DET KGL. DANSKE VIDENSKABERNES SELSKAB MATEMATISK-FYSISKE MEDDELELSER, BIND XXV, NR. 12

TENSIMETRIC AND X-RAY INVESTIGATIONS ON MAGNESIUM CARBONATE TRIHYDRATE AND ITS DEHYDRATION PRODUCTS

BY

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KØBENHAVN I KOMMISSION HOS EJNAR MUNKSGAARD 1949

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Printed in Denmark Bianco Lunos Bogtrykkeri

I. Introduction.

In a previous paper (1), we have put forward some observations on the course of dehydration in hydrated salts with special regard to the many conditions for the reversible dehydration of a hydrated salt. In connection with these observations, a detailed knowledge of the dehydration of magnesium carbonate trihydrate and the rehydration of the dehydration products is of considerable interest. The stable end product of the dehydration process, crystalline magnesite, is so hard (H 3.5-4.5) that it can not be expected to be produced at room temperature in the laboratory within a reasonable time. On the other hand, the process

 $\begin{array}{rcl} MgCO_3, 3 \ H_2O & \rightarrow & MgCO_3 + 3 \ H_2O \\ (Nesquehonite) & (colloidal magnesite) \end{array}$

is described by geologists as a rapid process. It could therefore be expected that the dehydration of MgCO, $3 H_2O$ should be further from the ideal state than the previous studied process $CaCl_2$, $H_2O \rightarrow CaCl_2 + H_2O$, that thus a study of this process would increase our knowledge of such non-ideal systems, but that it, on the other hand, should not be too slow to measure. This also proved to be the case. By non-ideal dehydrationrehydration systems we understand those in which the thermodynamic properties such as the equilibrium vapour pressure and its temperature coefficient are dependent on the way in which the system is built up; the systems will most often not be completely reversible.

Interest in the process is increased by the fact that comprehensive investigations on the solubility of magnesium carbonates have already been carried out by J. K. GIALDBÆK (2). In his paper, among other peculiarities, it was pointed out that different magnesite preparations have different solubilities; the

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explanation for this is now found in the results of our X-ray investigations. With regard to the properties, for example the solubilities of different labile magnesium carbonates, we can also supplement GJALDBÆK's basic work.

Our paper comprises the following main sections:

1) Preparation of the trihydrate, synthetic magnesite and amorphous "active" magnesium carbonates prepared partly by dehydration at two different temperatures and partly by precipitation.

2) Measurements of water vapour and carbon dioxide pressures of systems of magnesium carbonate trihydrate and its dehydration products, in addition to corresponding measurements of systems of amorphous "active" magnesium carbonate and its rehydration products.

3) X-ray examinations of different magnesites, of the "active" magnesium carbonates, of magnesium carbonate trihydrate and also of phases in the systems measured tensimetrically.

The results obtained will be communicated in the first section. After this will follow some general considerations on dehydrationrehydration in non-ideal systems, and then a section on the heats of hydration measured. Finally, a section with experimental details. The many vapour pressure data, the heats of hydration and detailed descriptions of the many systems measured, is appended, because it did not seem unlikely to us that these data could give a more detailed picture of the state in such non-ideal systems than that which we are able to outline at present.

II. Various Solid Systems Consisting of Magnesium Carbonate and Water, their Properties and Mutual Transformations.

The transformation of all known magnesium carbonates to magnesite and water is accompanied by a decrease in the free energy of the system. Nevertheless, it is an experience which our investigations confirm, that well crystallized magnesite can only be prepared by the heat treatment of hydrated magnesium carbonate—preferably in the presence of water—at high temperature. In systems with no liquid phase, even after heat treatments at temperatures up to about 200°, we were not able in any case to observe even an initial formation of magnesite; this is in agreement with MENZEL, BRÜCKNER and SCHULTZ (3), who only at 320° were able to obtain a small amount of crystalline magnesite in a similar system.

Our synthetic magnesite, produced by heating the trihydrate with water to 175°, gives a powder diagram of the greatest sharpness, which is exactly like a diagram of a coarsely crystalline, calcite-like magnesite, such as the Snarum magnesite, investigated by GJALDBÆK. When GJALDBÆK found that his synthetic magnesite was more easily soluble in water than Snarum magnesite, can we therefore not explain this simply by postulating that the synthetic magnesite is not so well crystallized as Snarum magnesite. The only difference between GJALDBÆK's method of preparation and ours has been that we heated for 20 hours at 175° , while GJALDBÆK reports that the process is complete in 1-2 hours at 160-175°; our crystals were 5-25 μ , while GJALD-BÆK states that his crystals were similar to Eubøa magnesite and consequently only 2–3 μ . It is possible that GJALDBÆK has had in his preparation a sufficient quantity of a still finer fraction and this has been responsible for the solubility measured.

Eubøa magnesite, which is stated by GJALDBÆK to crystallize with a particle size of 2—3 μ gives on X-ray investigation too wide lines; this shows that it is not so well crystallized as our synthetic magnesite or as Snarum magnesite. When GJALDBÆK found that this is considerably more soluble than the magnesites, which give sharp powder reflections, this is therefore only as expected. The increase in line width is not especially great, somewhat less than the $\alpha_1 \alpha_2$ separation. The increase in line width indicates that a considerable part of the substance consists of particles with a size of 800—1000 Å.

What impurities the four magnesites examined have contained, we have not investigated, but they can not all have been pure, since only two of them had the same lattice constants. We have not calculated the absolute values of the lattice constants. This has less interest, since we lack quantitative analyses and detailed information on the sites of origin of the four mineral samples.

On mixing of concentrated equimolar solutions of magnesium

chloride and alkali carbonate a voluminous white precipitate is produced, to which R. ENGEL (4) gives the formula $MgCO_3$, 2 H₂O by indirect analysis. This can not stand washing, hence it can not be analyzed directly or used for solubility experiments, and very little is known about the compound except that it is transformed to trihydrate on standing a few hours in its mother liquor. We succeeded in making a powder diagram of the compound before the formation of trihydrate became appreciable. The diagram contained (apart from weak sodium chloride lines from the dried mother liquor) only diffuse rings. The next day, definite crystals of trihydrate could be seen under the microscope. The experiment showed that ENGEL's "dihydrate" is quite amorphous. The water content can not therefore be considered important. The solubility and other properties of the compound will not supposedly differ much from those of other amorphous magnesium carbonates found and described below.

The equilibrium water vapour pressure over a system consisting of magnesite + a magnesium carbonate hydrate is not available for measuring at room temperature on account of the exceptional incrtness of magnesite. On the other hand the equilibrium pressure over systems of magnesium carbonate trihydrate + dihydrate, of trihydrate + amorphous "active" magnesium carbonate, of dihydrate + its amorphous dehydration product or of amorphous "active" magnesium carbonate + its amorphous hydration products can be measured. The irreversible "aging" phenomena, which most of the systems mentioned show to some extent, are slow processes compared with the equilibration of the equilibrium vapour pressure.

The starting material for the preparation of all the systems described was a crystalline magnesium carbonate trihydrate prepared according to $G_{JALDBEK}(2)$.

Rehydration systems.

On heating to $180-210^{\circ}$ in a stream of carbon dioxide, the trihydrate changes to an "active" magnesium carbonate, the water content of which decreases within 53 hours to 0.24 moles H₂O per moles MgCO₃. According to the X-ray diagram this

Table 1.

Water vapour pressure, carbon dioxide pressure and tensimetric heats of hydration of systems formed by rehydration of amorphous "active" magnesium carbonate, prepared from trihydrate dehydrated at 180—210°.

Sy- stem	H ₂ O		180			25°			350		kcal.	X-ray
No.	MgCO ₃	p_{H_2O}	log r 1	P_{CO_2}	$\mathrm{p}_{\mathrm{H_{8}O}}$	log r	р _{СОз}	P _{H2} O	log r	p_{CO_2}	$\mathrm{mole}\mathrm{H_2Oliq}.$	characteristic
$R_1 \ldots$	0.24	0.08	.71 -3	$\langle 0.01$								Amorphous
R ₂ ²	0.33	0.94	.78 - 2	0.05	1.26	.725 - 2	0.06				-3.2	Amorphous
R ₈	0.86	(1.34)	(.941-2)	0.02	(2.15)	(.957-2)	0.02	(4.00)	(.977 - 2)	0.02	(0.96)	Amorphous
R4	1.24	4.29	.443 - 1	(0.29)	6.12	.411-1	(0.31)	9.32	.344-1	(0.32)	-2.4	Amorphous
R₅a	1.40	(6.34)	(.612-1)	(0.22)	(8.06)	(.531 - 1)	(0.23)	(10.38)	(.391 - 1)	(0.27)	(-5.3)	-
R₅b	1.40	8.92	.761 - 1	0.13	10.08	.628 - 1	0.15	11.86	.449 - 1	0.18	-7.5	16 lines of trihydrate
R ₆	1.94	8.05	.716 - 1	0.24	8.98	.578 - 1	0.23	11.05	.418-1	0.23	-7.2	30 lines of trihydrate
$R_7\ldots$	2.38	11.07	.854 - 1	0.35	12.64	.726-1	0.43				-7.3	52 lines of trihydrate

 1 r = relative vapour pressure 3 R_2 : 0°: p_{H_2O} = 0.40, p_{CO_2} = 0.04

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Figure 1. The relative vapour pressure r at 18° as a function of the water content in rehydrated amorphous "active" MgCO₃, prepared at about 200°.

preparation is completely amorphous; it gives a pure liquid diagram. It is strongly hygroscopic, on suspension in water it is quickly transformed into a pure crystalline trihydrate. During intermittent measurements of the vapour pressure at 18, 25 and 35° (see table 1) we allowed this "active" magnesium carbonate to take up water. In fig. 1 we have given the relative vapour pressures at 18° as a logarithmic function of the water content. r is the ratio between the vapour pressure of the hydrate system and the vapour pressure of water at the same temperature. Even at a water content of 1.24 moles H₂O per mole MgCO₃ it was quite amorphous. Crystallization first begins between 1.24 and 1.40 mole H_2O . The trihydrate is produced. At the same time the water vapour pressure rises to 80 times the initial value. It is remarkable that this "active" magnesium carbonate can remain amorphous with a water content as high as 1.24 moles. On further uptake of water to 2.38 moles H_2O , the vapour pressure only increases 50 $^{0}/_{0}$. While the water content rises from 0.24 moles H_2O to 2.38 moles H_2O , the tensimetric heat of hydration calculated from the temperature coefficient of the vapour pressure—falls from about -2.8 kcal per mole H_2O to -7.5 kcal per mole H₂O.

It is noteworthy that we find negative tensimetric heats of hydration not only for this system, but for several others described in this paper. In a survey of the literature, positive heats of hydration of the order of a few kcal per mole liquid water will be found in most cases. In a previous paper (5) one of the authors has found positive tensimetric heats of hydration of up to 13.7 kcal per mole H_2O in systems of calcium chloride monohydrate + calcium chloride prepared from the former by dehydration at low temperature. This system contained extremely fine particles, but X-ray analysis showed that the calcium chloride was certainly not amorphous.

Negative heats of hydration are, however, not unknown. Thus H. MENZEL et al. (6) give the vapour pressure at 20 and 25° for a system of Na₂B₄O₇, 10 H₂O and its X-ray amorphous dehydration product, from which a tensimetric heat of hydration can be calculated of -4.5 kcal per mole liquid water.

Calculation of the solubility of amorphous magnesium carbonate.

It can be seen from fig. 1 that the tendency of "active" magnesium carbonate to take up the first few hundredths of a mole H_2O is considerable, but it sinks rapidly and is low for the last two moles of water. GJALDBÆK had already found that its reaction with water to form the trihydrate is so rapid that its solubility can not be measured. Numerical calculations of solubility from the vapour pressure are certainly very inexact because we are dealing with a non-ideal system, where we can not be sure of having single homogeneous phases. We will, however, carry through a few calculations to illustrate the information that vapour pressure can give us about the solubility of amorphous magnesium carbonate.

In general it can be said that it must be the most quickly reacting part of the system that determines the vapour pressure. Hence it must for example at the point where the trihydrate is formed, be trihydrate and the most quickly reacting part of the amorphous hydration product nearest to the trihydrate which determine the vapour pressure. This part of the amorphous hydration product must also be considered to be the most readily soluble, so that the water vapour pressure of the system is an expression of the upper limit for the solubility of the amorphous phase at the given water content.

GJALDBÆK (2) has estimated at 18° the solubility product L_3 and L_5 for trihydrate and pentahydrate, $L_3 = [Mg^{++}]_3 [CO_3^{--}]_3$ $= 10^{-5.05}$ and $L_5 = [Mg^{++}]_5 [CO_3^{--}]_5 = 10^{-4.89}$. The ionic symbols in square brackets with the indices 3 and 5 suffixed, indicate the activity of the corresponding ions in saturated solutions of trihydrate and pentahydrate respectively.

On the basis of vapour pressure measurements of a system, the rehydration system R_5b discussed later, consisting of incompletely crystallized trihydrate and an amorphous phase, which we assume to contain one mole H_2O , we will calculate the solubility product $L_1 = [Mg^{++}]_1 [CO_3^{--}]_1$ for the supposed monohydrate. The vapour pressure above this system which we designate $p_{1,3}$ was 8.92 mm at 18°.

The transformation of monohydrate to trihydrate:

 $MgCO_3$, $H_2O + 2 H_2O \rightarrow MgCO_3$, $3 H_2O$ can be carried out by evaporating 2 moles H₂O at saturated vapour pressure, p_{H,O}, expanding to $p_{1,3}$, the vapour pressure over the monohydrate-trihydrate system, and condensing the water vapour on this. By this we gain the work $A_1 = 2RT \ln p_{H,0}/p_{1,3}$. We can also effect the transformation by dissolving 1 mole MgCO₃, H₂O in the saturated solution of the compound with simultaneous reversible transfer of 1 mole anhydrous magnesium carbonate to a saturated solution of $MgCO_3$, $3 H_2O$ with simultaneous precipitation of 1 mole of the latter. By this we have transformed 1 mole $MgCO_3$, H_2O to $MgCO_3$, 3 H_2O , but at the same time diluted the saturated solution of monohydrate with 1 mole H_2O and concentrated the saturated solution of trihydrate by removing 3 moles H_2O by crystallizing out the trihydrate. Since the vapour pressure above the saturated solutions of monohydrate and trihydrate respectively are practically the same and both very near to the vapour pressure over pure water, we can neglect the work of transference for water and obtain for the work of transformation:

$$A_2 = RT \ln \frac{[Mg^{++}]_1 \ [CO_3^{--}]_1}{[Mg^{++}]_3 \ [CO_3^{--}]_3}.$$

Since $A_1 = A_2$, log $L_1/L_3 = 2 \log p_{H_2O}/p_{1,3}$ and we find $L_1 = 10^{-4,57}$ for our amorphous monohydrate at 18°.

Table 2.

.

Water vapour pressure, carbon dioxide pressure and tensimetric heats of hydration of systems formed by dehydration of magnesium carbonate trihydrate at room temperature.

System No.		H ₂ O	H ₂ O 18º			250			350			kcal.	X-ray	
		MgCO ₃	P _{H₂} o	log r	p _{CO2}	p_{H_2O}	log r	log r p _{CO2} p _{H2O} log r		log r	P _{CO1}	$\overline{\text{mole H}_2\text{O}}$ liq.	characteristic	
s 1	D ₁	2.52	2.50	.208–1	0.35	3.28	.140–1	0.36	4.70	.047–1	0.40	-3.9	{ 34 lines of trihydrate 2 lines of dihydrate	
Serie	D ₂	2.02	(6.01)	(.589–1)	0.20	(7.80)	(.516–1)	0.23	(9.78)	(.365–1)	0.25	(-5.4)	13 lines of trihydrate 6 lines of dihydrate	
	D ₃ a.	1.88	0.18	.066-2	0.07	0.32	.13-2	0.10	0.73	.238-2	0.16	4.2		
	D ₃ b.	1.88	0.24	.49-2	0.04	0.43	.26 - 2	0.05	0.91	.334 - 2	0.06	3.5	17 somewhat diffuse lines	
п Series 2 П	D4	1.64	0.044	.46–3	0.03	0.08	.53-3	0.04	0.18	.63–3	0.05	4.2	of dihydrate 10 diffuse lines of dihy- drate	
	D5	1.43	0.014	.96-4	0.07	0.027	.06-3	0.06	0.05_{5}	.11–3	0.05	3.8	6 diffuse lines of dihy-	
	D ₆	1.85	(1.90)	(.089–1)	0.21	(2.74)	(.062–1)	0.22	(4.57)	(.035-1)	0,25	(-1.3)	drate { 14 lines of trihydrate 9 lines of dihydrate	

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The difference between the solubility products of the two hydrates, $10^{-5.05}$ and $10^{-4.57}$, is small in proportion to the difference from the crystalline magnesite's solubility product $10^{-8.59}$, a figure we have calculated from GJALDBÆK's data.

The dehydration systems.

It has been shown previously by one of us (5) that the temperature of dehydration in a non-ideal system is determining for the energy state of the dehydration product. In order to investigate the part played by temperature of formation in the properties of the dehydrated trihydrate, another sample of "active" magnesium carbonate was prepared by dehydration of the trihydrate at room temperature over phosphorus pentoxide *in vacuo* for 309 days. The vapour pressures at 18, 25 and 35° were measured at 5 different stages (see table 2). A preparation of the composition MgCO₃, 1.43 H₂O was obtained. The rate of

Table 3.

Time of dehydration Days	Composition mole H ₂ O mole MgCO ₃	Rate of dehydration <u>mole H₂O</u> day	System No.
0	3.06	0.09	
0.8	2.99	0.024	
36	2.16	0.020	
50	1.88	0.011	D ₃
68	1.69	0.0015	
102	1.64	0.0013	D ₄
164	1.56	0.0013	
209	1.52	0.0009	
309	1.43	0.0009	D.

Dehydration of magnesium carbonate trihydrate in vacuo over P_2O_5 at room temperature.

dehydration fell in this period from 0.024 moles per day to 0.0009 moles per day (see table 3). Simultaneously with each estimation of vapour pressure an X-ray diagram was made. The lines of the trihydrate disappeared during gradual dehydration, and another line system appeared which we assume to originate from a dihydrate. The supposed dihydrate is identical with a crystalline phase, the existence of which MENZEL et al. (3) have already demonstrated by X-ray analysis in different dehydration products of magnesium carbonate, prepared by them. Our X-ray diagrams show the same lines as those published by MENZEL. MENZEL considered these to be due to a monohydrate. On this point we can not agree. In our diagrams the line system in question is most marked at a water content of a little below 2 moles, at the same time the last trihydrate lines disappear. On further dehydration there is a considerable fall in vapour pressure, and the lines of the new phase decrease in intensity; at a water content of 1.43 moles their intensity has fallen to roughly $\frac{1}{3}$ of the maximum. This is not in agreement with the supposition that the new phase is a monohydrate, neither do the diagrams presented by MENZEL et al. support this theory. Their diagram of a preparation with 2 H₂O shows the lines of the new phase most clearly, and another diagram of "magnesium carbonate monohydrate" which they have dehydrated under boiling toluol and according to the data is the completely pure monohydrate, is decidedly the most unsatisfactory of the X-ray diagrams presented by MENZEL.

In our investigations we did not wait for the disappearance of the last dihydrate lines.

A survey of the vapour pressure measurements of the dehydration systems at 18° is given in fig. 2. It can be seen here that the equilibrium pressure of the system dihydrate + trihydrate is rather high. When it is not the same for the two systems, which are later designated system D₁ and D₂, it is because they are not prepared in the same way, but D₂ which contains 2 moles H₂O must according to the method of preparation be considered more nearly a rehydration system. The dihydrate-trihydrate system is a non-ideal system, since the dihydrate is not an easily formed phase. The lines in its powder diagram are markedly diffuse.



Figure 2. Dehydration of $MgCO_3$, $3 H_2O$ at room temperature. The relative vapour pressure r at 18° as a function of the water content.

In fig. 3 we have given a survey of all the systems investigated. The ordinate expresses the relative water vapour pressure in logarithmic scale, the abscissa, the reciprocals of the absolute temperature. The curves with negative slope thus correspond to systems with negative heats of hydration, the dihydrate-trihydrate system's curves D_1 and D_2 have negative slopes, the calculated tensimetric heats of hydration are of the order of -4 and -5 kcal per mole liquid H_2O .

Comparing the first rehydration systems, R_2 and R_4 , with the last dehydration systems, D_3 , D_4 and D_5 in fig. 3, it can be seen that the amorphous carbonate, produced by dehydration of the dihydrate at room temperature contains more free energy than the "active" carbonate prepared from the trihydrate by heating to about 200°, although according to the X-ray diagrams both are amorphous.

The amorphous parts of the dehydration systems must contain water. This can be seen from the previously mentioned rate at which the dihydrate's lines vanish as the water content falls; at $1.43 \text{ H}_2\text{O}$ only 6 lines remain of the original 17, hence the amorphous part supposedly contains at least 1 mole H_2O per mole MgCO₃.

After dehydration at room temperature water vapour was led into the system in order to make the regeneration of the dihydrate as complete as possible and so insure that the alleged

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Figure 3. Relative vapour pressure r over rehydration systems (R) and dehydration systems (D) as a function of temperature. The systems R_2-R_7 are formed by gradual rehydration of amorphous "active" magnesium carbonate prepared from trihydrate, that was dehydrated at about 200°.

The systems $D_1 - D_2$ and $D_3 - D_6$ are formed by gradual dehydration of magnesium carbonate trihydrate at room temperature. The system D_6 is formed by partial rehydration of D_5 . (Table 3).

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dihydrate really contained 2 molecules of water. It appeared, however, that by this procedure trihydrate had already been formed before the system contained 2 molecules of water per molecule of magnesium carbonate. The dihydrate stage did not occur during rehydration. It is described above that the dihydrate stage did not occur during rehydration of "active" magnesium carbonate prepared at high temperature. As already pointed out, crystalline dihydrate is a compound which is produced with difficulty, as is probably consistent with its high solubility (see later), which also explains why the dihydrate is never obtained during precipitation of aqueous solutions at room temperature; instead the less soluble trihydrate is obtained.

Calculation of the solubility of the dihydrate.

We will calculate the solubility product L_2 for the imperfectly crystallized dihydrate. We choose the largest vapour pressure measured at 18°, $p_{2,3} = 6.01$ mm., over the dihydrate-trihydrate system, D_2 , as that which refers to the most well crystallized dihydrate. Similarly to the previous example we obtain

$\log L_2/L_3 = \log p_{H_2O}/p_{2,3}$

from which we find $L_2 = 10^{-4.64}$ for our dihydrate at 18° . In table 4 we have summarized the solubility products cal-

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Solubility products of magnesium carbonate hydrates and magnesite at 18° .

Prenaration	– log L	'MgCO₃ , mH₄O
	J. K. Gj.	A. L. + A. T. J.
Amorphous monohydrate	.,	4.57
Dihydrate		4.64
Pentahydrate	4.89	
Trihydrate	5.05	
Synthetic magnesite	~ 7.17	
Eubøa magnesite	\sim 7.83	
Snarum magnesite	~ 8.59	

culated by GJALDBÆK from experimental data and also the values calculated by us for the amorphous alleged monohydrate and for our incompletely crystallized dihydrate.

Observation on the loss of carbon dioxide.

Small amounts of carbon dioxide are evolved during the slow dehydration of the trihydrate at room temperature and also during rehydration of amorphous "active" magnesium carbonate. The neutral magnesium carbonates are not all stable at very low carbon dioxide pressure. During the vapour pressure measurements it was necessary to correct for this carbon dioxide as later described under section 4, experimental. We did not succeed either in detecting by X-ray diagrams the basic carbonate formed by the carbon dioxide loss, or in indicating the kind of basic carbonate which determined, in connection with the normal carbonate, the carbon dioxide tension measured. The method of dehydration used, where the system apart from short intervals was closed, guarantees, however, that only quite infinitesimal amounts of carbon dioxide are lost during both dehydration and rehydration. It can therefore be assumed that the content of basic carbonate has been very small during the whole period, and has not influenced the water vapour pressure at different stages of dehydration.

GJALDBÆK (2) has shown that magnesium hydroxide in aqueous suspension may change into magnesium carbonate trihydrate, when the carbon dioxide pressure exceeds $10^{-4.54}$ atm. or 0.022 mm. Hg, while it requires a carbon dioxide pressure of 0.2 and 5.5 atm. respectively to bring a granular or fibrous basic magnesium carbonate into equilibrium with the trihydrate.

III. Some Considerations of the Dehydration Processes and Discussion of the Thermodynamic Data.

In our opinion there are three factors which are especially important for the rate, and the greater or lesser reversibility of the dehydration-rchydration processes:

D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. XXV, 12,

1) The rate and reversibility are promoted by the maintenance of a not too low vapour pressure during dehydration.

2) The probability for reversibility decreases strongly with increasing hardness of the lower hydrate or anhydride, which are produced by the process.

3) The probability for reversibility during dehydration which proceeds to an anhydrous component, is greatest when the ratio, for this compound, between the temperature of dehydration and the melting point in degrees absolute is not too small.

Factor 1) becomes significant in less mobile systems, inert systems, where the processes first proceed with noticeable speed after the system being removed far from the state of equilibrium is brought into a strongly labile state. Compare the observations put forward by us on the kinetics of dehydration processes in an earlier paper (1).

We are not able to define any definite limit for the hardness, at which difficulties with the establishment of equilibrium become perceptible, but there is a strong indication that it lies between 2 and 3 in Mons's scale. By far the most hydrates are softer than H = 2, while many anhydrous salts are considerably harder; hence the closest approach to reversibility is often found in systems, where the dehydration product is a hydrate.

We will give a few examples to illustrate this. By dehydration in high vacuum at 20 and 40° of $CuSO_4$, 5 H₂O, the hardness of which is rather considerable, although less than 3 (the hardness of calcite), KOHLSCHÜTTER and NITSCHMANN (7) obtain as a dehydration product of constant weight a monohydrate, completely amorphous by X-ray analysis, while dehydration at 100° in air gives a well crystallized monohydrate.

Systems of gypsum, H = 2, and its metastable dehydration product, the X-ray crystalline so-called "soluble anhydrite", shows great difference in energy, varying regularly with the dehydration temperature and sintering temperature and time, as shown in a paper by E. S. NEWMAN and L. S. WELLS (8).

The production of the stable anhydrite, H = 3-3.5, of the "soluble anhydrite" is so slow, in spite of a molar heat of formation of 3 kcal, that even 145 hours of dry heat treatment at 200° does not give a yield demonstrable by X-ray analysis; this, however, is reached after 670 hours. Heating for $1^{1}/_{2}$ hours at 170° in the presence of water results, on the other hand, in an anhydrite identical with the natural compound.

Anhydrous calcium chloride, H = 2-3, is rather slowly formed and magnesite, H = 4, simply can hardly be produced by "dry" dehydration of a hydrate. On the other hand, the dehydration of sodium bromide dihydrate even under extreme conditions does not seem to give sodium bromide of abnormal energy. The hardness of anhydrous sodium bromide is also only about 1.5 (1).

G. TAMMANN's (9) observation of recrystallization in the inorganic salts which he investigated, at a temperature of $0.57 \times T_s$, where T_s is the melting point of the salt in degrees absolute, is of special interest in regard to factor 3.

According to the circumstances, one or several of the factors mentioned in dehydration of a hydrate may be of such a size that the dehydration product has such a fine particle size that it is characterized as amorphous. The thermodynamic properties of the system will then differ from those in a corresponding system with well crystallized phases, this can be shown by tensimetric or calorimetric measurements. On dehydration of magnesium carbonate trihydrate we obtain, apart from the dihydrate both at room temperature and at 180—210° amorphous dehydration products. By performing the dehydration in carbon dioxide and heating to 320° for several days, MENZEL et al. (3) have, however, by X-ray analysis, been able to demonstrate the formation of a small amount of magnesite.

Discussion of the thermodynamic data.

We will discuss the energy content of the products, and have in table 5 summarized the tensimetric heats of hydration for all pure rehydration systems produced from the 200°-preparation of amorphous "active" magnesium carbonate. The evolution of heat at the 200°-preparation's uptake of liquid water is seen to be negative during the whole process, but there is a clear difference in its size at different stages of water uptake. It is ca. -3 kcal per mole H₂O in the range from 0.24 H₂O to ca. 1.40 H₂O. From 1.40 H₂O to 2.38 H₂O it is about constant, a good -7 kcal. This is quite a remarkable result. Taking all

 2^*

Table 5.

System No.	mole H ₂ O mole MgCO ₃	Tensimetric heats of hydration kcal./mole H ₂ O _{liq.}	X-ray characteristic
\mathbf{R}_1	0.24	···	Amorphous
R_2	0.33	-3.2	Amorphous
R_4	1.24	-2.4	Amorphous
R_5b	1.40	-7.5	16 trihydrate lines
R_6	1.94	-7.2	30 trihydrate lines
\mathbf{R}_7	2.38	-7.3	52 trihydrate lines

Tensimetric heats of hydration of pure rehydration systems formed by rehydration of amorphous "active" magnesium carbonate (dehydrated at about 200°).

the figures together gives the following equation for the whole hydration:

 $\begin{array}{ll} MgCO_3, \ 0.24 \ H_2O + 2.76 \ H_2O_{1iq.} \rightarrow MgCO_3, \ 3 \ H_2O - 14.9 \ kcal \ (1). \\ (200^\circ\text{-amorphous}) & (cryst.) \end{array}$

The figure -14.9 is obviously rather inexact, because we have only a few measurements, the sign and the order of magnitude is, however, reliable.

The heat production on addition of liquid water to anhydrous salts or salt hydrates with crystalline hydrate as reaction product, tends as previously described, to be positive and of the order of magnitude of a few kcal per mole liquid H_2O . Such a heat evolution is—apart from being usually found—reasonable from a kinetic point of view. We find a positive heat evolution, because the water molecules are bound into the lattice and by this loose energy of translation and possibility of orientation.

When, on the other hand, a trihydrate lattice is built up from amorphous magnesium carbonate and liquid water, instead of a few kcal being liberated per mole H_2O some 15 kcal are taken up from the surroundings. Why more than 15 kcal exceeding the normal amount are bound in this hydrate formation is by no means obvious. When the trihydrate is formed from amorphous magnesium carbonate and water, the water molecules doubtless partly displace the carbonate ions from contact with the magnesium ions. The heat absorbed may therefore have been used to displace the carbonate ions to a distance from the magnesium ions and replace them by water molecules. According to this hypothesis, the carbonate ions are more firmly bound to the magnesium ions than are the water molecules. But this is strange, since the water molecules, all the same, are able to displace the carbonate ions.

It could also be supposed that the amount of heat absorbed is not used to overcome the mutual attraction of the magnesium and carbonate ions, but that it is taken up as heat energy by the trihydrate formed. This would take place, if the possibilities of vibration in the amorphous magnesium carbonate were strictly limited as compared with the crystalline trihydrate. It could be supposed that on hydration a deblocking of the vibrations of the carbonate ions occurred, this being accompanied by a considerable absorption of heat. If something like this occurs, it would not be necessary to assume that the carbonate ions are more firmly bound to the magnesium ions than the water molecules.

Both these assumptions are very unusual and it can therefore be asked whether our tensimetrically estimated heat productions are really identical with the calorimetric heats of production in the processes concerned. There is no doubt but that the vapour pressures, by which the heat absorptions are estimated, are real. They are reproducible and reversible for such large amounts of water, that they can not be explained as equilibrium pressures for the very small amount of water that adheres to the glass walls of the apparatus, or as experimental errors. We also find satisfying that we can calculate the tensimetric heat of hydration of -4.5 kcal per mole liquid water from the data of H. MENZEL et al. (6) for sodium borate and its X-ray amorphous dehydration product, as previously mentioned.

It might perhaps be supposed that the reversible hydration that we measure does not lead to the production of the crystalline trihydrate (Nesquehonite), but to an intermediate product which is then irreversibly transformed to the crystalline trihydrate with production of a considerable amount of heat. Such an assumption invalidates the gross equation for the hydration and does not give our amorphous magnesium carbonate with $0.24 H_2O$ a very low energy content in comparison with the crystalline trihydrate. On the other hand such an assumption gives the hypothetical intermediate product properties just as unusual as those we had to attribute to the amorphous magnesium carbonate on the supposition that the tensimetric heat of hydration was identical with the calorimetric, and the picture of the formation of the intermediate product from the amorphous magnesium carbonate becomes equally strange.

We can not calculate the heat production in the important process:

 $\begin{array}{l} \text{MgCO}_3, \ 3 \ \text{H}_2\text{O} \rightarrow 3 \ \text{H}_2\text{O} + \text{MgCO}_3 + \text{Q} \\ \hline \text{(Nesquehonite)} & \text{(Magnesite)} \end{array}$

but we can from equation (1) estimate that Q must be positive and large (some kcal greater than 15 kcal).

This can be explained by assuming that magnesium ions and carbonate ions are bound to one another in entirely different ways in the two compounds. In magnesite, the carbonate oxygen touches the magnesium ion, while the water oxygen touches the magnesium ion in magnesium carbonate trihydrate, and Q can scarcely be interpreted in any other way than by difference in strength of magnesium-oxygen bonds in the two cases.

The dehydration systems.

In table 6 we have tabulated the heat productions for hydration of the dehydration systems in different stages. From this we obtain the following equations, valid with the previously mentioned reservations with regard to the tensimetrically estimated heats of hydration,

 $\begin{array}{ll} \mathrm{MgCO}_3,\, 1.43 \ \mathrm{H}_2\mathrm{O} + 0.57 \ \mathrm{H}_2\mathrm{O}_{\mathrm{liq.}} \rightarrow \mathrm{MgCO}_3,\, 2 \ \mathrm{H}_2\mathrm{O} + 2.3 \ \mathrm{kcal.} \\ (20^\circ\text{-amorphous}) & (\mathrm{cryst.}) \end{array}$

Further this equation:

$$\begin{array}{c} \text{MgCO}_3, \ 2 \ \text{H}_2\text{O} + \text{H}_2\text{O}_{\text{liq.}} \rightarrow \text{MgCO}_3, \ 3 \ \text{H}_2\text{O} - 3.9 \ \text{kcal,} \\ \text{(cryst.)} & (\text{Nesquehonite}) \end{array}$$

where we do not need to make reservations with regard to the identity of tensimetric and calorimetric heat production, since X-ray examination shows that we have two crystalline phases. The state of equilibrium is reached slowly, and as expected in a system of two crystalline phases, one of which is rather hard.

Table 6.

Tensimetric heats of hydration of pure dehydration systems formed by dehydration of magnesium carbonate trihydrate at room temperature.

System No.	mole H2O mole MgCO3	Tensimetric heats of hydration kcal./mole H ₂ O _{liq.}	X-ray characteristic
D_5	1.43	3.8	6 diffuse dihydrate lines
\mathbb{D}_4	1.64	4.2	10 diffuse dihydrate lines
D_3b	1.88	3.5	17 diffuse dihydrate lines
D ₁	2.52	-3.9	{ 34 trihydrate lines 2 dihydrate lines

On addition of these two equations we obtain:

 $\begin{array}{ll} \mathrm{MgCO}_3 \text{, } 1.43 \ \mathrm{H_2O} + 1.57 \ \mathrm{H_2O}_{\mathrm{liq.}} \rightarrow \mathrm{MgCO}_3 \text{, } 3 \ \mathrm{H_2O} - 1.6 \ \mathrm{kcal.} \\ \text{(20°-amorphous)} & (\mathrm{Nesquehonite}) \end{array}$

The corresponding equation for the formation of Nesquehonite from $MgCO_3$, 1.40 H_2O , produced by rehydration of the amorphous 200°-preparation, gives:

It would be expected that the amorphous system prepared at 20° with 1.40 H₂O should contain more energy than that prepared by rehydration of amorphous MgCO_{3 (200°)}. The difference in energy content of the two systems found, 10 kcal, is of the expected order of magnitude.

IV. Experimental.

Preparation of Magnesium Carbonate Trihydrate, Synthetic Magnesite and Amorphous Magnesium Carbonates.

Magnesium carbonate trihydrate was prepared as described by J. K. GJALDBÆK (2) by mixing 400 cc. of 1 M magnesium sulphate solution with 300 cc. of 1 M sodium carbonate solution and allowing to stand at room temperature for 24 hours, by this procedure the voluminous precipitate first formed became crystalline. The preparation was washed free from sulphate ion. Under the microscope beautiful well formed needle-shaped crystals were seen in addition to nearly spherical aggregates, which, however, on exposure to the air until next day were for the most part broken. X-ray examination showed only one phase, the trihydrate. For further purification, half the preparation was suspended in 500 cc. of distilled water and dissolved in this on addition of carbon dioxide. Then air was bubbled through the solution, and after a few days only needleshaped crystals were formed, most of which were free, but a few were in bundles.

The molecular weight of the air dried preparation was determined by dissolving in a slight excess of 0.1 N hydrochloric acid, boiling and back titration with 0.1 N sodium hydroxide, using methyl red as indicator. The molecular weight of the first preparation was 139.4, corresponding to a composition of MgCO₃, 3.05 H₂O. The second preparation corresponded to the formula MgCO₃, 2.90 H₂O, while a preparation that had been kept in a weighing bottle with a glass stopper for $1^{1}/_{2}$ years gave the formula MgCO₃, 2.98 H₂O.

Synthetic magnesite was prepared from the trihydrate as described by J. K. GJALDBÆK (2). 1 gm. trihydrate and 5 cc. water were heated in a sealed thick-walled glass tube. To prevent the glass from breaking and in any case to prevent accidents, the sealed glass tube was put with some water into a specially constructed very solid steel bomb with a screw cap and lead washer. The whole was then heated in an electric oven to 175°. After heating for 20 hours the trihydrate had disappeared and rhombohedral crystals $5-25 \mu$ in size appeared; on X-ray examination these gave a very beautiful sharp magnesite diagram.

Amorphous "active" magnesium carbonate was prepared according to J. K. GJALDBÆK (2) by dehydrating the trihydrate in an atmosphere of carbon dioxide at $180-210^{\circ}$. 1.4 gm. trihydrate with the formula MgCO₃, 2.90 H₂O were heated in a weighing bottle in the electrical oven to 180° with constant addition of dry carbon dioxide. In the course of 15 hours water corresponding to 2.58 moles per mole MgCO₃ had been lost. After the heating had been continued for 4 hours the loss was 2.61 moles, a further 16 hours at 180° increased the loss to 2.62 moles. The product, which was rather hygroscopic at room temperature, was further heated for 18 hours at $180-210^{\circ}$, whereupon the loss increased to 2.67 moles H_2O . The composition of the preparation after a total of 53 hours heat treatment was calculated from the weight loss observed to be MgCO₃, 0.23 H₂O, titration gave the result of MgCO₃, 0.24 H₂O. These last 0.24 moles H₂O are thus retained with so much force that they can scarcely be present as a constituent of a crystalline hydrate. X-ray examination also showed the preparation to be completely amorphous.

A sample of the preparation, that on superficial examination had retained the structure of the starting material, when suspended in water changed within a few hours into clear crystalline needles, which microscopically and on X-ray examination proved to consist of pure trihydrate. It was thus confirmed that the loss of carbon dioxide from the carbonate during dehydration had not been considerable.

Amorphous "Active" Magnesium Carbonate Prepared at Room Temperature.

In order to avoid loss of carbon dioxide, the dehydration was carried out by means of phosphorus pentoxide in a closed evacuated system. 1 gm. trihydrate (MgCO₃, 3.06 H₂O) was put into a weighed flask, which was connected by a ground glass joint to another flask containing P_2O_5 . The system was rapidly evaporated with a mercury vapour pump. Apart from the small amount which served to maintain equilibrium pressure in the flasks, the dehydration can in this way be carried out without loss of carbon dioxide, since the experiment showed that the loss of weight—of water as well of carbon dioxide—during evacuation and the short time of pumping was insignificant.

Table 3 shows the progress of dehydration. After standing in vacuo for 18 hours, the loss of water corresponded to 0.07 moles per mole trihydrate. After a little more than a month, the phosphorus pentoxide had absorbed so much water, that the loss reached 0.90 mole. After a further 14 days the total loss was 1.18 moles H_2O per mole trihydrate. After measuring the water vapour and carbon dioxide pressures of this hydrate system (D₃), as described more fully in a following section, several samples—4 mg. in all—were taken for X-ray examination. The dehydration was then continued as previously, and several systems (D_4 and D_5) with decreasing water content were obtained and measured. For practical reasons the dehydration was not followed for longer than 309 days, by which time it had attained the composition MgCO₃, 1.43 H₂O.

Amorphous Magnesium Carbonate Prepared by Precipitation.

According to R. ENGEL (4), magnesium carbonate dihydrate is produced by precipitation of concentrated solutions of magnesium salts by concentrated solutions of alkali carbonates.

We precipitated 3 cc. 3 M magnesium chloride with 2 cc. 3 M sodium carbonate solution at room temperature. The mixture immediately stiffened to a gel forming an almost clear mass, on stirring a whitish suspension appeared. On taking a little up on filter paper, we obtained a damp mass which without washing was taken up on a glass rod for X-ray examination. This showed, as described, that the preparation was completely amorphous, some weak lines were present, originating from sodium chloride which had crystallized out from the mother liquor during the procedure.

Measurements of Water Vapour Pressure and Carbon Dioxide Pressure.

Method.

The vapour pressure measurements were carried out with the previously described KNUDSEN hot-wire manometer (10, 11, 12). For use in the carbon dioxide measurements, the apparatus was connected to a shortened McLeoD manometer constructed according to M. BRUNNER's (13) description for measurements from 0.01 to 1 mm. Hg. This BRUNNER manometer was constructed so that sufficient pressure was exerted during compression while measuring, that the water vapour present was condensed. The necessary correction for water vapour pressure could then be estimated, when the temperature of the instrument was known. At very low water vapour pressure, however, only the sum of the water vapour and carbon dioxide pressures can be measured; furthermore, this is rather inexact on account of the adsorption of the water vapour on the glass surfaces. As we shall see below, it is, however, possible in such cases to estimate by means of the hot-wire manometer the ratio between the pressures of water vapour and carbon dioxide in the mixture.

The hot-wire manometer, which was calibrated for measuring water vapour pressures from 0.001 to 20 mm., was in addition calibrated to measure carbon dioxide within the range, 0.01 to 1.20 mm.

Since the measurements of the relatively small carbon dioxide pressure here interested us most as correction to the often many times greater water vapour pressure, we consider the BRUNNER manometer to be sufficiently accurate. It was very practical to use, since it works with a volume of only 2 cc., hence the equilibrium in the water vapour-hydrate systems was not appreciably effected by the measuring.

During measurements of the magnesium carbonate hydrate systems, a reading (s volts) was first taken with the hot-wire manometer, which registered both water vapour and carbon dioxide pressure. By direct reading from the calibration curve for water vapour, we found an approximate value p' for the water vapour pressure, which was then corrected with half the value, we found at the same time for the carbon dioxide pressure estimated by the BRUNNER manometer. The water vapour pressure p' read off at once, was corrected with half the carbon dioxide pressure measured, because the p—s calibration curve for water vapour in the range concerned halves the ordinate values for the corresponding curve for carbon dioxide (see fig. 4). Even if this method of correction is not strictly accurate, it can, however, be taken as a very good approximation. The corrections were in general relatively small.

For water vapour pressure that was so small that we could not get the water to condense in the manometer, we estimated an approximate value for the sum of carbon dioxide and water vapour pressures in the BRUNNER manometer. When we then also measured with the hot-wire manometer, we obtained a s-value, which together with the value for the pressure (c) measured in the BRUNNER manometer, were co-ordinates to a point, which lay between the calibration curves for pure water vapour and pure carbon dioxide. Assuming that, corresponding



Figure 4. Estimation of the partial pressures of a mixture of CO_2 and H_2O with total pressure c by means of a reading s of the hot-wire manometer potentiometer. — The curves are calibration curves for pure CO_2 and pure H_2O vapour. c and s are co-ordinates to a point lying on a calibration curve for a certain mixture of CO_2 and H_2O vapour.

to the different mixtures of CO_2 and H_2O vapour, there are calibration curves of exactly the same type, lying between the calibration curves for pure water vapour and pure carbon dioxide and dividing the distance linearly in relation to the proportions of the mixtures, the partial pressures can be found from our measurements with the hot-wire manometer, when we know the sum of the pressures. This is most clearly demonstrated in fig. 4. To the s-value found, if this is only due to water vapour pressure, pressure a corresponds, and if only pure carbon dioxide is present, pressure b. We have, however, a mixture with pressure c, hence we calculate

$$p_{H_2O} = a \frac{b-c}{b-a}$$
 and $p_{CO_2} = b \frac{c-a}{b-a}$.

Immediately after the pressure measurements, samples were taken out for X-ray examination. When the flask with the preparation was weighed before and after sampling, we could still keep account of the remaining preparation's weight and composition. About 1 mg. of the compound was used for an X-ray specimen. To just the same extent as in previous papers, the difficulties in vapour pressure measurements are due to the very slow equilibration, occurring in many cases. As criterium for obtainment of equilibrium, we have taken that the same vapour pressure should be reached whether it is approached from a higher or lower vapour pressure. Since we measured at 18, 25 and 35°, it was especially the readings at 25°, that were most valuable in this connection. To illustrate this, we will give some extracts from the records of the measurements of water vapour pressure over two hydrate systems:

a) System R_4 , amorphous, 1.24 moles H_2O per mole MgCO₃ prepared 25-12-1943 from R_3 (0.86 H_2O) by leading in at room temperature water vapour at 13 mm. pressure in 25 hours, of which 0.0234 gm. $H_2O \sim 0.38$ moles was taken up. Stored until 15-3-44. The alteration in pressure, when the temperature was changed from 18° to 35° is 5 mm., which under the given experimental conditions corresponds to a change of 0.01 mole H_2O in the composition of this system or about $1^{0}/_{0}$ of the water content.

Date	Potentio- meter reading	Tempera- ture	₽ _{CO₂} mm	р _{н2} о mm	P _{H₂O} mm
16-3-44	9894	18°		2.37	
22 - 3 - 44	10422	18°			
23 - 3 - 44	12188	25°			
30 - 3 - 44	12650	25°			
1-4-44	14801	35°		9.20	
5 - 4 - 44	14907	35°	0.24	9.48	9.36
5-4-44	13747	25°		6.81	
17-4-44	13493	25°	0.32	6.33	6.17
19-4-44	12209	1.8°			
21 - 4 - 44	12216	18°	0.29	4.43	4.29
22 - 4 - 44	13431	25°			
24 - 4 - 44	13439	25°	0.31	6.27	6.12
25 - 4 - 44	14953	35°			
27 - 4 - 44	14937	35°	0.32	9.58	9.42
1 - 5 - 44	13486	25°			
3 - 5 - 44	13490	25°	0.33	6.33	6.17
4-5-44	12243	18°			
6 - 5 - 44	12202	18°	0.31	4.43	4.27

b) System D_3b , $MgCO_3$, 1.88 H_2O prepared by dehydration of 0.964 gm. $MgCO_3$, $3H_2O$ at room temperature. Measured after sintering at 35° from 22-9-43 to 8-10-43. The alteration in pressure at temperature change from 18 to 35^0 is 0.7 mm., corresponding to an alteration of 0.0007 moles H_2O in the composition or $0.037 \ ^0/_0$ of the water content.

Date	Potentio- meter reading	Tempera- ture	P _{CO2} mm	р'н ₂ 0 mm	Р _{п₂О} mm
8-10-43	2150	18°			
13-10-43	3623	18°			
14-10-43	3624	18°	0.02	0.21	0.20
20 - 10 - 43	4791	25°	•••		
20 - 10 - 43	4812	25°	0.03	0.41	0.39
22 - 10 - 43	6802	35°			
22 - 10 - 43	6818	35°	0.06	0.94	0.91
23-10-43	5012	25°			
25 - 10 - 43	5032	25°	0.05	0.46	0.43
27 - 10 - 43	3987	18°	0.04	0.26	0.24
2-11-43	3974	18°			

The water vapour measurements are by far the most important, since we did not expect that the carbon dioxide pressures were well defined; in any case, we have not been able to detect carbon dioxide pressure determining phases (apart from the MgCO₃ hydrates) by X-ray analysis. They may have occurred, but only in very small amounts, we think here in particular of magnesium hydroxide and basic magnesium carbonate.

The measurements were as a rule carried out at 18, 25 and 35°. We were therefore in a position to calculate the heats of hydration q for each system by means of CLAUSIUS-CLAPEYRON'S formula:

$$q = R \frac{\ln r_2 - \ln r_1}{\frac{1}{T_1} - \frac{1}{T_2}}$$

in which R is the gas constant, r_1 and r_2 , the relative water vapour pressures at absolute temperatures T_1 and T_2 , and q the tensimetric heat of hydration valid for 1 mole liquid H₂O. It must be stressed here that the values calculated in each case are only valid for that part of the system, which has been determining for the vapour pressure. As shown in a previous paper (5), it is not necessarily more than a small part of a system, which is determining the vapour pressure, when one or both phases are inhomogeneous. The tensimetric heats of hydration calculated from the vapour pressure data can under such conditions not be expected to be identical with the mean values obtained by calorimetry.

Measurements of Systems Produced by Rehydration of Amorphous "Active" Magnesium Carbonate.

Rehydration series. Table 1 and figure 3.

System R_1 . MgCO₃, 0.24 H₂O. The system consisted of the completely amorphous "active" magnesium carbonate prepared by dehydration of the trihydrate in an atmosphere of carbon dioxide at 180–210°. After repeated evacuation to remove all air, the pressure above the system rose in 5 days to 0.08 mm., which, however, was scarcely an equilibrium pressure.

System R_2 . MgCO₃, 0.33 H₂O. Prepared by leading water vapour at 12 mm. pressure for a few minutes at room temperature into system R_1 . Most of the water vapour was taken up within 24 hours, but final equilibrium was not obtained for quite a month. As soon as the water vapour was introduced, the pressure changed immediately, and within short periods almost reproducibly when the temperature was changed, hence the long accomodation time must be due to a slowly progressing alteration in the solid phases of the system, an aging or sintering must have taken place. No samples were collected for X-ray analysis, but the preparation must have been amorphous just as the next and the previous preparations. The heat of hydration was calculated to be -3.2 kcal per mole liquid H₂O.

System R_3 . MgCO₃, 0.86 H₂O. Water vapour at 15 mm. pressure was led at varying intervals for a total of 131 minutes into R_2 , while the flask was kept at 20° to avoid condensation of the water vapour. It was then allowed to stand in the flask for 4 months, after which samples were taken for X-ray analysis. The air was removed by direct evacuation. This caused a certain dehydration, which, in spite of later addition of a little water vapour, exerted some effect on the measurements which were carried out $1^{1}/_{2}$ months later. The water vapour pressures are quite certainly somewhat larger than those in R₂, but the shape of the curve places the system in the dehydration series, since the heat of hydration is positive, 0.96 kcal. These values are therefore put in paranthesis in table 1. X-ray examination showed that the preparation was completely amorphous.

System R_4 . MgCO₃, 1.24 H₂O. On addition of water vapour at 13 mm. pressure for 25 hours, system R_3 took up 0.38 moles H₂O per mole MgCO₃ at room temperature. The system was allowed to stand for $3^{1/2}$ months, after this the air present was removed without direct evacuation, but by repeatedly evacuating another part of the apparatus and then opening to the flask containing the preparation. By this procedure the air can be removed without appreciable alterations in the composition of the system. After evacuation of the air, measurements were carried out over a period of 2 months. A considerable increase in the water vapour pressure was noticed. The carbon dioxide pressure is given in parenthesis in table 1, since there was no possibility for analyzing the permanent gas a part of this may have been air. X-ray examination showed the preparation to be quite amorphous. The heat of hydration was negative, -2.4 kcal.

System R₅a and R₅b. MgCO₃, 1.40 H₂O. Prepared from R₄ by addition of water vapour as in the previous system, but for 76 hours. After 15 days the first single series was measured from higher to lower temperature, system R₅a. The results are given in the table, but in parenthesis, since it was not proved that equilibrium pressure had been obtained. The system was not investigated by X-ray analysis. By accident, air succeeded in entering the system, this was removed as previously described, and water vapour was introduced for 5 seconds. The measuring of system R₅b, which had practically the same composition as R₅a, was carried out over 3 weeks. On X-ray analysis a diagram was obtained with 16 diffuse magnesium carbonate trihydrate lines. We had previously registered 85 lines in a diagram of well crystallized trihydrate, taken in the same camera. The heat of hydration of system R_5a is given tentatively as -5.3 kcal, that of R_5b is -7.5 kcal.

System R₆. MgCO₃, 1.94 H₂O. Prepared from R₅b by ad-

dition of water vapour for 68 hours. The system was not very mobile. The small amounts of water vapour, liberated from or adsorbed by the glass walls of the apparatus outside the thermostat, when the temperature of the laboratory changed considerably during the day on account of lack of fuel, could not be taken up or liberated sufficiently quickly by the hydrate system, and the pressures therefore fluctuated periodically. The measurements of the system were therefore subject to an error of $2-3 \ 0/0$.

The X-ray diagram showed 30 somewhat diffuse lines, all belonging to the trihydrate diagram. No trace of dihydrate was found here, but we assume the system to be like the former, but with more trihydrate. The heat of hydration was of the same order as in the previous system, -7.2 kcal.

System R_7 . MgCO₃, 2.38 H₂O. Prepared from R_6 by introducing water vapour for 23 hours. On account of the relatively high vapour pressure, the measurements could only be carried out up to 25°. The vapour pressures were somewhat greater than in previous systems. If it is assumed, that the vapour pressure curve in fig. 3 is a straight line, it can be found that it will cut the vapour pressure curve for pure water at a value of 1/T corresponding to 10.4° C. (log r = 0). At about this temperature the system will have the same vapour pressure as the saturated solution of trihydrate, but we do not mean that a transition point is a reality, on the contrary that an irreversible transformation of the amorphous phase to the trihydrate will occur.

The heat of hydration was of the same order as in the previous systems, -7.5 kcal. The X-ray diagram showed 52 trihydrate lines.

Measurements of Systems Produced by Dehydration of Magnesium Carbonate Trihydrate at Room Temperature.

Dehydration series D_1 —(D_2) and D_3 — D_6 . Table 2 and figure 3.

System D₁. MgCO₃, 2.52 H₂O. Prepared by dehydration of trihydrate at room temperature for 9 days. Equilibration of the vapour pressure was very slow, occurring after changes in the temperature only after 5 days, but in a satisfactorily reprodu-D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. XXV,12. ³ cible way. The heat of hydration was calculated to -3.9 kcal. The X-ray diagram showed 34 trihydrate lines and 2 dihydrate lines.

System D_2 . On further dehydration of D_1 for 21 days in vacuo in a closed system, the composition was MgCO₃, 1.7 H₂O. Since it was especially interesting to obtain a system with as pure dihydrate as possible, water vapour was led in until the composition was MgCO₃, 2.02 H₂O. The measurements were carried out after 2 months. According to the method of preparation the system was almost a rehydration system. The relatively high vapour pressure, which is put in parenthesis in table 2, also fits best among the curves of the rehydration systems to R₅a. The X-ray diagram gave a disappointment, since apart from 13 lines of trihydrate it contained only 6 lines from the dihydrate. According to the composition we could scarcely expect to find a trihydrate, but the system must consist of dihydrate, trihydrate and amorphous magnesium carbonate. The heat of hydration was calculated to -4.5 kcal.

System D_3 . MgCO₃, 1.88 H₂O. The preparation, by dehydration of another portion of well crystallized magnesium carbonate trihydrate at room temperature in vacuo in a closed system, is given more fully in a previous section of this paper, where the time of dehydration and its rate for this and the next two systems are tabulated. The measurement of system D₃a was carried out between the 24th and 28th day after the dehydration. In the intermediate period the pressure at 18° was still rising, towards the end, however, extremely slowly. Measurements were therefore also taken at 25 and 35°; these results are given in the table. After measurement at 35° a slow rise in the pressure again occurs. At the end of this last rise, which we consider to be due to an aging or sintering of the solid phases in the system, the measurements which are given for system D₃b, were carried out. The heat of hydration was positive for both systems, 4.2 and 3.5 kcal respectively. The X-ray diagram of the sample removed after the measurements showed only 17 diffuse lines, which originate from the dihydrate, all the trihydrate lines have disappeared. By simple calculation from the width of the lines, the particle size of the dihydrate can be estimated to be of the order of 100 Å.

System D_4 . MgCO₃, 1.64 H₂O. From D_3b by continued dehydration at room temperature for 52 days. As in the previous system there was a strong sintering effect at 35°. The final measurements were therefore only carried out after 2 months. The small water vapour pressure was remarkable. The heat of hydration was calculated to 4.2 kcal. The X-ray diagram contained 10 diffuse dihydrate lines.

System D₅. MgCO₃, 1.43 H₂O. From D₄ by continued dehydration at room temperature for 207 days. Hence the preparation originated by intermittent dehydration of magnesium carbonate trihydrate for a total of 309 days. The sintering effect at 35° was noticed for 14 days, after which the measurements were reproducible at the 3 temperatures. The water vapour pressures at 25 and 18° are so low that no water could condense in the BRUNNER manometer. The measurements in this gave us therefore only the sum of water vapour and carbon dioxide pressures. The partial pressures had therefore to be found from the total pressure by means of simultaneous readings of the hotwire manometer as described in detail in the previous section. It should be noticed that while the dependance of the water vapour pressure on temperature is normal, this is apparently not so for carbon dioxide pressure. Even if a priori we can not expect any definite correlation, since the carbon dioxide pressure does not need to be defined, it is, however, most reasonable to assume similarity to the previous systems. Errors in carbon dioxide pressures do then not need to be greater than some few 1/100 mm. The errors in the water vapour pressures are probably of the same order. The heat of hydration is calculated from the given water vapour pressures to be 3.8 kcal. X-ray analysis gave us a diagram with 6 very diffuse dihydrate lines.

System D_6 (rehydrated). MgCO₃, 1.85 H₂O. In order to obtain a better diagram of the dihydrate and to be able to measure a system produced by rehydration, water vapour was led for 100 hours into system D_5 , which then attained the composition MgCO₃, 1.85 H₂O. The measurements were carried out after the system had stood for $3^1/_2$ months; they could be well reproduced. The heat of hydration calculated by the usual method is -1.3 kcal. The X-ray diagram, however, showed 14 trihydrate lines and only 9 dihydrate lines although the composition was MgCO₃,

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 $1.85 \text{ H}_2\text{O}$. This showed that the dihydrate crystallizes so extraordinarily slowly that most of the water vapour enters the trihydrate. The system is of course unstable from a thermodynamic point of view.

It is a pleasure for us to express our best thanks to professor N. BJERRUM for suggesting this work and for his continued interest and valuable criticism during its progress.

For the English translation we are indebted to CICILY ANDRESEN, B. Sc.

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Indleveret til selskabet den 5. januar 1949. Færdig fra trykkeriet den 8. december 1949.