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Remarks on the Crystallization and Dehydration of Copper Sulfate Pentahydrate

K. HEINZINGER and B. MAIWALD
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz, Germany

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Isotope effects have been used in studying crystallization and dehydration processes in hydrated crystals.[1-3] In drawing conclusions it has to be taken into consideration that there may exist different kinds of water molecules distinguished by their binding in the crystal. In copper sulfate pentahydrate there occur two kinds of bonding as shown by the neutron diffraction study of Bacon and Curry.[4] Four water molecules are bonded as ligands by a metal-oxygen bond and two hydrogen bonds and one water molecule by four hydrogen bonds. This grouping of the water molecules into two main classes is a general feature of hydrated crystals (see *e. g.* Hamilton and Ibers[5]). Another property of relevance for this discussion is, that the unit cell consists of two molecules $CuSO_4 \cdot 5H_2O$. To each of the copper ions four water molecules are coordinated. They form together with two sulfate oxygens two octahedra, slightly different in geometry.

The available hydrogen and oxygen isotope fractionation factors between the different kinds of water in the crystal, and between crystal water and the saturated solution which are relevant in respect to crystallization and dehydration processes are listed in Table 1. The reported oxygen isotope fractionation factors are still preliminary; exact numbers cannot be given yet but the direction of the enrichment alone is significant for this discussion.

Crystallization

In studying the crystallization process with the help of isotope effects, it would be an unjustified simplification to consider only the overall fractionation factor between saturated solution and total crystal water, α_{S-G}. In the case of the hydrogen isotopes, the two kinds of water in $CuSO_4 \cdot 5H_2O$ show different preferences for the isotopes.[3] This follows from the fact that the D/H ratios of four water molecules are equal in the limits of error while the D/H ratio of the fifth water molecule is bigger by 5.7%.

It has been shown that the enrichment of deuterium in the fifth molecule is not a result of a Rayleigh dis-

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[1] H. Tanaka and H. Negita, This Bulletin, **43**, 3079 (1970).
[2] H. Oki, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 3263 (1970).
[3] K. Heinzinger, *Z. Naturforsch.*, **24a**, 1502 (1969).
[4] G. E. Bacon and N. A. Curry, *Proc. Roy. Soc.* (London), **A266**, 95 (1962).
[5] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin Inc., New York (1968).

TABLE 1. HYDROGEN AND OXYGEN ISOTOPE FRACTIONATION FACTORS BETWEEN DIFFERENT KINDS OF WATER MOLECULES IN COPPER SULFATE PENTAHYDRATE AND BETWEEN CRYSTAL WATER AND THE SATURATED SOLUTION

α_{x-y}	α_{K_1-G}	α_{K_2-G}	α_{L-G}	α_{S-G}	Ref.
$(D/H)_x/(D/H)_y$	—	—	—	1.022	6
	0.988	0.988	1.045	1.023	3
$(T/H)_x/(T/H)_y$	—	—	—	1.044	1
$(^{18}O/^{16}O)_x/(^{18}O/^{16}O)_y$	α_{K_1-G} $>$	α_{K_2-G}	—	<1	7

K_1 refers to the first two moles of water per mol of $CuSO_4 \cdot 5H_2O$ liberated on dehydration, K_2 to the third and fourth and L to the fifth mol. G means total crystal water and S stands for saturated solution.

tillation. Therefore, the fractionation can only be caused by a difference in bonding. Then it can be concluded from the crystal structure together with α_{S-G} that in the water coordinated with the copper ion the light isotope is enriched, in the fifth water molecule bonded by four hydrogen bonds, the heavy isotope is enriched compared with the saturated solution, as can be seen from Table 1:

$$\alpha_{K_1-S} = \frac{\alpha_{K_1-G}}{\alpha_{S-G}} < 1, \quad \alpha_{L-S} = \frac{\alpha_{L-G}}{\alpha_{S-G}} > 1$$

This difference shows that the fractionation of the hydrogen isotopes is not a consequence of a diffusion isotope effect during crystallization, as has been suggested by Tanaka and Negita.1) This conclusion is supported by the result of the oxygen isotope effect measurement: $\alpha_{S-G} < 1$; for the overall enrichment of ^{18}O in the crystal water cannot be explained by the diffusion of the water molecules.

Therefore, it has to be concluded that during crystallization either the water on the surface of the crystal is in isotopic equilibrium with the water in the solution or that four water molecules are carried into the crystal with the cation and the fifth is taken from the bulk water. Both possibilities are reasonable, as it has been shown that in the solution a remarkable isotope fractionation between hydration water and bulk water exists. In the solution the hydration water of the cations is by a few percent enriched in the light hydrogen isotope and in ^{18}O compared with the bulk water (see *e.g.* Heinzinger and Weston,8) and Taube9)).

The similarity of the fractionation factors between hydration water and bulk water in the solution to those between the two kinds of water in $CuSO_4 \cdot 5H_2O$ can be understood by considering that the bonding of the hydration water in the solution is similar to the bonding of the four water molecules to the copper ion in the crystal, while the bonding of the water molecules in the bulk water of the solution is similar to the bonding of the fifth water molecule in the crystal. The vibrational spectra of concentrated solutions and hydrated crystals are similar (see *e.g.* Leung and Safford10)).

Dehydration

From the hydrogen isotope effect measurements it has been concluded that the fifth water molecule bonded in the pentahydrate by four hydrogen bonds becomes quantitatively the water molecule of the monohydrate at dehydration temperatures below 50°C.3) This conclusion is independent of a possible change of structure, because at these low temperatures the water molecules are not mixed up and the isotope ratios of the different kinds of water in the crystal are not changed during dehydration.

As there exists a slight difference in geometry between the two octahedra in the unit cell, it is not unreasonable to expect that at room temperature first one octahedron breaks up and looses its four waters and then the other, in agreement with the existence of a stable trihydrate. While the hydrogen isotope fractionation data do not allow a conclusion, because $\alpha_{K_1-G} = \alpha_{K_2-G}$ (Table 1), the oxygen isotope measurements support this assumption, for $\alpha_{K_1-G} > \alpha_{K_2-G}$. The enrichment of ^{18}O in the first water fraction relative to the second is necessarily a consequence of differences in the binding of the water molecules in the crystal. An isotope shift during dehydration could only be caused by some kind of a Rayleigh distillation, which would mean that the first fraction would have to be enriched in ^{16}O.

While it can be concluded from the oxygen isotope measurements that one octahedron breaks up after the other, the information from these measurements is still insufficient to decide which one of the two octahedra breaks up first. Analysis of vibrational spectra would be helpful for this decision.

Concluding this short discussion, it should be mentioned that the possibility to attribute the water molecules, collected on stepwise dehydration, to certain bonding situations in the crystal does not provide, by reversing the process, a possibility to produce a $CuSO_4 \cdot 5H_2O$ crystal with the water molecules of a given isotopic composition at given positions. The following simple experiment has been performed: $CuSO_4 \cdot 5H_2O$ was dehydrated to the monohydrate and then exposed to D_2O vapor. After the pentahydrate had formed again (checked by the amount of water taken up), dehydration in vacuum at room temperature was started. After 80% of the water was again collected, the isotopic composition was determined and it was found that deuterium and hydrogen were mixed up. This implies that the water of the monohydrate

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6) R. M. Barrer and A. F. Denny, *J. Chem. Soc.*, **1964**, 4677; M. Johansson and K. E. Holmberg, *Acta Chem. Scand.*, **23**, 765 (1969).

7) B. Maiwald and K. Heinzinger, to be published

8) K. Heinzinger and R. E. Weston, Jr., *J. Phys. Chem.*, **68**, 744 (1964).

9) H. Taube, *ibid.*, **58**, 523 (1954).

10) P. S. Leung and G. J. Safford, *ibid.*, **74**, 3696 (1970).

does not become quantitatively the fifth water molecule of the pentahydrate because of rearrangement during hydration.

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