

## High-energy Modification Hydrates of Copper(II) Sulphate: heats of solution and infrared spectrum

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### RINGKASAN

*Beberapa hidratan kuprum(II) sulfat bertenaga tinggi telah disediakan dan haba larutan bahan-bahan itu disukat. Haba ini didapati lebih besar daripada yang diperolehi sebelumnya. Satu mekanisme baru pengontangan dikemukakan dan disokongkan dengan kajian inframerah sampel yang mengandungi deuterium.*

### SUMMARY

*High-energy modification of lower hydrates of copper(II) sulphate have been prepared and their heats of solution measured. The values obtained are higher than previously found for the salt. A new mechanism of dehydration has been proposed and supported by ir study of deuterated sample.*

### INTRODUCTION

The plot of heat of solution data as a function of percent water content in a salt would generally give a relation similar to that shown in *Fig. 1* for the hydrates of copper(II) sulphate. In the figure, the lines AB and BC represent the heats of solution for the crystalline hydrates which were prepared by heating the pentahydrate in an oven (Badri and Jamieson, 1979). The value increases linearly from I, for the pentahydrate, to B, for the monohydrate. From the monohydrate to the anhydrous salt, A, there is an increase in the slope of the curve to give the line BA.

The line IJK, which is to be reported here, represents the values for the noncrystalline high-energy modification hydrates which were prepared by dehydrating the pentahydrate under vacuum. This line is parallel to the line AB and passes through I, the heat of solution of the starting material. To facilitate discussion, we propose this line be called the “maximum line” because it may not always be obtained experimentally (Badri and Jamieson, 1979; Jamieson and Frost, 1956) and because there are cases where intermediate lines have also been found together with this “maximum line” (Jamieson *et al.* 1965). In the case of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , only the intermediate line FGH was obtained

previously. This line intercepts the heat of solution line BC at F, the trihydrate composition (Badri and Jamieson, 1979).

It was suggested that under vacuum  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  would first form the crystalline trihydrate before proceeding to form the corresponding high-energy modification monohydrate. Even at sufficiently low pressures, and having desiccants such as barium oxide and carbon together with a liquid nitrogen cold trap, a maximum high-energy modification product with a heat of solution falling on the “maximum line” was not obtainable. Invariably all the vacuum dehydration products of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  under such conditions have heats of solution falling on a line with a lower slope. The reason for this seems to be that these products are mixtures of the starting material, the pentahydrate, and the high-energy modification monohydrate which originates from the crystalline trihydrate,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , with its heat of solution represented by the point G in *Fig. 1*.

Several investigations have been reported on the kinetics of dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and other salts. It is well known that the ambient pressure can influence the rate of dehydration and the nature of the products. Perhaps the most

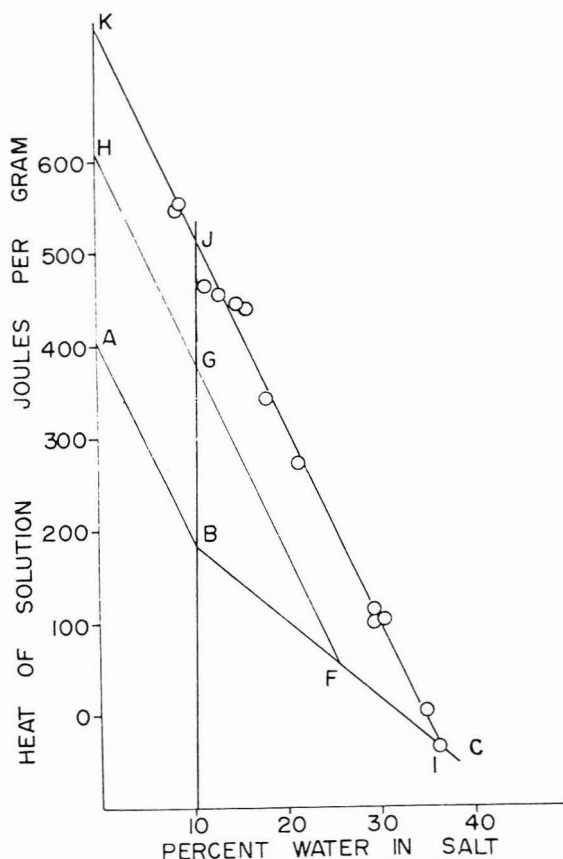


Fig. 1. Heats of solution for the hydrates of copper(II) sulphate.

pertinent are the experiments reported by Topley and Smith (1935) and Volmer and Seydel (1937) where the dependence of rate of dehydration on the pressure was shown to have a minimum. According to them, dehydration of a salt at a pressure greater than the minimum for the salt would yield a crystalline product.

It has also been suggested that the initial pressure of dehydration is particularly important as a crystalline product may be formed prior to further dehydration to the corresponding high-energy modification lower hydrates (Jamieson and Frost, 1956). This is certainly true as dehydration may start long before the apparatus is completely evacuated. In addition to this, the vapour pressure due to the decomposing sample is quite high and this alone may cause the formation of a crystalline lower hydrate as the product.

In this paper, we report the method of preparing the maximum possible high-energy modification for the hydrates of copper(II) sulphate and to use the ir spectrum to support the mechanism suggested.

## EXPERIMENTAL

### Heat of Solution

About 0.2 g sample of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  of BDH analar grade was put in a pyrex glass boat. The boat was then cooled with some liquid nitrogen in a watch glass covered with a beaker to prevent too much condensation of water vapour on the boat. When the sample was sufficiently cooled, the boat was introduced into a large glass chamber and evacuated to a pressure of about  $1 \times 10^{-5}$  Torr. Evacuation was carried on for a few hours after which dried air was introduced and the product was weighed. The composition of the salt was determined by the loss in weight. The heat of solution was measured immediately in a calorimeter.

The calorimeter was made up of a 200 ml silvered Dewar flask filled with distilled water. The flask was inserted into a cut plastic bottle which was placed at the centre of a plastic bucket containing decanoic acid (m.p.  $31^\circ\text{C}$ ). The bucket was thermostated at  $31^\circ\text{C}$  in a water-bath. The flask was fitted with a cover accommodating a stirrer, a heater, a small glass tube for the variable junction of a copper-constantan thermocouple and a glass funnel for sample delivery. The reference junction of the thermocouple was placed in a glass encasement and dipped into the decanoic acid equilibrated at its melting point. The thermocouple leads were connected to a DC microvoltmeter, (TOA electronic Ltd., Model PM-16A), and a recorder.

The heat capacity of the calorimeter was determined by the change in the thermally induced *emf* of the thermocouple caused by a known amount of the electrical energy supplied by the heater. This was registered on the voltmeter, amplified and recorded by the recorder.

### Infrared Study

About 0.1 g of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \cdot 2\text{D}_2\text{O}$  previously prepared (M. Badri and Jamieson, 1979) was introduced into a glass tube. The tube was stoppered and then cooled in liquid nitrogen for about 15 minutes. It was then connected to a vacuum line through a stopcock. The pressure was kept low, at about  $1 \times 10^{-4}$  Torr, by cooling the sample with ice. After about six hours the temperature was raised to that of the room ( $30^\circ\text{C}$ ) and dehydration was continued further for another 30 hrs at about  $1 \times 10^{-6}$  Torr. The ir spectrum was obtained from a Nujol mull of the product on a Beckman Acculab 7 ir spectrophotometer.

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## RESULTS

The heat capacity of the calorimeter was tested for its consistency by measuring the recorder deflections due to various amounts of energy input. The average value obtained was 39.6 J/in for ten different experiments with a deviation of about  $\pm 0.6$  J.

The heats of solution for the high-energy modification hydrates of copper(II) sulphate are listed in Table 1 and plotted as a function of percent water content in Fig. 1. The values were corrected for the dilution effect (Lange *et al.* 1933). They are shown by the circles which seem to fall on a straight line IJK in Fig. 1. By using the method of least squares, the equation for the line IJK was found to be

$$y_{IK} = -21.25x + 740.6 \pm 3$$

where  $y$  is the heat of solution and  $x$  is percent water in salt.

TABLE 1  
Heat of solution for high-energy modification hydrates of copper(II) sulphate.

% water in salt	heats of solution joules/gram
36.08	- 34.77
35.10	4.477
30.75	101.1
29.31	114.6
29.24	100.0
21.37	272.9
18.07	342.7
16.02	443.5
15.29	447.7
14.97	418.0
13.18	457.3
11.55	464.4
8.96	556.5
8.46	548.5

In Fig. 2, the ir spectrum of a vacuum dehydrated product is shown. The sample contains about 9.8% H<sub>2</sub>O and D<sub>2</sub>O, which is less than that of the monohydrate composition. The spectrum shows both the absorptions at 3300 cm<sup>-1</sup> and 2400 cm<sup>-1</sup> due to O - H and O - D stretching frequencies respectively. For clarity, the absorption band due to Nujol at about 3000 cm<sup>-1</sup> has been omitted.

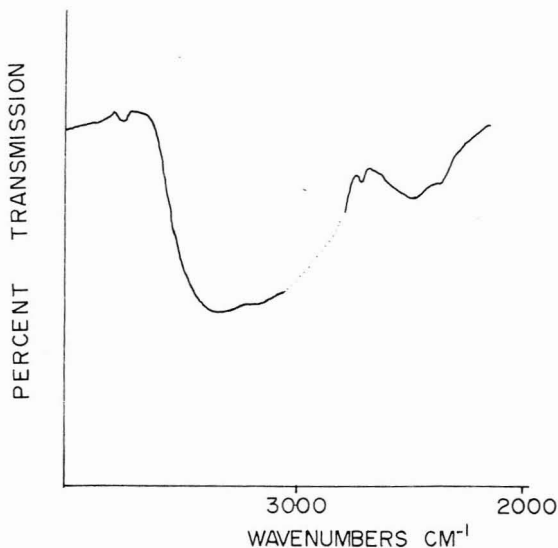


Fig. 2. Infrared spectrum for high-energy modification  $CuSO_4 \cdot xH_2O \cdot yD_2O$  where  $x + y < 1$

## DISCUSSION

The result clearly shows that it is possible to obtain the maximum heat of solution line for the high-energy modification hydrates if the initial dehydration pressure were kept very low. This could be achieved by reducing the temperature of the sample which in turn would reduce the rate of evolution of water vapour. It is in agreement with the suggestion of earlier workers that high water vapour pressures would facilitate crystallization of the products (Topley and Smith, 1935 and Volmer and Seydel, 1937). Such crystallization would undoubtedly result in the lowering of the heat of solution of a sample.

The occurrence of the intermediate heat of solution lines in some systems can now be explained. For example, in the case of cobalt(II) sulphate, this intermediate line seems to originate from the trihydrate (Jamieson *et al.* 1965) whereas in the case of zinc(II) sulphate there are two intermediate lines: one is from the trihydrate and the other is from the hexahydrate (Jamieson and Frost, 1965). However, contrary to the case of copper(II) sulphate, in both cases the maximum heat of solution line for the high-energy modification hydrates were obtained when various powerful desiccants were used.

Thus it is possible to assume that in those experiments the initial dehydrating pressures were high due to the rapid evolution of water vapour from the salts. The first stage of dehydration under such conditions would lead to the formation

of crystalline lower hydrates with their heats of solution falling on a line such as BC in Fig. 1. The manner in which the second dehydrating stage would proceed would depend on the salt concerned. In the case of copper(II) sulphate, the ambient pressure was low enough to cause the crystalline trihydrate formed to be further dehydrated instantly to the corresponding high-energy modification lower hydrate even though some parts of the sample were still of pentahydrate composition. Thus the final product would be a mixture of this high-energy form and the original pentahydrate. The heat of solution for such a mixture would then fall on a line joining the two individual values (Donnan and Hope, 1909). A truly intermediate line such as FGH in Fig. 1 could only be obtained by using the trihydrate as the starting material (Badri and Jamieson, 1979).

In the case of zinc(II) sulphate it seems that a slightly different mechanism is operating. The first stage of dehydration resulted in the complete formation of the crystalline hexahydrate (or the trihydrate). Only when all the heptahydrate was thus decomposed would the second stage proceed to the corresponding high-energy modification lower hydrate. The product is then a mixture of this high-energy lower hydrate and the crystalline hexahydrate and not the starting material, the heptahydrate. Thus the heat of solution of the sample would fall on an intermediate line originating from the hexahydrate. The purpose of having the desiccants in the system is to speed up the removal of water vapour. Consequently the initial dehydrating pressure would be low and this would facilitate the formation of the non-crystalline high-energy products directly from the starting material. In other cases, for example, the chlorides (Jamieson and Frost, 1956), desiccant alone seems to be insufficient to maintain a low initial pressure. Therefore in this case perhaps the maximum line could be obtained by applying the present technique.

It may not always be necessary that vacuum dehydration be carried out only after the samples were first cooled, particularly when small samples are used such as in the thermogravimetric technique. Here a sample weight of about 20 mg is typical. A good vacuum pump may be able to attain a very low pressure right from the start. Thus very little of the intermediate high-energy form would be formed.

However, in the experiments where samples of as much as 0.5 g were used for the measurement of some thermodynamic properties (Frost *et al.*

1951), the amount of water vapour evolved might have been a little bit excessive for fast evacuation. Thus the product might have been crystalline, or at most, might have assumed one of the several possible intermediate high-energy forms. As a result, its heat of solution would be lower than the maximum possible. This may be a reasonable explanation for such a low excess-energy content of vacuum dehydrated product of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  over that of the crystalline material (Jamieson and Frost, 1956).

The mechanism of dehydration under the present condition differs from the one described earlier (Badri and Jamieson, 1979). This is clearly shown by the spectrum of the deuterated salt,  $\text{CuSO}_4 \cdot x\text{H}_2\text{O} \cdot y\text{D}_2\text{O}$  with  $(x + y) < 1$ , Fig. 2. The presence of  $\text{D}_2\text{O}$  clearly indicates that vacuum dehydration of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \cdot 2\text{D}_2\text{O}$  does not completely remove what is supposed to be the less strongly bonded  $\text{D}_2\text{O}$ . Instead it shows that the removal of  $\text{D}_2\text{O}$ ,  $\text{H}_2\text{O}$  and anionic  $\text{H}_2\text{O}$  in the salt occur simultaneously and nonselectively. This is not impossible since at such a low pressure the driving force might have been large enough to overcome the slightly stronger bonds holding the anionic water in the lattice. This means that the remaining water molecules in the product are occupying different possible positions around the metal ions as well as on the sulphate ions. In this manner, the hydrated  $\text{CuSO}_4$  entities in the lattice are dissimilar and show different molecular structures. Thus there is no repetitive molecular or ionic pattern throughout the solid. Rearrangement of these ions to form a crystalline material is rendered impossible because they do not have a common feature in their structure even though they might have a similar composition. High water vapour pressure and heat would increase their mobility and the probability of rearrangement of the bonds so that the different entities are now able to have a more stable common structure to turn into and thus form a crystalline material.

## REFERENCES

- BADRI, M. and JAMIESON, J.W.S. (1979): Thermochemical measurement of the ligand field splitting energies for hexaaquocopper(II) and hexaamminecopper(II) ions. *Can. J. Chem.* 57, 1926-1931.
- JAMIESON, J.W.S. and FROST, G.B. (1956): The heats of crystallization of vacuum-dehydrated  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . *Can. J. Chem.* 34, 583.
- JAMIESON, J.W.S., LA MONTAGNE, R.A., PATERN, B.S. and BROWN, G.R. (1965): High-energy modification of the hydrates of zinc sulphate. *Can. J. Chem.* 43, 3129-3132.

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- TOPLEY, B. and SMITH, M.L. (1953): Kinetics of salt-hydrate dissociations:  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$ . *J. Chem. Soc.* 321.
- VOLMER, M. and SEYDEL, G. (1937): The velocity of dehydration of manganese oxalate dihydrate. *Z. physik Chem.* A179, 153-71.
- LANGE, E., MONHEIM, J. and ROBINSON, A.L. (1933): Heats of dilution of aqueous solutions of zinc, cadmium and copper sulphate and sulfuric acid at 25°C. *J. Amer. Chem. Soc.* 55, 4732.
- JAMIESON, J.W.S., BROWN, G.R., GRUENER, D.W., PEILUCK, R. and LA MONTAGNE, R.A. (1965): Possible calorimetric method for measurement of the ligand field splitting energies for the hexaaquocations of some transition elements. *Can. J. Chem.* 43, 2148-2156.
- DONNAN, F.G. and HOPE, G.D. (1909): Calorimetric Analysis of hydrated salts. *Trans. Faraday Soc.* 5, 244-50.
- FROST, G.B., MOON, K.A. and TOMPKINS, E.H. (1951): Amorphous intermediate products in the dehydration of certain hydrated salts. *Can. J. Chem.* 29, 604-32.

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