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The Temperature Dependence of the Fractionation of Tritiated Water in an Equilibrium between Crystalline Alum and Its Aqueous Solution

Haruhiko TANAKA*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-sendamachi, Hiroshima

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The temperature dependence of the fractionation of tritiated water (HTO) was examined during the crystal growth of alum from its tritiated aqueous solution. When the ratios of the mole fractions of HTO in the water of crystallization to that of the mother liquid, S, at various temperatures are compared, the following order is established:

$$S_{19.90} \approx S_{29.50} > S_{36.52} > S_{41.95} > S_{47.43} > S_{53.70} \approx S_{69.50},$$

where the suffixes represent the crystallization temperatures, and where $S_{19.90}=0.975$ and $S_{69.50}=0.949$. The concept of the hydration of ions developed recently was applied to the problem of the crystal growth from the solution. Two kinetic parameters, such as the relaxation time of the aluminum ion for entering the surface, τ_c, and that of the hydrated aluminum ion, $Al(OH_2)_6^{3+}$, for the exchange of the water with bulk water, τ_e, were taken into account to explain the fractionation. A surface-diffusion mechanism was suggested as essential in the crystal growth of alum from the solution. The activation free energy for the crystal growth from an unstirred solution was found to be 18.17 kcal/mol, a value which was in good agreement with the value given by Bennema.

Tritium has some advantages over deuterium for examining hydrogen isotope effects. However, the fractionation of tritium in a hydrated crystal in equilibrium with its aqueous solution had scarcely been studied before the results on several hydrated crystals were reported.[1,2] Moreover, the temperature dependence of the fractionation of heavy water has been examined neither by the use of deuterated water nor by that of tritiated water. In this connection, it seemed that it would be quite interesting to study the fractionation of tritium during the crystallization of an inorganic hydrate at various temperatures.

It has been pointed out in a previous report[2] that tritium-fractionation should be useful in the study of phase equilibria between hydrated crystals and their aqueous solutions. Such a study seems to have increasing significance in connection with the recent development of the ionic process in an aqueous solution, particularly with regard to the hydration of various ions. It has become possible to examine the mechanism of the crystal growth of inorganic hydrates from their aqueous solution, as well as the kinetics of the deposition of the hydration water of cations from the solution, in the light of tritium fractionation.

Recently, Fiat and Connick[3] have obtained the kinetic parameters of the hydrated aluminum ion in an aqueous solution by the use of the ^{17}O-NMR technique over a wide range of temperatures. Samoilov[4] has investigated the hydration of alkali metal ions in detail and found that the potassium ion diffuses in an aqueous solution without any hydration water. In addition, the crystal growth of alum from a very slightly supersaturated solution has been studied extensively by Bennema,[5,6] who measured the growth rate as a function of the relative supersaturation of the mother liquid. He concluded from his study that the crystal growth probably occurs by means of a surface-diffusion mechanism originally proposed by Burton *et al.*[7] As he pointed out himself, however, much study remains to be done before a sound theory of crystal growth from an aqueous solution can be worked out.

Potassium aluminum sulfate dodecahydrate, $KAl(SO_4)_2 \cdot 12H_2O$, has been chosen for the present study aiming at the elucidation of the mechanism of crystal growth from an aqueous solution. For this purpose, it seemed that it would be interesting to study the fractionation of tritiated water by slowly growing crystals from a tritiated aqueous solution at various temperatures. Another purpose of the present study is to discuss the behavior of water during the crystal growth from an aqueous solution, behavior which has not been clarified by any other study.

Experimental

Potassium aluminum sulfate dodecahydrate obtained from a commercial source was purified by recrystallization. The solvent was twice-distilled water which contained a trace of tritiated water (*ca.* 1.5×10^{-8} mol/l). The single crystals of the hydrated salt were obtained from a very slightly supersaturated solution at constant temperatures of 19.90°, 29.50°, 36.52°, 41.95°, 47.43°, 53.70°, and 69.50°C under unstirred conditions.[8] A seed crystal was obtained from the same solution as that used for the succeeding crystal growth. The form of the small seed crystal was nearly octahedral; the (111) face was well-developed in comparison

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* Present address: Shinonome Branch School, Faculty of Education, Hiroshima University, Shinonome, Hiroshima.

[1] H. Tanaka and H. Negita, This Bulletin, **43**, 3079 (1970).

[2] H. Tanaka and H. Negita, *ibid.*, **44**, 2075 (1971).

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

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

[5] P. Bennema, Thesis, The Technical University of Delft (1965).

[6] P. Bennema, *J. Cryst. Growth*, **5**, 29 (1969).

[7] W. K. Burton, N. Cabrera, and F. C. Frank, *Phil. Trans. Roy. Soc.*, **A243**, 299 (1951).

[8] This condition is necessary to determine the value of the activation free energy needed for the aluminum ion to integrate into the crystal surface, E_{sf}; this value will be discussed later.

with the other faces. The fluctuation of the temperature of the mother liquid was within ±0.02°C in a well-stirred thermostat. The rate of the evaporation of the solvent was so slow that only about 2 g of the well-developed (octahedral) single crystal of the salt was obtained in a week from a large amount of the mother liquid. The relative supersaturation of the mother liquid was kept below *ca.* 1.2×10^{-2} during each crystal growth.

Water from both the mother liquid and the single crystal was recovered by heating them in a stream of nitrogen gas until no further dehydration was observed. The tritium content in the water of crystallization was then compared with that in the corresponding mother liquid by an analysis of the activity of tritium. The activity was measured with a liquid scintillation counter (Packard Tri-Carb), using the scintillant described in a previous paper.[1]

Results and Discussion

The separation factor, S, for the equilibrium between solid and liquid phases can be given as follows in the case of a very low concentration of the relevant isotope (HTO in this case):

$$S = N_s/N_l,$$

where N_s and N_l are the mole fractions of HTO in the solid and liquid phases respectively. Table 1 gives the separation factor, S, together with the net counts per minute (cpm),[9] which are proportional to the amount of HTO, and the value of pH and the maximum relative supersaturation of the mother liquid during the crystal growth.

It may be seen that a considerable dilution of HTO occurs in the solid phase for the whole range of crystallization temperatures. The separation factors apparently decrease with an increase in the temperature in the 29.50°—53.70°C range, implying that more dilution of HTO in the hydrated crystal occurs at higher temperatures. On the other hand, no change in dilution can be seen within the limits of experimental error between 19.90° and 29.50°C or between 53.70° and 69.50°C.

Calculation of the Minimum Separation Factor, S. It has been reported in a previous paper[1] that HTO should be diluted in the crystal of inorganic hydrates during the growth from a solution, if free water behaves according to a surface-diffusion mechanism in which a growth unit essentially diffuses along the crystal surface before integrating into the kink.[7] On the contrary, the value of S has been calculated to be unity when the crystal growth follows a volume-diffusion mechanism; there is a direct integration from the solution into the kink without any surface diffusion.[5] It can thus be assumed here that free water should crystallize from the solution to give the water of crystallization in $KAl(SO_4)_2 \cdot 12H_2O$ by the surface-diffusion mechanism, since HTO was found to be diluted during the crystal growth of the salt.

Assuming an equilibrium between the free water in the solution and that on the crystal surface, the rate of the integration of the free water into the crystal, R, can be expressed as follows:[1]

$$R = \alpha C_0 \Omega N_0 (kT/2\pi m)^{1/2} (\sigma^2/\sigma_1) \tanh(\sigma_1/\sigma), \tag{2}$$

where

α=correction factor,
C_0=retarding factor,
Ω=volume of a growth unit,
N_0=equilibrium concentration of growth units per m*l* of the solution,
k=Boltzmann's constant,
T=absolute temperature,
m=mass of a growth unit,
σ=relative supersaturation, and
σ_1=parameter.

The R_{HTO}/R_{H_2O} ratio is thus obtained in the case of the crystal growth by the surface-diffusion mechanism, recognizing that all the factors other than m are independent of the hydrogen isotope:[1]

$$R_{HTO}/R_{H_2O} = (m_{H_2O}/m_{HTO})^{1/2} = 0.949, \tag{3}$$

where R_{HTO}/R_{H_2O} is the ratio of the integration of HTO to that of H_2O molecules into the crystal and where m_{H_2O}/m_{HTO} is the mass ratio of H_2O to HTO molecules. It follows from Eq. (3) that the minimum value of S (or the maximum dilution of HTO in the crystal) is equal to 0.949. This value was derived by assuming

TABLE 1. SEPARATION FACTOR, S, OF TRITIATED WATER, HTO, DURING THE CRYSTAL GROWTH OF ALUM FROM ITS AQUEOUS SOLUTION AT VARIOUS TEMPERATURES

Temp. (°C)	pH	σ_{max}[d]	Net cpm of HTO[a] Mother liq. (N_l)	Net cpm of HTO[a] Crystal (N_s)	S_{obs}
19.90±0.01	3.31	1.0×10^{-2}	27097±116[b]	26425±115[b]	0.975±0.004
29.50±0.02	3.20	1.2×10^{-2}	45678±210[c]	44477±55[c]	0.974±0.003
36.52±0.01	3.09	1.1×10^{-2}	70925±379[c]	68720±172[c]	0.969±0.004
41.95±0.01	3.05	9.0×10^{-3}	30128±119[b]	29000±143[b]	0.963±0.004
47.43±0.02	2.88	1.0×10^{-2}	67027±266[c]	64284±306[c]	0.959±0.005
53.70±0.01	2.70	1.0×10^{-2}	55500±273[c]	52495±234[c]	0.946±0.004
69.50±0.02	1.85	8.0×10^{-3}	32253±156[b]	30601±116[b]	0.949±0.004

a) cpm in each sample water of 0.1 g with mean square error.
b), c) Measured using counters of 35 and 45% efficiencies respectively.
d) degree of supersaturation.

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[9] Each cpm listed in Table 1 was obtained by averaging the activities per 0.1 g, which were measured 6—8 times for a given sample of water.

that the fractionation of the isotope results, if at all, only from the free water and, practically speaking, not from the hydration water of the cation.

Free Water in the Aqueous Solution. In the aqueous solution of alum, there are three hydrated ions: $K(OH_2)_p^+$, $Al(OH_2)_6^{3+}$, and $SO_4(H_2O)_q^{2-}$. The hydration number of the aluminum ion has been determined exactly,[10] while those of other ions are ambiguous at this stage. As will be seen, however, the result may be independent of the hydration numbers of K^+ and SO_4^{2-} ions, *i.e.*, p and q. It is improbable that the hydrated aluminum ion, $Al(OH_2)_6^{3+}$, is subject to dehydration in the solution as are the hydrated cations studied in a previous paper,[1] since $Al(OH_2)_6^{3+}$ is rather stable; the order of its lifetime was found to be 7.5 sec at room temperature.[3]

It can be assumed here that the apparent free water molecules may result from the hydration water when the relaxation time needed for $Al(OH_2)_6^{3+}$ to integrate into the crystal surface, τ_c, is longer than that needed for the hydrated ion to exchange its hydration water with bulk water, τ_e. This assumption may be explained by examining a given water molecule rather than the aluminum ion. That is, a given hydration water molecule of Al^{3+} is liberated during the integration into the crystal surface if $\tau_c > \tau_e$. The resulting hydration water of $Al(OH_2)_6^{3+}$ also exchanges with a free water molecule on the surface during the integration into the kink, since the sphere can reside on the surface over the interval of τ_c or a little longer.[6] The water molecules of $Al(OH_2)_6^{3+}$ which integrate into the kink from the surface are thus assumed to result from the originally free water on the surface. On the other hand, half of the hydration water may be taken statistically to come from free water molecules on the surface when τ_c is equal to τ_e.

The hydration of the sulfate ion is supposed to be generally negligible. As for the hydration of the potassium ion, a recent concept by Samoilov[4] may be properly referred to in the present case. According to him, the potassium ion diffuses in a solution without any accompanying hydration water. It follows from the preceding argument that the estimation of the fraction of the free water which plays an important role in the crystal growth can be deduced from the hydration of the aluminum ion.

τ_e of the Aluminum Ion. The relaxation time for the exchange of the hydration water with bulk water has been extensively studied by a number of methods. Although only the order of magnitude of the lifetime of the species, $Al(OH_2)_6^{3+}$, had previously been reported, the exact value has recently been found using a ^{17}O-NMR technique by Fiat and Connick.[3] The measurement was carried out over a wide range of temperatures and the activation free energy for the exchange and the relaxation time were both derived. The lifetime of the $Al(OH_2)_6^{3+}$ species is reproduced in Fig. 1 as a function of the reciprocal of the absolute temperature.

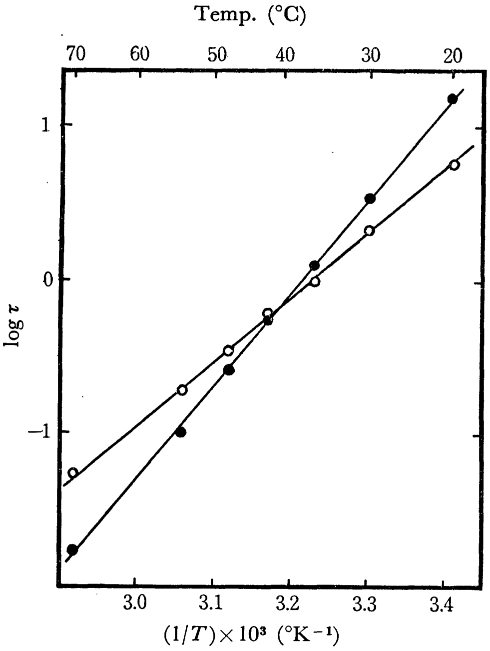

Fig. 1. Plots of τ_c and τ_e *vs.* $1/T$.

● τ_e calculated from Ref. 3.

○ τ_c calculated in terms of Eq. (4) using the value of E_{sf}, 18.2 kcal/mol.

Estimation of the Value of τ_c. The relaxation time of the aluminum ion for integrating into the crystal surface, τ_c, can be represented by the equation:[6]

$$\tau_c = (h/kT)\exp(E_{sf}/kT), \qquad (4)$$

where E_{sf} is the activation free energy of the ion for integrating into the crystal surface. It seems impossible at this stage to determine the value of E_{sf} accurately, since only the total activation energy for the crystal growth, E_t, can be obtained from the relation between the growth rate, R, and the temperature at a constant relative supersaturation, σ. However, the value of E_{sf} may be nearly equal to that of E_t or a little smaller, if the activation free energy of the aluminum ion for integrating into the kink from the surface, E_k, is relatively small. That is, it is possible to obtain the value of E_{sf} experimentally if the surface-diffusion mechanism is essential in which the integration of the cation into the surface is the rate-determining step. An energy diagram for the

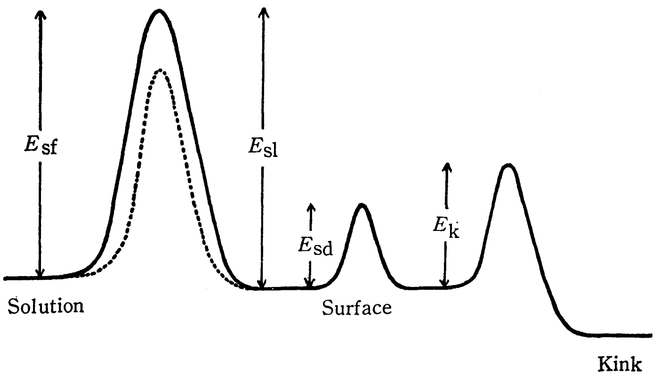

Fig. 2. The free energy diagram of the aluminum ion for integrating into the crystal from an unstirred solution. The dotted line denotes the barrier in the case of a well-stirred solution.

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[10] H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960); R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).

integration of the cation from the solution into the crystal is shown in Fig. 2.

On the other hand, the value of E_{sf} can also be estimated from a R-σ relation in which the growth rate, R, is expressed as a function of the relative supersaturation, σ, at a constant temperature. According to Bennema, the rate of the crystal growth of $KAl(SO_4)_2 \cdot 12H_2O$ from a well-stirred solution is given in the case of the surface-diffusion mechanism as follows:[6]

$$R = \beta C_0 \Omega (kT/h) \Lambda N_0 \{\exp(-E_{sf}/kT)\}(\sigma^2/\sigma_1)\tanh(\sigma_1/\sigma), \quad (5)$$

where β is a retarding factor and Λ is the thickness of the adsorption layer. He has thus estimated the value of E_{sf} to be 14.0 kcal/mol at 40°C in the case of a stirred solution. The value may, however, have some ambiguity at this stage due to the adjustable parameters, C_0 and Λ.

In the case of an unstirred solution, the following equation may hold:

$$E_{sf} = 14.0 + E_d, \quad (6)$$

where E_d is the activation free energy of the aluminum ion for diffusion in the solution. Equation (6) seems possible, for the activation processes of the cation for the diffusion and the integration into the surface should occur simultaneously. Accordingly, the value of E_{sf} becomes 18.2 kcal/mol in the case of an unstirred solution, assuming the value of E_d to be 4.2 kcal/mol, as was given by Eyring.[11] Neglecting the temperature dependence of the value of E_{sf}, it becomes possible to obtain the value of τ_c using Eq. (4) over the temperature range of 19.90°—69.50°C. Figure 1 shows the values plotted against the reciprocal of the absolute temperature.

Calculation of the Value of S. From the relation between τ_c and τ_e, the separation factor, S, can be calculated at a given temperature, taking account of Eq. (3). Since τ_e is larger than τ_c at 19.90°, 29.50°, and 36.52°C, as may be seen from Fig. 1, the aluminum ion should enter the crystal surface, accompanying the hydration water; that is, the species of the growth units are K^+, $Al(OH_2)_6{}^{3+}$, $SO_4{}^{2-}$, and H_2O for the crystal growth of alum. Assuming for the moment that the hydration water of $Al(OH_2)_6{}^{3+}$ is not subject to any fractionation of HTO from the bulk water, the value of S at 19.90°, 29.50°, and 36.52°C is calculated to be 0.975 as follows:

$$S = (6 \times 1.000 + 6 \times 0.949)/12 = 0.975. \quad (7)$$

At 41.95°C, τ_c is equal to τ_e. This means that the number of the hydration water of the cation, which integrates into the surface, is reduced to half of the preceding value; *i.e.*, the apparent species of the growth units may become K^+, $Al(OH_2)_3{}^{3+}$, $SO_4{}^{2-}$, and H_2O. The value of S is calculated as follows: $S = (3 \times 1.000 + 9 \times 0.949)/12 = 0.963$. The implication of the assumption that $\tau_c = \tau_e$ at 41.95°C seems quite important in that the value of E_{sf} (or the value of τ_c) can be determined rather exactly in terms of Eq. (4) if the value of τ_e is known, as is the case with the present study. It may be noted here, however, that the evaluated τ_c value may be a little ambiguous, as was pointed out before. As will be shown later, it is more reasonable to assume the reverse, that the $\tau_c = \tau_e$ equation holds when the observed value becomes 0.963.

At a higher temperature, the cation should integrate into the crystal surface apparently, without the hydration water, as was discussed before, because the $\tau_c > \tau_e$ relation holds in this case. It follows that all of the water of crystallization in alum should come from free water molecules, so the value of S becomes 0.949, as may be seen from Eq. (3).

At temperatures around 41.95°C, *i.e.*, at 36.52°C and 47.43°C, however, the separation factors are unlikely to take the extreme values of 0.975 and 0.949 respectively, because both τ_c and τ_e values should have some distribution and so should overlap to some degree. Accordingly, it is necessary to take account of the apparent loss of half of the hydration water of $Al(OH_2)_6{}^{3+}$ at 36.52°C. As a result, the apparent species of a growth unit for the aluminum ion at 36.52°C becomes $Al(OH_2)_m{}^{3+}$ with $3 < m < 6$. Similarly, the apparent species at 47.43°C can be given by $Al(OH_2)_n{}^{3+}$ with $0 < n < 3$. It follows that the separation factors, S, at 36.52° and 47.43°C are, at this stage, calculated to be in the ranges of 0.975—0.963 and 0.963—0.949 respectively. This also means that the apparent species of the growth unit changes continuously into the dehydrated aluminum ion, Al^{3+}, from the $Al(OH_2)_6{}^{3+}$ species with an increase in the temperature in the range of 29.50°—53.70°C, which thus leads to a continuous decrease in the value of S from 0.975 to 0.949 as the dehydration proceeds.

It should be noted here that the above treatment for the apparent dehydration of the species, $Al(OH_2)_6{}^{3+}$, is statistically true. The calculated value of S is given in Table 2, together with the values of τ_c and τ_e, and the apparent species of growth units. It seems worthwhile noting that the observed values are in good agreement with the calculated ones.

Factors Which May Influence the Value of S. It is well known that an aqueous solution of alum gives an acidic solution because a hydrolysis of the $Al(OH_2)_6{}^{3+}$ species occurs in the solution, a hydrolysis which is represented by a reaction such as:

$$Al(OH_2)_6{}^{3+} + H_2O \rightleftarrows Al(OH_2)_5(OH)^{2+} + H_3O^+.$$

It is thus necessary to obtain the concentration ratio of the tritiated hydronium ion, H_2TO^+, to the tritiated water, HTO. The T_3O^+ and HT_2O^+ species can be neglected as a source of tritium, since the mother liquid used contains a trace amount of HTO.

Salomon[12] has calculated the equilibrium constant of the reaction:

$$H_2O + H_2TO^+ \rightleftarrows HTO + H_3O^+,$$

to be 1.051 at 25°C. Therefore, the concentration

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[11] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York (1941), p. 557.

[12] M. Salomon, *Can. J. Chem.*, **44**, 689 (1966).

TABLE 2. CALCULATED SEPARATION FACTOR, S_{cal}, THE VALUES τ_c AND τ_e, AND APPARENT SPECIES OF GROWTH UNITS IN THE CRYSTAL GROWTH OF ALUM

Temp. (°C)	τ_c (sec)	τ_e (sec)	Apparent species of growth units		S_{cal}[c]
19.90	5.7	15.7	K^+, $Al(OH_2)_6{}^{3+}$,	$SO_4{}^{2-}$, and H_2O	0.975 (0.971)
29.50	2.1	3.4	K^+, $Al(OH_2)_6{}^{3+}$,	$SO_4{}^{2-}$, and H_2O	0.975 (0.971)
36.52	1.0_0	1.2_4	K^+, $Al(OH_2)_m{}^{3+}$[a],	$SO_4{}^{2-}$, and H_2O	$\begin{cases} <0.975\,(0.971) \\ >0.963 \end{cases}$
41.95	0.6_3	0.6_0	K^+, $Al(OH_2)_3{}^{3+}$,	$SO_4{}^{2-}$, and H_2O	0.963
47.43	0.3_6	0.2_7	K^+, $Al(OH_2)_n{}^{3+}$[b],	$SO_4{}^{2-}$, and H_2O	$\begin{cases} <0.963 \\ >0.949 \end{cases}$
53.70	0.2	0.1	K^+, Al^{3+},	$SO_4{}^{2-}$, and H_2O	0.949
69.50	5.4×10^{-2}	1.7×10^{-2}	K^+, Al^{3+},	$SO_4{}^{2-}$, and H_2O	0.949

a) $3<m<6$
b) $0<n<3$
c) The value corrected considering the species, $Al(OH_2)_5(HTO)^{3+}$, is given in parentheses.

ratio of H_2TO^+ to HTO in the solution is calculated to be *ca.* $[H_3O^+]/55.6$, where $[H_3O^+]$ refers to the concentration of H_3O^+. It follows that the H_2TO^+ species need not be considered as a source of tritium if $[H_3O^+]<10^{-1}$ gram ion/*l*. In the present study, the pH value of the mother liquid is larger than 1.85, so only HTO molecules have to be considered in calculating the value of *S*.

As for the crystal growth at 19.90° and 29.50°C, the $Al(OH_2)_6{}^{3+}$ species has been found to integrate into the crystal surface, accompanying the hydration water, as has been discussed before. Therefore, the $Al(OH_2)_5(HTO)^{3+}$ species should be taken into consideration in this case. The more tritiated species, *e.g.*, $Al(OH_2)_4(HTO)_2{}^{3+}$ are negligible, since the concentration of HTO is extremely low in the present case. Assuming the identical behavior of the species, $Al(OH_2)_5(HTO)^{3+}$, with a free water molecule in fixing into the crystal from the solution, the value of the separation factor for the species is estimated to be *ca.* 0.993 in terms of Eq. (2). The fractionation, if any, of HTO in the hydration water of the cation from bulk water is disregarded at this stage, which may lead to a little ambiguity in the calculation of *S*.

Mechanism of the Crystal Growth and the Fractionation of HTO. Since the $\tau_c=\tau_e$ relation is established when the species of a growth unit for the aluminum ion becomes $Al(OH_2)_3{}^{3+}$, as has been described above, the value of E_{sf} may be deduced in terms of Eq. (4), using the known value of τ_e.[3] The value of E_{sf} at 41.95°C is thus estimated to be *ca.* 18.17 kcal/mol in the case of an unstirred solution. It is interesting that the activation free energy for the exchange of the water in $Al(OH_2)_6{}^{3+}$ with bulk water, E_{ex}, becomes equal to the value of E_{sf} at this temperature, as may be seen from the equation:[13]

$$\tau_e = (h/kT)\exp(E_{ex}/kT). \tag{8}$$

The $E_{ex}=E_{sf}$ condition is important in that it is difficult to obtain the value of E_{sf} experimentally as well as theoretically, while the value of E_{ex} can be determined experimentally.

The mean displacement of the growth unit on the surface, x_s, can be estimated approximately, since the value of the activation free energy necessary for leaving the surface, E_{sl}, is nearly equal to the value of E_{sf}. The value of x_s for the aluminum ion is obtained in terms of the expression:[6]

$$x_s = a\exp\{(E_{sl}-E_{sd})/2kT\}, \tag{9}$$

where a is the shortest distance between neighboring growth units in the crystal and where E_{sd} is the activation free energy for the diffusion of the growth unit from one equilibrium position to a neighboring one on the surface. The value of E_{sd} is assumed to be *ca.* 7 kcal/mol according to Bennema,[5] so the value of x_s can be estimated to be *ca.* $7.6\times10^3\,a$. This implies that the cation diffuses over a wide range of the surface before integrating into the kink, because $x_s \gg a$. It follows that the surface-diffusion mechanism should play an essential role in the integration of the cation into the crystal, since the $x_s \gg a$ relation is a necessary condition for integration by means of this mechanism. This also implies that the integration of the cation into the surface should be the rate-determining step; therefore, the value of E_k is relatively small in comparison with the value of E_{sf} (*cf.* Fig. 2).

Accordingly, the crystal of alum should grow by the surface-diffusion mechanism, assuming that the rate of integration of the aluminum ion determines the overall growth mechanism. This assumption is supported by the facts that alum necessarily crystallizes from a slightly supersaturated solution in a stoichiometric way and that the cation has the lowest relaxation time for integrating into the crystal. The preceding discussion may be regarded as another argument for the mechanism of the crystal of alum which has been suggested by Bennema.[5,6] It may be concluded from the present study that isotopic fractionation in phase equilibria is largely influenced by the crystal-growth mechanism and the system of ions and water. The determination of the isotopic fractionation during the crystal growth of hydrated salts from a slightly supersaturated solution should thus contribute to an understanding of the growth mechanism and/or the system of the aqueous solution.

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[13] H. Eyring, *Chem. Rev.*, **17**, 65 (1935).