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*An I.R. and D.T.A. Study of the Hydrates of the Metal Sulfates of Cu^{2+} Co^{2+} Ni^{2+} Cd^{2+} Mn^{2+} Zn^{2+} and Mg^{2+}

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The structure of the polyhydrates of seven metal sulfates was studied by infrared and differential thermal analysis. The data were compared to those of the respective monohydrates and correlated with known results from X-ray diffraction measurements. An attempt is made to explain the «acidic» properties of the monohydrates on the basis of the special linkage of the water molecule to the central metal ion. It is maintained that the central ion is octahedrally coordinated, two bonds being M-H_2O bonds. The hydrogen atoms bonded to oxygen atoms of two different $SO_4^=$ groups are able, comparatively easily, to break free in the form of protons.

Introduction

In 1964, Jungreis and Ben-Dor[1] observed «acidic» properties in the monohydrates of several metal sulfates, as opposed to the polyhydrates and anhydrides. It was found that hydrochloric acid gas is evolved even at room temperature when mixing one of the abovementioned monohydrates with solid NaCl. The gas was indentified analytically and the conductivity of its solution in triple distilled water was measured.

Recently Tanabe *et al.*[2] also discussed the correlation between the acid property and the structure of solid metal sulfates. The acid property was tied with catalytic activity such as depolymerization, polymerization, etc. A full list of previous references dealing with this topic is given in Tanabe's paper.

Lendormy[3] compared the I.R. spectra of several monohydrates amongst themselves and with the respective monodeuterates. From the results, she suggested the existence of the group—SO_5H_2, so that the monohydrate is of the formula MH_2SO_5—the acid salt of mesosulfuric acid. In Lendormy's discussion there is no correlation between the observed spectra and the lowering of the symmetry by the crystalline structure. Gamo[4] compared I.R. spectra of mono- and polyhydrates. His results are consistent with ours, and differ from those of Lendormy. From the different vibrational modes of the monohydrates as compared to the polyhydrates, Gamo stated the existence of hydrogen bonding O_w - H .... O, where O_w is an oxygen atom from a water molecule and O from a $SO_4^=$ ion. Rocchiccioli[5] also discussed the structure of hydrates, but only the poly-, with no reference to the monohydrates. Oswald[6] compared the spectrum of the monohydrates to that of the monodeuterates and also the sulfates with the respective selenates, and our results are in perfect accord with these. However, Oswald does not give data on the polyhydrates and does not discuss their structure. Tanabe *et. al.*[2] deal only with the hydrates of nickel sulfate, giving I.R. spectra, amongst a variety of other physical methods, as a function of heat treatment. Their results are also in good agreement with ours.

Differential thermal analyses were carried out by a number of investigators,[7,8] but most of them concentrate on complete decomposition of the salt to the oxide or on the various intermediate hydrates giving little or no data regarding the monohydrates. Tanabe's D.T.A. information is extremely scanty.

Many X-ray and neutron diffraction measurements were carried out.[2,4,9-19] The results can be summarized thus: in the polyhydrates, the $SO_4^=$ group forms a tetrahedron, and the central metal ion is octahedrally coordinated to six molecules of water; the seventh water molecule, if present, is not attached to the central ion but is linked only to oxy-ions and other water molecules. In the case of Cu^{+2} where there are 5 water molecules, only 4 surround the central ion, while the fifth has a position similar to that explained above for the 7th water molecule. With the exception of copper, all the monohydrates are isomorphous with monoclinic $MgSO_4.H_2O$; $CuSO_4.H_2O$ is triclinic. Here, the central metal ion forms a somewhat distorted octahedron with four $SO_4^=$ groups and two H_2O molecules. The four $SO_4^=$ groups form an almost square plane, with the two water molecules ranged on a line perpendicular to the nearly square plane.

(*) Presented to the XXXV. Meeting of the Israel Chemical Society, Haifa, Israel, February, 1966. *Israel J. Chem.*, 3, 1p (1966).

(**) Based on M. Sc. thesis, Hebrew University of Jerusalem, 1966.

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Experimental Section

Samples: The following were Baker Analyzed Reagents: $MgSO_4.7H_2O$, $MnSO_4.H_2O$, $CoSO_4.7H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, $3CdSO_4.8H_2O$. $NiSO_4.7H_2O$ was obtained from The British Drug Houses Ltd., and $ZnSO_4.7H_2O$ from Union Chimique Belge, S.A.

The monohydrates, except for the commercially available $MnSO_4.H_2O$, were prepared from the polyhydrates by heating the latter 1 - 2 hrs to the desired temperatures (Table I) and keeping them in a desiccator above conc. H_2SO_4. Suitable drying temperatures were found from our D.T.A. results and from Lendormy's[3] T.G. experiments. The analysis of the monohydrates was confirmed by I.R. spectra, D.T.A. data, and their reaction with NaCl to split off HCl (a rection not given by any higher hydrate[1]).

Table I. Dehydrating temperatures of the various polyhydrates to the monohydrates

Monohydrate	Temp. (°C)
$MgSO_4 . H_2O$	120
$CoSO_4 . H_2O$	160
$NiSO_4 . H_2O$	150
$CuSO_4 . H_2O$	130
$ZnSO_4 . H_2O$	110
$CdSO_4 . H_2O$	110

Measurements. (a) Infrared. A Perkin Elmer model 21 infrared spectrophotometer with an NaCl prism for 2-15 μ was used. Samples were measured in 200 mg KBr discs containing ½-1% of the sample except in the case of cupric salts where KCl was used instead of KBr to avoid oxidation to free bromine.

(b) D.T.A. runs were carried out on a Stone D.T.A. KA-2H unit. Activated alumina (mesh size $\sim$ 200) was used both as a diluent and for reference. The linear change of temperature with time, and the temperature difference between sample and blank, were recorded automatically on two different recorders. The dehydrations were carried out both under atmospheric pressure and 44 psi Argon (dynamic gas technique) in the case of the polyhydrates; for the monohydrates all the reactions were carried out under atmospheric pressure only, as no significant difference in the results was obtained when using the dynamic gas technique.

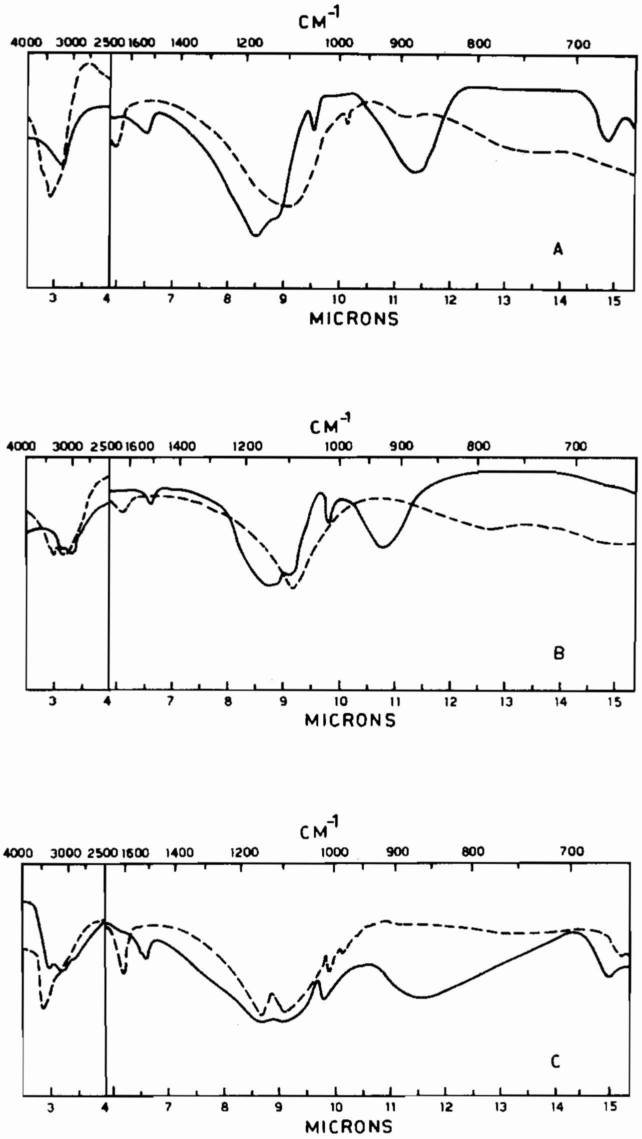

Figure 1. Infrared spectra of (A) $MgSO_4.7H_2O$ – – –; $MgSO_4 . H_2O$ ——— (B) $NiSO_4 . 6H_2O$ – – –; $NiSO_4 . H_2O$ ——— (C) $ZnSO_4 . 7H_2O$ – – –; $ZnSO_4 . H_2O$ ———.

Results

(1) A selection of infrared spectra is given in Fig. 1. and the key bands are given in Table II. The spectra are characterized by H_2O and $SO_4^=$ bands only. One would expect the appearance of stretching and bending O-H modes of H_2O and deformation (ν_4) and stretching (ν_3) degenerate vibrations of $SO_4^=$, but not the stretching symmetric (ν_1) and the deformation degenerate (ν_2) vibrations, which are not allowed in I.R. because of symmetry considerations.[20] ν_3 and ν_4 give rise to strong bands which are sometimes split because of the lowering of the symmetry in the solid matrix; for the same reason ν_1 and ν_2 do appear, but are rather weak. ν_2 peaking at $\sim$ 450 cm^{-1} was not observable being beyond the scanning range of the spectrophotometer.

From Table II it is seen that the strong stretching vibration of H_2O, appearing in the region 3350-3500 cm^{-1} for the polyhydrates, is shifted to 3000-3200 cm^{-1} for the monohydrates, and the bending vibration of H_2O is shifted considerably from $\sim$ 1640 cm^{-1} to $\sim$ 1520 cm^{-1}, all indicating a shorter metal-water bonding in the monohydrates. However, the rotating vibration of H_2O, which is usually inactive in I.R., appearing only for the monohydrates and peaking at $\sim$ 875 cm^{-1}, lends further support to the above assumption. Simultaneously with the shifting of the H_2O bands, a characteristic splitting of the $SO_4^=$ bands was observed in some cases, and in others, a deepening in the splitting, pointing towards removal of degeneracy owing to increasing co-ordination of $SO_4^=$, in exchange for water, with the metal ion on passing from the poly- to the monohydrate.

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(20) K. Nakamoto, «I.R. spectra of Inorganic and Co-ordination Compounds», John Wiley & Sons, N.Y., 1963.

Table II. I.R. bands (in cm^{-1}) of the polyhydrates compared to the monohydrates

Salt	Strong str.H_2O	Medium ben.H_2O	Strong str.$SO_4^=$	Weak str.$SO_4^=$	Medium rot.H_2O	Medium def.$SO_4^=$*
$MgSO_4 . 7H_2O$	3420	1665	1110	985	—	—
$MgSO_4 . H_2O$	3130	1525	1175; 1123	1050	883	673
$CoSO_4 . 7H_2O$	3350	1655	1105	985	—	—
$CoSO_4 . H_2O$	3400; 3230	1515	1175; 1110	1025	875	673
$NiSO_4 . 6H_2O$	3430; 3200	1640	1150; 1110	987	—	—
$NiSO_4 . H_2O$	3230; 3030	1525	1145; 1105	1023	933	—
$CuSO_4 . 5H_2O$	3350	1640	1215; 1170	967; 1005	—	667
$CuSO_4 . H_2O$	3010; 3300	1510	1195; 1065	1015	800; 865	622; 660
$ZnSO_4 . 7H_2O$	3500	1620	1150; 1100	1010; 985	—	656
$ZnSO_4 . H_2O$	3350; 3150	1525	1150; 1105	1020	870	667
$CdSO_4 . 8/3H_2O$	3500	1640	1118	(950-1000)	—	—
$CdSO_4 . H_2O^3$	3333; 3226	1540	1080; 1180	1020	875	657

(*) Scanning limit of spectrophotometer used.

(2) According to D.T.A. data, the dehydration of the various hydrates was found to be endothermic, as expected. The dehydration of the polyhydrates is stepwise, but some of the peaks indicate internal rearrangement and not the loss of water. This was shown by comparing weight loss curves with D.T.A. curves, where some of the D.T.A. steps have no counterpart on the T.G. curves. The dehydration energy consumed in the formation of the monohydrate is less than the energy required for the formation of the anhydride from the monohydrate, i.e. the bond holding the last water molecule is comparatively strong (Table III and Figs.* 2, 3 and 4).

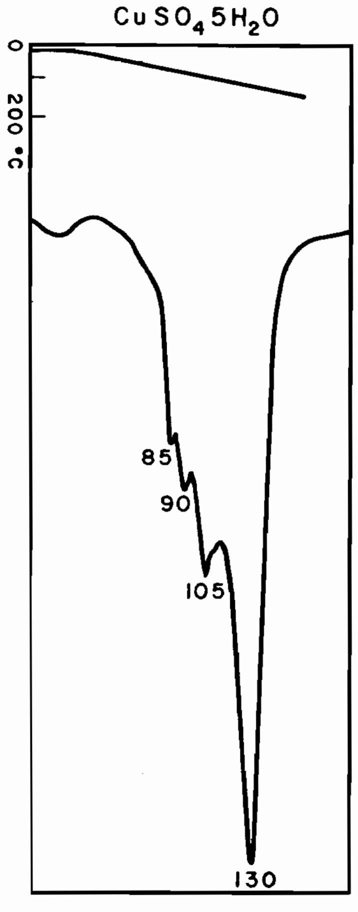

Figure 2. The dehydration of $CuSO_4.5H_2O$, rate of heating 6°C/min; dynamic gas technique (44 psi). Peak numbers show temp. in °C.

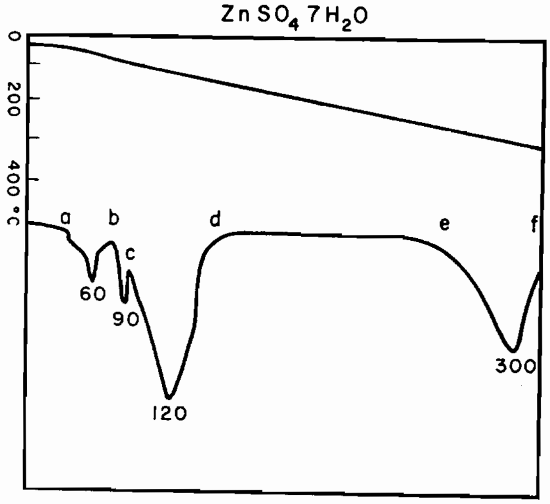

Figure 3. The dehydration of $ZnSO_4.7H_2O$; rate of heating 6°C/min; atmospheric pressure. Peak numbers show temp. in °C.

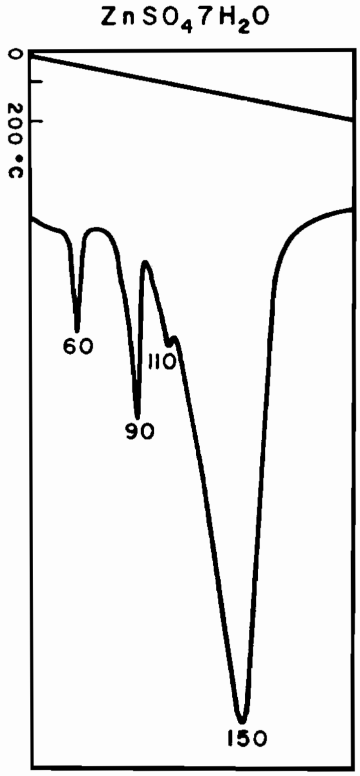

Figure 4. The dehydration of $ZnSO_4.7H_2O$; rate of heating 6°C/min; dynamic gas technique (44 psi). Peak numbers show temp. in °C.

(*) The upper curve in the figs. 2-7 is the heating curve and the lower is the differential curve.

Table III. Dehydration[a] of the polyhydrates to the respective monohydrates

Salt	% sample in alumina	No. of bands	Temperature of peaks in °C			
$MgSO_4.7H_2O$	16	3	70	105, 110 115, 117[c]	158-260	
$CoSO_4.7H_2O$	18	2	140	160		
$NiSO_4.6H_2O$	9	3	120	140	190	
$CuSO_4.5H_2O$	23	4	85	90	105	130
$ZnSO_4.7H_2O$[b]	18	3	60	90	120	
$ZnSO_4.7H_2O$	18	4	60	90	110	150
$CdSO_4\ 8/3H_2O$	30	2	105	110		

[a] Operating conditions: rate of heating - 6°C/min; technique used - dynamic gas at a pressure of 44 psi. This sample was dehydrated at atmospheric pressure for comparison. [c] Underlined number indicates temperature of formation of the monohydrate.

$MgSO_4.7H_2O$ presents a special problem in that there is no one characteristic peak for the dehydration: around the main 110°C band there are 3 weak bands (105°, 115°, 117°) and beyond them there is a series of 5 broad bands. Lendormy[3] observed the same phenomena in the thermogravimetric study of this salt. The loss in weight was continual and not in sharp steps. The series of bands between 158°C and 260°C might point to re-arrangement within the monohydrate and the beginning of a gradual dehydration towards the formation of the anhydride. Dell and Wheeler[21] suggested that, in general, several lower hydrates are formed during the decomposition and, in the presence of water vapor, recrystallization of each may occur. $NiSO_4.6H_2O$ dehydrates to the monohydrate at 140°C, and not at 190°C. This fact was verified by thermogravimetric analysis and I.R. spectra. The band peaking at 190° may be responsible for a re-arrangement or phase change within the monohydrate. This much was also suggested by Tanabe *et al.*[2]

In the case of copper, the band peaking at 85°C is responsible for the formation of the stable trihydrate which loses its water stepwise until 130°C, at which stage the monohydrate is formed. For zinc the hepta-, hexa- and monohydrates are kown. The hexahydrate forms at 60°C and the change into the monohydrate already starts at 90°C. This band might be responsible for reaction (i); the 110°C band for reaction (ii), and most of the energy involved in the 150°C band might be devoted to re-arrangement within the monohydrate.

$$\text{(i)}\quad ZnSO_4.6H_2O \ldots.\ H_2O \longrightarrow ZnSO_4.6H_2O + H_2O$$

$$\text{(ii)}\quad ZnSO_4.6H_2O + H_2O \longrightarrow ZnSO_4.6H_2O \longrightarrow$$
$$\longrightarrow ZnSO_4.H_2O + 5H_2O$$

Both figs. 3 and 4 deal with the dehydration of $ZnSO_4.7H_2O$; the difference being that the former is carried out at atmospheric pressure, while the latter, like all the other dehydrations (from poly- to mono-), was carried out at 44 psi in the dynamic gas technique. The reason for the use of this technique is that pressure slows down the reaction, and as a result, better separation of the bands is observable. For the dehydration of the monohydrates this special technique was superfluous as the dehydration involved either one or two well-separated bands.

The area under the dehydration bands is proportional to the dehydration energy. Thus, the area under the curve between points *a* and *b* Fig. 3 is proportional to the dehydration energy of one water molecule: from the hepta- to the hexahydrate. The area under the same curve between points *e* and *f* is also proportional to the dehydration energy of one water molecule: from the monohydrate to the anhydride. The area under the latter curve is larger than that under the former, that is, in comparison a greater amount of energy is consumed in the final stage of the dehydration. It should be stressed again that in most cases the intermediate steps in the dehydration point to the formation of varying mixtures of the highest polyhydrate with the monohydrate, and not to hydrates of definite composition.

The dehydration of the monohydrates is in most cases a one-step reaction, but with some cations the peak is split. This was observed in the case of Zn^{2+} and Cd^{2+}, while in the case of Co^{2+} and Cu^{2+}, two well-separated bands were observed (Table IV and Figs. 5, 6 and 7). The area of the first band is smaller than that of the second (if present) and might point to a recrystallization in the salt before the dehydration. The dehydration of the polyhydrates starts at *ca.* 50°C and the monohydrate stage is reached at a temperature near 100°C. However, the last water molecule is lost at much higher temperatures: above 200°C and in the case of Ni^{2+} at 420°C.

Only in the case of the above cobalt and cupric salts are there two distinct bands responsible for the dehydration. Comparing thermogravimetric[3] results, it can be stated that the bigger band peaking at the higher temperature indicates the actual loss of water, while the smaller band suggests a re-arrangement of phase-

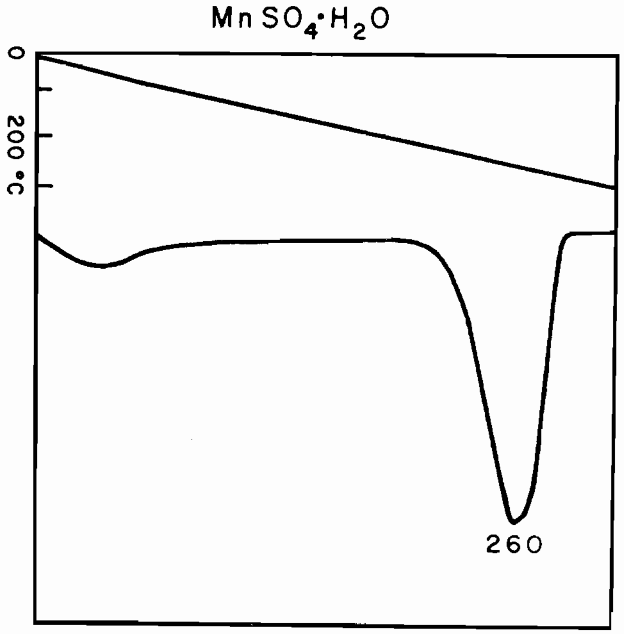

Figure 5. The dehydration of $MnSO_4.H_2O$; rate of heating 6°C/min; atmospheric pressure. Peak numbers show temp. in °C.

in °C.

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[21] R. M. Dell and V. J. Wheeler, «5th International Symposium on the Reactivity of Solids» (G.M. Schwab, Ed.), Elsevier, Amsterdam, 1965, p. 395

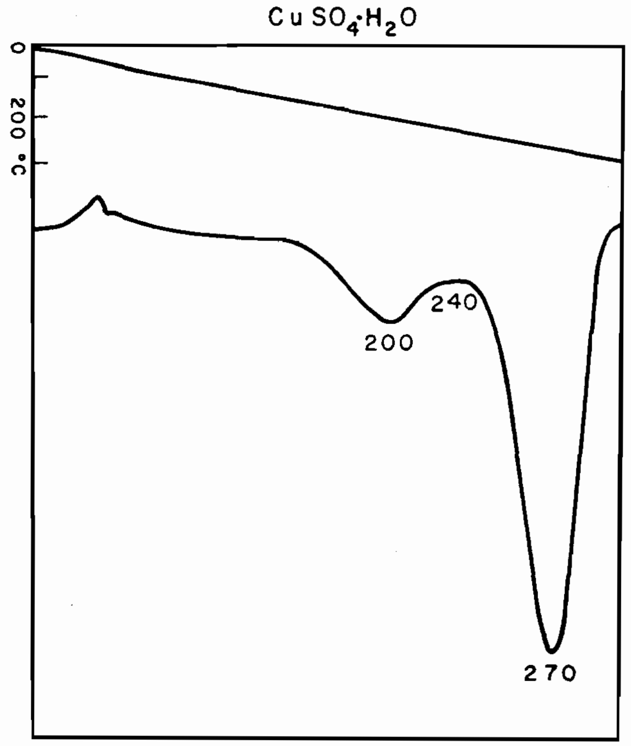

Figure 6. The dehydration of $CuSO_4.H_2O$; rate of heating 6°C/min; atmospheric pressure. Peak numbers show temp. in °C.

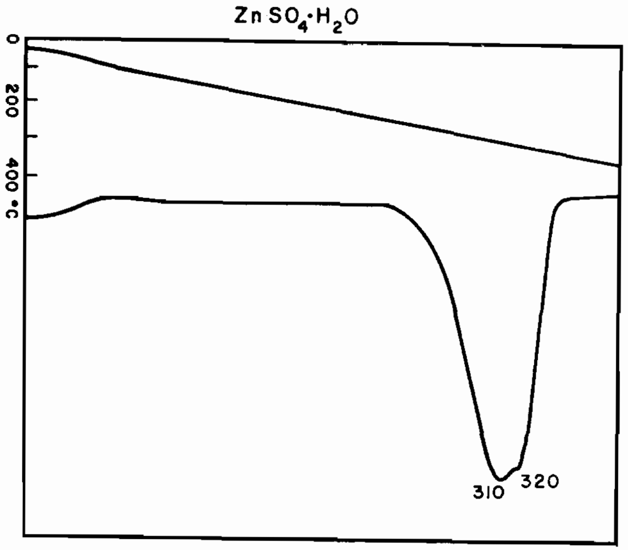

Figure 7. The dehydration of $ZnSO_4.H_2O$; rate of heating 6°C/min; atmospheric pressure. Peak numbers show temp. in °C.

Table IV. Dehydration of the monohydrates

Salt	% sample in alumina	No. of bands	Temp. of peaks in °C	Area ratio of bands
$MgSO_4 . H_2O$	100	1	354	—
$MnSO_4 . H_2O$	100	1	260	—
$CoSO_4 . H_2O$	45	2	215 320	2 : 10
$NiSO_4 . H_2O$	45	1	420	—
$CuSO_4 . H_2O$	45	2	200 270	2 : 10
$ZnSO_4 . H_2O$	33	2	310 320	1 : 1
$CdSO_4 . H_2O$	45	2	200 205	1 : 1

change of the monohydrate. Comparison of tables III and IV directly suggests the greater thermal stability of the monohydrates in comparison to any of the polyhydrates by as much as 100°C or more.

Assuming that the dehydration of the monohydrates is a first order reaction, yielding one band only, the activation energy for the dehydration can be estimated from

$$\frac{d(\ln \varnothing / T^2)}{d(1 / T)} = -\frac{Ea}{R}$$

provided errors due to geometry and particle size are recognized. This was done for the reaction $MgSO_4.H_2O \longrightarrow MgSO_4 + H_2O$. The ln of the rate of heating $\varnothing$ divided by T^2 was plotted *vs.* 1 / T, where T is the absolute temperature corresponding to the peak maximum on the dehydration curve. A straight line was obtained from which E_a was calculated and found to be 27.8 kcal/mole (Fig. 8).

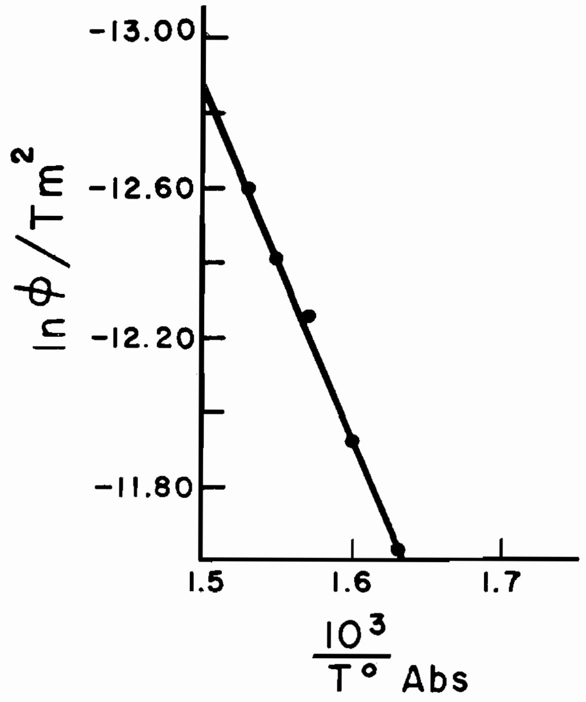

Figure 8. Estimate of activation energy (E_a).

This value is twice that known for common hydrates,[22] and is similar to the energy consumed when dehydrating $Mg(OH)_2$ or $Ca(OH)_2$. That is, the binding energy of the monohydrate is larger than that of coordinated water molecules, and may be compared to the energy of hydration of oxides.

Discussion

Definite acidity is shown by the above seven monohydrates judging from evolution of HCl when the solid monohydrates are mixed with NaCl. No other intermediate polyhydrate exhibits this behaviour, as proved from the «acidity» experiments. Also, the I.R. spectra and D.T.A. data showed a striking difference between all the polyhydrates on the one hand and the monohydrates on the other.

(22) M. Koishi, *Bull. Chem. Soc. Japan*, 37, 1150 (1964).

All the polyhdrates, irrespective of the number of water molecules which they contain above one, show the same I.R. spectra, while monohydrate I.R. spectra are clearly shifted and contain more new bands which appear because of lowering of the symmetry. The spectra obtained exclude the structure MH_2SO_5 or $M(OH)HSO_4$ for the monohydrates, as suggested by Lendormy. For the former formula, one would expect many more $SO_4^=$ bands, while for the latter, the appearance of the O-H band would be imperative. The shift of the bending mode of water from ~ 1600 cm^{-1} in the polyhydrates to ~ 1500 cm^{-1} in the monohydrates, and the stretching vibration from ~ 3600 cm^{-1} to ~ 3200 cm^{-1}, points to a change in the angle $H - O_w - H$ and the $O_w - H$ bond. O_w is bonded to two different $SO_4^=$ groups, thus hindering free rotation of the water molecule and favouring the appearance of a rotation band, ordinarily not allowed in I.R.

The D.T.A. data prove the extraordinary thermal stability of the monohydrates accompanied by a comparatively high dehydration energy. Increasing the atomic number in the 3d elements series causes the well-known change in ionic radii and hydration energies of the divalent ions. The temperature of dehydration of the monohydrates studied, except for cupric sulfate, follows the same trend, i.e., sarting from Mn^{2+} there is a continual rise until Zn^{2+} where there is a drop in the dehydration temperature. This explains the data presented in column 4 of table IV. Cupric salts were studied extensively by Borchardt and Daniels,[7] and the above mentioned anomalous behaviour might be explained by a partial hydrolysis or decomposition of the copper sulfate hydrate.

Our I.R. results concerning the structure of the monohydrates can be interpreted in the light of the structures which were determined by Oswald.[6] The $SO_4^=$ group forms a distorted tetrahedron, since one of its oxygen atoms is very close to the O_w; O_i—O_w = 2.71 Å. This, in fact, is a contact distance between the two oxygen atoms since the oxygen radius according to Pauling is 1.35 Å. Such a contact would force a hydrogen atom to be pushed as far out as possible. This of course is true about the second hydrogen atom too. The metal ion is hexa-coordinated with 6 atoms of oxygen: $2O_w$, $2O_i$ and $2O_{ii}$, where O_i is the atom nearest O_w. The specific charge on the cation is comparatively high, so that the oxygen ions are strongly attached to it and electrons are easily pulled off the «pushed-away» hydrogen, leaving it a proton. This explains the mentioned acidity of the monohydrates.

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