

A COMPARATIVE STUDY OF THE DEHYDRATION KINETICS OF SEVERAL HYDRATED SALTS¹

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ABSTRACT

Rates of dehydration under full vacuum, and also as the pressure of water vapor due to the dehydration process was allowed to increase, have been determined for a number of hydrated salts. The dehydration of manganous sulphate tetrahydrate, zinc sulphate heptahydrate, nickel sulphate hexahydrate, and magnesium sulphate heptahydrate has been found to proceed through the formation of amorphous intermediates, the last two of these being very stable. The dehydration of nickel nitrate hexahydrate, magnesium nitrate hexahydrate, and probably of ferrous sulphate heptahydrate and cobalt chloride hexahydrate at very low pressures takes place with the formation of crystalline intermediates. The results obtained are discussed in relation to the dependence of rate of dehydration on water vapor pressure previously reported for copper sulphate pentahydrate and for manganous oxalate dihydrate.

INTRODUCTION

It has been shown in an earlier paper (3) that when powdered samples of copper sulphate pentahydrate are dehydrated under vacuum at moderate temperatures, the dehydration proceeds to the monohydrate stage with a gradual decrease in rate. The product is amorphous in the sense that it does not diffract X-rays. However, if similar samples are placed in a closed and initially evacuated space, and the water vapor pressure due to the dissociation of the hydrate allowed to increase in the vessel, the rate of dehydration at first decreases to a minimum value, then increases to a value much larger than the minimum rate, this being followed, in turn, by a decline. The end product formed under these conditions is crystalline.

The minimum in rate occurs at a water vapor pressure of approximately 0.25 mm. and the periods of acceleration and decline, over a range in pressure of only a few millimeters, these pressures being far below those corresponding to possible phase equilibria. This marked effect of water vapor in a very narrow region of pressure has been observed also by carrying out dehydrations at a series of controlled pressures. The dehydration curves obtained for pressures below 0.25 mm. are quite different than for those above this value, the former showing a gradual loss in weight with time, while the latter show induction periods, the duration of which depends on the pressure.

The behavior of copper sulphate pentahydrate in this respect is similar to that of manganous oxalate dihydrate (6, 7), which for many years was regarded as unique in the dependence of its rate of dehydration on water vapor pressure. On vacuum dehydration this salt hydrate also yields a product which does not diffract X-rays.

Explanations of the form of these rate curves have been discussed elsewhere (1, 3, 4). The initial fall in rate is probably due to the retarding effect of water

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vapor on diffusion through a transition layer of amorphous material formed during the initial stages of dehydration, and the intermediate acceleration in rate, to an increase in porosity occurring on crystallization of the amorphous product in the presence of adsorbed water. The final decline is probably due to the gradually increasing impedance of the crystalline layer.

The purpose of the present work has been to survey the dehydration kinetics of a number of hydrated salts in order to obtain information regarding the generality of these effects. Rate determinations have been carried out for dehydrations at pressures of 10^{-5} mm. or less (designated as vacuum dehydrations in the following) and also while the pressure due to the liberated water vapor increased. For convenience, these latter are referred to as "increasing pressure" dehydrations. Determinations of rates of dehydration at externally controlled and constant pressures of water vapor have not been made in this work, although they give much more detailed information regarding the nature of the processes involved. However, such experiments are very time consuming, and it was desired to obtain comparative data for as many salts as possible.

EXPERIMENTAL METHOD

The salts used were reagent grade materials, recrystallized twice, air-dried, and screened, the "through 60 mesh on 80 mesh" fraction being used.

The essential features of the apparatus have been described (3). Powdered samples were placed in a small basket made of 100-mesh copper gauze, and suspended from a quartz spiral. The water vapor pressure in the system was measured by means of an oil manometer which had a conventional vertical arm and also an inclined arm for fine sensitivity in low pressure ranges. Readings of spiral extension and of pressure were made with a rigidly mounted cathetometer.

Vacuum dehydrations were carried out by allowing small samples (approximately 50 mgm. in most cases) to dehydrate while the pumps were in operation. Readings were plotted as weight-loss versus time. For several salts these curves were found to present points of interest, but they also served to establish the composition of the dehydration product. Increasing pressure dehydrations were carried out in the following manner. The samples were nucleated by allowing dehydration to proceed under vacuum to 10% of the total possible weight loss as determined by vacuum dehydration. The spiral case was then closed off from the pumps and the samples allowed to dehydrate and slowly build up a pressure of water vapor in the system. Readings of weight-loss were commenced at the beginning of the nucleation period, and those of pressure, at the time of closing off the spiral case, both of these being continued at a series of times for several hours. Determinations of rates of dehydration were made by evaluating tangents to the weight-loss versus time curves at a series of time values.

X-ray powder photographs were made using copper K_{α} radiation. For convenience, the term "X-ray amorphous" is used to describe products for which no diffraction lines were observed.

RESULTS

(1) *Manganous Sulphate Tetrahydrate*

Vacuum dehydration at 40°C. resulted in the smooth continuous weight-loss versus time curve shown in Fig. 1 (lower curve) the end product being of the monohydrate composition.

The results obtained on dehydration at 50°C. as the pressure of water vapor in the system increased are shown in Fig. 2.

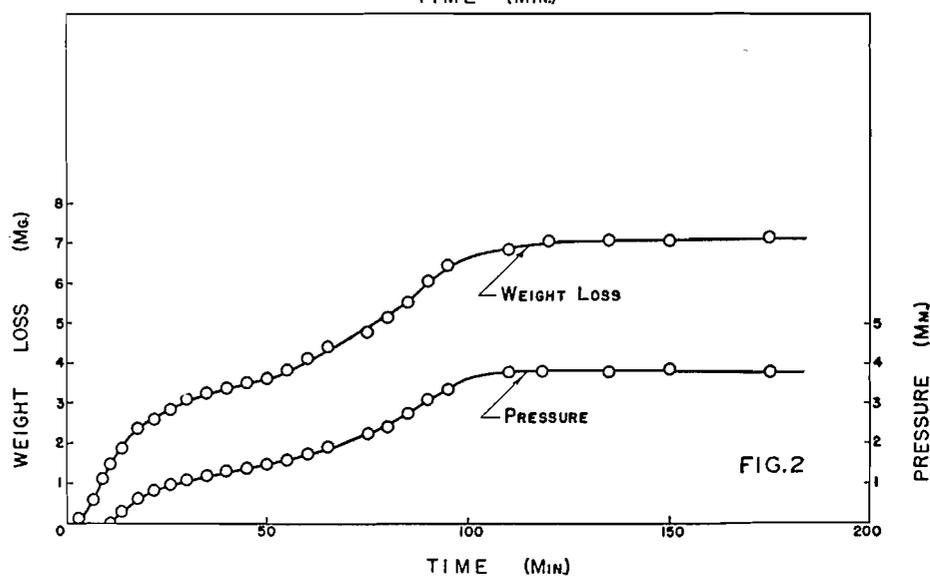
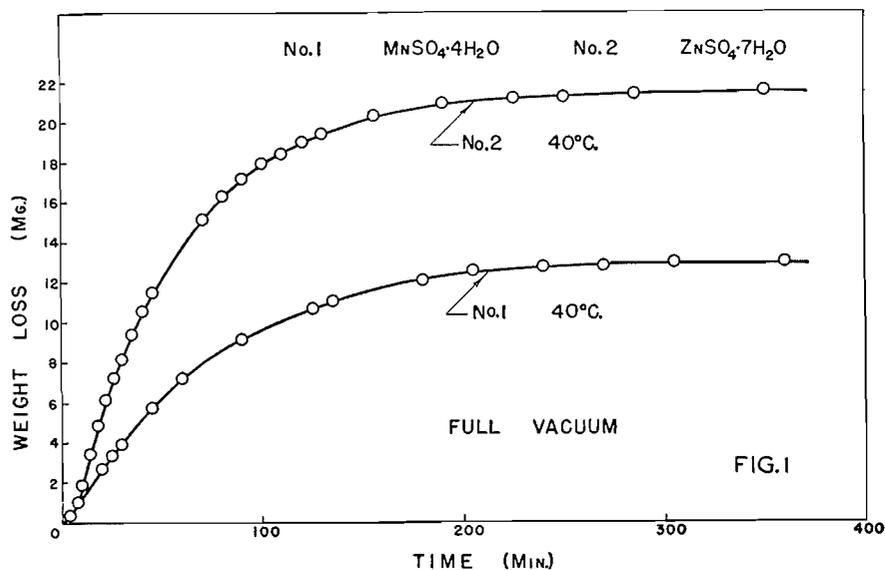


FIG. 1. The dehydration of zinc sulphate heptahydrate and of manganous sulphate tetrahydrate under vacuum.

FIG. 2. The dehydration of manganous sulphate tetrahydrate with increasing pressure of water vapor.

Following the period of nucleation under vacuum, the slope of the weight-loss curve gradually decreases as the pressure in the system becomes greater. The curve flattens somewhat at a weight-loss of about 3.5 mgm. which corresponds roughly to the trihydrate composition. An accelerated rate is then observed followed by a decline, the slope becoming zero at the dihydrate stage. These rates of dehydration plotted against the pressure, are shown in Fig. 3. Although the decline in rate to a minimum value, followed by an accelerated period, is similar to that reported for copper sulphate pentahydrate and for manganous oxalate dihydrate, the actual weight-loss versus time curve (Fig. 2) is slightly different in that a fairly rapid weight-loss persists for some time after the sample is exposed to water vapor, whereas with copper sulphate pentahydrate an induction period occurs almost immediately.

Unfortunately, X-ray data could not be obtained for this salt with the copper target available, since the absorption of the radiation was strong, resulting in fluorescent radiation.

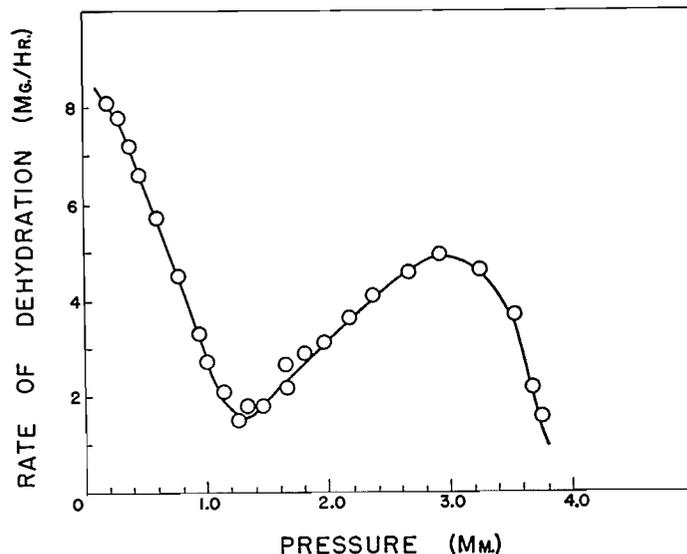


FIG. 3. The change in rate of dehydration of manganous sulphate tetrahydrate with pressure increase.

(2) *Zinc Sulphate Heptahydrate*

Vacuum dehydration at 40°C. again resulted in a smooth continuous curve (upper curve, Fig. 1), the end product being stoichiometrically of the monohydrate composition, and X-ray amorphous.

Measurements made at increasing pressure, and at 40°C., are shown in Fig. 4.

A small but reproducible induction period occurred immediately after nucleation, corresponding to the longer induction period observed for copper sulphate pentahydrate. Following this, the weight-loss curve has a slightly concave portion followed by a slightly convex portion, there being no clearly

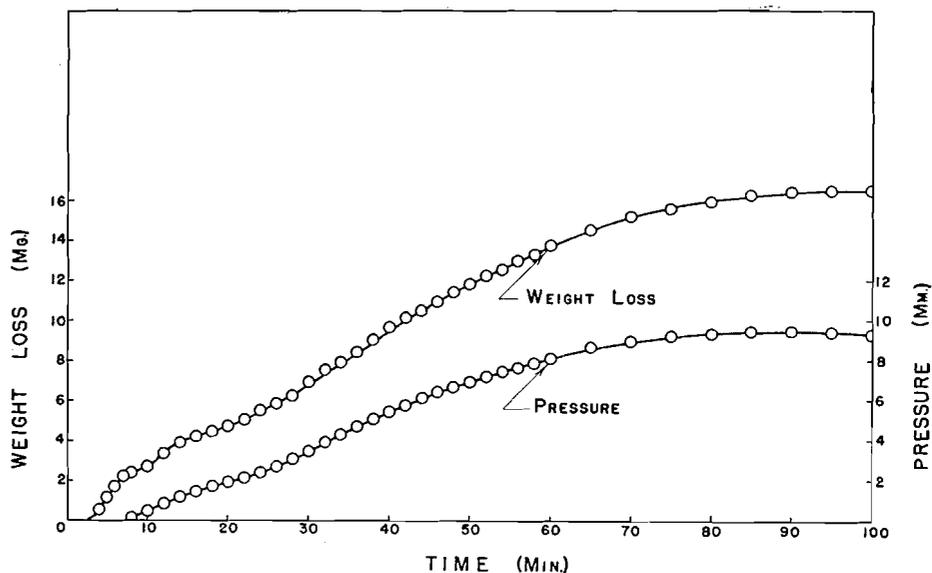


FIG. 4. The dehydration of zinc sulphate heptahydrate with increasing pressure of water vapor.

defined induction period. This resulted in two minima being obtained when the rate of dehydration was plotted against the pressure, as shown in Fig. 5.

X-ray powder photographs of the products obtained from these increasing pressure dehydrations showed a clearly defined diffraction pattern of monohydrate lines. Patterns identical with these were obtained when sealed samples of the amorphous product formed on vacuum dehydration were allowed to stand for several days.

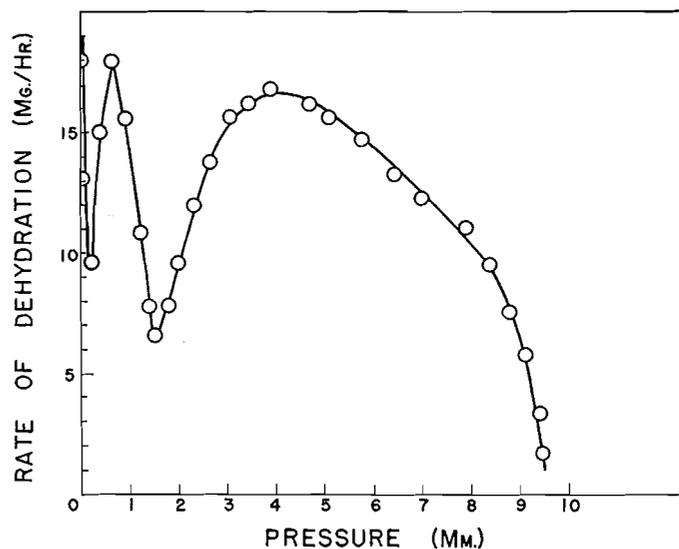


FIG. 5. The change in rate of dehydration of zinc sulphate heptahydrate with pressure increase.

(3) *Ferrous Sulphate Heptahydrate*

Dehydration under vacuum again exhibited a continuous loss of water from the heptahydrate to the monohydrate, the curve being similar to those shown in Fig. 1.

The weight-loss curve obtained on dehydration at increasing pressure at 60°C. is shown in Fig. 6.

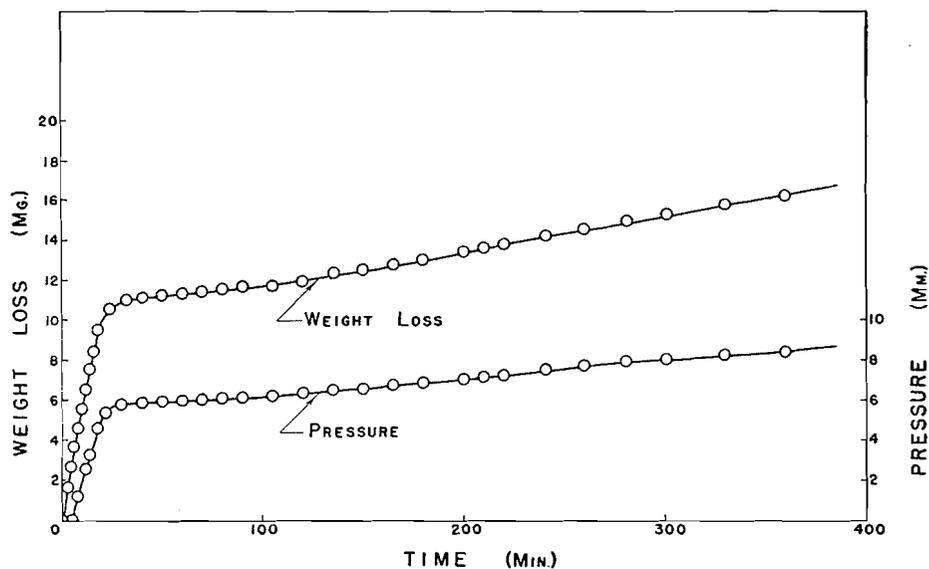


FIG. 6. The dehydration of ferrous sulphate heptahydrate with increasing pressure of water vapor.

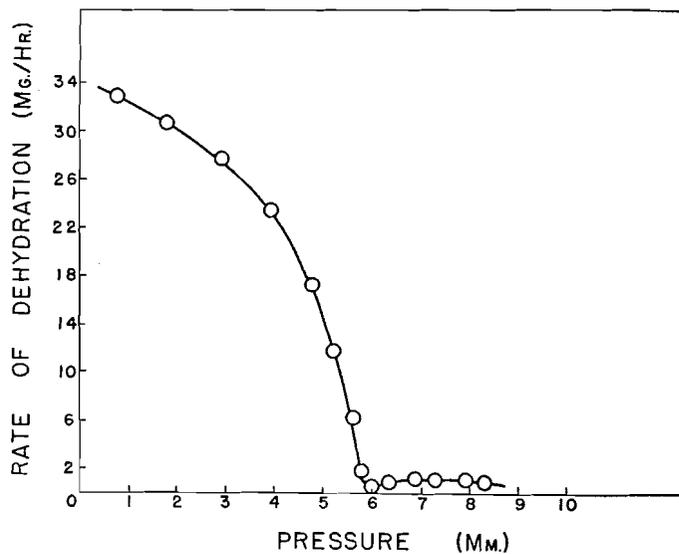


FIG. 7. The change in rate of dehydration of ferrous sulphate heptahydrate with pressure increase.

Following nucleation, rapid dehydration continued to somewhat beyond the tetrahydrate composition where an induction period set in followed by a slow increase in rate. This increase was diminished as the dehydration temperature was lowered, no increase being observed in a 21 hr. period at 40°C. The rate of dehydration at 60°C., plotted against the water vapor pressure, is shown in Fig. 7.

The curve is similar in character to that shown in Fig. 3, although the secondary increase in rate is much smaller, and the minimum occurs at a much higher pressure. It was not possible to obtain X-ray diffraction patterns for this salt for the reason that has been mentioned for manganous sulphate.

(4) *Nickel Nitrate Hexahydrate*

Vacuum dehydrations at several temperatures resulted in curves of different character than those described in the foregoing; the curve obtained at 40°C. is shown in Fig. 8, those obtained at other temperatures being similar. The initial loss of water is rapid and the rate nearly linear. After a weight-loss of about 6 mgm., the curve transforms to a second region which is also nearly linear, and then declines. If the two linear sections are extended to point A (Fig. 8), the point of intersection is found to be at approximately the tetrahydrate composition. The slopes of these linear portions were found to increase with temperature.

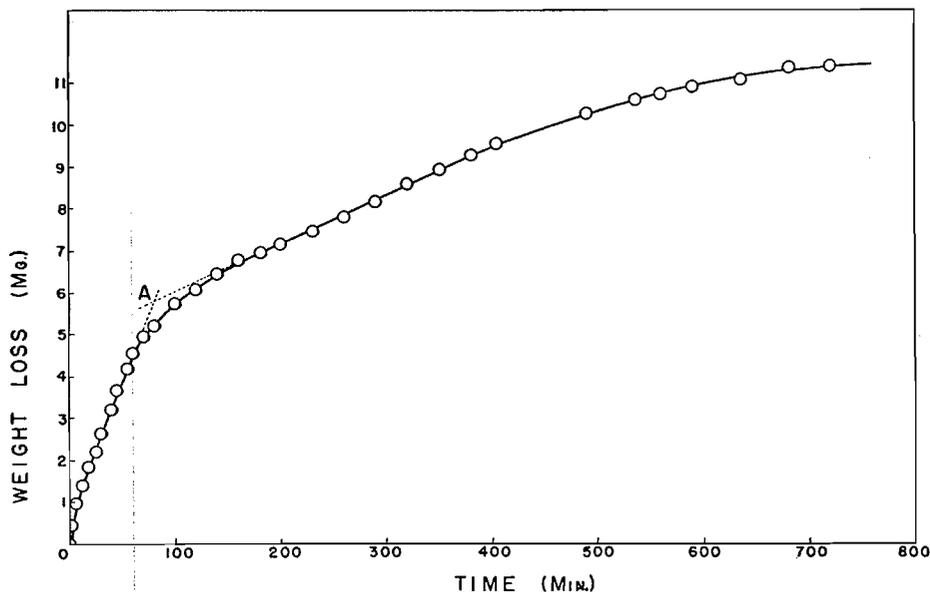


FIG. 8. The dehydration of nickel nitrate hexahydrate under vacuum.

The end product had the dihydrate composition. It appears, therefore, that under vacuum, dehydration takes place fairly rapidly to the tetrahydrate state, followed by the dehydration of this intermediate product to the dihydrate.

Unlike the examples reported in the foregoing, the end product of vacuum dehydration gave a definite X-ray diffraction pattern. However, if the time of preparation for the exposure were made as short as possible, the diffraction lines were very faint. It is possible that an amorphous material of very low stability was produced, subsequent handling being sufficient to cause the commencement of crystallization.

For dehydrations carried out at increasing pressure, an induction period was observed at the tetrahydrate stage followed by a slow and gradual increase in rate, the curves resembling closely those obtained for ferrous sulphate heptahydrate. Close examination of X-ray diffraction patterns obtained indicated the presence of tetrahydrate and dihydrate lines. It appears therefore that the first step in this process is the formation of crystalline tetrahydrate which then nucleates and forms crystalline dihydrate at a much slower rate. The rate of dehydration plotted against pressure is shown in Fig. 9, the curve again resembling that obtained for ferrous sulphate heptahydrate.

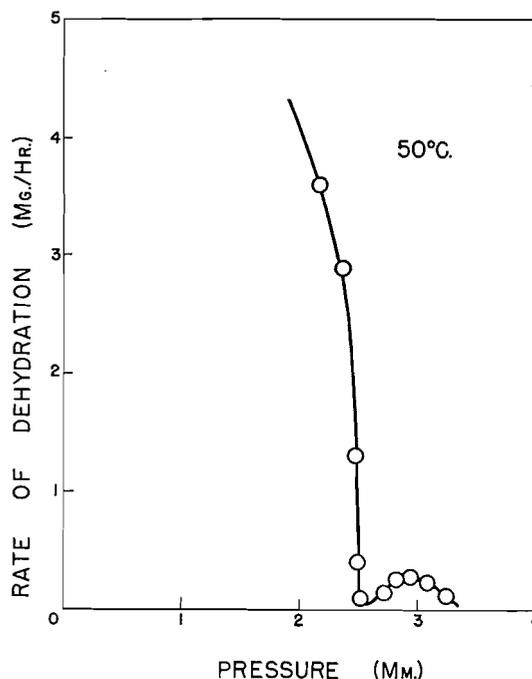


FIG. 9. The change in rate of dehydration of nickel nitrate hexahydrate with pressure increase.

The possibility of the formation of a basic salt in the dehydration process has been disregarded since it was found that the product formed both on vacuum and increasing pressure dehydration gave a pattern of only hexahydrate lines after standing in the room atmosphere for a few hours.

(5) *Magnesium Nitrate Hexahydrate*

Preliminary experiments with this salt indicated that effects occurred which were quite different from those observed for the other salts studied. Conse-

quently a number of dehydrations were carried out at several temperatures. The details of the experiments are given in Table I.

TABLE I
DEHYDRATION DATA FOR MAGNESIUM NITRATE HEXAHYDRATE

Expt. No.	Temp., °C.	Type of dehydration	Time of dehydration, min.	Sample wt., mgm.	Moles water lost per formula-wt.
1	30	Vacuum	1150	34.7	3.80
2	35	Vacuum	1166	40.2	3.92
3	40	Vacuum	1300	39.8	4.05
4	45	Vacuum	580	37.1	3.93
5	50	Vacuum	772	37.0	3.70
6	50	Vacuum	1370	37.3	3.98
7	55	Vacuum	510	38.9	2.39
8	40	Increasing pressure	1230	40.8	1.95
9	50	Increasing pressure	1415	35.4	3.42
10	40	Vacuum	35	32.3	1.89

Weight-loss versus time curves for the vacuum dehydration experiments Nos. 1, 3, 5, and 7 of Table I are shown in Fig. 10.

These dehydrations all displayed an induction period setting in at the tetrahydrate composition. These vacuum dehydration curves are, therefore, of the type which has been previously associated with dehydrations at increasing pressure. Furthermore, the period of acceleration following the induction period shows an interesting temperature dependence, the rate at 40°C. being higher than that at 30°C. and then declining as the temperature is raised.

Rate curves plotted against time, for these temperatures, are shown in Fig. 11. These curves show the minima and accelerated rates associated with increasing pressure dehydrations in the foregoing.

The end product of the vacuum dehydrations was found to be crystalline dihydrate, well defined and characteristic diffraction patterns being obtained. Clearly defined tetrahydrate lines were obtained with samples (Expt. 10) partially dehydrated to this stage. It appears quite definite, therefore, that on vacuum dehydration this salt forms crystalline tetrahydrate which then nucleates and forms crystalline dihydrate at rates which are markedly temperature dependent.

Experiments 8 and 9 of Table I were carried out at increasing pressure. Dehydration was observed to take place rapidly to the tetrahydrate stage at which an induction period set in, followed at 50°C. by a slow increase in rate, while at 40°C. no increase could be detected. The rate versus pressure curve obtained at 50°C. was found to be similar to that reported above for nickel nitrate hexahydrate.

Although many basic hydrated salts of magnesium have been reported, the formation of these takes place at dehydration temperatures exceeding 150°C. When the crystalline products obtained in the present experiments were allowed to stand in the humidity of the ordinary room atmosphere reversion to the hexahydrate crystalline form occurred.

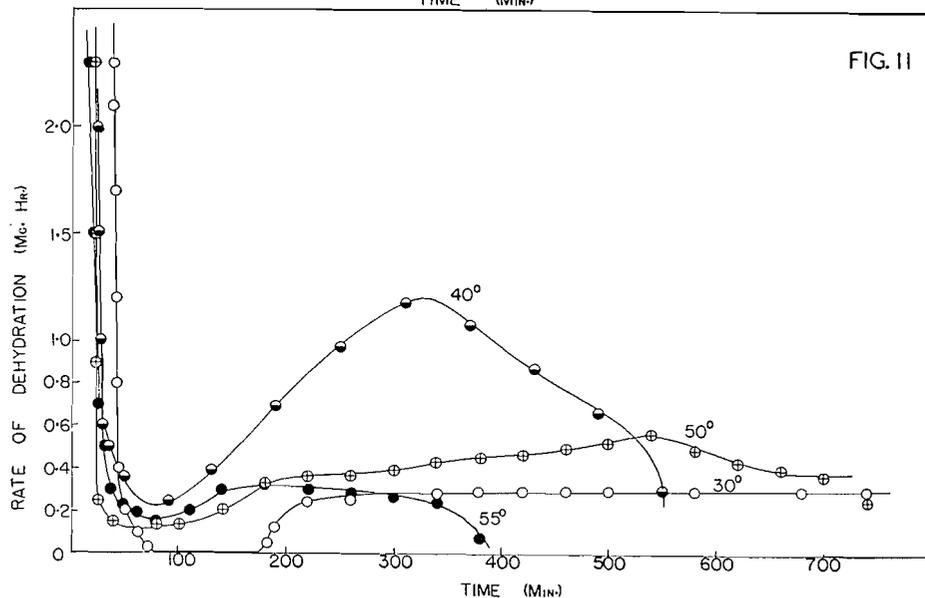
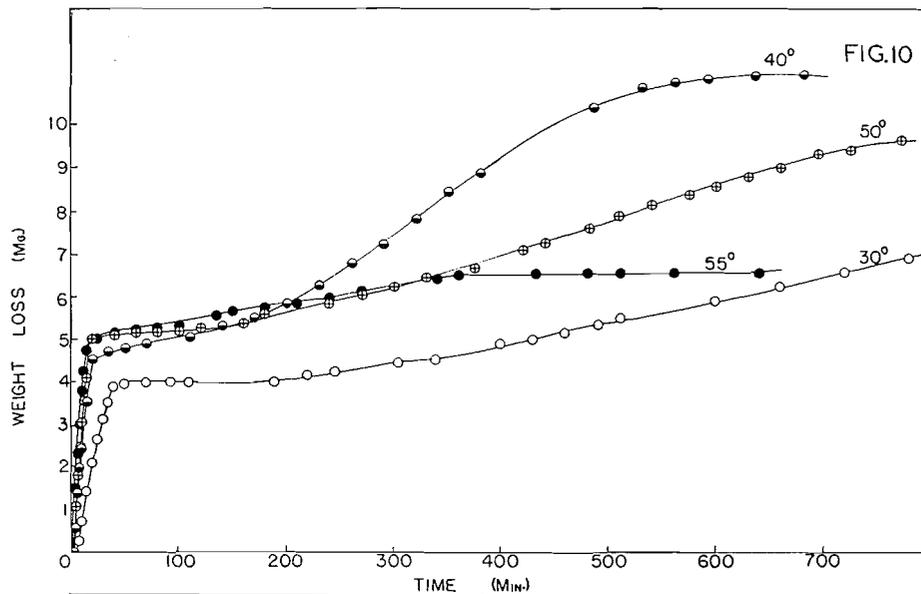


FIG. 10. The dehydration of magnesium nitrate hexahydrate under vacuum at several temperatures.

FIG. 11. The change in rate of dehydration of magnesium nitrate hexahydrate at several temperatures.

Since the dehydration from the tetrahydrate to the dihydrate stage has a temperature coefficient exhibiting a maximum in the region of 40°C., a careful survey of the rates in the temperature range from 30°C. to 55°C. was carried out. In order to make a comparison, the maximum rate of dehydration was found from the rate versus time curves (or from rate versus percentage decomposition curves) and converted to a rate per milligram of sample. (The com-

parison of maximum rates rather than rates obtained at the same percentage decomposition has been made in view of a suggestion by Colvin and Hume (1) that the maximum rates correspond to approximately the same interfacial conditions.) The results of these calculations are given in Table II and are

TABLE II
CALCULATED MAXIMUM RATES

Expt. No.	Temp., °C.	Maximum rate, mgm./hr./mgm.	Point Fig. 12
1	30.4	10.06	A
2	35.1	44.62	B
3	40.2	48.20	C
4	45.0	37.81	D
5	49.0	21.10	E
6	50.1	22.70	F
7	55.1	12.06	G

plotted in Fig. 12. From this figure it is clear that at temperatures above approximately 40°C., the mechanism of the dehydration process is in some way adversely affected by increase in temperature, the rate of dehydration becoming negligible above approximately 55°C.

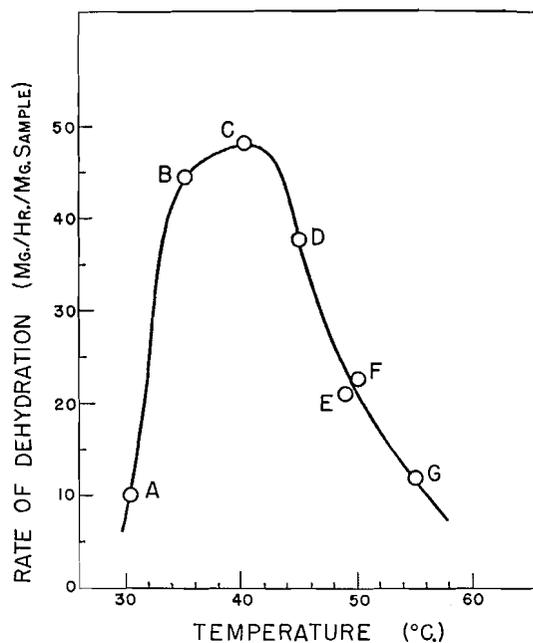


FIG. 12. The dependence of the second stage of the rate process on temperature for magnesium nitrate hexahydrate.

(6) *Magnesium Sulphate Heptahydrate*

Vacuum dehydration of this salt resulted in a smooth continuous curve of the same type as those shown in Fig. 1. The end product had the monohydrate

composition and was X-ray amorphous. Lines characteristic of the crystalline monohydrate appeared when amorphous samples were sealed and heated for two days at 130°C.

However, the behavior of this salt on dehydrating at increasing pressure was very different from that of any of the salts mentioned in the foregoing. It was found that the rate of dehydration gradually decreased with corresponding increase in pressure, no induction periods being observed. The product obtained was X-ray amorphous. The change of rate with pressure increase is shown in Fig. 13.

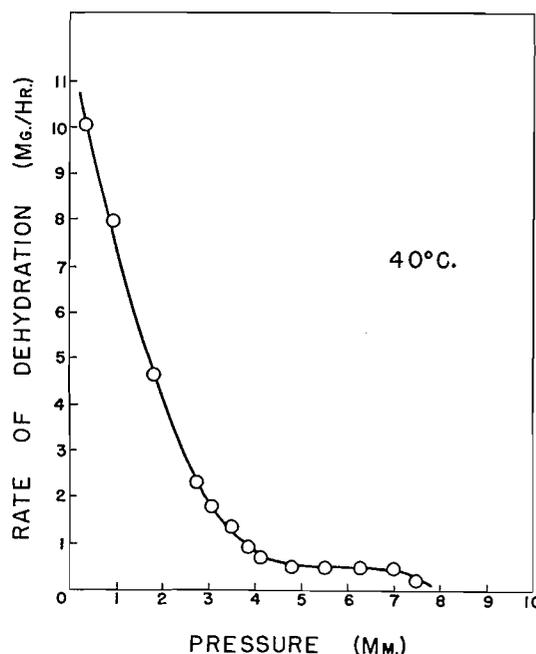


FIG. 13. The change in rate of dehydration of magnesium sulphate heptahydrate with pressure increase.

(7) *Nickel Sulphate Hexahydrate*

This salt was found to behave in similar manner to magnesium sulphate heptahydrate. The product of vacuum dehydration had the monohydrate composition and was X-ray amorphous. The effect of increasing water vapor pressure on the dehydration rate is similar to that shown in Fig. 13. Faint hexahydrate lines were obtained in this sample, indicating incomplete dehydration.

(8) *Cobalt Chloride Hexahydrate*

Vacuum dehydration resulted in curves similar to those obtained for nickel nitrate hexahydrate. These are shown in Fig. 14.

The rate of dehydration proceeds rapidly to the dihydrate stage followed by a much slower rate. Prolonged dehydration yields a product having the mono-

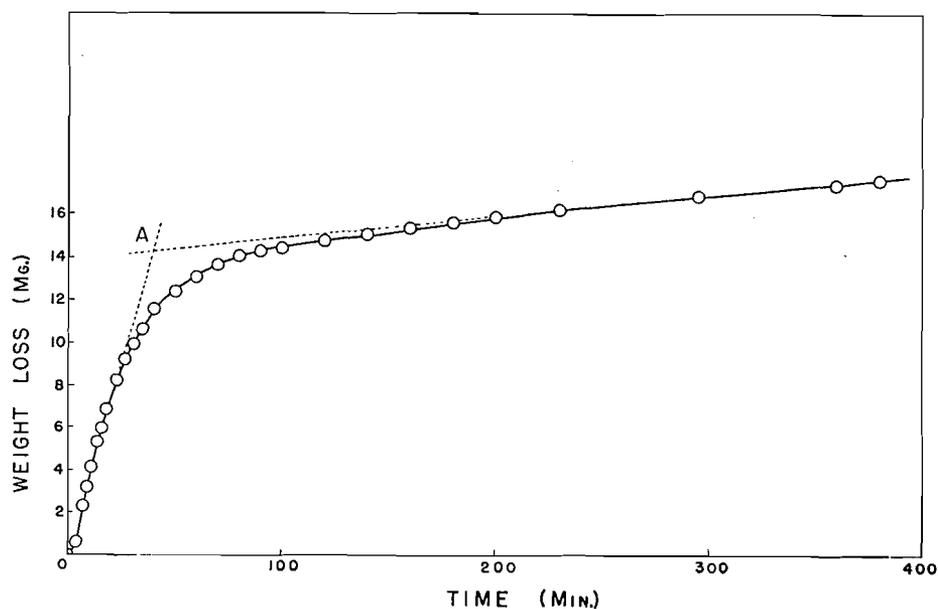


FIG. 14. The dehydration of cobalt chloride hexahydrate under vacuum.

hydrate composition. Unfortunately, the crystalline or amorphous character of the end product could not be definitely determined by X-ray diffraction for reasons which have been mentioned.

On dehydrating at increasing pressure, a rapid loss of water occurred to approximately the dihydrate composition, beyond which no change was observed. The change in rate with pressure increase is shown in Fig. 15.

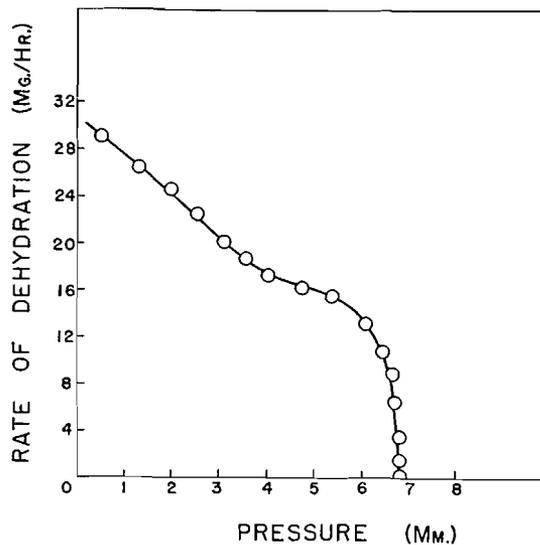


FIG. 15. The change in rate of dehydration of cobalt chloride hexahydrate with pressure increase.

DISCUSSION

Although it has not been possible to determine from X-ray evidence whether or not the product obtained from the vacuum dehydration of manganous sulphate tetrahydrate is amorphous, the similarity of the dehydration curves to those previously reported for copper sulphate pentahydrate (3) and for manganous oxalate dihydrate (6, 7) suggests that the dehydration process is the same in each case and is subject to the same interpretation. However, the minimum in the rate curve for the manganous salt occurs at about 1.2 mm., whereas for copper sulphate pentahydrate it occurs at about 0.25 mm., and for manganous oxalate dihydrate at less than 0.2 mm.

The dehydration process for zinc sulphate heptahydrate is more complex. Since an X-ray amorphous product is formed on vacuum dehydration, it is certain that this forms during the nucleation period. It is possible that the short induction period following nucleation (or therefore the first minimum in the rate curve) is due to the crystallization of this product at very low pressure. No adequate interpretation can be made of the second minimum at higher pressure on the basis of the present data and a more comprehensive study of the dehydration kinetics of this salt hydrate should be made.

Magnesium sulphate heptahydrate is of particular interest in that the dehydration curves obtained indicate that an X-ray amorphous product is formed not only on vacuum dehydration but also in the presence of water vapor at a pressure much higher than those observed for the other salts. The amorphous product is therefore very stable. This result suggests that this salt might be found to behave in a manner similar to copper sulphate pentahydrate if investigated over a wide range of controlled and constant pressures of water vapor. Experiments of this type are being carried out in this laboratory and will be reported in a later paper. The data given for nickel sulphate hexahydrate suggest a similar type of behavior.

The formation of crystalline products in the vacuum dehydration of nickel nitrate hexahydrate and magnesium nitrate hexahydrate indicates that if an amorphous product is formed at all, it must crystallize at extremely low water vapor pressures. Although the decomposition products obtained from ferrous sulphate heptahydrate could not be characterized by X-ray diffraction, the similarity of the dehydration curves to those obtained for nickel nitrate hexahydrate suggests that these products may be also crystalline. The minima observed in the rate versus pressure curves for these salts must be interpreted therefore in a somewhat different manner than has been done for copper sulphate pentahydrate. Instead of a process involving the crystallization of amorphous material, it must be assumed that as nuclei develop on the surfaces of the crystalline intermediates, the development of macrocrystalline aggregates is catalyzed by adsorbed water molecules.

The curves obtained for the dehydration of cobalt chloride hexahydrate are also similar to those obtained for nickel nitrate hexahydrate and it is probable that this dehydration also proceeds through the formation of a crystalline intermediate. However, with this salt the dehydration at increasing pressure does not proceed past the dihydrate stage, the corresponding pressure being

much lower than the equilibrium pressure reported by Derby and Yngve (2) for the hexahydrate - dihydrate - water vapor equilibrium. The behavior of this salt is of interest in comparison with that of magnesium sulphate heptahydrate, and a more comprehensive study of its dehydration kinetics is in progress.

The dehydration of magnesium nitrate hexahydrate is of particular interest, since the sequence of changes occurring on vacuum dehydration is that which is observed for other salts as the pressure of water vapor increases. Dehydration takes place rapidly with the formation of crystalline tetrahydrate which then nucleates and forms crystalline dihydrate. If it is assumed that the development of macrocrystals from these nuclei is catalyzed by water vapor, then this process must occur at the very low pressures prevailing in the transition layer as the water molecules liberated from the hexahydrate lattice pass through the crystalline tetrahydrate layer into the external evacuated space. The rate of escape of water molecules from the dehydrating tetrahydrate lattice will increase with temperature. However, any slight adsorption in the transition layer will decrease with the temperature. The opposition of these two effects may qualitatively explain the over-all dependence of rate on temperature which has been observed. However, any such explanation must be regarded as highly tentative in view of the lack of more comprehensive data. It will be observed from Fig. 10 that the rate of dehydration of the primary hexahydrate lattice increases with temperature in the normal manner, as also does both the primary and secondary rate for nickel nitrate hexahydrate.

It is clear from all the data presented in the foregoing that the effect of water vapor is first decreasing and then accelerating the over-all rate of dehydration, first observed by Topley and Smith for the decomposition of manganous oxalate dihydrate, is quite general and is always associated with an induction period in which a crystalline lower hydrate is formed from an intermediate. The intermediate may be an X-ray amorphous product or it may be crystalline. The nature of the X-ray amorphous product is, therefore, of interest. It may consist of an aggregate of microcrystals with dimensions of only a few unit cells, these being below the limiting size required for X-ray diffraction (about 100 Å). If this is so, the nature of the process whereby macrocrystals are formed in the presence of water molecules from X-ray amorphous intermediates does not differ in any essential way from that in which macrocrystals of the end product are formed from a nucleated crystalline intermediate. However, the heats of transition from the X-ray amorphous to the crystalline states which have been reported for the monohydrates of copper and zinc sulphate (4) are higher than might be expected from consideration of surface energy only, and it is possible that, for these salts at least, some condition other than high state of division results from low pressure dehydration of the primary lattices. The determination of such heats of transition for other salts is in progress.

The limiting pressure of water vapor above which amorphous products crystallize varies greatly from one salt hydrate to another, being virtually zero for nickel nitrate, magnesium nitrate, and cobalt chloride, and ranging to

presumably relatively high values for magnesium sulphate and nickel sulphate. Experiments carried out in this laboratory suggest that this effect is related to differences in the surface areas and capillary structures of the transition layer, although the nature of the amorphous material itself may also be a factor (5).

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