Mechanisms and Kinetics of the Thermal Decomposition of Sodium Sulphide Pentahydrate under Controlled Water Vapour Pressure †

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The kinetics and mechanism of the thermal decomposition of sodium sulphide pentahydrate to an essentially anhydrous form was investigated, in the pressure range 3—20 Torr, using thermogravimetry and X-ray powder diffractometry under controlled temperature and water vapour pressure. A two-step dehydration reaction pathway involving an intermediate dihydrate phase was observed: $Na_2S \cdot 5H_2O \longrightarrow Na_2S \cdot 2H_2O + 3H_2O$ (g); $Na_2S \cdot 2H_2O \longrightarrow Na_2S + 2H_2O$ (g). The latter reaction is shown to be relatively more inhibited than the first. The intermediate phase was studied by means of simultaneous thermogravimetry and X-ray powder diffraction methods. A structural transformation is proposed in terms of a topotactic process, which readily accounts for the readiness with which the first reaction takes place and which is also consistent with the overall structural transformation from the pentahydrate to the anhydrous product.

A wide variety of hydrated sodium sulphide species has been quoted in the literature as being formed either by crystallization from solutions or by thermolysis in the solid state.[1] The occurrence of $Na_2S \cdot 9H_2O$ is acertained beyond doubt, whereas for the lower hydrates a number of controversial results are found in the literature.
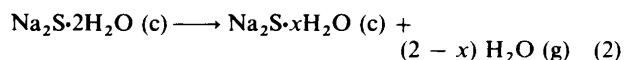
In their solubility studies, Parravano and Forniani[2] claimed the existence of a hexahydrate and a 5.5 hydrate in the temperature ranges 48—91.5 and 91.5—94 °C. The latter hydrate was also found to be metastable between 48.9 and 91.5 °C. Using various different preparative procedures, Böttger,[3] Sabatier,[4] and Lemoine[5] obtained a pentahydrate, $Na_2S \cdot 5H_2O$. Later on, Sanfourche[6] described an intermediate stable above 85 °C, which was supposed to be a monohydrate. In a more recent work Kopylov[7] reported the existence of a pentahydrate and a hemihydrate, $Na_2S \cdot 0.5H_2O$, between 49 and 97 °C, and between 84 and 88 °C, respectively. These hydrates were obtained by crystallization from aqueous solutions.

Concerning the thermal decomposition of sodium sulphide hydrates, the information available in the literature is very scarce. It is generally believed that at temperatures below 100 °C the nonahydrate begins to loose its water down to the monohydrate.[8] The last water molecule is removed only with difficulty, e.g. in a hydrogen atmosphere at 700 °C. The high stability of the monohydrate has also been noticed by Kerby and Hughson[9] in their thermoanalytical work embracing thermogravimetric and high-temperature X-ray powder analysis. Sanfourche[6] and Damoiseau[10] prepared a 4.5-hydrate and a trihydrate, respectively, merely by keeping $Na_2S \cdot 9H_2O$ crystals under vacuum over sulphuric acid solutions.

Apart from the well known anti-fluorite type lattice of anhydrous sodium sulphide,[11] complete crystal structures have been determined for $Na_2S \cdot 5H_2O$[12] as well as for $Na_2S \cdot 9H_2O$,[13] which unambiguously proves the existence of these hydrates.

In the last few years there has been renewed interest in the chemistry of sodium sulphide, because of its practical applications in chemical heat pumping, based on solid–gas reactions, as well as in industrial paper technology.[14—17] In the present work we have concentrated our efforts on investigating the thermal decomposition of sodium sulphide pentahydrate under controlled pressure and temperature, in an atmosphere of pure water vapour. This study has two major goals. (i) To elucidate the mechanism of the dehydration reaction, which proceeds through a hitherto unknown dihydrate intermediate, according to the scheme in equations (1) and (2), where $0.2 < x < 0.5$.

$$Na_2S \cdot 5H_2O \text{ (c)} \longrightarrow Na_2S \cdot 2H_2O \text{ (c)} + 3H_2O \text{ (g)} \qquad (1)$$

$$Na_2S \cdot 2H_2O \text{ (c)} \longrightarrow Na_2S \cdot xH_2O \text{ (c)} + (2 - x) H_2O \text{ (g)} \qquad (2)$$

(ii) To get a better understanding of the overall structural transformation, which unexpectedly is a facile process. The reactions (1) and (2) are reversible and display relatively small dehydration–rehydration hysteresis in a manner similar to a few other salt hydrates possessing layer structures, viz. copper formate tetrahydrate, manganese formate dihydrate, and uranyl nitrate.[18—21]

Experimental

Materials.—In all experiments fresh sodium sulphide nonahydrate of reagent grade (Merck pa) was utilized and only well developed, colourless, and transparent crystals were selected for the study. If not otherwise stated, this salt was further purified by recrystallization from distilled water before use. This procedure gave prismatic tetragonal crystals with sizes in the range 0.5—1 mm, which were used as the starting material.

In the thermogravimetric experiments the amount of sample was about 15—20 mg $Na_2S \cdot 9H_2O$, which corresponds approximately to a monolayer of particles in the balance pan. In the X-ray diffractometry studies, 0.5—1 g of material were used. All the samples were unsieved, and the various hydrates were prepared *in situ*, to avoid possible oxidation or hydrolysis.[17,22]

Due to their high hygroscopicity, stoicheiometries for lower sodium sulphide hydrates can be determined only indirectly in the following manner. Using an iodometric titration procedure,[23] fresh, crystalline $Na_2S \cdot 9H_2O$ was analysed for water by determining its sulphide content, and it was confirmed that the stoicheiometry corresponds to 9.0 mol water per mol Na_2S. The impurities of sulphite and thiosulphate were less than 1%. Thus for a thermogravimetric run with a known amount of nonahydrate, which when handled rapidly shows no problems with hygroscopicity, it is sufficient to measure the sample mass in order to determine the water content at different times. The mol ratio n (mol water per mol Na_2S) corresponding to a sample weight m is inferred from equation (3), where m_9 is the weight of the nonahydrate used as the starting material.

$$n = 13.34(m/m_9) - 4.34 \qquad (3)$$

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† *Non-S.I. unit employed:* Torr $\approx$ 133 Pa.

The deuterium oxide utilized in the H_2O–D_2O exchange experiments was of reagent grade with 99.8 atom% deuterium (Ciba-Geigy).

Instrumentation and Experimental Procedure.—(*a*) *Thermogravimetric (t.g.) equipment. The McBain balance.* The McBain quartz-spring balance, described elsewhere,[24,25] is well suited for experiments in both temperature-scanning and isothermal modes. The scanning rate may be set down to 3 °C h⁻¹. It is equipped for operation under controlled water vapour pressure according to the cold-point method, and both weight and temperature changes are continuously recorded. Hereafter, the constrained pressure and temperature in the apparatus are denoted as T_c and p_c, respectively. The sensitivity of the balance is 0.05 mg for weight-change measurements, which gives an absolute accuracy of about 0.03 in the molar ratio n. Prior to an experiment the device was thoroughly evacuated and degassed.

In all the experiments the pentahydrate was initially prepared *in situ* from the nonahydrate, by dehydration at 7 Torr and *ca.* 35 °C. Precautions were taken to avoid melting of the material, since the nonahydrate possesses a peritectic point at 49 °C, at which it decomposes to pentahydrate and solution.[1,7] The pentahydrate is stable up to its (congruent) melting point at 98 °C. The identity of the dehydration product with $Na_2S\cdot5H_2O$ was inferred from the following observations: first, the molar ratio n of the dehydration product was 5.0, as recorded by t.g.; secondly, X-ray diffraction studies performed under similar pressure and temperature showed that the powder diffractogram was identical with that reported previously for the pentahydrate.[12] The powder diffractogram displayed sharp, well defined reflections, indicating a good crystallinity.

In the temperature-scanning experiments the scanning rates were either 3 or 12 °C h⁻¹. In the pressure-jump experiments the reaction was initiated by means of a pressure jump, which was performed by switching from one evaporator to another, kept at a different temperature. In these measurements $T_c = 70$ °C and the initial pressure 21 Torr.

The determination of vapour pressures was performed using a kinetic procedure, whereby the reaction rate of a sample was recorded at different T_c and constant p_c, or *vice versa*. The sample consisted of a mixture of the two hydrates which participate in the reaction, and was prepared *in situ* by partial dehydration of the hydrate having the higher water content. In this way, a large solid–solid interface develops between the two hydrates, which is necessary for fast equilibration times. Reaction rates were calculated from the slope of the mass *vs.* time recordings as obtained by t.g. Equilibrium temperatures (or pressures) were then determined by plotting the reaction rate *vs.* T_c (or p_c) and finding the intersection at the T_c (or p_c) axis. This method is only applicable when the sorption–desorption hysteresis is small.

The H_2O–D_2O exchange studies were performed as described by Kraft[26] and Franklin and Flanagan.[27] Sodium sulphide pentahydrate was initially prepared *in situ* in the McBain thermobalance, as already described, at $T_c = 70$ °C and $p_c = 19.8$ Torr. The experiment was started by changing to another evaporator, containing deuterium oxide at 22 °C, which yielded a vapour pressure of 18 Torr. The mass change of the sample was then continuously recorded and from this the $D_2O:Na_2S$ molar ratio was calculated.

The Cahn electrobalance. The Cahn RG electrobalance, modified to allow for experiments in a pure water vapour atmosphere, is suitable for measuring the water contents of samples when T_c is varied in a stepwise manner. The sensitivity of the balance is about 1% in the pertinent measuring range. The sample is located in a glass pan suspended from the balance lever, and is surrounded by a jacketed glass tube connected to a thermostatting bath. Prior to the experiments the system is throughly evacuated and degassed. The water vapour pressure is kept constant by means of a temperature-controlled evaporator containing distilled water.

In the course of the experiments, T_c was changed in a stepwise manner and sufficient time was given for equilibrium to be established at each setting. Complete equilibrium was usually reached within 2 h.

(*b*) *X-Ray diffraction equipment.* The θ—2θ X-ray powder diffractometer consisted of a CRG basic X-ray unit (wavelength Cu-$K_\alpha = 1.54$ Å), modified to allow for either isothermal or temperature-scanning measurements under controlled water vapour pressure. The modification, which comprises a specially built X-ray furnace, is described in ref. 28. The furnace with the sample holder has a thermostatted outer jacket, and can be operated under vacuum conditions.

With the combined θ—θ diffractometer and thermobalance, simultaneous recordings of X-ray diffractograms and sample weight are easily made.[29] The sample, the weight of which was about 1 g, is placed in a metal cup, which in turn is connected to a vertical metal bar of an electrobalance mounted below it. In addition, the sample which is immobile serves as a target for X-rays. The X-ray and the counter move in opposition with the same speed about a horizontal axis through the sample.

The X-ray diffraction experiments were conducted in two different ways. First, the structural transformation was followed in time by selecting a narrow Bragg angle (2θ) interval, comprising the characteristic d spacings, known to be altered in the course of the structural transformation. By fixing the X-ray detector between two reversing switches, a sequence of forward and backward narrow diffractograms was thus recorded. Secondly, when the equilibrium structure was reached, an overall diffractogram was recorded for the purpose of identification.

In the pressure-jump experiments, the furnace of the X-ray diffractometer was connected to two evaporators, one containing pure water and the other saturated calcium chloride solution. Both the evaporators were kept at 20 °C. A few grams of sodium sulphide nonahydrate were fixed in the sample-holder cavity by means of a grid. The sample temperature was maintained at about 70 °C in these experiments.

Results

Characterization of the Hydrate Phases.—(*a*) *Stoicheiometric characterization using thermogravimetry. Isobaric conditions: temperature-scanning mode.* Dehydration thermograms were recorded under isobaric conditions in the temperature-scanning mode, in the range 40—85 °C. The thermograms obtained are presented in Figure 1 for $p_c = 3.2, 6.7, 9.3$, and 17.6 Torr, where only those recorded at 3 °C h⁻¹ are included since no significant change was observed when increasing the scanning rate to 12 °C h⁻¹. In all circumstances these thermograms exhibit some noteworthy features.

(*i*) When heating the pentahydrate a small amount of water corresponding to a molar ratio change $\Delta n = 0.05$—0.15 (mol water per mol Na_2S) is gradually lost before the salt is converted to the lower hydrate. (*ii*) An intermediate plateau is observed at $n = 1.6$—1.8. (*iii*) The dehydrated material still contains 0.2—0.9 mol water per mol Na_2S in the temperature range investigated. This value varies somewhat with the scanning rate. The water content is higher for lower scanning rates. (*iv*) In some runs a weak shoulder was found to appear at a molar ratio n lying between 2.3 and 3.0.

The pentahydrate, the intermediate *ca.* 2 hydrate, and the dehydration product all exhibit a more or less extensive divariance (see below).

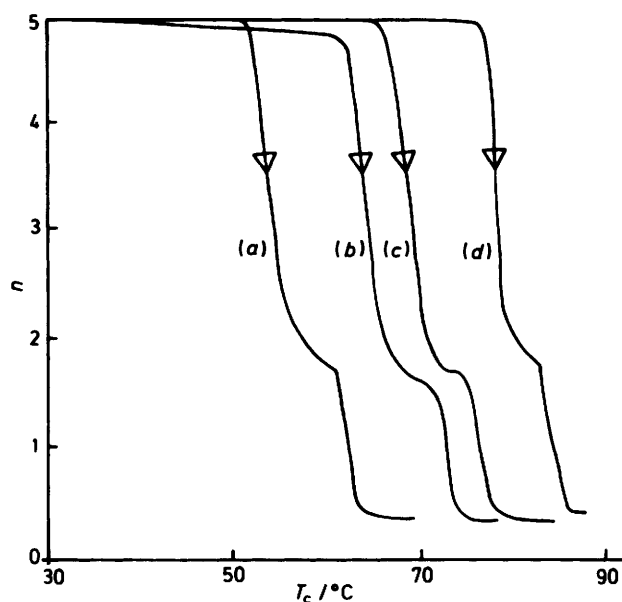As is clear from Figure 1, the transition temperatures change

Figure 1. Thermograms for decomposition of sodium sulphide penta-hydrate, recorded at four p_c values: 3.3 (a), 6.7 (b), 9.3 (c), and 17.6 Torr (d). Temperature range ca. 30—85 °C, scanning rate 3 °C h^{-1}

with pressure, but the water content of the intermediate hydrate is fairly constant between $n = 1.6$ and 1.8. The decomposition temperatures of the pentahydrate and ca. 2 hydrate as given by temperature-scanning thermograms are displayed in the pressure–temperature diagram in Figure 3, for the purpose of comparison.

When the particle size is chosen to be ca. 3—5 mm no significant change in the transition temperatures or the stoicheiometries of the participating species is observed.

Isobaric conditions: stepwise temperature variation. In order to check whether the temperature-scanning results correspond to equilibrium conditions and to ascertain the reversibility of the intermediate steps, independent experiments using the Cahn electrobalance were carried out at p_c ca. 7.0 Torr. The results are presented in Table 1, where two different experimental series 1 and 2 are included. According to series 1, the pentahydrate decomposes into an intermediate phase with $n = 2.10$ at 66.0 °C. On attempting to rehydrate it by lowering T_c to 60.5 °C, n increased to 4.91. If it is reheated to 65.5 °C, $n = 2.33$ results, and n decreases abruptly to 2.04 when T_c is increased to 71.1 °C. It is thus possible to cycle between the pentahydrate and the ca. 2 hydrate, in a reversible manner. At 74.9 °C the sample dehydrates to $n = 0.94$, and at 80.8 °C to 0.70. In series 2, where T_c was increased throughout, the intermediate phase has a composition with $n = 1.90$.

It should be noted that the changes in the mass occur abruptly, when the characteristic temperature of that particular transition is reached. The only exception to this observation is the divariance found for all the phases.

When the temperature-scanning runs are interrupted at 85 °C, the dehydrated phase still contains a small amount of water. This water was shown to disappear gradually when T_c was increased and the anhydrous state was reached at ca. 200 °C.

(b) *Structural characterization.* In situ X-ray measurements. X-Ray diffraction measurements, using the θ—2θ X-ray powder diffractometer, were performed under similar p_c and T_c conditions as those for the Cahn electrobalance, i.e. 7 Torr and various T_c. These measurements give evidence of the formation of a crystalline intermediate corresponding to the ca. 2 hydrate,

Table 1. Water content of sodium sulphide at varying temperatures and isobaric conditions, as recorded by the Cahn electrobalance

Series no.	p_c/ Torr	T_c/ °C	$n \pm 1\%$ (mol H_2O per mol Na_2S)	Remarks
1		20	9.00	Crystallized sample
	7.0	49.8	5.00 ⎫	
	5.7	66.0	2.02	
	7.0	66.0	2.10	
	6.5	60.5	4.91	
	6.5	65.5	2.33	
	6.5	67.7	2.33 ⎬	n Slightly decreasing
	6.5	69.4	2.12	
	6.5	71.1	2.04	
	6.5	72.5	2.04	
	6.5	74.9	0.94	
	6.5	80.8	0.70 ⎭	
2	7.0	22.5	9.00 ⎫	
	7.0	33.0	5.04	
	6.8	43.0	5.02	
	6.7	52.4	5.01 ⎬	Crystallized sample
	6.7	68.4	1.90	
	6.7	77.4	0.19 ⎭	
	0.0	77.4	0.11	Vacuum

Table 2. X-Ray powder diffractogram of the ca. 2 hydrate, obtained by dehydrating $Na_2S\cdot5H_2O$. $\lambda = 1.54$ Å (Cu-K_a)

θ/°	d/Å	Intensity/%
11.0	4.04	10
12.0	3.70	10
13.8	3.23	10
14.5	3.08	15
15.0	2.98	0—80 *
15.9	2.81	20
16.6	2.70	20
17.3	2.59	35
18.3	2.45	100
19.0	2.36	35 *
20.1	2.24	35 *

* Varying.

previously observed by t.g. The diffractogram of this species is presented in Table 2. By a stepwise increase in the temperature, it was clear that the pentahydrate and dehydrated product correspond to the previously determined pentahydrate and anhydrous sodium sulphide *structures* respectively.[11,12] However, the anhydrous compound could be obtained in a pure form only through forced pumping and/or heating in order to remove contamination by the ca. 2 hydrate.

The diffractograms of the pentahydrate, ca. 2 hydrate, and dehydrated product all display narrow, well defined reflections, indicating a crystalline product. The same applies when the pentahydrate is dehydrated under vacuum conditions. However, a noteworthy observation is that a few lines (see Table 2), which are present while the ca. 2 hydrate is being formed as well as immediately after its formation, disappear when T_c is increased. This is clearly shown for the 15.0° line in Figure 2, where the most prominent lines of these three phases, viz. 16.4, 18.3 and 15.0, and 19.5°, respectively, are included. The temperature was continuously increased at a rate of ca. 10 °C h^{-1}. Since the 15.0° reflection reappeared when lowering T_c, this transformation seems to be fully reversible. Furthermore, the line intensities for the ca. 2 hydrate increase when those of the pentahydrate
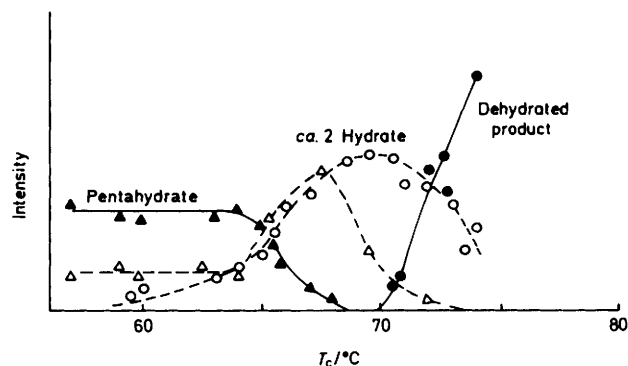
Figure 2. Intensities of prominent X-ray diffraction lines of a $Na_2S \cdot nH_2O$ sample *vs.* T_c at $p_c = 7$ Torr. Scanning rate *ca.* 10 °C h^{-1} (free heating). The intensity axis refers to diffraction peak height (arbitrary scale) $\theta = 15.0$ ($\triangle$), 16.4 ($\blacktriangle$), 18.3 ($\bigcirc$), or 19.5° ($\bullet$)
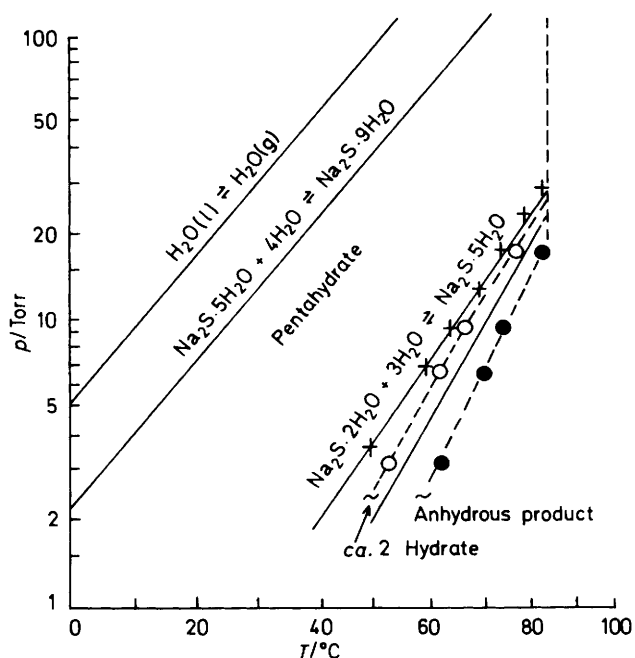

Figure 3. Pressure *vs.* temperature diagram for the Na_2S–H_2O system. $+$, Equilibrium data recorded for a mixture of the pentahydrate and *ca.* 2 hydrate; $\bigcirc$, temperatures of the onset of decomposition of the pentahydrate, measured from the thermograms in Figure 1. $\bullet$, temperatures of onset of decomposition of the *ca.* 2 hydrate (*cf.* Figure 1)
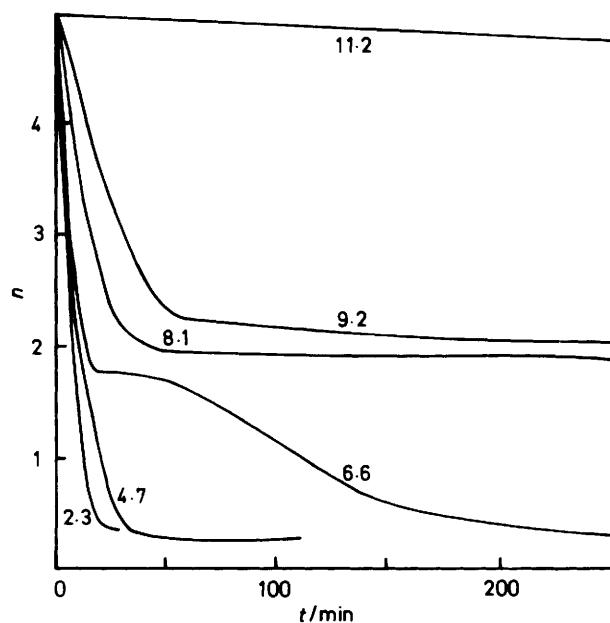

Figure 4. Pressure-jump dehydration curves for the pentahydrate recorded at 70.0 °C. Initial pressure: 21 Torr. Final pressures (Torr) are shown

disappear, whereas when the line of the dehydrated product starts to increase those of the *ca.* 2 hydrate decline. It is interesting that the intensities of the lines 15.0 and 18.3° increase simultaneously, which is indicative of the build up of one and the same phase.

Combined X-ray and thermogravimetric measurements. These measurements confirmed the correspondence between the changes in water content as recorded by t.g. measurements and the structural changes as indicated by X-ray crystallography. Both temperature-scanning and stepwise varying-temperature experiments were performed. It is evident from these measurements that the different steps of the t.g. scanning thermograms correspond to the pentahydrate, *ca.* 2 hydrate, and anhydrous salt structures, respectively.

(*c*) *Equilibrium vapour pressure data for pentahydrate* $\rightleftharpoons$ ca. 2 *hydrate + water vapour.* Vapour pressures at different

temperatures for this equilibrium were recorded using the kinetic method described above by changing T_c while keeping p_c constant (see the Experimental section), and are presented in Figure 3, together with data for the sodium sulphide–water system reported previously by Brunberg.[14] The presence of these phases obtained *in situ* was merely inferred from the total water content. The accuracy of these data relies upon the fact that very little inhibition was found for this step (see below), consistent with the decomposition temperatures obtained from the recorded thermograms (see Figure 1).

A linear relationship between ln p and $1/T$ is found for reaction (1), as expressed by equation (4). The calculated

$$\ln(p/\text{Torr}) = 23.9 - \frac{7\,290}{(T/\text{K})} \qquad (4)$$

(average) thermodynamic parameters are $\Delta H^\circ = 60.6 \text{ kJ mol}^{-1}$ H_2O and $\Delta S^\circ = 199 \text{ J K}^{-1} \text{ mol}^{-1}$ H_2O, in the relevant temperature range.

Kinetic Measurements.—Reaction rate measurements, using the pressure-jump technique. Kinetic measurements using the pressure-jump technique were made at $p_c = 3$—12 Torr at 70 °C (Figure 4). At higher pressures (>8 Torr) the reaction stopped at $n = 2.0$—2.1 and no further reaction took place within 1 d. In the medium-pressure range (*ca.* 7 Torr) a distinctive plateau was obtained at $n = 1.8$. At the lowest pressures, *viz.* <5 Torr, the relaxation curve only revealed a shoulder at $n = 1.7$—1.8, which was obtained from the derivative curve. The water content of the *ca.* 2 hydrate increased with increasing p_c. The two steps observed at pressures below 7 Torr are associated with reactions (1) and (2).

When the maximum rates of reactions (1) and (2) are plotted against p_c straight lines are obtained intersecting the p_c axis at 10.7 and 7.0 Torr, respectively (see Figure 5). Thus no Smith–Topley effect is detected in the p_c and T_c range investigated.[20,30]

Inhibition of reactions (1) *and* (2). The rates of reaction (2) were measured at different pressures, at 70 °C (see Figure 6). The hydrate mixture was prepared by starting with the
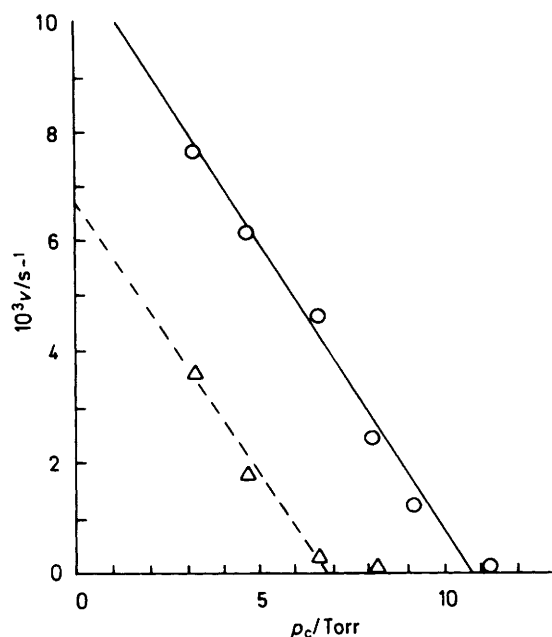
Figure 5. Plots of maximum reaction rate $v = dn/dt$ vs. p_c for the reactions: ○, pentahydrate ⟶ ca. 2 hydrate; △, ca. 2 hydrate ⟶ anhydrous product (cf. Figure 4)

Figure 6. Plots of reaction rate (dn/dt) vs. p_c for mixtures of the pentahydrate and ca. 2 hydrate (●, ▲) and of the ca. 2 hydrate and anhydrous product (○, △). The arrows indicate the direction in which the pressure was changed

pentahydrate and decomposing it by lowering p_c from 21 to 6.6 Torr. The formation of the ca. 2 hydrate is detected by its characteristic plateau. Thereafter, by further dehydration (cf. Figure 4) a final mixture of this phase and the dehydrate product corresponding to a water composition of about $n = 1.2$ was obtained. Figure 6 shows a pronounced inhibition plateau (i.e. a region where the reaction rate is zero) at about 3 Torr around the equilibrium pressure. To ensure the exclusive participation of this mixture, the sample was subsequently rehydrated at 12.8 Torr, whereby the characteristic plateau of the ca. 2 hydrate (at $n = 2.2$ Torr) reappeared. The formation of this phase, in the course of a rehydration, was also confirmed by X-ray diffraction. Similar measurements were made for a mixture of the pentahydrate and ca. 2 hydrate, and the resultant data are also included in Figure 6. A relatively small inhibition (ca. 1 Torr) is observed for this case.

Exchange rate studies. The results of the H_2O–D_2O exchange experiments showed that only four (experimentally 3.8) among five possible water molecules are exchanged when the pentahydrate is subjected to deuterium oxide vapour. Moreover the exchange is rapid. Since the plot of $D_2O:Na_2S$ molar ratio vs. time was very nearly exponential a time constant of 50 min could be extracted from it.

Discussion

Formation and Stability of the ca. 2 *Hydrate.*—It is well known that metastable intermediate formation may occur during dehydrations. Lallemant[31,32] showed that magnesium sulphate and magnesium chromate hydrates ($MgSO_4 \cdot 4H_2O$ and $MgCrO_4 \cdot 5H_2O$) may decompose into metastable phases, prior to the attainment of the stable phase, provided that the pressure and temperature are appropriate. These intermediate phases, if there are more than one, often possess X-ray diffractograms resembling each other. The line positions may change slightly and some lines may disappear or arise. Lallemant examined the metastability by storing the inter-
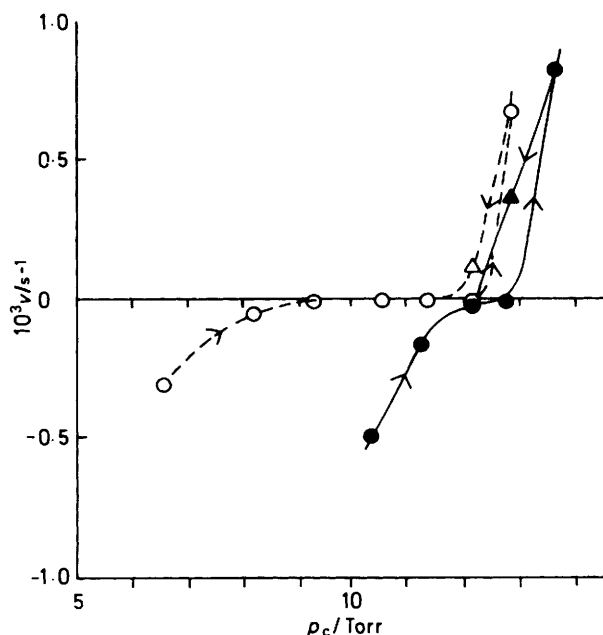
mediate species for a very long time, i.e. 1 month for some samples, and found that they decomposed, but only at comparatively low pressures.

It may be expected that conducting the thermal dehydration from the pentahydrate to the ca. 2 hydrate more or less closely to equilibrium may lead to more or less disordered ca. 2 hydrates with varying water content. This explains the stoicheiometric discrepancies between results obtained using the temperature-scanning mode (see Figure 1) and those with the Cahn technique (see Table 1). This effect is also clearly displayed by three of the dehydration processes. The intensity of some diffraction lines associated with the ca. 2 hydrate tends to diminish when the temperature increases. This is most evident for the 15.0° line, which has almost disappeared when the dehydrated phase builds up (cf. Figure 2). Such observations seem to indicate some kind of reorganization occurring in the lattice of the ca. 2 hydrate. This is corroborated by the different decay behaviour found at higher temperatures (cf. Figure 2) for the 18.3 and 15.0° lines. Since this effect is evidently reversible and takes place within a T_c range of three degrees, it is tentatively ascribed to a reversible order–disorder transformation.

In contrast to what was found for magnesium sulphate and chromate, experiments with sodium sulphide show that the ca. 2 hydrate is a stable intermediate, since it may equilibrate with the dehydrated product. The pronounced inhibition of the conversion of the ca. 2 hydrate to the dehydrated product (cf. Figure 6) prevented an accurate determination of the equilibrium vapour pressure for reaction (2) using the kinetic procedure. However, the stability domain may be estimated, if one can find the boundaries of the inhibition region. This may be done in the following manner. It has generally been observed[33] that the inhibition of the reaction anhydrous phase ⟶ ca. 2 hydrate ceases as soon as the pentahydrate starts to form. Since the reaction of the ca. 2 hydrate to go into the pentahydrate possesses a very small inhibition region (cf. above), it is reasonable to assume that its equilibrium line represents a low-temperature limit to this region. The high-temperature limit is given by the decomposition temperatures as
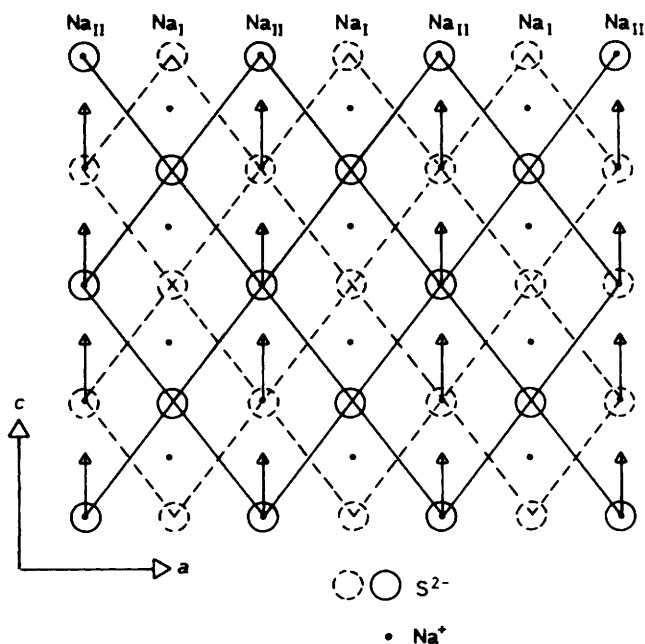
Figure 7. A simplifed sketch of the $Na_2S\cdot 5H_2O$ structure, showing a projection onto the ac plane, with two superimposed sulphide layers and one sodium layer between. The arrows indicate the motion of the Na_{II} ions, during the transition to the $ca.$ 2 hydrate, according to the suggested mechanism (see text)

obtained from the thermograms in Figure 1. An approximate equilibrium line is calculated by taking the average of the temperatures for the two boundaries (see Figure 3), and is given by equation (5). The thermodynamic parameters corresponding

$$\ln(p/\text{Torr}) = 26.5 - \frac{8\ 300}{(T/\text{K})} \quad (5)$$

to this expression are $\Delta H^\circ = 69.0$ kJ mol^{-1} H_2O and $\Delta S^\circ = 220$ J K^{-1} mol^{-1} H_2O.

Possible Topotactic Processes.—As mentioned above, only a few other salt hydrates have been reported which are both reversible and show small hysteresis, *e.g.* copper formate tetrahydrate, manganese formate dihydrate, and uranyl nitrate hexahydrate.[18–21] Franklin and Flanagan[27] explained the ease with which the reaction of $UO_2(NO_3)_2\cdot 6H_2O$ occurs in terms of the large diffusion constant of water in the solid hydrate lattice. It is noteworthy that all these hydrates are similar to sodium sulphide pentahydrate in the sense that they all possess layer structures.

The structure of sodium sulphide pentahydrate may be described as consisting of alternating layers of sulphide, sodium, and water,[12] represented by •••-S-O-Na-O-S-•••. In this structure, which is orthorhombic with $a = 6.47$, $b = 12.54$, and $c = 8.65$ Å, the layers are perpendicular to the b axis. Figure 7 shows a projection into the ac plane, with two superimposed sulphide layers and a sodium layer lying between them. For the sake of clarity the water molecules have been omitted. There are two structurally non-equivalent types of sodium ions, denoted Na_I and Na_{II}, with an abundance ratio $1:1$. As seen from Figure 7, the sodium ions are located in alternating Na_I and Na_{II} chains parallel to the c axis. The water molecules may be divided into two different types O_I and O_{II}, with an abundance ratio $1:4$. In both cases they are tetrahedrally bound to two sulphide and two sodium ions. In the Na_I chains the sodium ions have an

octahedral co-ordination with respect to the water molecules, the octahedra having common O_I corners. Together with four O_{II} molecules and one sulphide ion, the Na_{II} ions form a square pyramid. The sulphide ions can be visualized as forming distorted octahedral cages with common faces. In half of these cages the Na_I are centrally located, whereas the Na_{II} are unsymmetrically positioned in their faces. The D_2O-H_2O exchange experiments show that only four of the five possible water molecules are exchangeable, which implies a high mobility of the O_{II} molecules. It is therefore reasonable to presume that during the thermal decomposition process these molecules are the first to be expelled. On the other hand, the dehydration experiments show that only three molecules are being lost, yielding a dihydrate. This finding may be understood by considering a topotactic process, in which the Na_{II} ions become destabilized in their unsymmetrical face position, as a result of the loss of three of the O_{II} molecules, and move towards the cage centre. The initial Na_{II} sites are thereafter occupied by the last O_{II} molecule. This leads to a structural equivalence of the sodium ions as well as of the water molecules, and the latter are each tetrahedrally bound to two sulphide and two sodium ions, which is structurally favourable.[34] A topotactic process is thus expected, taking into the account the readiness of the pentahydrate ——→ $ca.$ 2 hydrate reaction, despite the low temperature.[35,36] Attempts to verify these possibilities on the basis of a complete structural determination of the dihydrate are currently being made.

Finally, it should be stated that these lattice motions remind one very much of the case of shear transformation.[37,38] It was proposed that such a transformation takes place during the dehydration of the hydroxides as well as for monovariant and divariant salt hydrates, and that this is what accounts for their topotactic behaviour.

It should be stressed that the overall reaction of the pentahydrate to anhydrous product is relatively facile compared to other dehydration reactions. Taking into account the mechanism suggested above, it may be deduced that the process $ca.$ 2 hydrate ——→ anhydrous product is also topotactic.

References

1 Gmelin, Handbuch der Anorganischen Chemie, Bd 21, 8. Aufl., Verlag Chemie, Weinheim, 1927.
2 M. Parravano and M. Forniani, *Gazz. Chim. Ital.*, 1907, **37**, 521.
3 H. Böttger, *Liebigs Ann. Chem.*, 1884, **223**, 335.
4 P. Sabatier, *Ann. Chim. Phys.*, 1881, **22**, 18.
5 C. Lemoine, *C.R. Acad. Sci. (Paris)*, 1884, **98**, 45.
6 M. A. Sanfourche, *Bull. Soc. Chim. Fr.*, 1922, **31**, 966.
7 N. Kopylov, *Zh. Neorg. Khim.*, 1968, **13**, 276.
8 J. Mellor, 'Comprehensive Treatise on Inorganic and Theoretical Chemistry,' Longmans, London, 1961, vol. 2, suppl. 2, p. 981.
9 R. C. Kerby and M. R. Hughson, Research Report R262, Department of Energy Mines and Resources, Ottawa, 1973.
10 A. Damoiseau, *J. Pharm. Chem.*, 1884, **10**, 351.

11 E. Zintl, A. Harder, and B. Dauth, *Z. Elektrochem.*, 1934, **40**, 588.
12 D. Bedlivy and A. Preisinger, *Z. Kristallogr.*, 1965, **121**, 131.
13 D. Bedlivy and A. Preisinger, *Z. Kristallogr.*, 1965, **121**, 114.
14 E-Å. Brunberg, Department of Electron and Plasma Physics, The Royal Institute of Technology, personal communication, 1984.
15 E-Å. Brunberg, Colloquium: Dynamics of Solid/Gas Processes for Energy Conversion, The Royal Institute of Technology, Stockholm, Sweden, 1982, 23 (TRITA-FYK-8201).
16 M. Ucar and B. Pounder, *J. Therm. Insul.*, 1982, **6**, 48.
17 S. Andersson, *Chem. Scr.*, 1982, **20**, 164.
18 P. M. Fichte and T. B. Flanagan, *Trans. Faraday Soc.*, 1971, **67**, 1467.
19 T. A. Clarke and J. M. Thomas, *J. Chem. Soc. A*, 1969, 2227, 2230.
20 M. L. Smith and B. Topley, *Proc. R. Soc. London, Ser. A*, 1931, **134**, 224.
21 M. L. Franklin and T. B. Flanagan, *J. Chem. Soc., Dalton Trans.*, 1972, 192.
22 E. Rosen and R. Tegman, *Acta Chem. Scand.*, 1971, **25**, 3329.
23 B. Eriksson, R. Rådeström, and L. Sjöström, SCAN-Forsk No. 315, Research Report, Swedish Forest Products Research Laboratory, Stockholm, Sweden, 1982, and refs. therein.
24 J. Andersson, M. Azoulay, and J. de Pablo, *Thermochim. Acta*, 1983, **70**, 291.

25 F. Lavanant, Doctoral Thesis, Dijon, 1963.
26 H. Kraft, *Z. Phys.*, 1938, **110**, 303.
27 M. L. Franklin and T. B. Flanagan, *J. Phys. Chem.*, 1971, **75**, 1272.
28 N. Gerard and G. Watelle-Marion, *Bull. Soc. Chim. Fr.*, 1963, 2631.
29 N. Gerard, *J. Phys. Educ.*, 1974, **7**, 509.
30 G. Bertrand, M. Lallemant, A. Mokhlisse, and G. Watelle-Marion, *J. Inorg. Nucl. Chem.*, 1978, **40**, 819.
31 M. Lallemant, Doctoral Thesis, Dijon, 1974.
32 M. Lallemant and G. Watelle-Marion, *C.R. Acad. Sci., Ser. C*, 1971, **272**, 139.
33 J. Y. Andersson, M. Azoulay, and J. de Pablo, unpublished work.
34 M. Falk and O. Knop, in 'Water: a Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1973, vol. 2, ch. 2.
35 C. N. R. Rao and K. J. Rao, 'Phase Transitions in Solids,' McGraw-Hill, New York, 1978.
36 N. Datta, S. Chatterji, J. W. Jeffrey, and A. L. Mackay, *Mineral Mag.*, 1969, **37**, 250.
37 J-C. Niepce, G. Watelle-Marion, and N. H. Brett, *J. Chem. Soc., Faraday Trans. 1*, 1978, 1530.
38 R. K. Osterheld and P. R. Bloom, *J. Phys. Chem.*, 1978, **82**, 1591.