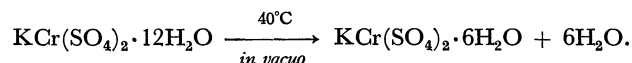# Fractionation of Tritiated Water in Potassium Chromium Sulfate Dodecahydrate

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A considerable dilution of tritiated water in the water of crystallization was observed in the crystal-growth process of $KCr(SO_4)_2 \cdot 12H_2O$ from a slightly supersaturated aqueous solution. This was explained in terms of an ionic process in aqueous solution and a surface-diffusion mechanism of crystal growth. It was also found that the tritium content in the hexahydrate was appreciably smaller than that in the liberated water during the course of reaction;

$$KCr(SO_4)_2 \cdot 12H_2O \xrightarrow[\text{in vacuo}]{40^{\circ}C} KCr(SO_4)_2 \cdot 6H_2O + 6H_2O.$$

It seems that the stepwise dehydration supports the dehydration mechanism proposed by Garner.

It has been reported that an examination of the fractionation of tritiated water in the crystallization of some hydrated salts from an aqueous solution helps clarifying the crystal-growth mechanism and/or the behavior of water during the course of crystallization.[1] We might expect that examination of the possible fractionation of tritiated water during the course of stepwise dehydration also leads to understanding of the dehydration mechanism. Though various studies have been carried out on the dehydration processes, not much has been done to clarify its mechanism. So far such an elucidation does not seem to have been made in the light of the fractionation of tritiated water.

Recently, the hydration of ions in an aqueous solution has been studied extensively by various methods, the life-time of a hydrated cation being determined.[2] Eigen stated from the relaxation technique that alkali metal ions are very weakly hydrated in aqueous solutions, i.e., the life-time of the hydrated cations is ca. 10^{-9} sec.[3]

On the contrary, it is well-known that the water of hydration of a chromium ion is very rigidly held in the sphere, i.e., the life-time of the Cr^{3+} ion is ca. 10^5—10^6 sec.[4]

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1) H. Tanaka, This Bulletin, **45**, 339 (1972).

2) F. Basalo and R. Johnson, "Coordination Chemistry," W. A. Benjamin, Inc., New York, N. Y. (1964), p. 154.
3) M. Eigen, Pure Appl. Chem., **6**, 97 (1963).
4) J. P. Hunt and R. A. Plane, J. Amer. Chem. Soc., **76**, 5960 (1954).

The crystal growth of a few salts from very slightly supersaturated solutions has been studied extensively by Bennema.[5] He concluded from his study that the crystal growth may occur by means of the surface-diffusion mechanism originally proposed by Burton *et al.*

Hepburn and Phillips reported that the water coordinated to the univalent cation is primarily dissociated *in vacuo* in the case of alum:[6]

$$[M^+(OH_2)_6][M^{3+}(OH_2)_6](SO_4)_2 \longrightarrow$$

$$M^+[M^{3+}(OH_2)_6](SO_4)_2 + 6H_2O$$
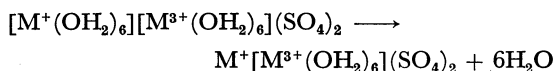
On the contrary, Garner suggested that the exchange of the water coordinated to each cation in alum occurs during the course of stepwise dehydration, the excess water being dissociated to give the hexahydrate.[7] A study from a new view point is desirable for the elucidation of the mechanisms of the crystal growth and dehydration. It seems to be of interest to examine the possible fractionation of tritiated water in alum which would be caused by the crystal growth from a solution and stepwise dehydration.

For this purpose, potassium chromium sulfate dodecahydrate, $KCr(SO_4)_2 \cdot 12H_2O$, was chosen.

Experimental

Commercial potassium chromium sulfate dodecahydrate was purified by recrystallization. Twice-distilled water containing a trace amount of tritiated water (HTO) was used as a solvent. The single crystal of $KCr(SO_4)_2 \cdot 12H_2O$ was grown from a slightly supersaturated tritiated aqueous solution at 20.2°C by evaporating the solvent gradually.

Half of the water of crystallization was removed from the single crystal at 40°C *in vacuo*. Another half of the water was dehydrated completely by heating at 350°C. Water from the dodecahydrate was also recovered by heating at 350°C until no further dehydration was observed. The recovery of water is shown in Fig. 1.

The tritium contents were compared by analyzing the activity of tritium. Measurements were carried out with a liquid scintillation counter, a Packard Model 2002 Tri-Carb Scintillation Spectrometer. As a scintillant we used
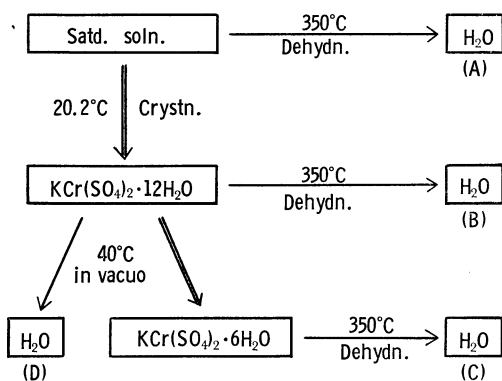

Fig. 1. The scheme for the recovery of water.

5) P. Bennema, Thesis, The Technical University of Delft (1965); P. Bennema, *J. Cryst. Growth*, **5**, 29 (1969).

6) J. R. I. Hepburn and R. F. Phillips, *J. Chem. Soc.*, **1952**, 2569.

7) W. E. Garner, "Chemistry of the Solid State," Butterworths, London (1955), p. 213.

a solution composed of toluene, ethylene glycol monomethyl ether, 2,5-diphenyloxazole (PPO) and 1,4-bis-2′-(5′-phenyl-oxazolyl) benzene (POPOP).

Results and Discussion

The separation factor S_1 of HTO for the crystal growth of a hydrated salt from a slightly supersaturated aqueous solution has been defined as $S_1 = N_s/N_l$, where N_s and N_l are the mole fractions of HTO in the solid and liquid phases, respectively.[8] On the contrary, the separation factor S_2 for the dehydration $KCr(SO_4)_2 \cdot 12H_2O \longrightarrow KCr(SO_4)_2 \cdot 6H_2O + 6H_2O$ can be defined as the ratio of the mole fraction of HTO in the hexahydrate to that in the dodecahydrate. The separation factor S_3 can thus be given by the ratio of HTO content in the primarily liberated water to that in the dodecahydrate.

TABLE 1. SEPARATION FACTOR OF HTO
IN $KCr(SO_4)_2 \cdot 12H_2O$

Comparison of watr	Ratio of cpm[a]	Separation factor
(B)/(A)	$(17469 \pm 170)/(18191 \pm 83)$	$S_1 = 0.960 \pm 0.007$
(C)/(B)	$(17222 \pm 71)/(17469 \pm 170)$	$S_2 = 0.986 \pm 0.007$
(D)/(B)	$(17895 \pm 173)/(17469 \pm 170)$	$S_3 = 1.024 \pm 0.009$

a) Mean of 5–6 measurements with a counter of 35% efficiency.

Table 1 shows the observed fractionation of tritiated water. (A), (B), (C), and (D) denote the kinds of water shown in Fig. 1. The average net counts per minute (cpm) for 0.1 g of water and the values of the separation factor which are equal to the ratios of cpm are given, each cpm being in proportion to the mole fraction of HTO.

We see from the S_1 value 0.960 that tritiated water is considerably diluted in the dodecahydrate during the course of crystallization from its aqueous solution. It is found from the S_2 value 0.986 that tritiated water is appreciably diluted in the hexahydrate during the course of stepwise dehydration; $KCr(SO_4)_2 \cdot 12H_2O$

$$\xrightarrow[\text{in vacuo}]{40°C} KCr(SO_4)_2 \cdot 6H_2O + 6H_2O.$$ The dilution in the hexahydrate can also be seen from the S_3 value 1.024.

Tritium Fractionation on the Crystal Growth of KCr(SO₄)₂· 12H₂O. It has been reported that the S_1 value is found to be nearly equal to unity if the crystal grows according to a volume-diffusion mechanism; there is a direct integration of the growth unit from the solution into the kink without any surface diffusion.[9] On the contrary, tritiated water may be diluted in the water of crystallization, if a surface-diffusion mechanism in which the growth unit diffuses over a wide range of the crystal surface before integrating into the kink, controls the crystal growth from a solution.[1]

It has been shown in the crystal growth of potassium aluminum sulfate dodecahydrate $KAl(SO_4)_2 \cdot 12H_2O$ that HTO can be diluted in the water of hydration of

8) H. Tanaka and H. Negita, This Bulletin, **43**, 3079 (1970).

9) H. Tanaka and H. Negita, *ibid.*, **44**, 2075 (1971).

the K^+ ion in the crystal and the fractionation may not actually take place for the hydration water of the Al^{3+} ion in the crystal.[1] The R_{HTO}/R_{H_2O} ratio has been obtained for the free water on the crystal growth of the hydrated salt *via* surface diffusion:

$$R_{HTO}/R_{H_2O} = (m_{H_2O}/m_{HTO})^{1/2} = 0.949, \qquad (1)$$

where R_{HTO}/R_{H_2O} is the ratio of the integration of HTO into the crystal to that of H_2O, and m_{H_2O}/m_{HTO} the mass ratio of H_2O to HTO.

Although the hydration number of an ion in an aqueous solution can not be defined in a strict sense, it may be conveniently taken as the number of water molecules directly coordinated to the central ion, for example, six for the Cr^{3+} ion.[10] The hydration water of the K^+ ion may, as is the case for $KAl(SO_4)_2 \cdot 12H_2O$, be assumed to become free to be integrated into the crystal from a solution, since the life-time of the hydrated cation is extremely short; *ca.* 10^{-9} sec.[3] This seems to be in line with the suggestion of Samoilov that the K^+ ion diffuses in an aqueous solution practically without any hydration water.[11]

It is well-known that the water is strongly bound to the Cr^{3+} ion as compared with the Al^{3+} ion, *i.e.*, the life-time of $Cr(OH_2)_6^{3+}$ and $Al(OH_2)_6^{3+}$ is 10^5—10^6 sec[4] and 1—10 sec,[12] respectively. Thus, the Cr^{3+} ion can be assumed to enter the crystal accompanying the hydration water, since such a behavior may be the case with Al^{3+} ion.[1] As for the sulfate ion, hydration may be negligibly weak in that the ion may be integrated into the crystal practically without accompanying hydration water as is the case for the K^+ ion.

Accordingly, it appears that half of the water in $KCr(SO_4)_2 \cdot 12H_2O$, *i.e.*, the water of crystallization coordinated to the K^+ ion, comes from the free water and another half from the hydration water of the Cr^{3+} ion in the solution. It can be assumed that HTO is diluted in $K(OH_2)_6^+$ of the dodecahydrate according to Eq. (1) and that no practical fractionation takes place in $Cr(OH_2)_6^{3+}$ of the crystal, if we neglect the possible slight enrichment of HTO in the hydration water of the Cr^{3+} ion in the solution.[13]

Although the calculated value of S_1 deviates a little from the observed one, the considerable dilution of HTO in the crystal is explained not by the volume-diffusion but surface-diffusion mechanism and the ionic process.

Validity of the Calculation of S *in Relation to the Data with HDO.*   Studies have been carried out on the fractionation of deuterated water (HDO) in the crystallization of hydrated salts from solutions and some important data have been given.[14-16] The data by Barrer and Denny[14] include the S value of HDO less than the lower limiting value of 0.973 which is obtained

if the present assumption for the calculation of S of HTO is applied to that of HDO.

Johansson and Holmberg[15] found that HDO is slightly enriched in some hydrated crystals. The enrichment of heavy water in the crystal can not be explained well by the present treatment, *i.e.*, the maximum S value may be estimated to be unity in the case of the volume-diffusion mechanism.[9]

The discrepancy may be due to the following factors: (1) The S value should depend on experimental conditions, especially on the crystallization rate and temperature. (2) Strictly speaking, the fractionation of heavy water in the hydration water is not always negligible in the aqueous solution. (3) The S value might also be influenced by the bond character of the water of crystallization in the crystal.

Factor (1) seems to be the most important at this stage since the well developed single crystal we obtained was grown from a very slightly supersaturated solution under strictly controlled conditions, where the theory of crystal growth can be applied.

Tritium Fractionation on the Dehydration of $KCr(SO_4)_2 \cdot$ $12H_2O$.   Studies have been carried out on the dehydration of hydrated salts *in vacuo*.[17] Numerous examples reveal that an interfacial mechanism is frequently operative during the course of dehydration. It is also assumed generally that water molecules dissociate from the surface of a hydrated crystal to cause a partially dehydrated structure which then leads to a partly amorphous state. A further rearrangement then occurs giving crystalline nuclei of a new phase.

Hepburn and Phillips suggested that (1) the water coordinated to the univalent ion is primarily dissociated *in vacuo* in the case of alum without any exchange of the water with the hydration water of the trivalent ion, and (2) the hexahydrated crystal is then formed in which the structure differs from that of the original dodecahydrate.[6]

It has been suggested that tritiated water is diluted in the hydration water of the K^+ ion in the crystal of the dodecahydrate during the course of crystallization from a solution. Thus, the S_2 and S_3 values can be estimated to be larger and smaller than unity, respectively, if the mechanism proposed by Hepburn and Phillips is the case in the dehydration process.

However, contrary to expectation, the S_2 and S_3 values were found to be 0.986 and 1.024, respectively, implying that the dehydration does not proceed by means of the above mechanism. Thus it can be expected that an alternative mechanism controls the stepwise dehydration of $KCr(SO_4)_2 \cdot 12H_2O$ *in vacuo*.

The dehydration process of $KCr(SO_4)_2 \cdot 12H_2O$ to $KCr(SO_4)_2 \cdot 6H_2O$ is assumed to be followed by three steps.[7] (1) Collapse of the lattice of the dodecahydrate to give an amorphous intermediate and gradual growth of the nuclei of the hexahydrate, (2) diffusion of the dissociated water through the product, and (3) evaporation of the water from the surface of the product. A diagram of the dehydration mechanism is given in Fig. 2. Such a dehydration process implies that the ex-

10) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **71**, 627 (1971).

11) O. Ya. Samoilov, "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions," Consultants Bureau Enterprises, Inc., New York (1965), Chap. 5.

12) D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, **90**, 608 (1968).

13) H. Taube, *J. Phys. Chem.*, **58**, 523 (1954).

14) R. M. Barrer and A. F. Denny, *J. Chem. Soc.*, **1964**, 4677.

15) M. Johansson and K. E. Holmberg, *Acta Chem. Scand.*, **23**, 765 (1969).

16) K. Heinzinger, *Z. Naturforsch.*, **A24**, 1502 (1969).

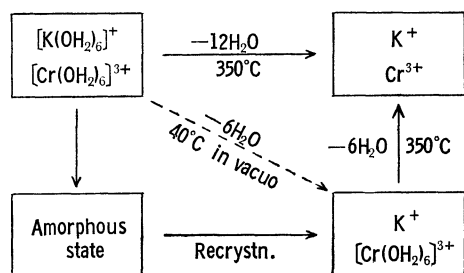17) For example; W. J. Dunning, *J. Mater. Sci. Res.*, **4**, 132 (1969).

Fig. 2. The mechanism of the stepwise dehydration of KCr-$(SO_4)_2 \cdot 12H_2O$. The dotted line refers to the mechanism by Hepburn and Phillips.

change of the hydration water of the Cr^{3+} ion with the other water molecules occurs during the course of dehydration. Such an exchange seems to be supported by the work of Okazaki et al.[18]

We believe that Garner's suggestion is appropriate and can be used to account qualitatively for the separa-

18) N. Okazaki, A. Okumura, and K. Nakagawa, This Bulletin, **34**, 983 (1961).

tion factors, S_2 and S_3. Under the present experimental conditions, the dodecahydrate seems to decompose to give an amorphous intermediate with the adsorbed water molecules on the surface as well as in the interior. The dilution of tritiated water in the hexahydrate may occur in the succeeding rearrangement, since the hydration water of the Cr^{3+} ion is interchangeable with that of the K^+ ion. That is, the hexahydrate may recrystallize from the amorphous state, when the dilution occurs in a similar manner to that in the crystallization of a hydrate from an aqueous solution by means of a surface-diffusion mechanism.

It can be concluded that the dehydration, KCr-$(SO_4)_2 \cdot 12H_2O \xrightarrow[in\ vacuo]{40°C} KCr(SO_4)_2 \cdot 6H_2O + 6H_2O$, proceeds by the mechanism of Garner and not by that of Hepburn and Phillips.