

## Thermal Transitions in Copper Sulphate Pentahydrate Molecular Rotation and the Dehydration of Hydrates

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positive deviation from the Mosotti law. As the density is increased, this deviation becomes smaller, and vanishes when  $v$  is approximately equal to  $b$  or  $2\pi Na^3/3$ . The corresponding density is about twice ordinary liquid densities. This is reasonable, for one might expect translational fluctuations to become relatively unimportant not only in solids but also in liquids. Not much significance is to be attached to the value  $v=b$  predicted by the above formula since it is probably necessary to take terms of higher order in  $P_0/v$  into account as liquid densities are approached. It should be emphasized, however, that although the Mosotti value of  $(\epsilon-1)v/(\epsilon+2)$  is approached

at some particular density, the Mosotti formula cannot give the correct variation of  $\epsilon$  with density. This consideration may at first sight seem to make the application of our equations to liquid pentane seem questionable. However, we must remember that although the translational fluctuation may become small at liquid densities, this is not true of the rotational fluctuation. It might, therefore, be better to suppose that the  $\gamma$  contribution to the slope vanishes and that only  $\sigma$  is important. The value of  $\sigma$  in liquid pentane would then be  $-0.05$ , with a ratio of  $0.86$  instead of  $0.5$ . It is apparent that we can attach only qualitative significance to these figures.

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## Thermal Transitions in Copper Sulphate Pentahydrate Molecular Rotation and the Dehydration of Hydrates

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A study of the thermal transitions in copper sulphate pentahydrate has been made from warming curves obtained by a differential thermocouple method. Small transitions were observed at  $29^\circ\text{C}$ ,  $35^\circ\text{C}$ ,  $53.7^\circ\text{C}$ , and dehydrations at  $96.5^\circ\text{C}$ ,  $102^\circ\text{C}$ , and at  $113^\circ\text{C}$ . The first three of these may be interpreted as transitions from oscillation to rotation of the water molecules in the crystal. The last three are associated with the stepwise dehydration to the tetra-, tri-, and monohydrates, respectively. The existence of the tetrahydrate, not previously known, has been demonstrated. A discussion of the dehydration in the light of its crystal structure is given. A mechanism of dehydration by heat, based on the concept of molecular rotation, has been suggested.

SINCE Pauling's explanation<sup>1</sup> of certain observed transitions in solids on the basis of a gradual transition from oscillational motion of the molecules about equilibrium positions to complete rotation, the phenomenon has proved to be of rather wide occurrence in accordance with his prediction. In many substances the excitation of rotation of the molecules or groups is accompanied by gradual and sometimes sharp changes in such properties as dielectric constant, heat capacity, specific volume, coherent scattering of x-rays, and crystal structure. Pohlman<sup>2</sup> has studied the adsorption spectra of a number of ammonium salts in the neighborhood of the transition temperatures. Shearin<sup>3</sup> has also recently found that there is an infrared absorption at wave-lengths of about  $3.7\mu$  for solid hydrogen

chloride which indicates hindered rotation. This observation is in contrast to the results of Errera and Sack<sup>4</sup> working with Hertzian waves. Evidence that molecular rotation in certain organic crystals is initiated simultaneously with atomic vibrations has been given by White and Morgan<sup>5</sup> and Yager and Morgan.<sup>6</sup>

As is shown by x-ray studies of the transitions observed in certain crystals, for example, sodium nitrate,<sup>7</sup> ammonium nitrate,<sup>8</sup> and *n*-amyl ammonium chloride,<sup>9</sup> rotation of the molecules or groups may or may not be initiated at a polymorphic inversion. If the transition is accompanied by a change in crystal structure, the con-

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<sup>1</sup> Pauling, *Phys. Rev.* **36**, 430 (1930).

<sup>2</sup> Pohlman, *Zeits. f. Physik* **79**, 394 (1932).

<sup>3</sup> Shearin, *Phys. Rev.* **48**, 299 (1935).

<sup>4</sup> Errera and Sack, *Trans. Faraday Soc.* **30**, 687 (1934).

<sup>5</sup> White and Morgan, *J. Am. Chem. Soc.* **57**, 2078 (1935).

<sup>6</sup> Yager and Morgan, *J. Am. Chem. Soc.* **57**, 2071 (1935).

<sup>7</sup> Kracek, Posnjak and Hendricks, *J. Am. Chem. Soc.* **53**, 3339 (1931).

<sup>8</sup> Hendricks, Posnjak and Kracek, *J. Am. Chem. Soc.* **54**, 2766 (1932).

<sup>9</sup> Southard, Milner and Hendricks, *J. Chem. Phys.* **1**, 95 (1933).

version may be rather abrupt though not necessarily discontinuous. This behavior is shown by such solids as hydrogen chloride,<sup>10</sup> nitrogen,<sup>11</sup> sodium cyanide,<sup>12</sup> and others.<sup>13</sup> With other crystals such as sodium nitrate or *n*-amyl ammonium chloride the transition is more gradual without a definite change in crystal structure. The definiteness of all these transitions is generally explained by assuming a cooperative phenomenon in which it is supposed that as soon as a molecule changes from the oscillatory state to the rotational state its whole surroundings will be involved and the other molecules will follow immediately. The resulting changes in lattice or molecular forces often result in a change in crystal structure.

In Pauling's theoretical treatment of a simple diatomic molecule, he considered the molecule bound like a harmonic oscillator in the crystal fields. The potential function representing the averaged interaction of the molecule with its surrounding molecules is given in its simplest form by

$$V = V_0(1 - \cos 2\theta),$$

in which  $V_0$  is a constant obtainable from specific heat data and  $\theta$  is the angle made by the figure axis of the molecule with some fixed direction. The transition from oscillation to rotation is assumed to start when the kinetic energy of the molecules becomes of the order of magnitude of  $2V_0$  or at a temperature of  $T = 2V_0/k$  when rotation weakens the binding forces. Thus the binding force is found to depend upon the temperature. For lower temperatures the molecules oscillate about  $\theta = 0$ , while above the transition they ro-

tate, being hindered in their motion by the crystal fields.

Since Pauling's work, a number of more complete mathematical treatments of wider application have been given. Some of these consider molecules of different three-dimensional configurations; others try to represent more fully the magnitude of the crystal fields and their effects on dielectric constant and specific heat. Of these the work of Stern,<sup>14</sup> Nielson,<sup>15</sup> Frenkel and his co-workers,<sup>16</sup> Fowler,<sup>17</sup> and Devonshire,<sup>18</sup> may be mentioned.

The purpose of this paper is to study the dehydration of copper sulphate pentahydrate and to show that transitions occur which may be interpreted as transitions from oscillation to rotation of the water molecules. Since the crystal structure of this hydrate has recently been determined<sup>19</sup> it lends itself to a rather complete analysis. A theory of dehydration on the basis of molecular rotation of the water molecules in certain salt hydrates as mentioned by one of us recently<sup>20</sup> is suggested and may be extended after further data are available. It seems possible at the present time that the vapor pressure of certain hydrates may be related to the statistical probability of the molecules acquiring enough vibrational-rotational energy to break away from the crystal lattice.

## EXPERIMENTAL

A thermal analysis of copper sulphate from  $-75^\circ\text{C}$  to  $160^\circ\text{C}$  was made by taking the heating curves with differential thermocouples. A diagrammatic illustration of the apparatus is given in Fig. 1. Double silk covered copper (B. S. No. 40) and constantan (B. S. No. 30) wire were used for both the differential and the temperature thermocouples. Calibration curves were obtained from the melting point curves of the following carefully purified substances: chloroform, monochlorobenzene, carbon tetrachloride; ice point; and sodium sulphate decahydrate, naphthalene,

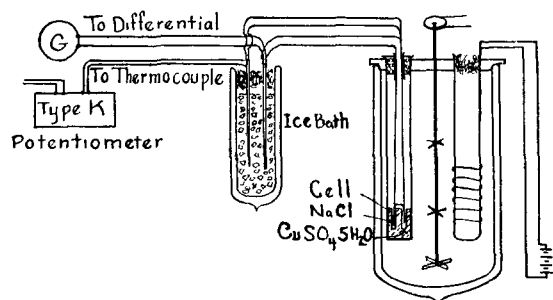


FIG. 1. Apparatus for heating and cooling curves.

<sup>10</sup> Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 101 (1928).

<sup>11</sup> Ruhemann, *Zeits. f. Physik* **76**, 368 (1932).

<sup>12</sup> Bijvoet and Verweel, *Rec. Trav. Chim.* **54**, 631 (1935).

<sup>13</sup> See for example, Pauling, reference (1).

<sup>14</sup> Stern, *Proc. Roy. Soc.* **A130**, 551 (1931).

<sup>15</sup> Nielson, *J. Chem. Phys.* **3**, 189 (1935).

<sup>16</sup> Frenkel, Tode and Ismailow, *Acta. Phys. U. R. S. S.* **1**, 97 (1934).

<sup>17</sup> Fowler, *Proc. Roy. Soc.* **A149**, 1 (1935).

<sup>18</sup> Devonshire, *Proc. Roy. Soc.* **A153**, 601 (1936).

<sup>19</sup> Beevers and Lipson, *Proc. Roy. Soc.* **A146**, 570 (1934).

<sup>20</sup> Taylor and Taylor, *J. Ind. Eng. Chem.* **27**, 672 (1935).

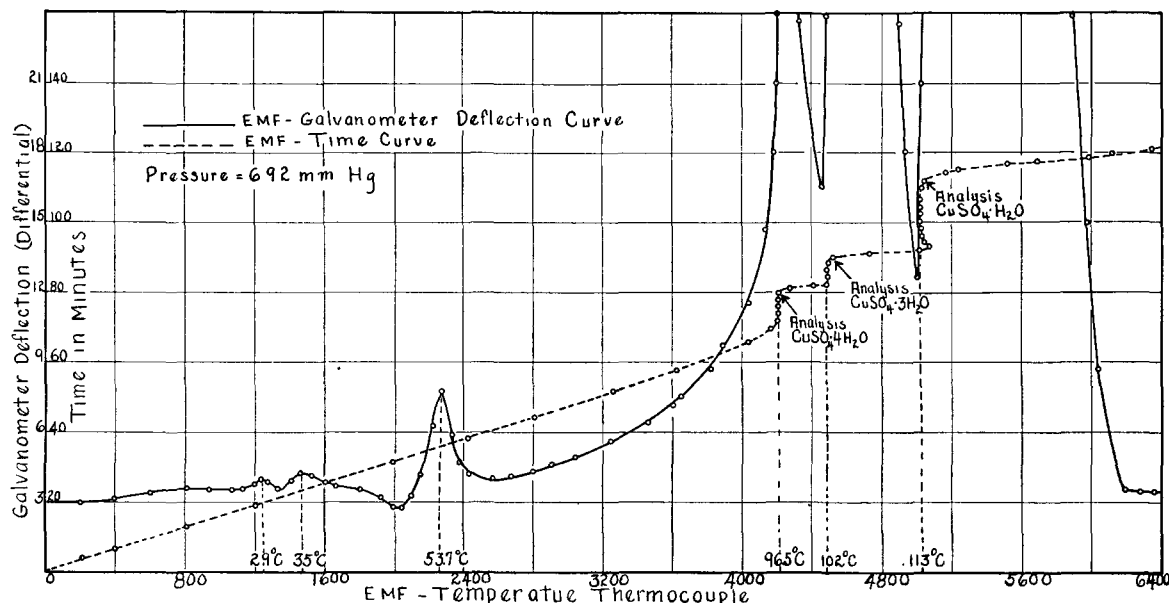


FIG. 2. Heating curves for copper sulphate pentahydrate.

benzoic acid, and salicylic acid. Different bath liquids were used according to the temperature range.<sup>21</sup> Over the transition ranges three different bath liquids were used to eliminate any uncertainties which might arise due to the possibility of transitions in them.

The cell was made by drilling two holes in a copper block and fitting them with thin-walled glass tubes. One tube was filled with about 1.5 g of copper sulphate pentahydrate and the other with an equal quantity of sodium chloride. Sodium chloride was chosen as a blank to run against copper sulphate because it has nearly the same specific heat and is known to have no transitions over the temperatures range studied.

A Leeds and Northrup type R-2500 C galvanometer with a sensitivity of 1.6 microvolts per mm was connected directly to the differential thermocouple. The scale was placed at about 75 cm from the galvanometer, so that one centimeter deflection corresponds to about one-third degree. The e.m.f. of the temperature thermocouple was read to the nearest 2 microvolts by means of a Leeds and Northrup type K potentiometer in conjunction with a type HS galvanometer (L. and N., year 1913).

In making a run the bath was cooled with solid

carbon dioxide and then heated at a constant rate. Readings of the temperature thermocouple and the galvanometer deflection were taken every minute, or every half minute in the neighborhood of a transition. Twenty-five to thirty runs were made over different temperature ranges. Some were made using different rates of heating, varying from 2°C per minute to 0.5°C per minute. Other runs were made in which the particle size of the copper sulphate was varied. Most runs were made at pressure of about 690 mm of mercury,<sup>22</sup> but a few runs were made under partial vacuum (5 cm Hg). The higher rates of heating give larger changes in galvanometer deflections, but there is a loss in detail and accuracy of temperature readings. Large particles do not give as sharp breaks in the latter part of the time temperature curves because the second stage of the dehydration probably starts before the first has reached to the center of the particle. On the other hand, too small particles prevent escape of liberated water vapor from the center of the sample. The most favorable conditions seemed to be a rate of heating of from 1°C to 1.5°C per minute and a particle size of >100<150 mesh (about 0.09 mm).

The curves for the temperature range -75°

<sup>21</sup> *International Critical Tables*, Vol. I, p. 61.

<sup>22</sup> The average atmospheric pressure at Moscow, Ida., is about 690 mm of mercury.

to 10°C are not reproduced because there was no abnormal deflection of the galvanometer and the temperature rose at a constant rate. Curves showing typical behavior above these temperatures are given in Fig. 2, which gives the results over the range 10°C at 160°C obtained by use of a two junction differential thermocouple. The analyses represented on Fig. 2 were obtained by stopping different runs at the points indicated and analyzing for both copper and water remaining. The results of the analyses for different runs did not vary more than 0.20 percent from the theoretical values calculated from the formulae  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . The value of 2270 microvolts for the higher of the small maxima could be reproduced under the same conditions on the same or different samples to within 5 to 10 microvolts using the same differential. The smaller maxima at about 1220 microvolts and 1470 microvolts were not so reproducible, different runs varying from 5 to 50 microvolts. This larger variation may be due in part to the smallness of the changes and the comparatively high rate of heating. It was found difficult to reproduce these smaller maxima later using different differentials with heavier wire, or with too much insulation. Instead of rising to a maximum there was simply a definite change in the slope of the differential curve at 50° to 55°C. The changes corresponding to the dehydrations shown, however, were always obtained.

#### DISCUSSION OF THE WARMING CURVES

As the temperature of the cell containing the sodium chloride and the copper sulphate was raised there should have been no abnormal deflection of the galvanometer connected to the differential thermocouple unless there is a fairly sudden change in the heat capacity or heat adsorption of the copper sulphate. Apparently there is such a change at about 29°C, 35°C and especially at 53.7°C. Greater sensitivity probably would reveal further detail in regard to the lower transitions. In the light of previous work on the rotation of molecules in solids, these changes may be interpreted as changes from oscillation to rotation of the water molecules. This is in accord with the suggestion of Pauling<sup>1</sup> that the water molecules in potassium alum must be rotating at room temperatures in order to explain certain

x-ray data showing high crystallographic symmetry. The rotation of the water molecules in some complex cyanide hydrates was also suggested by Errera and Sack<sup>4</sup> to explain some sharp changes in dielectric constants. Further, Fowler's treatment<sup>17</sup> of the dielectric constant of Rochelle salt assumes rotation of the water molecules. A transition in copper sulphate in the neighborhood of 50°–55°C has been observed by a number of investigators by measurement of conductivity, electromotive force, solubility and dilation. These have been summarized by Abraham and Lucasse.<sup>23</sup>

The three small transitions observed may possibly be due to rotation of all the water molecules about the three crystallographic axes following Fowler's treatment<sup>17</sup> of Rochelle salt, but it seems possible in this case that the ones at 29°C and 35°C are due to initiation of rotation of the two water molecules which first come off to give the trihydrate and the one at 53.7°C to the next two occurring together. Since the effects observed here are small, much smaller than similar ones for ammonium chloride for example, the rotations seem to be associated with a particular axis rather than end for end or free rotation. A few runs at slightly higher pressures where thermal changes were not masked by the high rate of dehydration indicated the possibility of a change to free rotation at or just below the temperature of spontaneous decomposition. This point requires further investigation. Similar transitions were observed in a number of other hydrates as well as in the heavy water hydrates of copper sulphate. At present it appears that in certain hydrates such as sodium sulphate decahydrate there is a complete breakdown and dehydration at the initiation of rotation giving a solution of the salt in its water of crystallization.

On heating the sample of copper sulphate above the 53.7°C transition at a pressure of 692 mm of mercury,<sup>22</sup> the rate of dehydration gradually increases up to 96.5°C where dehydration continues at a constant temperature until one molecule of water is lost leaving a residue of  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ . Then at 102°C the second molecule of water comes off until the composition is  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . At 113°C two more molecules of

<sup>23</sup> Abraham and Lucasse, *J. Phys. Chem.* **37**, 521 (1933).

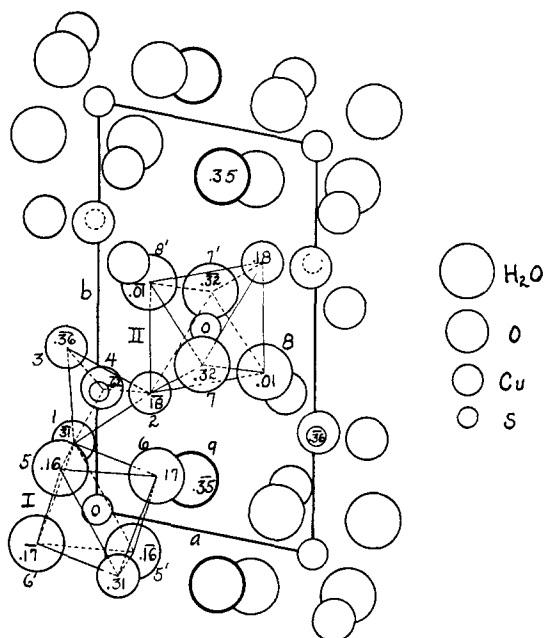


FIG. 3. Projection of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  structure on a plane normal to the  $c$  axis. Examples of the coordination octahedra around the copper atoms, and the  $\text{SO}_4$  tetrahedra are shown. Noncoordinated water molecules are drawn heavier. The numbers outside the circles correspond with the numbering of the various atoms by Beevers and Lipson. The numbers inside the circles are the  $z$  parameters.

water come off together at a constant temperature. In these experiments the fifth one was not lost at a definite temperature but only gradually with increased temperature. The heat change in these processes corresponds roughly to the heat of efflorescence, that is, the heat of hydration plus the heat of vaporization whereas the heat change in the case of those hydrates melting in their water of crystallization corresponds roughly to the heat of hydration. When a sample was run at a pressure of 5 cm of mercury, the copper sulphate dehydrated at a constant temperature of  $55^\circ\text{C}$  without any indication of a stepwise dehydration.

The results definitely indicate the existence of a tetrahydrate of copper sulphate and they have been reproduced as many as twenty times. This finding is difficult to interpret in view of the large amount of data on the vapor pressure of copper sulphate showing the existence of only the 5, 3, and 1 hydrates even up to fairly high temperatures.<sup>24</sup> A possible explanation lies in the assumption that the vapor pressure curve

<sup>24</sup> Carpenter and Jette, J. Am. Chem. Soc. **45**, 578 (1923).

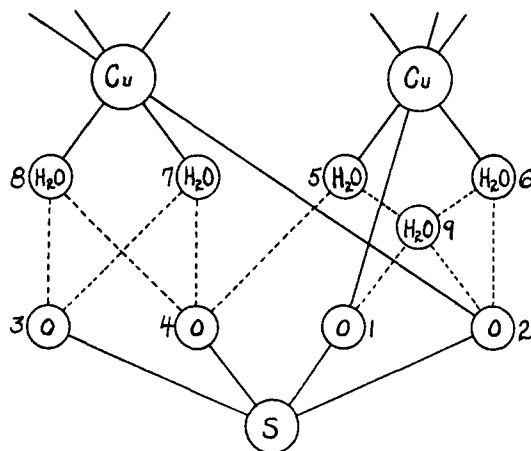


Fig. 4. Schematic diagram of the arrangement of bonds in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Hydrogen bonds are represented by dashed lines, other bonds by solid lines. The  $\text{SO}_4$  oxygens do not all belong to the same  $\text{SO}_4$  group.

of the pair  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 4\text{H}_2\text{O}$  crosses the vapor pressure curve of  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  at the higher temperatures. The vapor pressure of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  pair would then be higher at lower temperatures where most of the measurements have been made. It is also not unreasonable in view of the structure relations of copper sulphate that at lower temperatures the vapor pressure of the pair  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 4\text{H}_2\text{O}$  may be very nearly the same as the pair  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O} - \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , the difference becoming significantly greater only at higher temperatures. We can say, however, that at  $97^\circ\text{C}$  and a pressure of 692 mm of mercury,<sup>22</sup> the vapor pressure of the pair  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \text{CuSO}_4 \cdot 4\text{H}_2\text{O}$  is higher and that the tetrahydrate does exist, though possibly unstable. The definiteness of the temperature of dehydration and the analyses show that the observed curves are not due to any type of mixture of the five and three hydrate but to a definite compound.

#### CRYSTAL STRUCTURE OF $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ AND ITS DEHYDRATION

Beevers and Lipson<sup>19</sup> have recently made a rather complete determination of the crystal structure of copper sulphate pentahydrate. The crystal is triclinic and contains two molecules to the unit cell. The copper atoms lie on centers of symmetry at (000) and  $(\frac{1}{2}, \frac{1}{2}, 0)$  and the other atoms are in the general positions  $\pm(xyz)$  of the space

group  $C_4$ <sup>1</sup> with the parameters of the sulphur atoms being (0.01, 0.29, and 0.64). Each copper atom is surrounded by a slightly distorted octahedron consisting of four water molecules in an approximate plane and two oxygens from the sulphate groups. The odd water molecule touches two oxygens of different sulphate groups and two waters of a copper octahedron. It is apparently bound very firmly with a tetrahedral arrangement of bonds while the other waters have only a coplanar system of three bonds. A projection of the atomic arrangement in the unit cell, and a schematic diagram of the bond structure are shown in Figs. 3 and 4.

Beevers and Lipson have attempted to explain the dehydration of copper sulphate pentahydrate to the trihydrate by assuming that the water molecules first break up around the copper at (000) due to the greater instability of the distorted coplanar arrangement of bonds, and then around the copper at  $(\frac{1}{2}\frac{1}{2}0)$  giving the monohydrate. In the light of the results of this paper their explanation is hardly complete. In fact their structure determination seems to be in even better agreement with our results and conclusions.

Dehydration will occur when the thermal agitation of the water molecules becomes great enough to break the binding forces holding them in the lattice. This thermal agitation will be mostly distributed between vibrational and rotational motion. The increase in rotational motion with temperature contributes to the weakening of the binding forces. The strength of these bonds will depend upon their nature, the interatomic distances, and the amount of bond distortion in their formation. The four water molecules in the coordination octahedra are bonded to the copper atom by covalent square bonds.<sup>25</sup> Harker<sup>26</sup> has shown the square covalent radius of copper to be 1.32Å. The covalent Cu—O distance should then be 1.98Å. In Table I the interatomic distances (Cu—5), (Cu—6), and (Cu—8) are seen to be in excellent agreement with this value. The other Cu—O distance (Cu—7) is of the same type, its appreciably greater value indicating a weaker bond than the other three cases. The bonds from

the copper atom to the sulphate oxygens in the octahedra are electrostatic in type. The water molecules of the coordination octahedra, as well as the fifth water molecule, probably form hydrogen bonds with oxygen atoms of the sulphate groups, the oxygen atoms of the octahedra, and the oxygen of the fifth water molecule (Fig. 4). No water molecule, however, forms a hydrogen bond with the oxygen atoms of its own octahedron. The hydrogen bond is an electrostatic or ionic type of bond,<sup>27</sup> and in the case of such bonds involving water molecules the hydrogen is much closer to the one oxygen than the other. Pauling<sup>28</sup> has shown that in ice these distances are 0.95Å and 1.81Å, respectively. The former is the normal electron-pair bond distance while the longer distance constitutes the ionic or electrostatic part of the hydrogen bond. Such bonds have been reported in the following hydrates,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ <sup>29</sup> and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .<sup>30</sup>

The strength of the hydrogen bond will depend, as in the case of any ionic bond, on the interatomic distance, becoming weaker as the bond distance becomes longer. It will also depend on the positions of the oxygen atoms involved, being more stable when the  $\text{O}—\text{H}:\ddot{\text{O}}:\text{H}—\text{O}$  angle approximates  $105^\circ$ , the angle found in the gaseous water molecule, and less stable as this angle suffers greater and greater distortion.

By means of the complicated trigonometrical formulas for distances within a triclinic cell, the interatomic distances listed in Table I have been calculated from the parameters given by Beevers and Lipson.<sup>19</sup>

The transitions observed at  $96.5^\circ\text{C}$  and  $102^\circ\text{C}$  correspond with dehydration to the tetrahydrate

TABLE I. *Interatomic Distances in the Unit Cell of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .*

Octahedron No. I (Octahedron about Cu at 000)	(Cu—1)* = 2.32Å (Cu—5) = 1.97 (Cu—6) = 1.97	(6—1) = 3.18Å (5—1) = 2.92 (6'—1) = 2.86	(5'—1) = 3.18Å (6—5) = 2.75 (6'—5) = 2.85
Octahedron No. II (Octahedron about Cu at $\frac{1}{2}\frac{1}{2}0$ )	(Cu—7) = 2.08 (Cu—8) = 1.95 (Cu—2) = 2.44	(8—2) = 3.06 (8—2') = 3.19 (7—2) = 3.12	(7—2') = 3.25 (8—7) = 2.85 (8—7') = 2.80
Distances between oxygens of water molecules and sulphate groups	(8—3) = 2.58 (8—4) = 2.66 (7—4) = 2.58 (7—3) = 2.90	(5—4) = 2.71 (5'—9) = 2.71 (6—9) = 2.74	(6—2) = 2.78 (9—1) = 2.71 (9—2) = 2.96

\* These numbers correspond to the numbers given to the oxygen atoms in the cell by Beevers and Lipson.<sup>19</sup> see Fig. 3.

<sup>25</sup> We are indebted to Professor Linus Pauling for this suggestion.

<sup>26</sup> Harker, *Zeits. f. Krist.* **93**, 136 (1936).

<sup>27</sup> Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

<sup>28</sup> Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).

<sup>29</sup> Zeigler, *Zeits. f. Krist.* **89**, 456 (1934).

<sup>30</sup> Zachariasen, *Zeits. f. Krist.* **89**, 442 (1934).

and thence to the trihydrate. That they are associated with the break up of the II octahedron rather than the I octahedron as postulated by Beevers and Lipson is evident from the following. It has been noted in II that water molecules (7) and (7') are bonded to the copper by much weaker bonds than water molecules (8) and (8'), the interatomic distances being 2.08Å and 1.95Å, respectively. Furthermore the hydrogen bond between the water molecule (7) and sulphate oxygen atom (4) is very weak as evidenced by the interatomic distance of 2.90Å. The other hydrogen bond distances (7-3), (8-4), and (8-3) are somewhat stronger, the interatomic distances being 2.58Å, 2.66Å, and 2.58Å, respectively. In fact from a consideration of the bond strengths as based on the interatomic distances throughout the crystal it is seen that water molecules (7) and (7') are the most loosely bound water molecules in the cell. Bond distortion likewise further contributes to the weakness of binding of these molecules. Beevers and Lipson have found the angle between oxygen atoms (3-7-4) to be 122° while that between oxygen atoms (3-8-4) is 108°. Hence water molecules (7) and (7') would be expected to start rotating at lower temperature than any of the rest of the water molecules in the cell. It seems possible, therefore, to interpret the small transition at 29°C as the point at which they start rotating. Once two of the water molecules of the II octahedron are set to rotating the other two would be expected to do likewise soon, as a result of the disturbed equilibrium among the binding forces. The transition at 35°C is, thus, expected and is interpreted as the point where water molecules (8) and (8') start rotating. This is in line with the dehydration to the trihydrate with the loss of molecules (8) and (8') following that of (7) and (7') at 96.5°C very closely, namely at 102°C provided the loss of the first two molecules does not materially affect the structure so as to change the binding of the next two in the unit cell.

Assuming that the breaking up of the first octahedron (II) to give the trihydrate does not materially affect the binding forces of the water molecules in the next octahedron (I), the transition at 53.7°C may be associated with the dehydration of the trihydrate at 115°C to give the monohydrate. This stage of the dehydration is,

we believe, associated with the break up of the I octahedron instead of the II octahedron as postulated by Beevers and Lipson. From interatomic distances (Table I) the bond strengths for the four water molecules (5), (5'), (6), and (6') are seen to be almost the same. They would therefore be expected to all start rotating at once and to all come off at once in dehydration. Bond distortion of the hydrogen bonds here contributes to the weakening of the bonds about equally for all four water molecules. The angles between oxygen atoms (9'-5-4) and (2-6-9) are 122° and 129° respectively. That this distortion does not result in the I octahedron breaking up first is probably to be attributed to the stabler bond arrangement due to the practically equal Cu-O distances for the water molecules in the I octahedron.

Concerning the fifth water molecule it is evident that its original tetrahedral bonding arrangement should be quite stable, and that it would hardly be expected to start rotating until after the water molecules of the I octahedron have done so. From its dehydration behavior one would be led to believe that possibly after the break up of the I octahedron it becomes more firmly bound to the sulphate groups or that it becomes bound into the lattice by new bonds. Data are lacking for any further consideration of it at this time.

The results of this paper showing the new stage in the dehydration of copper sulphate pentahydrate do not necessarily mean that any of the previous work has been in error. It may simply mean that the difference between  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  becomes significantly great only at higher pressures and at temperatures higher than those ordinarily used (about 50°C). This deserves further study.

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