

The Hydrated Magnesium Ion Deaquation in Zinc Potassium Sulphate Hexahydrate

Dr. Sevak Kumar*

Assistant Professor, Department of Physics, MBPG College, Dadri, Gautam Buddha Nagar, UP, India

Email: Sevaknagar@gmail.com

Abstract: *The interatomic distances and angles are listed in Tables-2.1 and 2.2. All water molecules are coordinated to magnesium ions, six to each one. The crystal structure (Fig. 2.2) consists of a packing of these octahedrally hydrated magnesium ions and unhydrated ammoniums, among the tetrahedral sulphate ions. From the tables it follows that the water octahedra are not regular with their four equatorial bonds being almost equal but greater than the two nearly equal axial (polar) bonds.*

Keywords: *Hydrated Magnesium, Ion Deaquation, Zinc, Potassium Sulphate Hexahydrate*

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Thermal Deaquation :

Earlier thermal measurements (DTA, TG & DTG) made by Ben-Dor & Margalith [1] have proved to be suitable methods for studying deaquation steps in some metal hydrates. These authors have reported the deaquation to occur in two broadly classified steps: firstly all but one molecules of water are evolved at lower temperatures beginning say 60°C & the remaining water molecule is evolved after significant rise in the temperature of the salt. Therefore, the last molecule was found to be bound very strongly within the crystal lattice. The thermal decomposition data for two more systems are given below.

Studies in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$:

As show in Fig. 1.2, from the work of Sarig [2] regarding DTA, TG & DTD, it is seen that three weight loss steps of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ accompanied by three DTG curves and three corresponding endothermic DTA peaks can be distinguished at 85, 107 & 231°C. The sample weight in the measurement of Sarig[2] was 23.83 mg; therefore the theoretical weight loss on the evolution of one molecule of water should be 1.71 mg. The experimental values obtained for different steps were as follows: first step (AB) 3.33 mg, second (BC) 3.32 mg. & the last (DE) 1.68 mg. These weight loss values approximately correspond to 2 moles, 2 moles & 1 mole loss of water in the sequence of deaquation for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It is seen that four moles of water leave the crystal lattice by about 107°C, whereas the last fifty mole leaves around 231°C, a much higher temperature.

Studies in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$:

As shown in Fig. 2.1, for the system $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, four deaquation steps are seen as AB, BC, CD & DE. In the work of Sarig[2] for the initial sample weight of 21.30 mg. for $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, the loss of one molecule of water corresponds to the weight loss of 1.37 mg. The respective weight losses of different steps in Fig. 2.1 were as follows: first step (AB) 1.25 mg, second (BC) 4.35 mg, third (CD) 2.92 mg. & the last (DE) 1.35 mg. These results indicate the sequence of deaquation steps as 1 mole, 3 moles, 2 moles & finally 1 mole. It is again seen that six moles leave the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ crystal lattice by about 130°C; but the last 7th mole finally leaves at a much higher temperature of 230°C.

Resolution of deaquation steps :

Sarig[2] has further pointed out that gas (water vapour) diffusion equilibrium established over the sample during heating, checks identification of peaks in the deaquation process plot. However by using inert gas flow in controlled manner Sarig[2] was able to prevent such an equilibrium to be established and obtain good separated deaquation steps.

Electric Field assisted deaquation :

Kher et al [4] & Nandi et al[5] proposed that during the process of deaquation of a hydrates salt, a very small fraction of water groups released from the bondage of crystal lattice, get dissociated into H^+ and OH^- ions. They[4,5] actually measured the current flowing through the hydrated salts at a linear heating rate of the sample to yield information about deaquation steps and also further about the

dissociation energies of different water groups in the lattice.

In the light of the works of Kher et al [4] and Nandi et al [5], it seems that H^+ and OH^- ions, obtained after dissociation of even a small fraction of water groups, were sufficient to check smooth outflow of water groups during deaquation. The dissociated water groups must be getting temporarily adhered to negative & positive ions respectively in the lattice of the hydrated salt and thus blocking the space within the lattice to check gas (water vapour) outflow from within the lattice to outer space. Electric field assisted heating is thus a useful process parallel to inert gas flow envisaged and actually realized by Sarig [2] in his work on $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 7H_2O$.

Srivatsa and Pandey [5-7] have made a number of studies pertaining to electrical field assisted deaquation process in some hydrated Tutton salts. They have obtained such results about the arrangement H_2O octahedra around the divalent cations in the lattice, as could otherwise be obtained only by detailed quite involved crystallographic investigations. To appreciate this point, further, it would therefore be interesting to discuss the known crystallographic data about the Tutton salts.

Crystal Structure of Tutton Salts :

The Tutton salts have the general composition $A_2^+ B^{2+}(XO_4) \cdot 6H_2O$, where A is a monovalent cation K, Rb, Cs or NH_4 , B is a divalent cation Mg, Zn, Fe, Co, Ni or Cu and X is S or Se. These salts were extensively studied by the goniometric method around the turn of century by Tutton [8-10] and proved to be an early example of a large iso-structural series. The structure of the one member of the series magnesium ammonium sulphate hexahydrate was investigated in detail by Margulis and Tempeleton [11] and is shown in Fig. 2.2. This was found to be in the space group $P_{21/2}$ with two molecules per unit cell. The space group indicates that the divalent cations be located at $(0, 0, 0)$ & $(\frac{1}{2}, \frac{1}{2}, 0)$ and all other atoms at general positions with coordinates $\pm(x, y, z; x + \frac{1}{2}, -y + \frac{1}{2}, z)$. The hydrogen bonding of water molecules in this system is shown in Fig. 2.3.

The cell dimensions of the monoclinic unit cell of magnesium ammonium sulphate hexahydrate Tutton salt at room temperature are :

$$a = 9.324 \pm 0.007 \text{ \AA}$$

$$b = 12.597 \pm 0.009 \text{ \AA}$$

$$c = 6.211 \pm 0.005 \text{ \AA}$$

$$\angle \beta = 107.14^\circ \pm 0.020^\circ$$

The interatomic distances and angles are listed in Tables-2.1 and 2.2. All water molecules are coordinated to magnesium ions, six to each one. The

crystal structure (Fig. 2.2) consists of a packing of these octahedrally hydrated magnesium ions and unhydrated ammoniums, among the tetrahedral sulphate ions. From the tables it follows that the water octahedra are not regular with their four equatorial bonds being almost equal but greater than the two nearly equal axial (polar) bonds.

The Sulphate ion :

The shape of the sulphate ion is close to that of a regular tetrahedron. The O-S-O angles range from 108.4° to 110.7° with standard deviation of 0.3° . The S-O distances, before correction for thermal motion, range from 1.459 to 1.481 \AA with standard deviations of 0.005 \AA , the average being 1.473 \AA .

The Hydrated Magnesium Ion :

The octahedron of water molecules is slightly distorted from regular. The Mg-O distances differ by upto 0.03 \AA , independent of how the thermal correction is applied, while each has a standard deviation of 0.005 \AA . The small distortions are attributed to the lack of symmetry of the neighbours to which the water molecules are hydrogen bonded. Two equatorial bonds Mg-O₇ and other two equatorial bonds M-O₈ are nearly equal and greater than the remaining two axial bonds of water octahedron surrounding Mg^{2+} ion.

Deaquation in Zinc Potassium Sulphate Hexahydrate :

Srivatsa and Pandey [6] have reported electric field assisted deaquation in Zinc Potassium Sulphate Hexahydrate Tutton salt in its pelletized samples. Fig. 2.4 shows Log I versus Time (min.) plot obtained at the heating rates of $1^\circ\text{C}/\text{min.}$ & $2^\circ\text{C}/\text{min.}$ The graphs obtained show one peak around 90°C and another composite peak with components at 112°C and 115°C . Srivatsa and Pandey [6] also successfully attributed the first peak to H^+ and OH^- ions arising from a fraction of water groups released around 90°C from the equatorial positions in the Tutton salt lattice and the second peak to H^+ and OH^- ions created due to such ionisations of water groups released from axial water groups. Crystallographically, the axial $M^{2+}-H_2O$ bonds are shorter in length and hence differ from equatorial $M^{2+}-H_2O$ bonds. The simple electric field assisted deaquation process distinguishes axial water groups from those of polar water groups and thus provides information close to that provided by X-ray studies. Srivatsa and Pandey [6] have further obtained dissociation energies of different types of water groups within the Tutton salts using above experimental data.

Proposed work:

In this thesis, it is therefore, proposed to present results of electric field assisted deaquation in two hydrated salts, $Na_2WO_4 \cdot 2H_2O$ & $Na_2MoO_4 \cdot 2H_2O$ and

further obtain information about dissociation energies of water groups within such salts.

Table – Interatomic distances (Å) in Mg(NH₄)₂·(SO₄)₂·6H₂O Tutton salt single crystals:

SO₄²⁻ tetrahedron:

S –O ₃	1.459±0.005	O ₃ –O ₅	2.419±0.006
S –O ₄	1.474±0.005	O ₃ –O ₆	2.396±0.007
S –O ₅	1.481±0.005	O ₄ –O ₅	2.417±0.006
S –O ₆	1.476±0.005	O ₄ –O ₆	2.393±0.006
O ₃ –O ₄	2.387±0.005	O ₅ –O ₆	2.417±0.006

Mg (H₂O)₆²⁺ Octahedron:

Mg –O ₇	2.083±0.005	O ₇ –O ₉	2.924±0.007
Mg –O ₈	2.073±0.005	O ₇ –O' ₉	2.922±0.007
Mg –O ₉	2.051±0.005	O ₈ –O ₉	2.953±0.007
O ₇ –O ₈	2.945±0.007	O ₈ –O' ₉	2.879±0.007
O ₇ –O' ₈	2.932±0.007	—	—

Table – (Continued)

H₂O Hydrogen Bonding :

O ₇ –O ₃	2.722±0.006	O ₈ –H ₁₉
O ₇ –O ₅	2.756±0.006	O ₉ –H ₁₂
O ₈ –O ₄	2.792±0.006	O ₉ –H ₁₈
O ₈ –O ₅	2.844±0.006	O ₃ –H ₁₃
O ₉ –O ₄	2.777±0.006	O ₄ –H ₁₁
O ₉ –O ₆	2.713±0.006	O ₅ –H ₁₅
O ₇ –H ₁₃	1.0±0.1	O ₆ –H ₁₂
O ₇ –H ₁₅	0.9±0.1	O ₄ –H ₁₈
O ₈ –H ₁₁	0.8±0.1	O ₅ –H ₁₉

NH₄⁺ Hydrogen bonding:

N –O ₃	3.102±0.009	N –H ₁₇
N –O ₄	2.837±0.008	N –H ₂₀
N –O ₅	2.916±0.008	O ₅ –H ₁₄

N –O ₆	2.949±0.008	O ₆ –H ₁₆
N –O ₆	3.059±0.009	O ₄ –H ₁₇
N –H ₁₄	1.0±0.1	O ₃ –H ₂₀
N –H ₁₆	0.9±0.1	O ₆ –H ₂₀

Table- Bond angles (degrees) in Mg(NH₄)₂·(SO₄)₂·6H₂O Tutton salt single crystals:

O–S–O Angles:

O ₃ –S–O ₄	108.9	O ₄ –S–O ₅	109.7
O ₃ –S–O ₅	110.7	O ₄ –S–O ₆	108.4
O ₃ –S–O ₆	109.4	O ₅ –S–O ₆	109.6

H₂O Hydrogen bond angles:

O ₃ –O ₇ –O ₅	101.2	O ₃ –O ₇ –H ₁₃	8
O ₄ –O ₈ –O ₅	115.3	O ₅ –O ₇ –H ₁₅	2
O ₄ –O ₉ –O ₆	102.9	O ₄ –O ₈ –H ₁₁	7
H ₁₃ –O ₇ –H ₁₅	110.0	O ₅ –O ₈ –H ₁₉	5
H ₁₁ –O ₈ –H ₁₉	111.0	O ₄ –O ₉ –H ₁₈	6
H ₁₂ –O ₉ –H ₁₈	106.0	O ₆ –O ₉ –H ₁₂	6

O–Mg–O Angles:

O ₇ –Mg–O ₈	90.3	O ₈ –Mg–O ₉	91.5
O ₇ –Mg–O ₉	90.0	—	—

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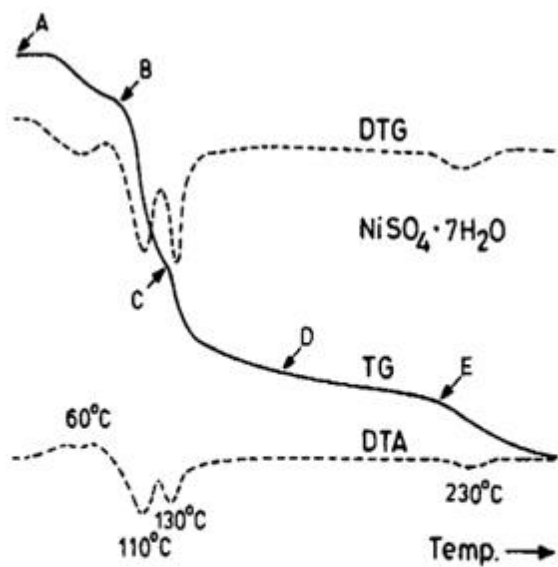


Fig. DEAQUATION OF NICKEL SULFATE HEPTAHYDRATE.

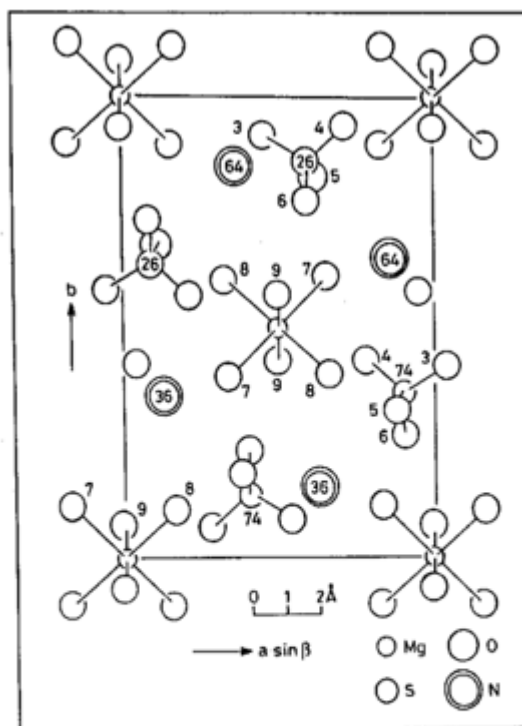


Fig. CRYSTAL STRUCTURE OF $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_6 \cdot 6\text{H}_2\text{O}$: THE NUMBERS AT THE SULFUR AND NITROGEN ATOMS INDICATE THEIR Z-COORDINATES.

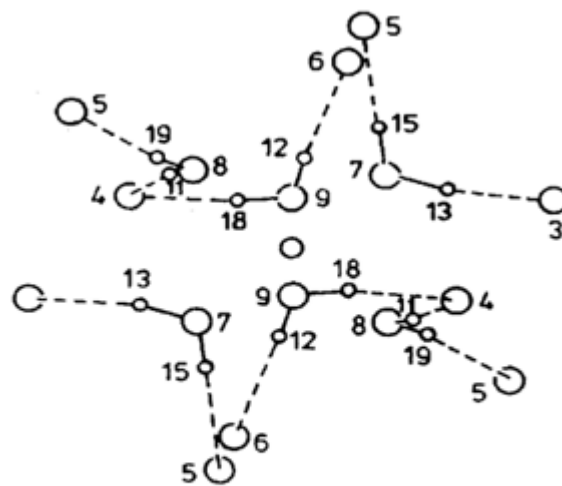
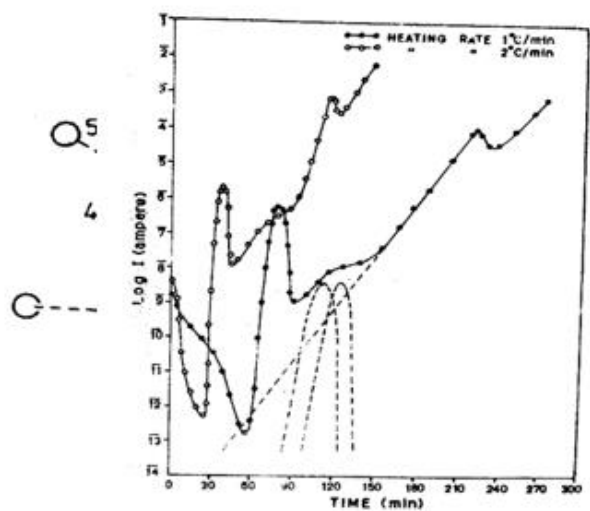


Fig. HYDROGEN BONDING OF WATER



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Fig. TIME VARIATION OF CURRENT THROUGH A CRYSTAL OF $Zn(NH_4)_2(SO_4)_6 \cdot 6H_2O$ FOR TWO DIFFERENT HEATING RATES.

Corresponding Author

Dr. Sevak Kumar*

Assistant Professor, Department of Physics, MBPG
College, Dadri, Gautam Buddha Nagar, UP, India

Email: Sevaknagar@gmail.com