Dehydration steps in CuSO₄·5H₂O crystals

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Abstract. Measurement of electrical conductivity (DC), dielectric constant (at 10 kHz), dynamic and isothermal TGA of $CuSO_4 \cdot 5H_2O$ in single crystals and poly-crystalline form have been carried out in the temperature range 30-300°C. It has been observed that the dehydration takes place in the steps of 1 mol, 1 mol, 2 mols and 1 mol at temperatures 111, 124, 190 and 275°C respectively in one of the sets. The DC electrical conductivity and dielectric constant also show a large increase and decline near about the first two dehydration temperatures confirming the results of TGA study. This behaviour has been explained on the basis of the release of water molecules at the respective dehydration temperatures and dissociation of a fraction of the released water molecules into H^+ and OH^- ions. Availability of these charged particles increases the conductivity and formation of space charge increases the dielectric constant.

1. Introduction

The thermal and electrical measurements have proven to be convenient methods for studying deaquation steps in many metal-salt.hydrate systems. The sequence of deaquation steps in many polyhydrated metal sulfates, as reported by Ben-Dor and Margalith (1967), consist of two definite steps: First all but one molecule of water are evolved at relatively low temperatures (beginning at 60° C), then after a significant rise in temperature the last molecule is evolved. Four distinct steps in the DTA analysis were detected by them using a relatively high heating rate of 6°C/min. Paulik *et al* (1966) extensively studied the effect of experimental condition on reproducibility of thermal analysis result and detected three distinctive deaquation steps of $CuSO_4.5H_2O$ namely 2 mols, 2 mols and 1 mol of water. By the simultaneous TG, DTG and DTA analysis Sara Sarig (1973) also detected three deaquation steps of $CuSO_4.5H_2O$. Wiedemann Bayer (1975) and Chupakhin *et al* (1975) have studied the thermal decomposition process and effect of vapour pressure on kinetics of nuclear growth during dehydration of $CuSO_4.5H_2O$. The detection of quadruple point (i.e., the temperature at which four phases are simultaneously present in the system) have been done using thermal analysis and electri-

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cal conductivity by Wendlandt (1970) and Simmon and Wendlandt (1972). Simultaneous electrical conductivity and DTA analysis was carried out by Halmos and Wendlandt (1973) with a special apparatus. They have detected the previously reported quadruple points in case of $CuSO_4.5H_2O$ (Wendlandt 1970; Borchardt and Daniels 1957; Wendlandt 1970; Halmos and Wendlandt 1972). Thermal decomposition of $CuSO_4.5H_2O$ was investigated by Bonilla *et al* (1975) using DTA and dielectric measurements. The fact that materials undergoing phase transitions show an anomalous behaviour of dielectric constant at the transition temperature was used in the study. Das and Sharma (1969) have studied electrical behaviour of $CuSO_4.5H_2O$ with successive loss of its water of crystallization. Their measurements show that temperatures at which the successive water of crystallisation are lost depend on the direction of the crystal axes, viz., $\parallel a, \parallel b$, or $\parallel c$ with respect to the electrical field.

It has been observed from the reports of several authors that the exact dehydration temperatures indicating the different deaquation steps never coincided. Even the measurement of the same sample by different methods resulted in giving different number of steps for the dehydration process. Different studies require different form of the sample namely powder form of the material is used for the DTA study whereas pellet or crystal is needed for electrical conductivity and dielectric measurements. As the number of dehydration steps and their dehydration temperatures depend on the nature, size and shape of the sample, in the present study crystals and pellets of different thicknesses are used to study the deaquation steps in $CuSO_4.5H_2O$ using electrical conductivity, dielectric constant and thermogravimetric techniques.

2. Experimental

2.1. *Nature of samples*

Crystals were grown from aqueous copper sulfate solution by slow evaporation process. Big pieces of crystals with perfectly reflecting surfaces were obtained. Small pieces of one to two mm thickness and area about 0·2 sq cm were obtained by cleaving big crystals for electrical and thermal study. Similar measurements were also carried out using pellets. The pellets were prepared by pressing the powdered crystal (104 μ) in a hydraulic press to a pressure of 5,000 kg/cm².

2.2. *Measurement of electrical conductivity*

The electrical conductivity was measured by a BPL meg meg ohm meter type RM 160/3 in the temperature range from 30 to 300°C. The rate of increase of temperature being 1° C/min. The variation of log σ with T is shown in figure 1a. The conductivity measurements in case of crystals show two very sharp peaks at 110°C and 124° C respectively which correspond to dehydration temperatures. The height of the second peak is much larger than that of the first (larger by about 4 orders). The third dehydration step at 190°C is observed only in a few cases (depending on atmospheric humidity). However, as will be described, in TGA study, the third peak is invariably present. As the sample is cooled from 300°C to room temperature the conductivity shows a continuous decrease up to about 120° C below which
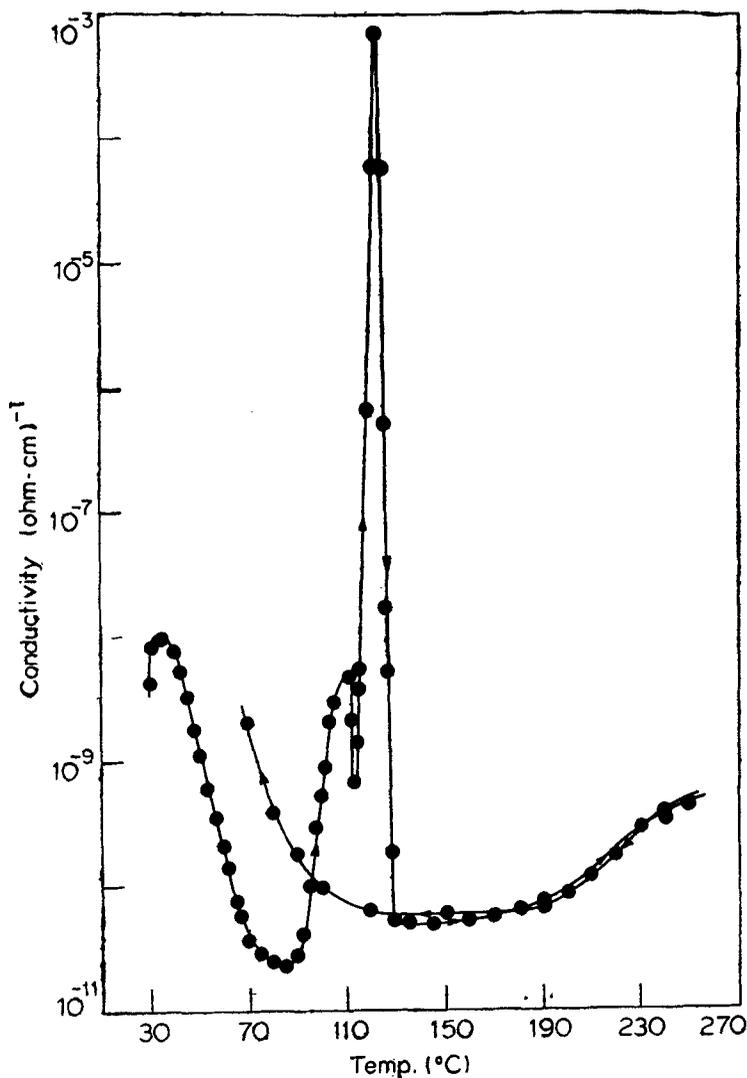
Figure 1a. Variation of **DC** electrical conductivity with temperature of $CuSO_4 \cdot 5H_2O$ crystal.

it increases considerably as it begins to absorb moisture from the atmosphere. The conductivity peaks due to dehydration obtained during heating are completely missing during cooling. The pelleted samples, however, show two broad peaks at 114° C and 190° C (figure 1b). The first broad peak at 114°C corresponds to the release of first two water molecules at 110° C and 124° C in the case of crystals. The second peak at 190° C agrees with the TGA peak. The observed rate of change of conductivity in case of crystals is much higher than that in case of pellets. The experiment was repeated for several crystals and pellets. Mean dehydration temperatures are calculated from several such observations. Table 1 summarises the deaquation temperatures.

Table 1. Dehydration temperatures from DTG, conductivity and dielectric constant studies.

	Dehydration temperatures ° C	Mean temperature ° C	Mean temperature ° K	Mean deviation	% error
1st Peak	110				
	111				
	114				
	115	113·12	386·12	2·095	0·542
	110				
	115				
	115				
	115				
2nd Peak	126				
	122				
	124				
	123				
	127·5	124·94	397·94	3·044	0·7625
	130				
	130				
	122				
	120				
3rd Peak	185				
	190				
	190	192·66	465·66	6·99	1·50
	195				
	198				
	198				
4th Peak	273				
	275				
	275				
	275	277·57	550·57	9·14	1·659
	280				
	285				
	280				

2.3. *Measurement of dielectric constant*

The dielectric constant ϵ' was measured by a Marconi Bridge type TF 868/1 at 10 kHz in the same temperature range. The variation in ϵ' with temperature for crystals is shown in figure 2a. Two sharp peaks of nearly the same height with slow rate of heating (0·5° C/min) are obtained at 110° C and 127° C respectively. The variation in ϵ' is from 30 to 156. The two higher dehydration steps are not observed in the dielectric study. With high rate of heating the accurate deaquation temperatures cannot be determined (as the balancing of the bridge takes some time during which the transition is missed). In the pelleted form the dielectric constant measurement shows a single broad peak at 120° C (see figure 2b). The dielectric constant varies from 6·25 to 16330 near this temperature. In both the
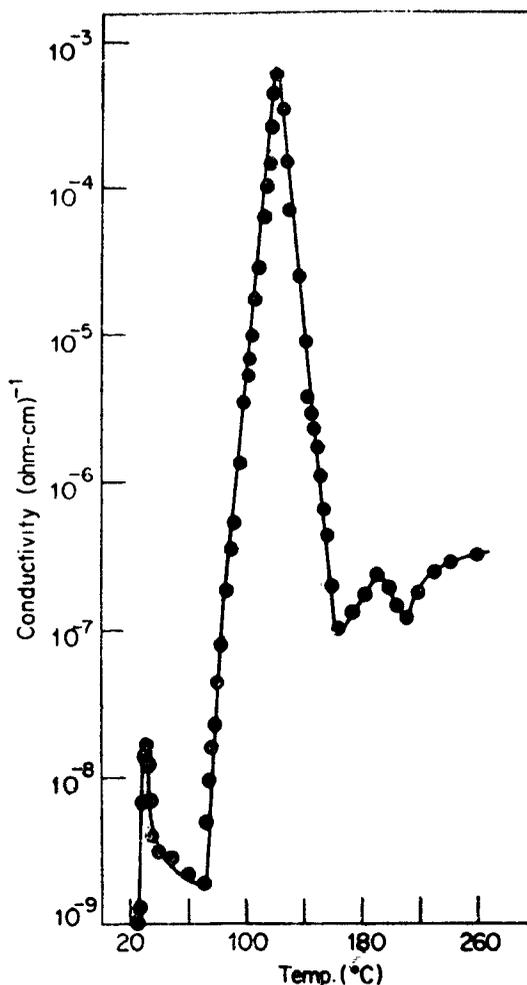
Figure 1b. Variation of DC electrical conductivity with temperature of $CuSO_4 \cdot 5H_2O$ pellet.

cases while cooling from 300° C to the room temperature the dielectric constant is found to remain constant.

2.4. *Thermogravimetric analysis*

The measurement of loss in mass of copper sulfate pentahydrate crystals as well as pellets were carried out in the temperature range from 30°C to 400°C with the help of a sensitive monopan balance (sensitivity 0·1 mg) having an arrangement for suspending the crystal. The sample was heated at a constant rate of 5° C/min. The loss in mass and time were measured at an interval of 5°C. The values of $\Delta m / \Delta t$, i.e., rate of change in mass (in mg/min) at different temperatures were calculated. Figures 3 and 4 show a plot between Δm versus temperature and $\Delta m / \Delta t$ versus temperature respectively. Figure 4 shows several peaks corresponding to different

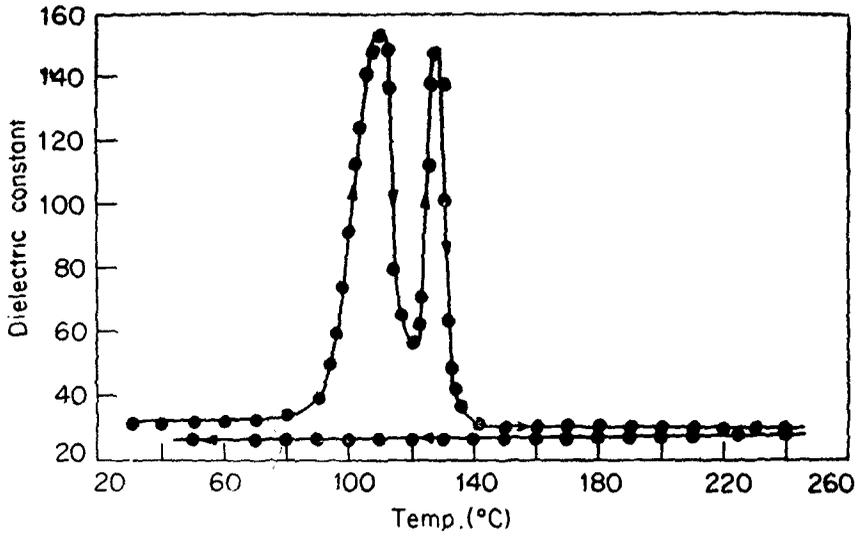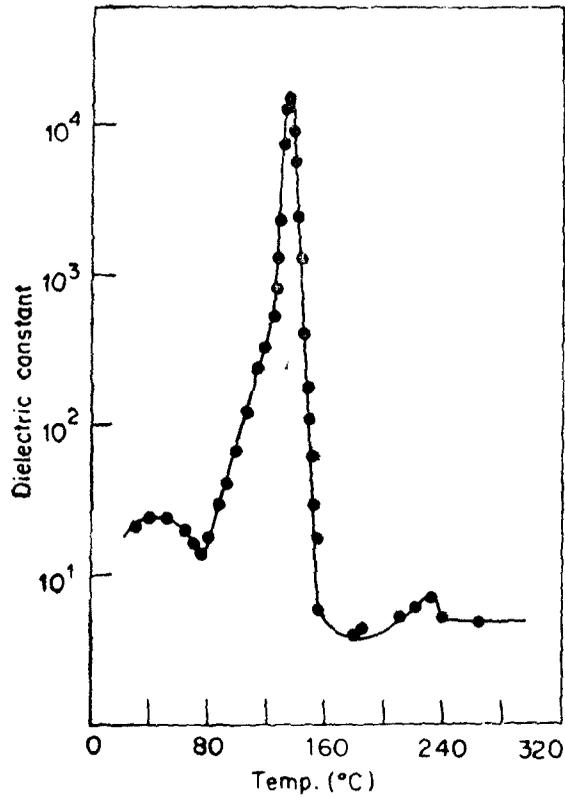**Figure 2a.** Variation of dielectric constant with temperature of $CuSO_4 \cdot 5H_2$ crystal (frequency 10 kHz).

Figure 2b. Variation of dielectric constant with temperature of $CuSO_4 \cdot 5H_2O$ pellet (frequency 10 kHz).
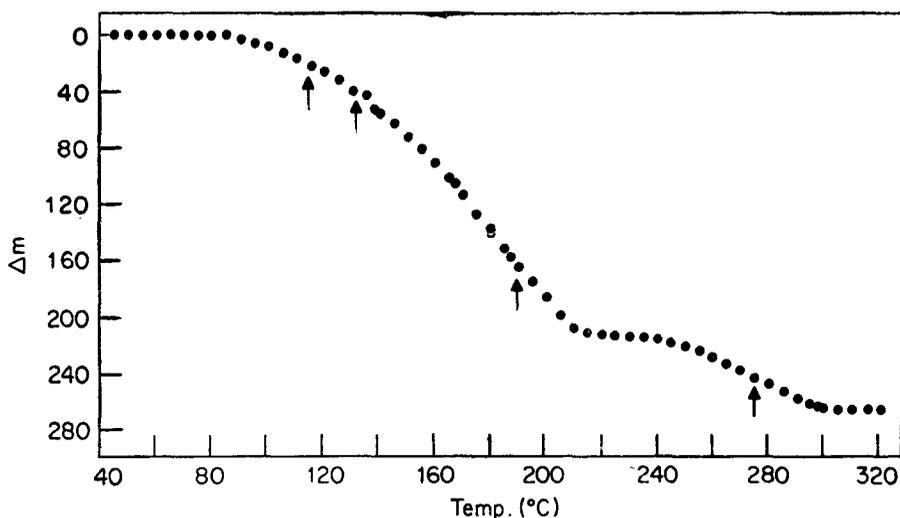
Figure 3. Plot of loss in mass of copper sulfate pentahydrate crystal with temperature.
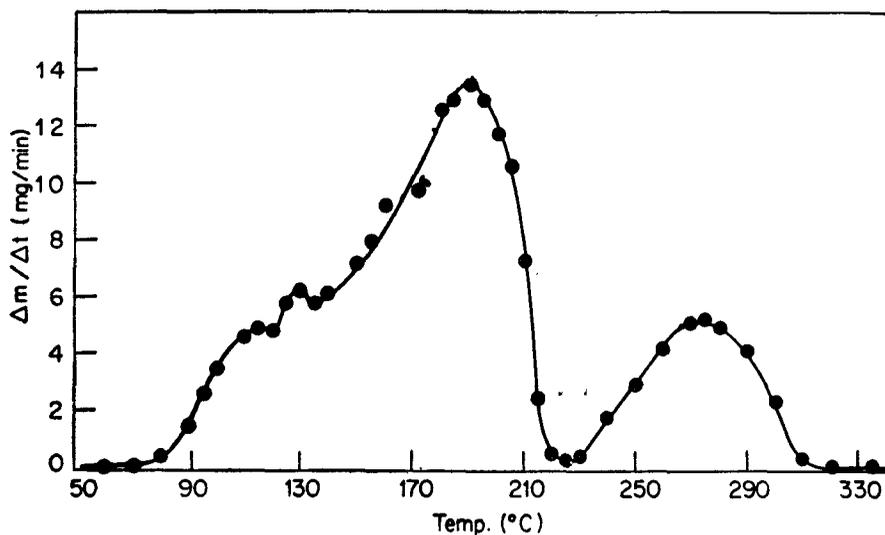

Figure 4. Variation of rate of loss of mass (mg/min) with temperature of copper sulfate pentahydrate crystals.

dehydration steps. The second and third peaks are equally broad. The first and fourth peaks are also equally broad but broader than the second and third. The heights of the first and the fourth peaks are equal and the height of the third peak is nearly double that of the first. The first two peaks at 110° C and 130° C correspond to the release of the first and second water molecules. The third broad peak of larger height at 190° C corresponds to the release of the next two water molecules. Another broad peak of smaller height at 275° C is observed for the

release of the last water molecule. Table 1 also summarises mean deaquation temperatures from dielectric as well as TGA measurements.

2.5. *Static or isothermal TGA study*

In the isothermal TGA study, the crystal was maintained at constant temperatures of 60° C, 80° C, 120° C and 200° C. Measurements of variation of mass of the sample with time were carried out at these temperatures. It is observed that when the crystal is maintained at 60° C it loses all the water molecules in nearly 40 hr. As the crystal temperature is increased the rate of loss of water with time increases. The time required for the release of all the water molecules at 200° C is about 30 min.

3. Results and discussion

3.1. *TGA study*

The dynamic TGA study shows occurrance of several peaks of different heights at the respective dehydration temperatures. The first two peaks corresponding to the release of first two water molecules are smaller in height than the third which corresponds to the release of next two water molecules.

Bonding of the water molecules in cupric sulfate is described by Evans (1966) and Sara Sarig (1973). Four water molecules are coordinatively bonded to the cupric ion and each of these water molecules is also coordinated by the oxygen atom of two SO_4 groups. The fifth water molecule is coordinated only by other water molecules and oxygen atoms and is called structural water. Several authors (Ben-Dor and Margalith 1967; Sara Sarig 1973; Graham 1835; Rinne 1899; Guareschi 1915, etc.) describe the dehydration in copper sulfate in the steps 2, 2 and 1. But unfortunately the temperatures at which the water is lost are not reported by many and there is no agreement in the reported values. The present TGA study shows two distinct peaks at 110° C and 120° C for the corresponding loss of first two water molecules. The mass loss observed corresponding to first two peaks in the TG curve at 110° and 130° C is in agreement with the mass loss calculated corresponding to the loss of first and second molecule of water of crystallization. This shows that the bonding of the second molecule is slightly altered making it more firmly bound to Cu and O atoms after the release of the first molecule. Hence the dehydration temperature for the second molecule will be slightly higher.

As seen from the static study and suggested by Ben–Dor and Margalith (1967) the decrease in mass of the sample due to release of water molecules begins even if the temperature of the crystal is 60° C. The rate of loss of water molecules is lower, larger the difference between the actual dehydration temperature and the temperature of the sample. Coming back to the dynamic study, the observed value of $\triangle m/\triangle t$ at 110° C is due to contribution from the water molecules which have the dehydration temperatures of 110° C, 130° C and 190° C respectively. The contribution will be greatest for the molecule whose deaquation temperature is 110° C and will be smaller for the second molecule and negligible for other molecules,

Hence the area under the first two peaks are smaller as single molecule is coming out of the crystal and contribution due to other remaining four molecules is quite small. The area under the third peak is larger than those under other peaks as two molecules are involved in the dehydration process.

Calculations from molecular weight show that 1/5th of the total mass of water of crystallization comes out of the sample at $110°$ C, 2/5th at $140°$ C, 4/5th at $245°$ C and 5/5th at $308°$ C respectively. These temperatures are higher than the dehydration temperatures corresponding to the release of first, second, third, fourth and fifth molecules. Thus it is clear that up to the instant of the first peak all the molecules corresponding to the first deaquation temperature are not released but continue to be released till a slightly higher temperature is reached. However, the rate of release of water molecules decreases above the dehydration temperature as the total number of this type of water molecules available after this instant is much smaller. Similar is the case for the other peaks.

The x-ray data reported by Ben–Dor and Margalith (1967) for $CuSO_4 \cdot 5H_2O$ gives a deaquation temperature at a much lower temperature ($< 75°$ C). The dynamic study shows that there is no change in mass of the crystal up to about $80°$ C. On the other hand the static TGA study shows that water molecules are released from the structure at as low a temperature as $60°$ C if sufficiently large time is allowed for the process. For the structure determination by x-ray method, the sample has to be maintained at a particular temperature for several hours. Hence looking into the results of TGA studies it may be concluded that the reported lower deaquation temperature obtained by x-ray study actually corresponds to the first deaquation temperature of $110°$ C indicated by dynamic study.

3.2. *Conductivity and dielectric constant measurements*

The large increase in conductivity at the transition temperature indicates a sudden and enormous increase in the concentration of mobile charge carriers in the samples. It is, therefore, assumed here that a very small fraction of one of the water molecules that are detached from the structure at $110°$ C gets dissociated into H^+ and OH^- ions. At $124°$ C the second water molecule gets detached and a small fraction of such molecules dissociates into H^+ and OH^- ions. This increases the concentration of mobile charge carriers causing the observed large increase in conductivity. The number of charged particles n collected during the peak of conductivity curves can be determined experimentally by calculating the area (current *vs* time curve, figure 5) corresponding to the total charge released near the respective dehydration temperatures and dividing this by e the charge of electron. The values of current were calculated experimentally from the measured values of resistance and constant applied voltage. The number of charged particles n obtained in this way comes out to be $5 \cdot 774 \times 10^{13}$ for the first peak and $6 \cdot 1 \times 10^{18}$ for the second peak in one case. The dissociation energy for the H_2O molecules is $1 \cdot 2$ eV in the liquid state. Let the fraction f'

$$f' = \frac{\text{number of water molecules dissociated}}{\text{total number of water molecules detached}}$$
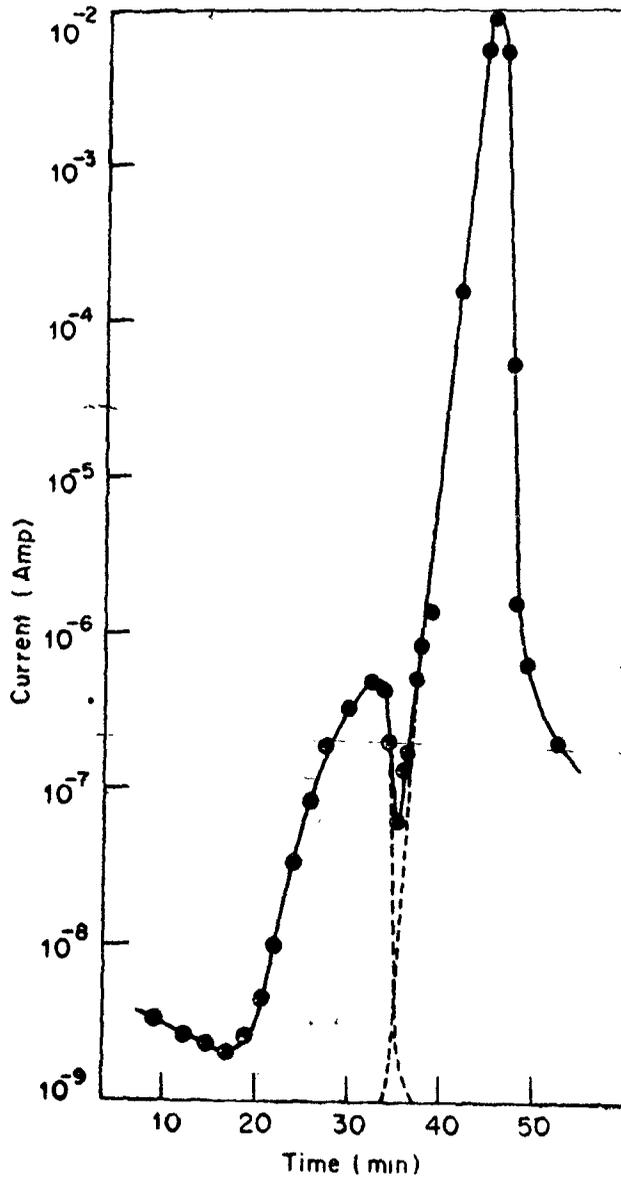
$$= n_2/n_1$$

Figure 5. A plot of change of current with time for calculating the number of charge carriers produced by dissociation.

where n_2 is the number of water molecules which receive thermal energy greater than $(kT + 1 \cdot 2)$ eV and n_1 is the number of water molecules which receive thermal energy greater than kT. From Maxwellian distribution

$$f' = n_2/n_1 = \frac{\int_{(kT+1\cdot2)\,\text{eV}}^{\infty} \epsilon^{-E/kT}\, dE}{\int_{kT}^{\infty} \epsilon^{-E/kT}\, dE}$$

Let f be the ratio of the number n_2 of water molecules dissociated to the number N of water molecules corresponding to the first deaquation temperature.

$$f = n_2/N$$

where

$$N = \int_0^\infty \epsilon^{-E/kT} \, dE.$$

The number of water molecules dissociated, that is, the number of free positive and negative charges produced at the deaquation temperature will be equal to fX (total number of water molecules, N corresponding to the first deaquation temperature). N is of the same order of magnitude as n_1, *i.e.*, $N \cong n_1$. Hence f will be equal to f'. Therefore the number of water molecules dissociated is $(N \times f)$. The number N can be calculated by imagining that one out of the five water molecules is involved for the two peaks. The calculated value of the number of charged particles produced by dissociation comes out to be $9 \cdot 5 \times 10^5$ for the first peak and $3 \cdot 02 \times 10^6$ for the second peak, which are lower than the experimentally observed values. This may be explained by assuming that the dissociation energy depends on the strength by which the H^+ and OH^- ions in the H_2O molecule are pulled in opposite directions in the structure, and will therefore be lower in solids than in liquids where the molecules are free. Calculations of $n_2 = f \times N$ for various values of dissociation energy have been carried out. From these it is found that if the dissociation energy of water in the solid is $0 \cdot 333$ eV for the first water molecule detached at $110°$ C and $0 \cdot 14$ eV for the next water molecule detached at $124°$ C, the statistical calculations give the value of the number n_2 as $4 \cdot 42 \times 10^{13}$ for the first peak and $6 \cdot 28 \times 10^{18}$ for the second peak which are in close agreement with the experimental values. As pointed out above the decrease in dissociation energy of water molecules inside $CuSO_4 \cdot 5H_2O$ solid may be due to the pulling of the hydroxyl ion by the Cu^{+2} ions in one direction and hydrogen ion by the SO_4^{-2} ions in the opposite direction. The value of the fraction f_1 for the first peak is calculated to be $1 \cdot 02 \times 10^{-7}$ and the fraction f_2 for the second peak is calculated to be $1 \cdot 45 \times 10^{-2}$. This shows clearly that the height of the second peak is about four orders larger than the height of the first peak as is observed. At about $110°$ C almost all the attached water molecules are released and a fraction f of it is dissociated. All the water molecules so released and dissociated are not able to come out of the sample immediately and many of them remain trapped in the interstitial space. The dissociated and trapped H^+ and OH^- ions are made mobile by the applied field contributing to the enhanced increase in the conductivity of the sample. As the temperature crosses the dehydration point the number of trapped ions decreases at a high rate as they are driven by the applied field and collected by the respective electrodes, while the trapped H_2O molecules can come out relatively slowly by the diffusion process. Hence $\triangle m / \triangle t$ in TGA study does not become zero immediately after the peak but takes considerable time to do so.

The observed change in dielectric constant is due to orientation of the permanent dipole moments of water molecules and space charge polarisation produced by the trapped positive and negative charges generated by dissociation. In the pelleted form of the sample the number of trapping centre increases and therefore the orientation polarisation increases considerably. The TGA study shows that the

deaquation peaks are quite broad indicating that the diffusion process has slowed down to a considerable extent. The increase in the number of trapping centres and the decrease in the rate of diffusion causes an increase in the concentration of the trapped water molecules. Since such molecules remain trapped for a considerable time, the concentration of positive and negative charges due to dissociation also increases. Hence the orientation and space charge polarisations increase to a great extent as is observed.

4. Conclusions

It is concluded from the study that in crystals the dehydration temperatures are 111°, 124°, 190° and 275° C respectively at which 1 molecule, 1 molecule, 2 molecules and 1 molecule are released. The fraction of the released water molecules that are dissociated is large for the first two water molecules contributing to the observed conductivity and dielectric peaks at the respective temperatures. In the pelleted form the first two steps merge into one giving deaquation steps as 2 molecules, 2 molecules and 1 molecule.

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