Thermochimica Acta, 13 (1975) 409–418

AN EXPERIMENTAL STUDY OF THE SALT HYDRATE $MgSO_4 \cdot 7H_2O$

S. EL D. HAMAD
Department of Geology, University of Khartoum (Sudan)
(Received 2 July 1975)

ABSTRACT

Thermogravimetry was used to study the characteristic features of the salt hydrate $MgSO_4 \cdot 7H_2O$. The kinetics of dehydration of $MgSO_4 \cdot 7H_2O$ in vacuum and in the temperature range 25–120°C was studied. Further experiments on the salt were performed under isobaric conditions and in the temperature range 19–90°C to study the equilibrium conditions for some phases in the system $MgSO_4$–H_2O. The results showed that the reaction $MgSO_4 \cdot 7H_2O = MgSO_4 \cdot 6H_2O + H_2O$ is reversible.

INTRODUCTION

In the system $MgSO_4$–H_2O, epsomite $MgSO_4 \cdot 7H_2O$ is the most common crystalline phase[1] and other low hydrates occur as scarce deposits. These are: hexahydrite ($MgSO_4 \cdot 6H_2O$), pentahydrite ($MgSO_4 \cdot 5H_2O$), leonhardite ($MgSO_4 \cdot 4H_2O$) and kieserite ($MgSO_4 \cdot H_2O$). From the early days the study on the salt hydrate, $MgSO_4 \cdot 7H_2O$, was centred on the measurement of its dissociation pressure. In this connection the attention of many investigators was concentrated on refining the different volumetric techniques they used. Foote and Scholes[2], Wilson[3], and others had shown that at 25°C $MgSO_4 \cdot 7H_2O$ transforms to hexahydrate at a vapour pressure of ~ 12.0 mm Hg. However, under conditions where the water vapour pressure is lower, other phases with less water are formed. Other research workers used the thermobalance in their studies of this salt hydrate. Fruchart and Michel[4] showed that the dehydration of $MgSO_4 \cdot 7H_2O$ as a function of slowly rising temperature was step-wise. They reported the existence of the trihydrate and the dihydrate in addition to those quoted previously as intermediate phases. On the other hand Duval[5] found that heating the salt hydrate at a higher rate of temperature was continuous and that the end product was the monohydrate.

In the present study a thermogravimetric apparatus incorporating a sensitive spring balance was built for performing some dehydration–hydration experiments on artificial $MgSO_4 \cdot 7H_2O$ in an attempt to revise the existing data reported in the literature and to elucidate the nature of interaction between the solid phases and water vapour. The apparatus is shown in Fig. 1A and B.

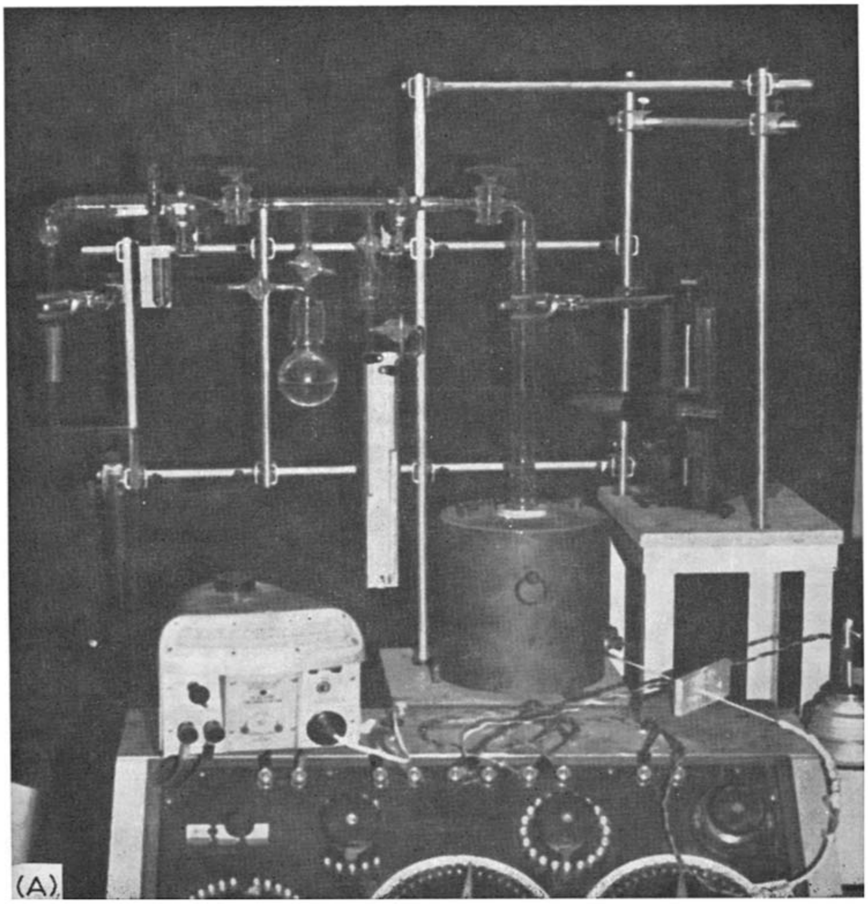

Fig. 1. (A) Thermogravimetric apparatus. (B) Schematic diagram of thermogravimetric apparatus.

SPECIMEN

The material used throughout this study was the Hopkins and Williams Analar Grade magnesium sulphate heptahydrate, No. 5406 with no less than 99.5% $MgSO_4 \cdot 7H_2O$. Necessary precautions were taken to ensure that all portions of the specimens used in the various experiments did not dehydrate under the dry conditions of the laboratory. Powdered $MgSO_4 \cdot 7H_2O$ was kept under an atmosphere of saturated water vapour at room temperature. The water content was determined on a 1-g sample using the penfield tube method. The weight-loss was 49.51% which was equivalent to 6.79 moles of H_2O per mole of $MgSO_4 \cdot 7H_2O$. Taking the impurities in the specimen into consideration, the difference was within the experimental errors. Under the microscope the specimen was biaxial negative with a prismatic shape and a negative elongation. The indices of refraction $\gamma = 1.459$, $\alpha = 1.435$ were measured to an accuracy of ± 0.002 using carefully calibrated immersion liquids. These data were in close agreement with those in the literature.

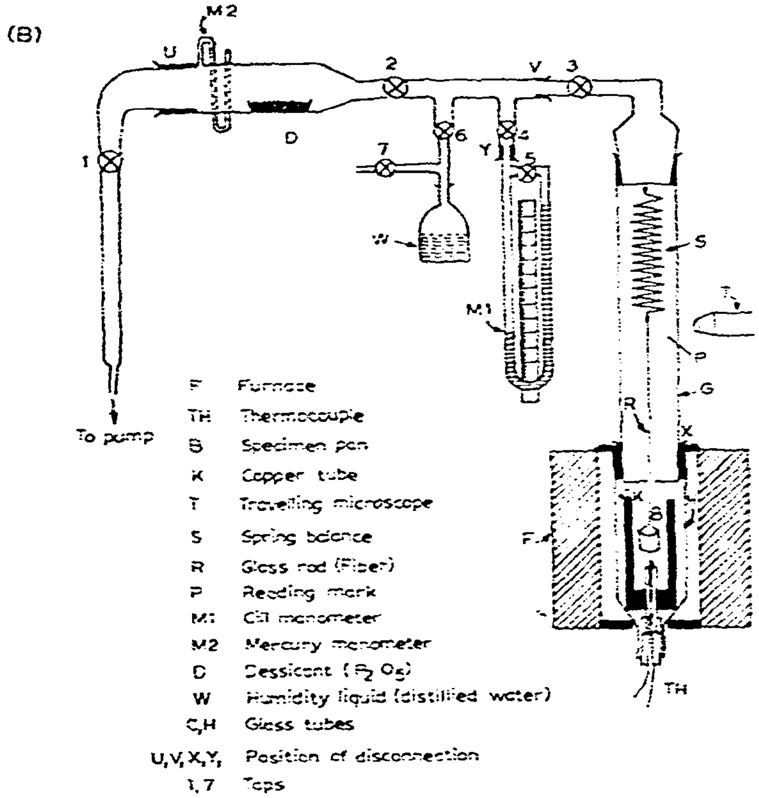

Fig. 1 (B).

THE KINETICS OF $MgSO_4 \cdot 7H_2O$ THERMAL DEHYDRATION

Experiment

In the thermal decomposition of $MgSO_4 \cdot 7H_2O$ the expulsion of water occurs with an activation energy which may be determined under the conditions where the water is continuously removed from the specimen, thus preventing the establishment of a solid–vapour equilibrium. In such experiments performed under isothermal conditions, the values of the rate constant k are obtained from the plots of the percentage loss of weight versus time. Using these values and the integrated form of the Arrhenius equation $\ln k = \ln A - E_a/RT$, the activation energy, E_a, of the reaction in the temperature range studied can be calculated.

The dehydration of $MgSO_4 \cdot 7H_2O$ was carried out under vacuum and in presence of P_2O_5, which continuously removed the water vapour. The plots of percentage loss of weight as a function of time performed in the temperature range 25–120°C are shown in Fig. 2. The data for each curve were obtained on a fresh powdered sample of $MgSO_4 \cdot 7H_2O$ weighing ~200 mg. It was introduced into the specimen chamber of the thermobalance after the temperature was brought to the desired value. As soon as the sample was outgassed the rate of loss of weight was followed by observing the position of the spring balance at suitable intervals. At the same time the temperature was measured accurately with the Pt/Pt–13% Rh thermocouple, the variation was better than ±0.5°C.

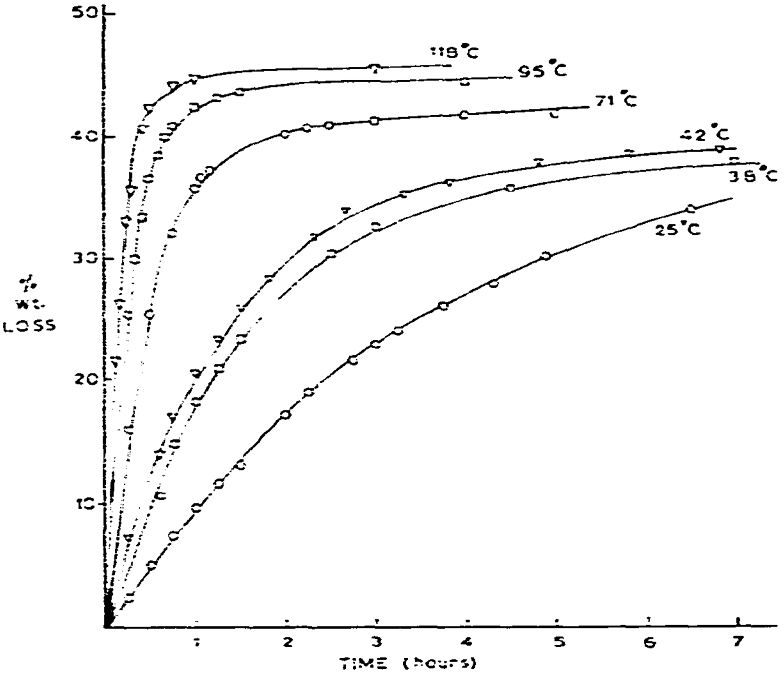

Fig. 2. Rate of dehydration of $MgSO_4 \cdot 7H_2O$ under vacuum conditions and over P_2O_5 at the indicated temperatures.

Results

From the shape of the dehydration curves (Fig. 2) it is clear that the initial weight-loss was rapid and the reaction tended to have a linear rate, but in the final stage of each dehydration the rate of weight-loss decreased. Moreover, the absence of induction periods in the early stages of the reactions is noticeable: the curves appeared to be exponential rather than sigmoidal. This indicates that there was no impedance to the escape of water from the lattice and that dehydration had resulted in immediate formation of the solid product.

The results of the experiments show that the amount of water lost from the specimen at the three low temperatures 25, 38 and 42°C was equivalent to 5 moles of H_2O per mole of $MgSO_4 \cdot 7H_2O$, but the dehydration at the three higher temperatures, viz., 71, 95 and 118°C had caused the rapid loss of approximately six water molecules.

From the slopes of the initial straight parts of the curves values of the rate constants *k* were calculated as shown in the table on page 413.

The high speed of the reactions at 71.0, 95.3 and 117.6°C which was indicated by the shape of the respective dehydration curves is also reflected in the higher values of the rate constants shown in the table.

T (°C)	k ($sec^{-1} \times 10^{-3}$)
25.0	2.61
38.0	5.04
42.5	6.29
71.0	14.06
95.3	24.85
117.6	36.67

Using the integrated form of the Arrhenius equation values of ln k were plotted against $(T\,°\mathrm{K})^{-1}$ (Fig. 3). From these plots two straight lines were obtained. Their point of intersection is at 47.35 °C. This point lies between those temperatures at which 5 moles of H_2O were expelled from $MgSO_4 \cdot 7H_2O$ and those temperatures at which 6 moles of H_2O were lost rapidly. Assuming that the frequency factor A is independent of temperature, the experimental activation energy E_a was calculated from the slopes of the two straight lines:

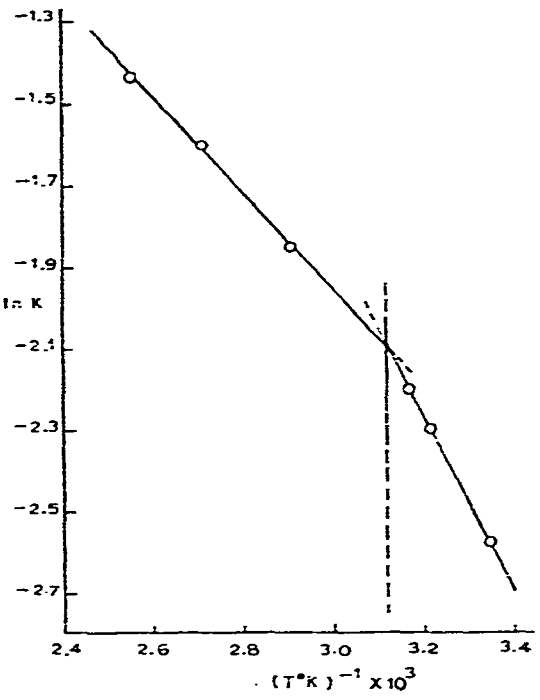

Fig. 3. Temperature dependence of the rate constants for the dehydration of $MgSO_4 \cdot 7H_2O$.

(i) At temperatures <47.35 °C when weight-loss ~$5H_2O$ moles; $E_a = 9.880$ kcal mol^{-1}.

(ii) At temperatures >47.35 °C when weight-loss ~$6H_2O$ moles; $E_a = 5.398$ kcal mol^{-1}.

Under the microscope the dehydrated products appeared as finely grained materials. Most of the grains were clustery and consisted of aggregates of granular material. The original crystalline form of $MgSO_4 \cdot 7H_2O$ characterised by the prismatic shape and perfect (010) cleavage had disappeared. This lack of crystallinity in the residues was reflected in the general appearance of the X-ray powder photographs, Cu–K_α radiation. The specimens dehydrated at 117 and 71 °C did not produce any diffraction patterns but instead the photographs showed heavy backgrounds in the low angle regions. This indicated that the crystalline $MgSO_4 \cdot 7H_2O$ was completely transformed into a disorganised product with an amorphous texture. At the same time the sample dehydrated at 25 °C, yielded a powder pattern with a small number of lines and broad halo at the low angle region which made it difficult to distinguish some of the reflections from the general background. This seems to indicate a lower degree of disorder in the lattice structure of the residue.

ISOBARIC EXPERIMENTS

Methods

Two experiments under isobaric conditions and in the absence of air were carried out on samples of $MgSO_4 \cdot 7H_2O$ to explore the extent of dehydration and the reversible hydration and to determine the critical temperatures for the onset of water sorption. In these experiments the vapour pressure was maintained at a fairly constant value to within ±0.02 mm Hg and the temperature of the specimen was allowed to rise and fall at a controlled rate while the change in weight was recorded

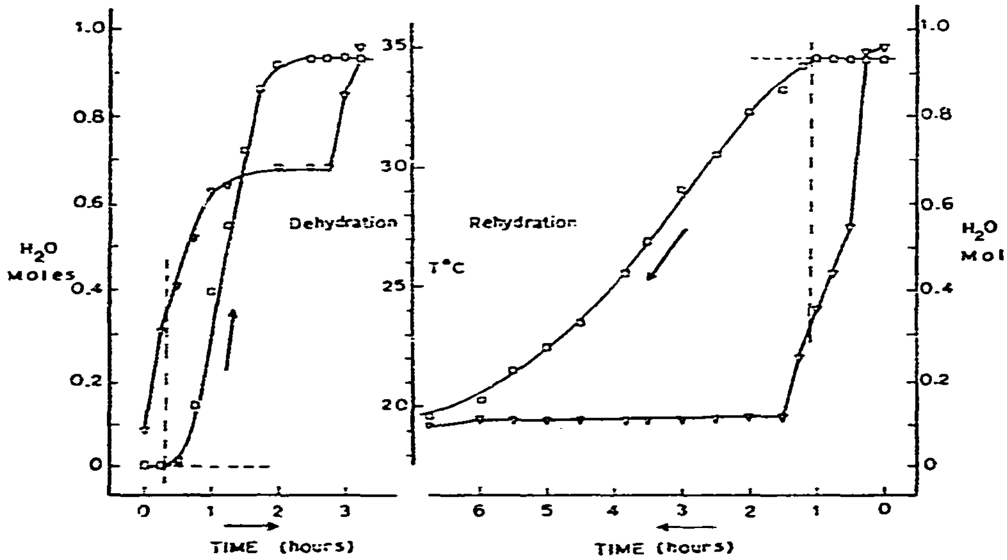

Fig. 4. Rate of isobaric dehydration and hydration in the reaction $MgSO_4 \cdot 7H_2O = MgSO_4 \cdot 6H_2O + H_2O$. Vapour pressure, 12.5 mm Hg; □, moles of H_2O; ▽, change of temperature. Onset of dehydration and hydration indicated by dotted lines.

at definite time intervals. The first experiment was conducted in the temperature range 18–35°C and at a vapour pressure of 12.50 mm Hg on 200 mg of powdered $MgSO_4 \cdot 7H_2O$. The average rate of change in temperature was ~10°C per hour. The data obtained from this experiment are illustrated in Fig. 4.

The second experiment was carried out on a fresh portion of 200 mg of powdered $MgSO_4 \cdot 7H_2O$. The temperatures selected were in the range 19–90°C and the vapour pressure was 12.30 mm Hg. The rate of temperature increase varied from ~2.4°C per hour in the first stage of the dehydration reaction to ~6°C per hour in the last stages. When the temperature reached 90°C the specimen was cooled by allowing the temperature to fall slowly to 25°C. The weight of specimen remained unchanged and there was no sign of rehydration. The complete data of the dehydration reaction are illustrated in Fig. 5.

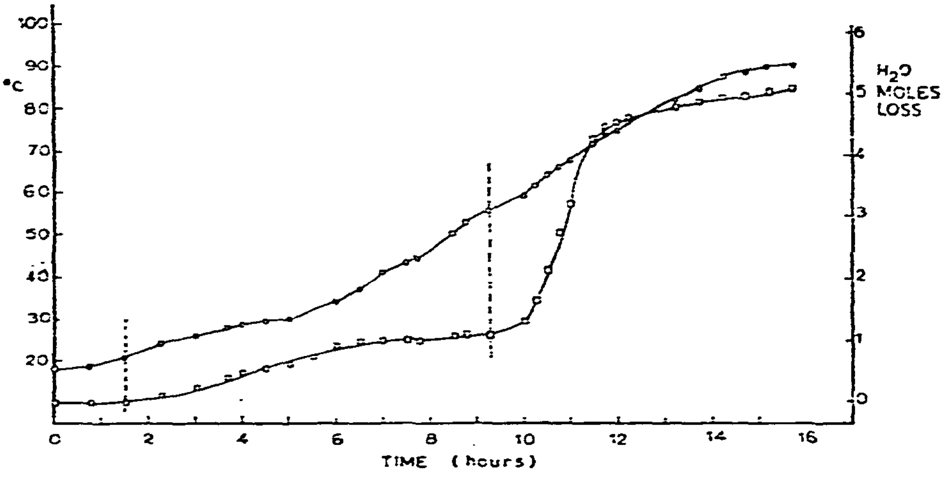

Fig. 5. Rate of isobaric dehydration of $MgSO_4 \cdot 7H_2O$ as a function of slowly rising temperature. Vapour pressure, 12.3 mm Hg; ⊡. moles of H_2O lost; ○, change of temperature. Onset of dehydration indicated by dotted lines.

Results

It is clear from the data obtained in the temperature range 18–35°C (Fig. 4) that one mole of H_2O was lost reversibly from $MgSO_4 \cdot 7H_2O$ and that the critical temperature for the onset of hydration (23.2°C) is very close to the corresponding temperature for the onset of dehydration (23.8°C). McConnell[6] found that when complete hydration occurs rapidly and reversibly in a narrow temperature range, the onset of hydration can be considered as defining equilibrium conditions for the total water fraction. In the equilibrium reaction studied, viz., $MgSO_4 \cdot 6H_2O + H_2O = MgSO_4 \cdot 7H_2O$ the amount of water lost and regained was one mole of H_2O. Hence, the vapour pressure imposed (12.50 mm Hg) may be considered as the equilibrium vapour pressure at 23.2°C for the above reversible reaction. This result is in close agreement with the dissociation pressure for the reaction $MgSO_4 \cdot 7H_2O = MgSO_4 \cdot$

$6H_2O + H_2O$ which was obtained by many investigators at 25°C. The value they obtained ranges between 11.5 to 12.0 mm Hg (ref. 3).

Using Cu–K_α radiation, data from an X-ray powder photograph of the residue were similar to those obtained for the original specimen. No significant alterations in the position and shape of the lines were observed.

The isobaric curve (Fig. 5) obtained in the temperature range 19–90°C is characterised by distinct horizontals. This indicates that the dehydration was stepwise. The formation of the hexahydrate began at 21°C and dehydration continued in a steady rate until the weight-loss was equivalent to one mole of H_2O per mole of $MgSO_4 \cdot 7H_2O$. The horizontal corresponding to the hexahydrate persisted up to 55°C. Above this value dehydration proceeded in a steady rate until equilibrium was reached at approximately 80°C. The total weight-loss at this temperature was equivalent to $\sim 5H_2O$ per mole of $MgSO_4 \cdot 7H_2O$.

The X-ray powder pattern of the residue was characterised by line broadening and a heavy background which obscured some of the reflections in the low angle regions. This is an indication of a disorganised material.

DISCUSSION

From the temperature dependence of the rate constant for $MgSO_4 \cdot 7H_2O$ (Fig. 3) it is clear that between 25 and 47.35°C, 5 moles of water were released from the lattice with an activation energy of 9.880 kcal mol^{-1}, and that between 48.35 and 117°C, 6 water molecules were expelled with an activation energy of 5.398 kcal mol^{-1}. These results seem to indicate the transformation of $MgSO_4 \cdot 7H_2O$ to the dihydrate and the monohydrate under suitable experimental conditions. However, the overall low values of the activation energies obtained suggest that the energy barrier for the reaction was very small and support the views of Garner[7] and Galwey[8] that the expulsion of water from salt hydrates occurs with activation energies of small values that the rate-controlling process may be comparable to a liquid evaporation.

It is evident that under the experimental conditions undertaken one mole of water appears to be firmly bound in the crystal structure of $MgSO_4 \cdot 7H_2O$. Leonard and Weiss[9] reported that kieserite, $MgSO_4 \cdot H_2O$ loses its water at 350°C, while Fruchart and Michel[4] and Wells[10] gave figures in the range 178–300°C for the release of the last water molecule in the heptahydrate. It is possible that this variation in temperature was due to the different environments of the specimens during the experiments.

The occurrence of the dihydrate $MgSO_4 \cdot 2H_2O$ has not been reported in nature but the data obtained are similar to those of Chihara and Seki[11], Duval and Duval[12] and Fruchart and Michel[4] who showed that it existed as an intermediate phase in the dehydration of the heptahydrate. Tate and Warren[13] found that once it was formed it decomposed to give the monohydrate.

The residues obtained in the course of dehydration under vacuum conditions were non-crystalline and tended to have an amorphous texture. This was evidenced by the appearance of the X-ray powder patterns. Partington[14], Cooper and Garner[15], Garner[7] and Garner and Jennings[16] postulated that, in the dehydration of salt hydrates under vacuum conditions a two-stage reaction takes place.

(a) Formation of an unstable and amorphous lower hydrate or an anhydrous phase.

(b) Rearrangement of this disorganised amorphous material and its transformation into nuclei of a new crystalline phase. This process is accelerated in the presence of water vapour.

The results of the dehydration of $MgSO_4 \cdot 7H_2O$ over P_2O_5 indicate that water was lost from the surface without appreciable rearrangement in the remaining lattice structure. It is possible that the continuous expulsion of water had created vacant sites in the lattice structure of $MgSO_4 \cdot 7H_2O$ which led to its collapse and the formation of an amorphous material.

Examination of the residue obtained after dehydration of $MgSO_4 \cdot 7H_2O$ in the temperature range 19–90°C and over water vapour pressure showed that the lattice structure had been distorted to a certain degree. The presence of water vapour (12.5 mm Hg) had little catalytic effect on the formation of a good crystalline phase. It is possible that this value of the vapour pressure was very low for any recrystallisation to take place.

Considering the results of the experiment, performed under isobaric conditions and in the temperature range 18–35°C, in which one mole of water was lost reversibly, i.e., $MgSO_4 \cdot 7H_2O \rightleftharpoons MgSO_4 \cdot 6H_2O + H_2O$, it is clear that this mole of water is relatively loosely held within the lattice structure of $MgSO_4 \cdot 7H_2O$. Baur[17] found that six water molecules are coordinated to Mg^{2+} ion and the seventh water molecule is linked to one oxygen atom of the SO_4 group and to three other water molecules. Palache et al.[18] indicated that the water molecule involved in the reaction $MgSO_4 \cdot 7H_2O \rightleftharpoons MgSO_4 \cdot 6H_2O + H_2O$ is the seventh water molecule.

Much work is needed on the dehydration of $MgSO_4 \cdot 7H_2O$ under different isothermal and isobaric conditions in order to obtain more information on the optimum conditions of equilibration of the various intermediate phases which will throw light on their physicochemical properties. It is believed that the results obtained in the present study have paved the way towards this goal.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. D. C. McConnell for his encouragement and advice during the progress of this research. Thanks are also due to the Department of Mineralogy and Petrology, Cambridge, for providing the facilities for the research.

REFERENCES

1 I. Kostov, in P. G. Embrey and J. Phemister (Eds.), *Mineralogy*, Oliver and Boyd, London, 1968.
2 H. W. Foote and S. R. Scholes, *J. Amer. Chem. Soc.*, 33 (1911) 1309.

3 E. E. Wilson, *J. Amer. Chem. Soc.*, 43 (1921) 704.
4 R. Fruchart and A. Michel, *Compt. Rend.*, 245 (1958) 1222.
5 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 2nd ed., 1963, p. 217.
6 J. D. C. McConnell, *Mineral. Mag.*, 34 (1965) 327.
7 W. E. Garner, *Chemistry of the Solid State*, in W. E. Garner (Ed.), Butterworth, London, 1955, ch. 8, p. 213.
8 A. K. Galwey, *Chemistry of Solids*, Science paperbacks, Chapman & Hall, London, ch. 5, 1967, p. 163.
9 J. Leonard and R. Weiss, *Naturwissenschaften*, 44 (1957) 338.
10 A. F. Wells, *Structural Inorganic Chemistry*, Oxford, 3rd ed. Oxford, 1962, Ch. XV, p. 565.
11 H. Chihara and S. Seki, *Bull. Chem. Soc. Japan*, 26 (1953) 88.
12 T. Duval and C. Duval, *Anal. Chim. Acta*, 2 (1948) 45.
13 F. G. H. Tate and L. W. Warren, *Analyst*, 61 (1936) 367.
14 J. R. Partington, *J. Chem. Soc.*, (1911) 466.
15 J. A. Cooper and W. E. Garner, *Proc. Roy. Soc.*, 174A (1940) 487.
16 W. E. Garner and T. J. Jennings, *Proc. Roy. Soc.*, 224A (1954) 460.
17 W. H. Baur, *Acta Crystallogr.*, 17 (1964) 1361.
18 C. Palache, H. Benman and C. Frondel, *Dana's System of Mineralogy*, Vol. II, J. Wiley, New York, 1951.