard deviation for ΔH_u .

$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ dissolves partially in H_2O so that in mixtures with an H_2O excess the phase change is superimposed with a solution process. As a result different values are obtained for T_u which depend on whether the phase change was determined during the heating process, e.g. in the DTA test cell - T_u (DTA) - or during the cooling process, e.g. by a recording of cooling curves - T_u (cooling tests). Both values of T_u are important for the practical use of such mixtures as storage medium, since both temperatures provide a guide value for the temperature range, in which a real storage unit will operate. A comparison of the values of selected mixtures determined for the heating process - T_u (DTA) - and for

/55

Table 10 Results for various mixtures with $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
as base component

composition weight %		T_u $^{\circ}\text{C}$	ΔH_u J/g
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O		
100	-	32.5	251 ± 11
94.7	5.3	32	237 ± 10
90.4	9.6	32	214 ± 11
84.9	15.1	29	199 ± 12
79.9	20.1	27	178 ± 12
75.1	24.9	24	159 ± 11
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O		
	H_2SO_4		
88.8	10.1	1.1	31
78.8	20.1	1.1	26
74.1	24.9	1.0	24
76.7	19.4	3.9	23
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O		
	NaOH		
74.5	24.5	1.0	24

the cooling process - T_u (cooling test) - is given in table 11.

The decrease of the phase change enthalpy of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ in mixtures with increasing H_2O content is shown in figure 19. Within the range shown one can observe the linear decrease. For comparison a second straight line is also possible which is obtained by calculation and with the assumption that $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ is not water soluble. In this case H_2O can be considered to be an inert secondary component, and the phase change enthalpy of the mixture is

Table 11: Comparison of T_u (DTA) and T_u (cooling test)

composition weight %			T_u (DTA) °C	T_u (cooling test) °C
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O			
90	10		32	32.6
75	25		24	31.5
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O	H_2SO_4		
89	10	1	31	32.1
74	25	1	24	31.8
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	H_2O	NaOH		
74	25	1	24	31.8

obtained from the particular $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ portion. The difference between the two straight lines shows clearly that during estimates concerning storage capacities the solution effect of the salt must absolutely be taken into account if the storage media are composed of salt hydrate and water.

4.3 Systems with $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ / $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ as base components /56

The system $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ / $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ exhibits miscibility over the entire phase range. For a composition of 47 mol % (41.3 weight %) $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and 53 mol % (58.7 weight %) $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ a eutectic is present according to the investigations by Yoneda and Takanashi [61]. The authors list a melting point of 59.1°C ; for the phase change enthalpy ΔH_u an experimentally determined value of 147 J/g and a calculated value of 145 J/g are listed.

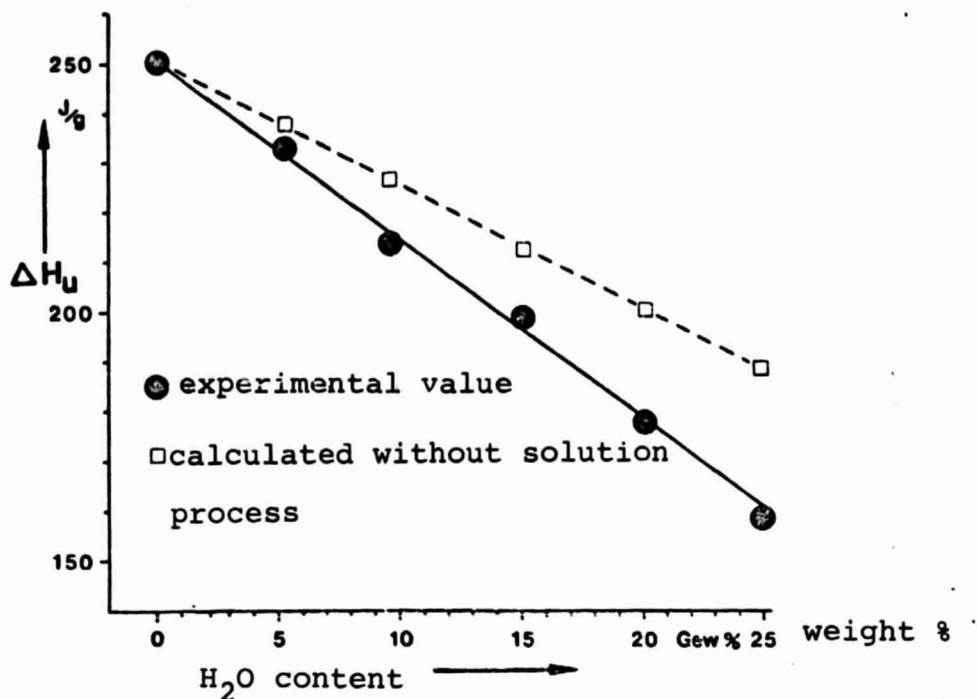


Figure 19: Phase change enthalpy ΔH_u as a function of the H_2O content for the system $Na_2SO_4 \cdot 10 H_2O/H_2O$

For the thermal analyses laboratory chemicals (Merck, crystalline, 57 extremely pure) were used as starting components. The DTA test curve produced an ideal shape with a sharp endothermic peak, such as appears for congruently melting substances. For the eutectic a phase change temperature of $59^\circ C$ and a phase change heat of $146 J/g$ was determined so that the literature statements were fully confirmed.

In addition to the pure eutectic mixtures with low water proportions were also measured. One could observe a distinct decrease of T_u and ΔH_u already for an H_2O content of 2% or 4%. The results are summarized in table 12.

Table 12: Results for mixtures with $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ / $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ as base component

comparison in weight %			T_u °C	ΔH_u J/g
$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	H_2O		
41.3	58.7	-	58	146 ± 6
40.5	57.5	2.0	53	107 ± 6
39.7	56.4	3.9	41	95 ± 6

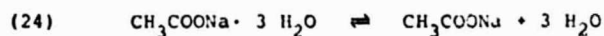
The graphic representation of the test results (figure 20) clearly shows the effect of the third phase H_2O . The large decrease of ΔH_u for already very low H_2O content can be explained by the extremely high solubility of the individual components.

For the use as a storage medium this means that for the attainment of a high storage capacity the starting components must be practically free of water. This requirement cannot be satisfied problem-free especially for $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ since it is very hygroscopic and since technical-grade products of the magnesium chloride hexahydrate have a not-to-be-neglected portion of water.

4.4 System with $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ as base component

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In the system sodium acetate/water only $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ appears as hydrate. For conversion into the anhydride the literature lists values between 58 and 59°C [26]. The phase change according to the following equation:



can be classified as a nearly congruent melting since the anhydride dissolves at a temperature of ca. 70°C completely in the water of crystallization. For the phase change enthalpy the literature

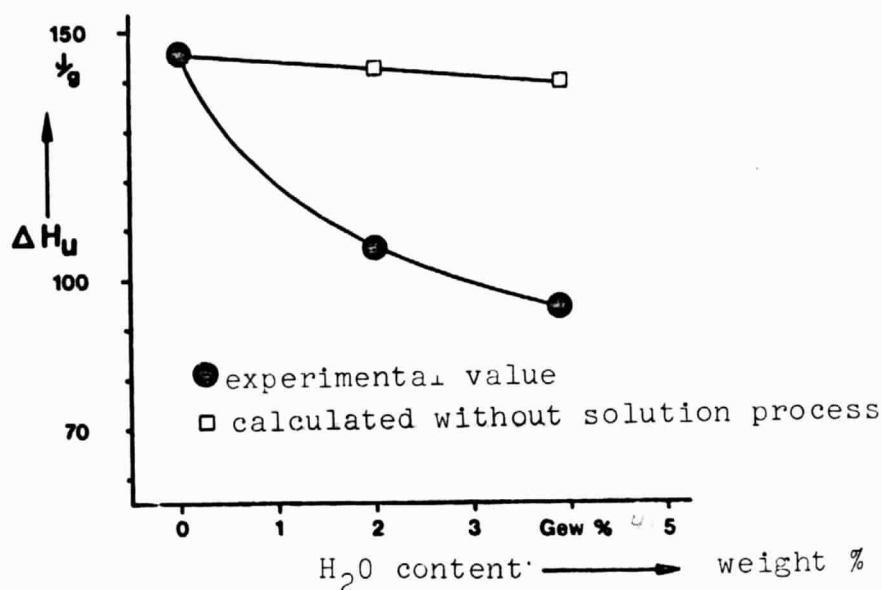


Figure 20: Phase change enthalpy ΔH_u as a function of the H_2O content for the system $MgCl_2 \cdot 6 H_2O / Mg(NO_3)_2 \cdot 6 H_2O$

contains contradictory statements. Values of 160 J/g [32], 161 J/g [62], 180 J/g [8] and 265 J/g [4,6] are listed.

For the system $CH_3COONa/H_2O/NaOH$ investigations are available /59 for the temperature range from $0.5^\circ C$ to $20^\circ C$. As a general result it is reported that NaOH reduces the solubility of $CH_3COONa \cdot 3 H_2O$ and that for a very high NaOH content the anhydride [63] is preferably formed.

During the course of the thermal analyses we measured in addition to the pure sodium acetate trihydrate also mixtures with an H_2O content of 5% up to 20 % (test series 1). Starting with an H_2O content of 5% congruent melting was observed. Additionally we also tested mixtures with an excess of the two equal-ion compounds CH_3COOH and H_2O .

Quantitatively we determined the effect of NaOH on T_u and ΔH_u of mixtures with a starting composition of 95% $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ / 5% H_2O (test series 2) and 90% $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ / 10% H_2O (test series 3). All samples used in test series 2 exhibit incongruent melting behavior which increased noticeably with increasing NaOH content. In test series 3 we observed congruent melting for mixtures with an NaOH content of 1% and 2%. A higher NaOH proportion led to a clearly incongruent phase change.

A summary of the results is shown in table 13. For mixtures with high H_2O - or NaOH content only approximation values were obtained. For this no standard deviation is listed. The phase change enthalpy of the pure $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ was determined to be 260 J/g. Thus it lies near the upper limit of the various literature values.

The effect of H_2O on the phase change heat obtained for the particular mixtures is shown graphically in figure 21. Up to an H_2O content of 10% there results a nearly linear decrease. Just as in the already discussed systems a second straight line is plotted on the graph, which is calculated with the assumption of insolubility of $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$. A comparison shows that for mixtures in the range from 5% to 10% H_2O content the difference is not serious.

The test results obtained for test series 2 and 3 are shown in figure 22. For the mixtures with 5% H_2O content we found altogether higher values for mixtures with an H_2O proportion of 10%. In both cases a qualitatively similar shape was obtained, showing that an addition of NaOH first brings about an increase in the phase change enthalpy. From a maximum value for NaOH there then follows a distinct decrease of the thermal effect. The shape of the curve can be interpreted in such a way that through the equal-ion addition of NaOH the solubility of $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$ is reduced so that compared to the starting mixtures a higher salt hydrate proportion is available for the phase change. /60

Table 13: Results for various mixtures with $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$
as base component

$\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$	composition in weight %		T_u $^{\circ}\text{C}$	ΔH_u J/g
	H_2O	NaOH		
100	-	-	58.5	260 ± 11
95	5	-	55	220 ± 9
90	10	-	52	190 ± 10
80	20	-	(50)*	(100)*
94	5	1	53	239 ± 9
92	5	3	51	248 ± 10
90	5	5	46	189 ± 10
85	5	10	(39)*	(110)*
89	10	1	51	198 ± 8
88	10	2	50	205 ± 8
87	10	3	48	211 ± 8
86	10	4	47	190 ± 9
80	10	10	(40)*	(150)*

* approximation value

4.5 Systems with $\text{NaOH} \cdot \text{H}_2\text{O}$ as base component

/61

For the system $\text{NaOH}/\text{H}_2\text{O}$ one can find in the literature statements concerning a large number of hydrates, especially for low temperatures. Unequivocal assurance is given for the existence of $\text{NaOH} \cdot \text{H}_2\text{O}$. The results of the investigations of numerous works have been summarized [26] to form a real phase diagram. For the temperature range of interest here it exhibits in addition to the monohydrate also a eutectic in the phase area richer in NaOH. It is composed of $\text{NaOH} \cdot \text{H}_2\text{O}$ and $\alpha\text{-NaOH}$ and can be described as an approximation by the gross formula $\text{NaOH} \cdot 0.75 \text{H}_2\text{O}$.

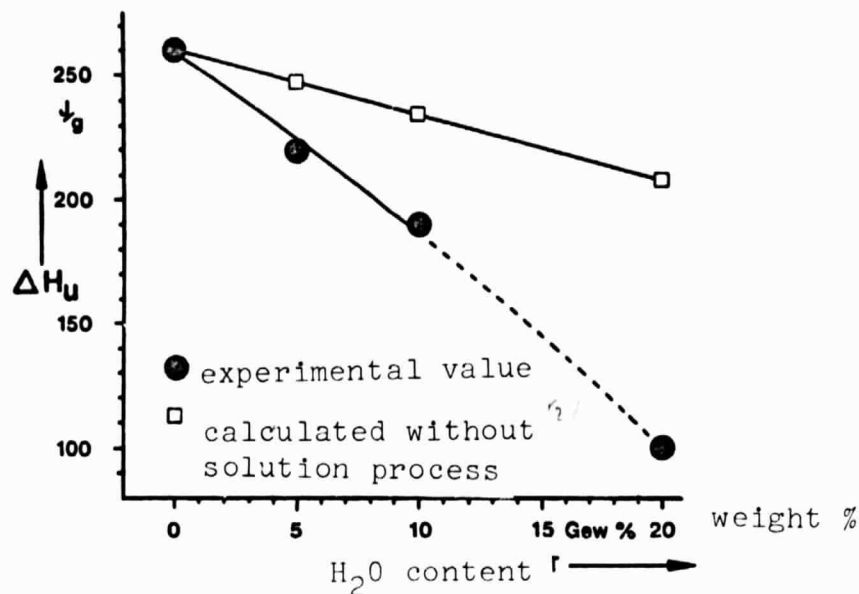


Figure 21: Phase change enthalpy ΔH_u as a function of the H_2O content for the system $CH_3COONa \cdot 3 H_2O/H_2O$

For $NaOH \cdot H_2O$ a congruent melting point of $64^\circ C$ to $65^\circ C$ is listed. The literature values for the phase change enthalpy lie in the range from $272 J/g$ [4,7,8] and $275 J/g$ [5,6]. For the eutectic one can derive from the phase diagram a melting point of ca. $62^\circ C$. Information concerning the heat of melting is not available as far as we now.

During the DTA investigations we used in addition to the pure $NaOH \cdot H_2O$ two mixtures with an H_2O content of 7% and 11% as well as a mixture richer in $NaOH$. The sample consisting of 94% $NaOH \cdot H_2O$ and 6% $NaOH$ corresponds approximately to the composition of the eutectic. The results are shown in table 14.

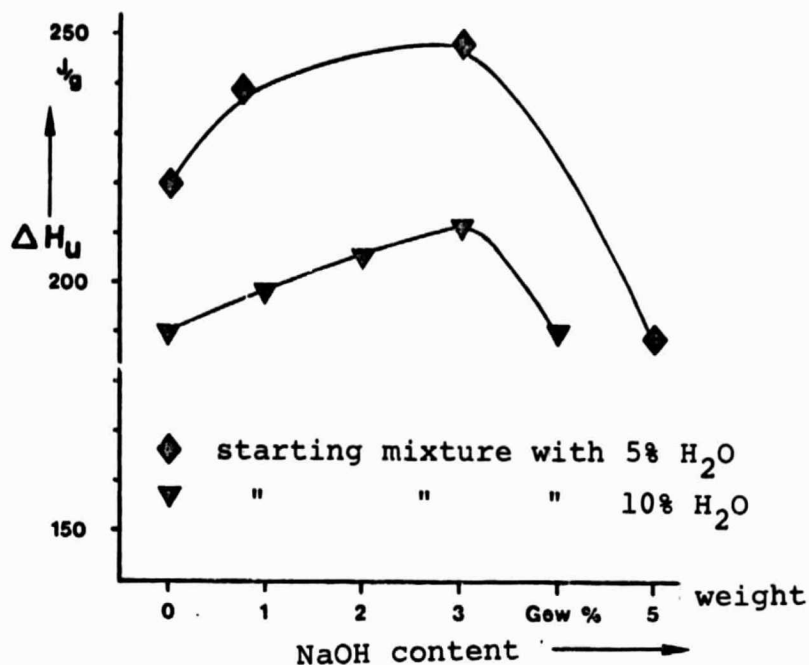


Figure 22: Phase change enthalpy ΔH_u as a function of the NaOH content for $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}/\text{H}_2\text{O}$ mixtures with a share of 5% and 10% H_2O

Table 14: Results for various mixtures with $\text{NaOH} \cdot \text{H}_2\text{O}$ as base component

NaOH · H ₂ O	composition in weight %		T _u °C	ΔH_u J/g
	H ₂ O	NaOH		
100	-	-	64	259 ± 10
93	7	-	53	150 ± 9
89	11	-	44	95 ± 8
94	-	6	61	255 ± 10

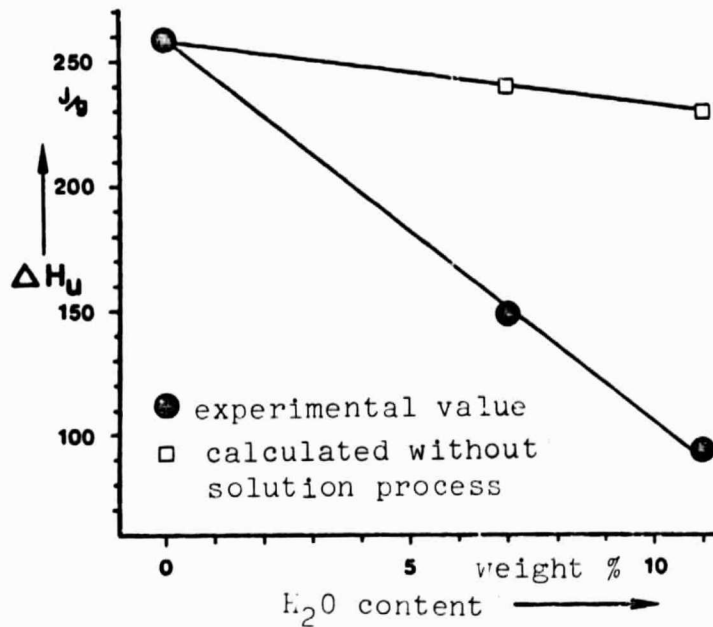


Figure 23: Phase change enthalpy ΔH_u as a function of the H_2O content for the system $NaOH \cdot H_2O/H_2O$

The effect of the second phase H_2O in mixtures with $NaOH \cdot H_2O$ can be derived from figure 23.

One can see for the range investigated a very pronounced nearly linear decrease of the phase change enthalpy. The shape of the curve reminds one of the system $MgCl_2 \cdot 6 H_2O/Mg(NO_3)_2 \cdot 6 H_2O$ which, however, exhibits a still stronger H_2O effect. The decrease of the phase change enthalpy calculated by neglecting the solubility of $NaOH \cdot H_2O$ is also plotted in the graph. The considerable deviation of the two curves shows that the very high water solubility must absolutely be taken into account when $NaOH \cdot H_2O$ is to be used as storage medium.

4.6 Systems with $Ba(OH)_2 \cdot 8 H_2O$ as base component

$Ba(OH)_2 \cdot 8 H_2O$ crystallizes from aqueous barium hydroxide solutions between -0.5 and $78.5^\circ C$. In the old literature a somewhat higher water content - $9 H_2O$ - is listed occasionally;

however, this deviation must probably be attributed to adsorption. Additionally it is mentioned that the octahydrate is able to include into its crystal structure smaller amounts of excess H_2O . For the melting point values between $78^\circ C$ and $79^\circ C$ [64] are predominantly listed.

The thermal investigations have shown that $Ba(OH)_2 \cdot 8 H_2O$ undergoes a phase change at $78^\circ C$ whereby it was not clarified unequivocally whether the solid material occurring in small amounts in addition to the saturated solution is $Ba(OH)_2$ or $Ba(OH)_2 \cdot H_2O$. A small water addition or a temperature increase by ca. $10^\circ C$ leads to a solution of the precipitate so that according to the stipulated definition (compare chapter 3.1) the melting behavior can be designated as being nearly congruent. The evaluation is made more difficult because the $Ba(OH)_2 \cdot 8 H_2O$ used contains a small proportion of $BaCO_3$. It is insoluble in the melt and can thus make it appear that incongruency existed.

For the DTA measurements we used in addition to the various laboratory preparations also a technical-grade product. It is represented by the mixture with the composition of 94% $Ba(OH)_2 \cdot 8 H_2O$ and 6% H_2O . Table 15 presents a summary of the mixture used along with the test results obtained.

/65

Table 15 Results for various mixtures with $Ba(OH)_2 \cdot 8 H_2O$ as base component

composition in weight %		T_u $^\circ C$	ΔH_u J/g
$Ba(OH)_2 \cdot 8 H_2O$	H_2O		
100	-	78	301 ± 12
94	6	77.5	280 ± 12
85	15	73	230 ± 10
75	25	69	207 ± 9
69	31	67.5	171 ± 9
62	38	66	147 ± 9

The test curve observed for the pure octahydrate showed an identical shape. It was therefore also used as calibration substance for the determination of the temperature-dependent correction factor (compare chapter 2.3.3). The effect of water as a second phase on the shape of the curve is not significant up to an H₂O content of 15%. Only at the higher H₂O content does the typical baseline shift resulting from solution effects appear (compare figure 18).

The test results are shown graphically in figure 24. The decrease of the phase change enthalpy is nearly linear within the ranges shown. The deviation from the straight line calculated by neglecting the water solubility is not serious. Thus Ba(OH)₂ · 8 H₂O also exhibits in H₂O-containing mixtures (up to ca. 15%) a very high heat of melting and is an extremely interesting compound from the point of view of high storage capacity.

66

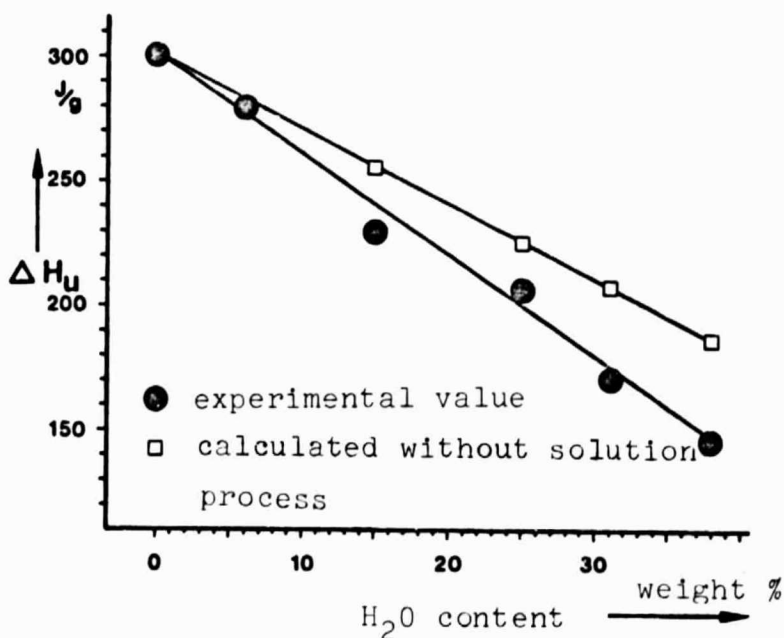


Figure 24: Phase change enthalpy ΔH_u as a function of the H₂O content for the system Ba(OH)₂ · 8 H₂O/H₂O

5. Summary

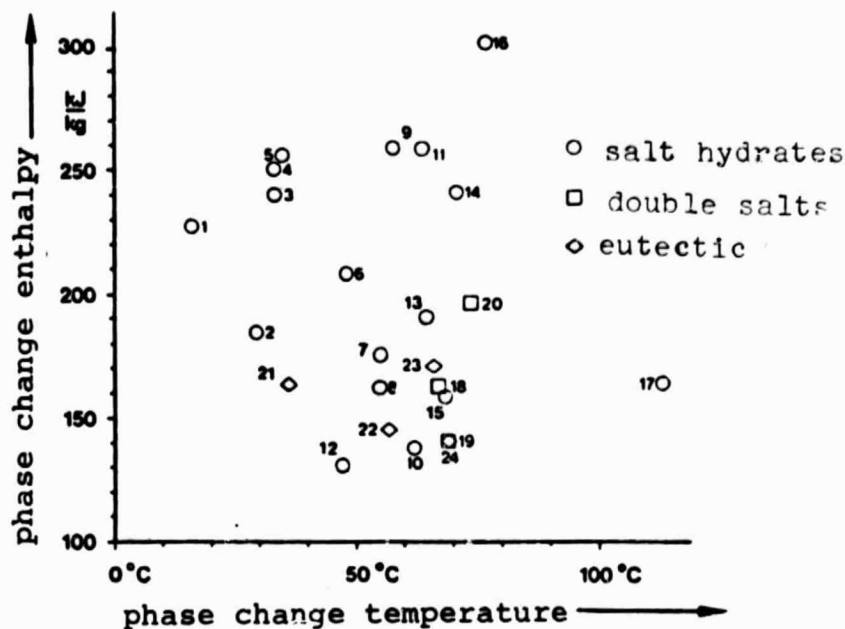
In the subject paper the result of the thermal analyses of selected salt hydrate systems in the temperature range from 15 to 115° C are presented. The key point of the work was the determination of the phase change temperatures and the phase change enthalpies, which in this way provide base values for the working range and the storage capacity of potential storage media.

Based on the chemical properties of salt hydrates the DTA measurements were carried out in a special test cell. The results could be evaluated quantitatively after the various influence parameters had been determined and the necessary correction factors had been established. /67

For the investigations we used 17 salt hydrates, 3 double salts and 4 eutectics. Here these were primarily compounds with alkali- and earth alkali metals as cations and with halogenized, nitrate-, sulfate-, phosphate-, and hydroxide ions as anion.

The phase change temperatures and phase change enthalpies determined for salt hydrates, double salts and eutectics are summarized in figure 25. The graph shows that the substances with high phase change heat - above 200 J/g - are represented exclusively by the pure salt hydrates. These are especially congruently or nearly congruently melting compounds $\text{KF} \cdot 4 \text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$, $\text{NaOH} \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$. Under the aspect of the thermal behavior these salt hydrates seemed to be the most promising candidates for additional investigations for media development. Additional compounds with high heat conversion are $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$, and $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$ which, however, because of their pronounced incongruent melting behavior they are suited only conditionally for use as storage media. They must first be converted into systems with congruent phase change, which was done successfully for $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ by the use of the saturated sodium sulfate solution.

The effect of additives - water, acids, and hydroxides - on the phase change temperature and the phase change enthalpy was determined for five different material systems. For $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ / $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and for $\text{NaOH} \cdot \text{H}_2\text{O}$ a very pronounced decrease of the heat of conversion sets in for an excess of water so that only the pure salt hydrates appeared to be suitable media. The effect is not as pronounced for $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$. For this there result even for pronounced deviations from the composition of the pure hydrates sufficiently high heat exchange rates, so that for the further media development a wider composition range is still possible.



- | | | | | | | |
|-----------------|----|---|----|--|----|--|
| salt hydrates ○ | 1 | $\text{KF} \cdot 4\text{H}_2\text{O}$ | 7 | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 12 | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ |
| | 2 | $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ | 8 | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 14 | $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ |
| | 3 | $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | 9 | $\text{NaCH}_2\text{COO} \cdot 3\text{H}_2\text{O}$ | 15 | $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ |
| | 4 | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 10 | $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ | 16 | $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ |
| | 5 | $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ | 11 | $\text{NaOH} \cdot \text{H}_2\text{O}$ | 17 | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| | 6 | $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ | 12 | $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ | | |
| double salts □ | 18 | $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ | | | | |
| | 19 | $(\text{NH}_4)\text{NaSO}_4 \cdot 2\text{H}_2\text{O}$ | | | | |
| | 20 | $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ | | | | |
| eutectic ◇ | 21 | $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | | | | |
| | 22 | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} / \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | | | | |
| | 23 | $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | | | | |
| | 24 | $\text{NaBr} / (\text{NH}_2)_2\text{CO}$ | | | | |

Figure 25 Phase change temperatures and phase change enthalpies of the salt hydrates, eutectics, and double salts used in the thermal analyses.

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