Studies on Crystal Hydrates. VI[1]. *Thermodynamics of Dehydration of Crystal Hydrates. A New Criterion for the Continuous Zeolitic Dehydration. Capillary Condensation of Water Vapor into Exactly Uniform Pores and an Experimental Test of the Kelvin Equation. Case of* DL-*Tris-ethylenediamine-cobalt(III) Chloride Hydrate*

By Hideaki CHIHARA

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A criterion has generally been adopted as to the manner of dehydration of a crystal hydrate, which makes use of the dehydration isotherm[1]. The experimental determination of a complete dehydration isotherm, however, is sometimes quite an elaborate matter owing to difficulty in obtaining the true equilibrium of dehydration[2]. It was found that a new criterion, which is equivalent to the "isotherm criterion", can be obtained by the measurement of dehydration pressures at different temperatures for a fixed content of water in the solid phase; the water content needs not be accurately known. This may be termed "entropy criterion" as it is based on the value of the entropy of dehydration.

Although the entropy criterion is exactly as useful as the isotherm criterion, both were found to fail to apply to a particular case of DL-tris-ethylenediamine-cobalt(III) chloride hydrate, in which only one kind of channel filled with water molecules runs parallel to the direction of the c-axis[1]. This cobalt complex presents a remarkable model substance as a crystal

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[1] Report V: H. Chihara and K. Nakatsu, This Bulletin, 32, 903 (1959).

[2] Report IV: H. Chihara and S. Seki, ibid., 32, 897 (1959).

hydrate of zeolite type, as a porous adsorbent having exactly uniform capillaries, as a host-lattice of an *Einchlussverbindung* like a urea adduct, and as an isothermal order-disorder assembly of water molecules.

Thermodynamics of Dehydration

For a dehydration equilibrium

$$A\cdot nH_2O \rightleftarrows A\cdot (n-1)H_2O + H_2O(g)$$

the change in the standard entropy $\varDelta S$ is given by

$$S_H - S_A = S_W - \varDelta S$$

where S_H, S_A and S_W are the standard entropies of the hydrate, the lower hydrate (or the anhydrous crystal) and the water vapor (45.1 cal./deg. mol.), respectively. $S_H - S_A$ can be obtained from the measurements of the heat capacities and $\varDelta S$ from the tensiometric measurements. Table I lists these values for a few hydrate systems. It is seen in Table I that $S_H - S_A$ is nearly constant being around 10 e. u., which is also nearly equal to the entropy of ice at the standard state. This shows that an additivity rule holds for these crystalline solids. The values of $S_W - \varDelta S$, on the other hand, scatter far and wide, being as large as 21.6 e. u. and as small as −2.5 e. u. One of possible reasons for the discrepancies between $S_H - S_A$ and $S_W - \varDelta S$ would be that the stable equilibrium may not have been attained in the tensiometric measurements. This may undoubtedly cause a serious discrepancy. However, it is readily shown that a discrepancy can naturally occur even if the equilibrium was obtained in both thermal and tensiometric measurements.

TABLE I. ENTROPY PER MOLE OF WATER IN CRYSTALLINE HYDRATES

Hydrate	$S_H - S_A$[3]	$S_W - \varDelta S$
$MgCl_2\cdot 2H_2O$	10.2	10.8[4]
$MgCl_2\cdot 4H_2O$	10.1	10.4[4]
$MgCl_2\cdot 6H_2O$	12.2	13.9[5]
$CaSO_4\cdot \frac{1}{2}H_2O$	11.4	−2.5[6]
$ZnBr_2\cdot 2H_2O$	11.7	21.6[7]
$ZnSO_4\cdot 2H_2O$	10.4	8.5[8]
$ZnSO_4\cdot 7H_2O$	5.6	2.9[8]
$CdBr_2\cdot 4H_2O$	10.7	9.9[9]
$CdSO_4\cdot \frac{8}{3}H_2O$	10.1	12.6[10]
$CuSO_4\cdot H_2O$	8.7	7.9[11]
$CuSO_4\cdot 3H_2O$	9.0	11.6[10]
$CuSO_4\cdot 5H_2O$	9.6	8.0[10]
$NiCl_2\cdot 6H_2O$	8.3	13.2[4]
$BaCl_2\cdot 2H_2O$	8.5	6.8[12]

Let us consider a system consisting of a hydrate phase (denoted by the subscript 1), the anhydrous phase (subscript 2) and the water vapor phase (subscript 3) in equilibrium. The molar Gibbs free energy of the whole system is given by

$$G_m = (1-\theta)\mu_1 + \theta\mu_2 + c\theta\mu_3 \tag{1}$$

in terms of the chemical potentials μ_i where θ corresponds to the degree of dehydration or the mole fraction of the anhydrous phase in the solid components. One mole of the hydrate is assumed to produce c moles of water vapor. The conditions for the stable equilibrium are

$$\frac{dG_m}{d\theta} = 0 \qquad \frac{d^2G_m}{d\theta^2} > 0 \tag{2}$$

Case A.—The simplest case in which

$$\left(\frac{\partial\mu_1}{\partial\theta}\right)_{P,T} = \left(\frac{\partial\mu_2}{\partial\theta}\right)_{P,T} = 0 \tag{3}$$

leads to the ordinary condition of equilibrium

$$\mu_1 = \mu_2 + c\mu_3 \tag{4}$$

By defining the absolute activity λ_i by

$$\mu_i = kT\log\lambda_i \tag{5}$$

the equilibrium constant K is then obtained as

$$K \equiv \frac{\lambda_1}{\lambda_2\cdot(\lambda_3{}^+)^c} = \left(\frac{p}{P^+}\right)^c \tag{6}$$

where λ^+ and P^+ are the standard-state quantities. The pressure equation will then be

$$\log p - \log P^+ = \frac{1}{c}(\log\lambda_1 - \log\lambda_2 - c\log\lambda_3)$$
$$= -\frac{\varDelta h}{kT} + \frac{\varDelta s}{k} \tag{7}$$

where

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3) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", NBS Circular 500, National Bureau of Standards, U. S. Department of Commerce, U. S. Government Printing Office, Washington (1952).

4) I. Sano, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*) **59**, 1145 (1938).

5) J. H. Derby and V. Yngve, *J. Am. Chem. Soc.*, **38**, 1439 (1916).

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10) C. D. Carpenter and E. R. Jette, *J. Am. Chem. Soc.*, **45**, 583 (1923).

11) A. Siggel, *Z. Elektrochem.*, **19**, 349 (1913).

12) G. F. Hüttig and Ch. Slonim, *Z. anorg. Chem.*, **181**, 65 (1929).

and
$$\left.\begin{aligned}\Delta h&=(h_2+ch_3-h_1)/c\\ \Delta s&=(s_2+cs_3-s_1)/c\end{aligned}\right\}\tag{8}$$

Eq. 7 is the integrated form of the Clapeyron-Clausius equation. The second condition (Eq. 2) gives

$$\frac{\mathrm{d}\log p}{\mathrm{d}\theta}=\frac{\mathrm{d}}{\mathrm{d}\theta}\left\{-\frac{1}{kT}(\mu_1-\mu_2-c\mu_3{}^+)\right\}=0\tag{9}$$

showing that the dehydration pressure should be constant over the range of the θ values or, in other words, the dehydration should be stepwise as is the case for $CuSO_4\cdot 5H_2O$ and its lower hydrates. Eqs. 7 and 8 then indicate that the Clapeyron-type equation gives the integral heat and entropy of dehydration when the condition (3) is satisfied. The heat and entropy thus obtained should be comparable with the third-law values S_H-S_A. It is inferred that the condition (3) holds in hydrates for which one sees approximate agreement between S_H-S_A and $S_W-\Delta S$ in Table I.

Case B.—In a general case where the condition (3) is not satisfied,

$$\left(\frac{\partial\mu_1}{\partial\theta}\right)_{P,T}\neq 0\qquad\left(\frac{\partial\mu_2}{\partial\theta}\right)_{P,T}\neq 0\tag{10}$$

the condition for the equilibrium gives

$$\begin{aligned}-\log\lambda_1+\log\lambda_2+c\log\lambda_3+(1-\theta)\left(\frac{\partial\log\lambda_1}{\partial\theta}\right)_{P,T}&\\ +\theta\left(\frac{\partial\log\lambda_2}{\partial\theta}\right)_{P,T}=0&\end{aligned}\tag{11}$$

which then leads to the pressure equation

$$\begin{aligned}c\log(p/P^+)=\frac{1}{kT}\{&\bar{h}_1-\bar{h}_2-ch_3{}^+\\ &-T(\bar{s}_1-\bar{s}_2-cs_3{}^+)\}\end{aligned}\tag{12}$$

where $\bar{h}$ and $\bar{s}$ are the differential molar heat and entropy. The shape of the dehydration isotherm must satisfy the second condition for the equilibrium:

$$\begin{aligned}\frac{\mathrm{d}^2G_m}{\mathrm{d}\theta^2}=\frac{\mathrm{d}}{\mathrm{d}\theta}\bigg\{&-\mu_1+\mu_2+c\mu_3+(1-\theta)\left(\frac{\partial\mu_1}{\partial\theta}\right)_{P,T}\\ &+\theta\left(\frac{\partial\mu_2}{\partial\theta}\right)_{P,T}\bigg\}>0\end{aligned}\tag{13}$$

which then leads to

$$\frac{\mathrm{d}}{\mathrm{d}\theta}(\bar{\mu}_2+c\mu_3{}^+-\bar{\mu}_1)=\frac{\mathrm{d}}{\mathrm{d}\theta}(\bar{\mu}_2-\bar{\mu}_1)>0\tag{14}$$

Differentiating Eq. 12 with respect to θ gives

$$\begin{aligned}ckT\frac{\mathrm{d}\log(p/P^+)}{\mathrm{d}\theta}&=\frac{\mathrm{d}}{\mathrm{d}\theta}(\bar{\mu}_1-\bar{\mu}_2-c\mu_3{}^+)\\ &=\frac{\mathrm{d}}{\mathrm{d}\theta}(\bar{\mu}_1-\bar{\mu}_2)\end{aligned}\tag{15}$$

Therefore we have

$$\frac{\mathrm{d}\log p}{\mathrm{d}\theta}<0\tag{16}$$

This shows that the dehydration pressure decreases constantly with increasing θ, or it corresponds to the zeolitic dehydration. The Clapeyron-Clausius equation gives differential molar heat and entropy in this case.

S_H-S_A as obtained from the calorimetric results corresponds to the difference in the integral entropies s_1-s_2 which is related to ΔS by Eq. 8.

Now, it will be evident that the discrepancies between S_H-S_A and $S_W-\Delta S$ may naturally occur if the dehydration proceeds zeolitically as the differential and the integral entropies of dehydration do not usually coincide with each other*, except for accidental coincidence.

In view of the fast that the integral entropy assigned to water molecules within a hyrate lattice is nearly constant being approximately 10 e. u., ΔS values obtained by the tensiometric measurements can be used to determine whether or not the dehydration is zeolitic even if the corresponding calorimetric data are unavailable. In Table I, the discrepancy is appreciable in $CaSO_4\cdot\frac{1}{2}H_2O$, $ZnBr_2\cdot 2H_2O$ and $ZnSO_4\cdot 7H_2O$. The hemihydrate of $CaSO_4$ undergoes zeolitic dehydration as shown by the isotherm reported by Gregg and Willing[13]. The cases of $ZnBr_2$ and $ZnSO_4$ hydrates have not been examined in detail and it is not clear if these are really zeolitic cases.

TABLE II. COMPARISON OF THE ISOTHERM AND ENTROPY CRITERIONS FOR THE TWO TYPES OF DEHYDRATION

	For dehydration by which crystal lattice collapses	For dehydration by which lattice does not collapse
S_H-S_A	about 10 e. u.	about 10 e. u.
$S_W-\Delta S$	equal to S_H-S_A	not equal to S_H-S_A
Clapeyron eq. gives	integral heat and entropy	differential heat and entropy
Pressure vs. deg. of dehydration	constant pressure	monotonous decline

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* It is possible to calculate the intergral entropy for zeolitic hrdrates, if complete data of isotherms are available particularly at a very low presure region. See T. L. Hill, P. H. Emmett and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5102, 5933 (1951).

[13] S. J. Gregg and E. G. G. Willing, *J. Chem. Soc.*, **1951**, 2373, 2916.

Table II summarizes and compares the "isotherm" and "entropy" criterions. The "entropy criterion" is thus entirely equivalent to the "isotherm criterion" which has widely been accepted. The applicability or the inapplicability should be the same for both criterions. The advantage of the "entropy criterion" rests on the fact that the measurements of the dehydration pressure at different water contents are not necessary.

A Notable Case in which the Criterions Fail to Apply

When one correlates a thermodynamic relation to an atomistic interpretation, there is a risk of his over-relying upon empirical rules. Thus the "isotherm criterion" depends on a lot of experimental facts on the isotherm determinations and the structural studies before and after dehydration. This is in a way based on the analogy between zeolitic dehydration and adsorption. The phase rule of course can make judgement if the number of phases is known unambiguously.

The case of DL-$[\mathrm{Co\ en_3}]\mathrm{Cl_3}\cdot n\mathrm{H_2O}$ ($n \leq 4$), the dehydration of which was reported in the preceding paper[1)], provides us with a notable exception to both criterions, which are however mutually consistent. Fig. 1 shows the change in $S_W - \Delta S$ as the hydration proceeds. $S_W - \Delta S$ is nearly constant between $n=0.2$ and 3 except for a minimum occurring around $n=2.6$[1)]. Below and above this range of values of n, $S_W - \Delta S$ tends to increase, deviating from the additivity value of 10 e. u. The entropy criterion tells that the crystal undergoes zeolitic dehydration when $n \leq 0.2$ and when $n \leq 3$ and the lattice-destructive dehydration when n is between 0.2 and 3. This apparent conclusion is consistent with the isotherm criterion as judged from the isotherm given in Fig. 7 of the preceding paper[1)], in which the pressure remains constant between $n=0.2$ and 3. However, as already reported[1)], this conclusion is not justified by the crystal structure studies by which we see that the structure is unchanged by dehydration except for the loss of water molecules in the channels. This must evidently correspond to zeolitic dehydration and thus the failure of both criterions is apparent.

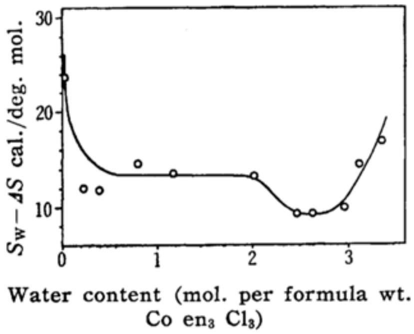

Fig. 1. Change with the water content in the differential molar entropy of water in $[\mathrm{Co\ en_3}]\mathrm{Cl_3}$ hydrate.

The extreme uniformity of the pore structure of this crystal seems to be responsible for the failure. There exists only one kind of pore running parallel in the direction of the c-aixs of the crystal. Such uniformity has never been realized in actual hydrate systems or adsorption systems and has been out of reach of empirical rules mentioned in the first paragraph of the present section. This type of isotherm should lead to a sharp distribution function of pore sizes if we treat it by a standard method utilizing the desorption branch of sorption isotherm[14)].

The most reliable criterion would be the structure investigation by the X-rays but in most of zeolite minerals and gels there is a broad distribution of pore size, which necessarily gives rise to the isotherm corresponding to the *Case B*; $[\mathrm{Co\ en_3}]\mathrm{Cl_3}$ hydrate is one of the rarest exceptions. The "entropy criterion" as well as the "isotherm criterion" is, therefore, considered to be still valid in judging which type of dehydration a particular hydrate would undergo.

Comparison of Capillary Radius as Determined by Dehydration Isotherm and by X-ray Study

It will be interesting to see to what extent the well-known Kelvin equation

$$\log(p_r/p) = -2\sigma M/(\rho r R T) \qquad (17)$$

gives reasonable pore radius when it is applied to the system of pores of molecular dimensions. p is the saturation pressure over a plane surface of the adsorbate liquid (water in the present case) whose surface tension is σ, density is ρ, and molecular weight is M. p_r is the saturation pressure over the surface, its radius of curvature being r. This equation has been known to hold for a macroscopic pore or a macroscopic droplet of liquid but we

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14) C. Pierce, *J. Phys. Chem.*, 57, 149 (1953).

seem to have available no direct experimental test of the equation down to pores of a few Ångstroms in radius.

The horizontal portion of the isotherm given in Fig. 7 of the preceding paper[1] gives $r=5.8$Å if $\rho=0.9971$, $\sigma=71.97$ dyn./cm., $p=23.756$ mmHg and $p_r=2.85$ mmHg are inserted in Eq. 17. It would not be necessary to add to r the thickness of a monolayer or of statistical layers as the capillary condensation begins at $n=0.2$, far below the monolayer capacity $n=3$**. On the other hand, the result of the crystal structure analysis[15] gives the distances from the origin (the center of a pore, see Fig. 3 of the preceding paper), in the plane parallel to the base of the hexagonal cell, 2.9 Å to the periphery of the van der Waals radius of the nearest CH_2 group and 3.4Å to the periphery of the nearest chloride ion (the inner wall of the pore is a little pleated).

We are now led to the conclusion that for water vapor as the adsorbate the Kelvin equation gives only the order of magnitude of the pores radius of micropores. We shall undertake experiments with nitrogen as the adsorbate later. For macropores the discrepancy would be much smaller. In view of the fact that the concept of the surface tension would undoubtedly lose its significance in such systems of water molecules, the Kelvin equation has been applied beyond its reasonable limit of application, although the method has been in extensive use for evaluating the pore size distribution in many adsorbents. The use of the Kelvin equation was partly justified for macropores by the experimental results that it gives the pore sizes in good agreement with those obtained by the mercury porosimeter method[16]. The present result gives some clue to the error caused by the use of the Kelvin equation for micropores.

Summary

A simple theory of the thermodynamics of hydrates is developed, which is able to show that the differential molar entropy of dehydration changes with the water content continuously if the hydrate undergoes zeolitic (continuous) dehydration. In this case the integral molar entropy of dehydration does not agree with the differential entropy. The same is true for the heat contents. For stepwise dehydration, on the other hand, both differential and integral entropies coincide in values. A new criterion, termed "entropy criterion", is presented that if the differential entropy of the water of crystallization, obtained by subtracting the entropy of dehydration (determined by the pressure measurements) from the standard entropy of water vapor 45.1 e. u., differs greatly from 10 e. u., the hydrate should undergo zeolitic dehydration and should have water molecules weakly bonded to the crystal lattice, from which water can be removed without causing collapse of the lattice. This new criterion is equivalent to using the current "isotherm criterion".

DL-[Co en$_3$] $Cl_3 \cdot nH_2O$ ($n\leq4$) presents a notable exception to both criterions in that the crystal undergoes zeolitic dehydration in spite of its entropy of dehydration and its isotherm indicating the stepwise dehydration. The failure of the criterions in this crystal is due to the extreme uniformity of pore structure of the hydrate. The Kelvin equation for calculating the pore radius (giving 5.8Å) from the dehydration isotherm is tested against the pore radius obtained by the X-ray crystal structure analysis (giving 2.9 to 3.4Å). It may be concluded that the Kelvin equation is considered to give only the order of magnitude for micropore size. This cobalt complex hydrate is one of the rarest examples having exactly uniform pores and the criterion for the type of dehydration here presented is still effective in most cases.

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Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

** It is rather surprising to note the capillary condensation is completed just befor the monolayer is filled.

15) K. Nakatsu, Y. Saito and H. Kuroya, This Bulletin, **29**, 428 (1956).

16) E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.* **73**, 373 (1951).