Studies on Crystal Hydrates. IV. Dehydration and Rehydration, Stable and Metastable Equilibria and Transition between Hydrate Modifications of Potassium Mercury(II) Chloride Monohydrate, $K_2HgCl_4 \cdot H_2O$*

By Hideaki CHIHARA and Syûzô SEKI

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Numerous reports may be found in the literature of the subject as to the dehydration and rehydration of crystal hydrates, but there are few investigations based on the exact thermodynamical precautions. Atomistic interpretation of the phenomena related to the behavior of water molecules in the dehydration reaction seems to have insufficient ground to advance. One of the principal reasons for this seems to be that there are complexities which enable us to obtain a material at the well-defined thermodynamical as well as molecular state only with extreme difficulty. Dehydration can frequently produce amorphous or colloidal material which gradually changes to stable crystalline solids[1]. Different methods of preparation sometimes produce materials of different free energy[2].

Many hydrates undergo phase transitions prior to dehydration in the heating experiments[3]. A study of the mechanism of such transitions will assist in understanding the law governing the dehydration reaction.

In the present paper, another example of the difficulty of obtaining the true equilibrium will be presented. It was inferred that $K_2HgCl_4 \cdot H_2O$ might undergo "zeolitic" dehydration, from its crystal structure[4], in which water molecules are packed in channel-like interstices. Although the direct evidence of such type of dehydration was not obtained, a consideration of the entropy of dehydration let us conclude that this is the case. An X-ray diffraction study of the phase transition and the rehydration will be briefly reported.

Experimental

Material. — KCl: Takeda Co., first grade. Purified by recrystallization from water.

$HgCl_2$: Takeda Co., analytical grade. Recrystallized from water. $K_2HgCl_4 \cdot H_2O$: Crystals were prepared according to the phase diagram[5] of the system KCl-$HgCl_2$-H_2O which is reproduced in Fig. 1. Because amorphous samples were often obtained depending on the method of preparation as will be described later, the following procedure was found most satisfactory by analogy of the system $MnCl_2$-NH_4Cl[6]. A saturated solution corresponding to the point a in Fig. 1 (25°C) was

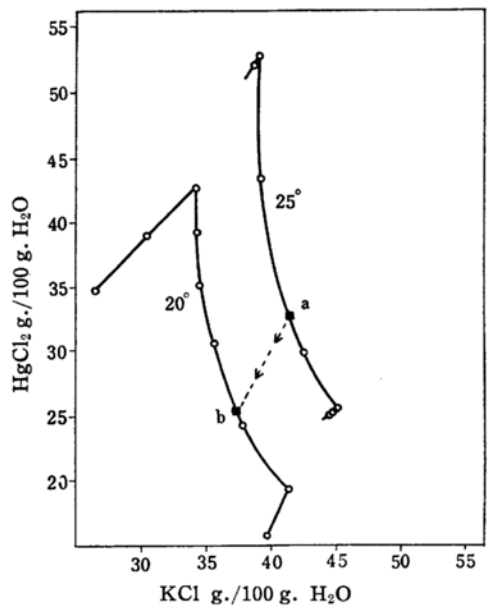

Fig. 1. Solution equilibrium diagram of the system KCl-$HgCl_2$-H_2O. Only a portion corresponding to the solid composition $K_2HgCl_4 \cdot H_2O$ is shown.

slowly cooled down to 20°C. A calculation shows that the solution changes its composition along the line a→b. The precipitate was filtered with a glass filter, pulverized, and then returned to

* The Report III may be found in This Bulletin, **30**, 674 (1957).

1) H. Chihara and S. Seki, This Bulletin, **30**, 674 (1957); G. B. Erost, K. A. Moon and E. H. Tompkins, *Can. J. Chem.*, **29**, 604 (1951); H. W. Quinn, R. W. Missen and G. B. Frost, ibid., **33**, 286 (1955); R. C. W. Wheeler and G. B. Frost, ibid., **33**, 546 (1955).

2) W. F. Giauque, *J. Am. Chem. Soc.*, **71**, 3192 (1949).

3) H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).

4) C. H. MacGillavry, J. H. de Wilde and J. M. Bijvoet, *Z. Krist.*, **100**, 212 (1938).

5) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds", 3rd Ed., Vol. 1, D. Van Nostrand Co., New York (1940), p. 624.

6) A. L. Greenberg and G. H. Walden, Jr., *J. Chem. Phys.*, **8**, 645 (1940); A. Grenall, ibid., **17**, 1036 (1949).

the mother solution for ten days in a closed vessel, being occasionally shaken. The X-ray photograph of the precipitate finally filtered was entirely consistent with the reported crystal structure[4].

Measurements of the Dehydration Pressures.—The dehydration pressures were measured by a simple mercury-in-glass manometer with the help of a traveling microscope to within ±0.01 mmHg. The water thermostat was kept at constant temperatures to within 0.005°C. In the experiment of the isothermal dehydration, the water vapor was trapped into a small capillary and weighed. The amount dehydrated was corrected for the mercury vapor condensing from the manometer into the trap.

Dehydration Equilibrium

The dehydration pressures of the crystalline $K_2HgCl_4 \cdot H_2O$ were measured between 26 and 40°C and the results are plotted in Fig. 2 by squares. The pressure equation is

$$\log P(\text{mmHg}) = 8.538 - (2161/T) \qquad (1)$$

The heating and cooling data were perfectly coincident within the experimental error and it was ascertained that equilibrium was attained with no hysteresis effect. The heat, the entropy, and the free energy of dehydration are given in Table I.

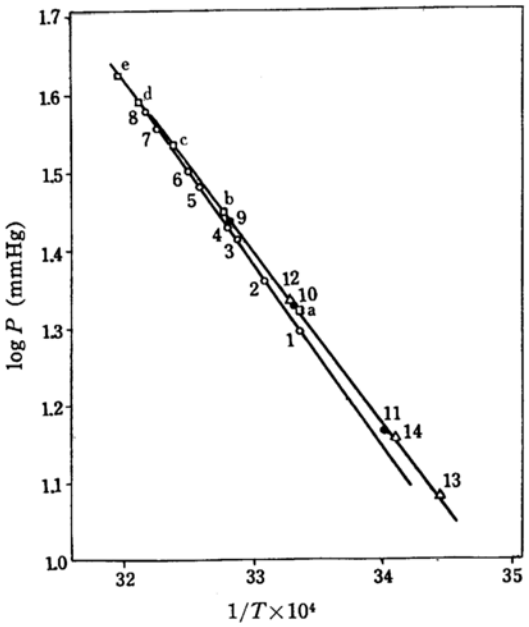

Fig. 2. Dehydration pressures of $K_2HgCl_4 \cdot H_2O$; □, crystalline hydrate (equilibrium data) (a-e); ○, heating direction of partly amorphous hydrate (1-8); ●, cooling direction of partly amorphous hydrate (9-11); △, subsequent heating and cooling measurements with partly amorphous hydrate (12-14).

TABLE I. CHANGES OF THE HEAT CONTENT, THE ENTROPY AND THE FREE ENERGY BY DEHYDRATION OF $K_2HgCl_4 \cdot H_2O$

ΔH kcal./mol.	ΔS cal./mol. deg.	ΔG at 25°C kcal./mol.
9.50	25.9	2.18

Results for Partly Amorphous Samples.—KCl 12.227 g. and $HgCl_2$ 15.459 g. were mixed with water 20 cc. and the solid was dissolved completely at high temperature by preventing evaporation. The solution was then cooled down to and kept at 20°C. It was deeply supercooled and no precipitation occurred before the entire solution reached 20°C. The solid precipitate after a few hours had the composition corresponding to $K_2HgCl_4 \cdot H_2O$ and the solution contained KCl 7.11 g. and $HgCl_2$ 6.13 g. The X-ray powder photograph of the solid thus prepared, however, showed that it was partly amorphous. The Debye rings, though faint, were consistent with the reported crystal structure of the hydrate[4]. The dehydration pressure of the partly amorphous hydrate showed a hysteresis phenomenon according to the pressure equations:

$$\log P(\text{mmHg}) = 9.139 - (2359/T) \quad \text{in heating direction} \qquad (2)$$

$$\log P(\text{mmHg}) = 8.595 - (2180/T) \quad \text{in cooling direction} \qquad (3)$$

The results are shown by open circles (heating direction) and by solid circles (cooling direction) in Fig. 2. The results of the subsequent heating and cooling experiments are indicated by triangles. It took about 20 days to reach an apparent dehydration equilibrium as compared with a few minutes in the case of the crystalline sample at 24.03°C.

The experiments of isothermal dehydration were made at 34.13°C. The initial formula of the hydrate was $K_2HgCl_4 \cdot 0.997 H_2O$. The constant value of the dehydration pressure was reached only after about 280 days (see Fig. 3). The calculated pressure from Eq. 2 was 31.09 mmHg and the apparent coincidence was good. The second equilibration with the composition $K_2HgCl_4 \cdot 0.965H_2O$ (water 0.032 mol. was taken from the original hydrate) was much slower than the first and then it was felt that further dehydration might accelerate the approach to the equilibrium. The third run, however, was even slower,

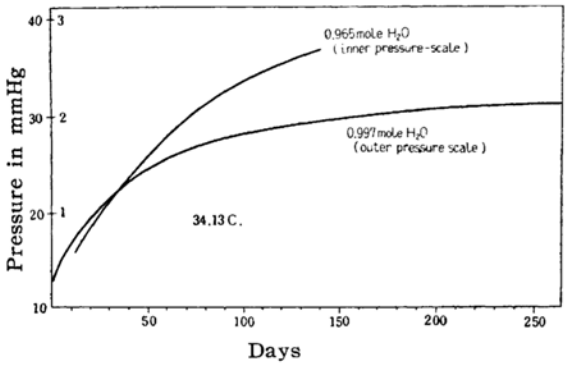

Fig. 3. Approach to the apparent equilibrium of isothermal dehydration of partly amorphous sample.

with 0.809 mol. of water per formula weight. The sample used in this experiment was taken out of the apparatus and examined by the X-rays. It was still partly amorphous but the crystallization seemed to have proceeded during the pressure measurements (longer than two and half years).

The differential thermal analysis of the partly amorphous sample gave only ill-defined peaks in comparison with the result for the crystalline sample which will be discussed below.

These results show that the crystallization of an amorphous solid is a very slow reaction at room temperature and that care must be exercised in the preparation of the solid substances, because an inadequate method of preparation sometimes produces materials of higher free energy than the one for the equilibrium product**.

Entropy of Dehydration

The value of entropy may be assigned to water molecules in the hydrate crystal by subtracting the experimental entropy of dehydration from the standard entropy of water vapor 45.1 cal./deg. mol. This method gives for the present case 19.2 cal./deg. mol. which amounts to roughly twice as large a value as in average hydrate crystals and shows that the dehydration is "zeolitic".

Transition and Dehydration in Air

The results of the differential thermal analysis are given in Fig. 4 which shows two heat-absorption peaks at 114 and 123°C, with a fine structure in the former peak. The shoulder at 107°C always appeared in several runs but one at 117.6°C was not always reproducible.

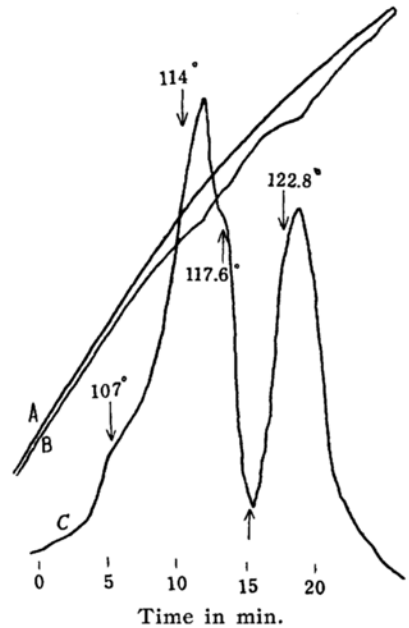

Fig. 4. Differential thermal analysis of crystalline $K_2HgCl_4 \cdot H_2O$; curve A, temperature of the reference NaCl powder; curve B temperature of the sample; curve C the temperature difference.

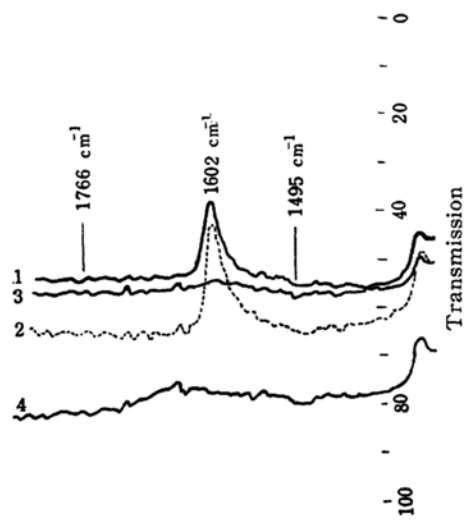

Fig. 5. Infrared spectra. (1) Room-temperature phase, (2) heated to 118°C, (3) heated to 130°C, (4) daifloil background.

There are evidences for the fact that the first peak at 114°C is due to a transition between two hydrate modifications

** A similar case is the dehydration and transition of $NiSO_4$ hexahydrate as reported by Simon and Knauer (*Z. anorg. u. allgem. Chem.*, **242**, 375 (1939)).

7) Full discussion of the entropy of dehydration is given in Part VI (This Bulletin, **32**, 908 (1959)).

and the second peak at 123°C is due to dehydration. There occurred no detectable evaporation and condensation of water in the apparatus of the thermal analysis[3] at the temperature between the two peaks, and also the infrared absorption spectrum*** of the hydrate crystals quenched from 118°C, at which the first heat effect completed its peak, retained the 6-micron absorption band of water (Fig. 5). The hydrate heated beyond the second heat-absorption temperature was not absorbed in this wavelength region; the heat absorption at 123°C is apparently due to dehydration.

An X-ray study was made of the transition of $K_2HgCl_4 \cdot H_2O$ at 114°C. The crystals were heated to 117°C in the apparatus of the differential thermal analysis (the transition was observed) and was rapidly cooled to room temperature and examined by the Norelco X-ray diffractometer. The scanning of the goniometer started about ten minutes after the sample was taken out of the heating vessel, with the scanning rate $2\theta = 0.5°$/min. The scanning was repeated according to the following succession:

12—61°, 35—46, 10—42, 10—35, 34—27 (reversely), 26—34, 10—14, 23—26, 28—31, 45—47, in 2θ values.

It took about 5.5 hr. for this series of scanning. The scanning was then repeated every day for the following six days. The change in the diffraction patterns with time was bewildering during the first few hours. Some of the typical results are reproduced in Fig. 6. The diffraction

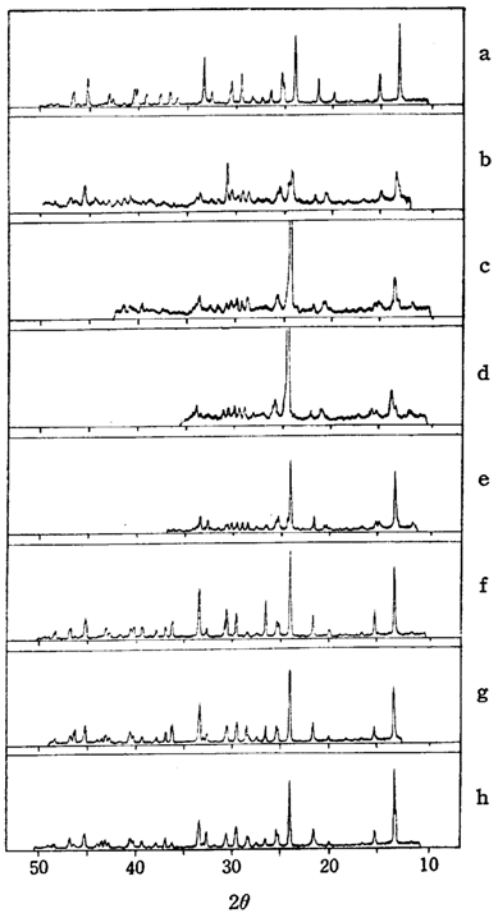

Fig. 6. Change of X-ray diffraction diagrams due to the transition; (a) α-modification of the hydrate, (b) ten minutes after once heating the hydrate to 117°C, (c) 40 min. after b, (d) 60 min. after b, (e) 18 hr. after b, (f) 42 hr. after b, (g) 90 hr. after b, (h) 138 hr. after b.

*** The infrared absorption spectra were recorded with Hilgar Model H800 Spectrophotometer.

TABLE II. POWDER DIFFRACTION LINES IN 2θ VALUES (deg.)

α-Hydrate	β-Hydrate	Anhydrous crystal
13.08 (110)	11.62 (210)	11.25
15.14 (020)	13.16 (021)	11.74
19.9 (002)	13.45 (220)	12.54
21.5 (200)	15.0 (040) (201)	13.14
23.9 (112)	20.7*	13.8
25.1 (022)	21.9 (400)	14.8
25.3 (130)	24.2 (222)	18.2
26.4 (220)	24.5	19.8
27.3 (131)	25.5 (042)	20.2
28.3	25.7 (260)	20.4
29.4 (202)	28.6**	20.6*
30.4 (212)	29.2	21.5
30.6 (040)	29.7* (402)	21.9
32.5 (140)	30.4	23.8
32.9	30.8 (422) (080)	24.1
33.3 (220) (310)	31.8	24.6
36.0 (320)	32.3	25.0
36.1	33.5 (442)	25.4
36.8 (042)	33.6 (620)	27.1
37.7 (240)	34.0	27.4
39.2	36.4 (640)	27.7
40.1 (330)	37.5 (082)	28.3**
40.4 (150) (004) (223)	38.9	28.9
42.6	39.6	29.5
43.0, 43.1 (242)	40.8**	30.0
	41.4	
43.4	42.2	
45.1 (340) (303) (250) (401)	43.0	
	44.4	
46.6 (420)	45.4	
	45.6	

* Diffraction lines due to $HgCl_2$.

** Diffraction lines due to KCl.

patterns of the anhydrous crystal (Fig. 7a) and of the hydrate (Fig. 6a) which is stable at room temperature (α modification) are also given for the sake of reference. The series of patterns shows the change in the crystal structure from the high-temperature modification (β modification) to the low-temperature modification (α modification) slowly occurring at room temperature. Fig. 6b is itself an intermediate or a mixture of the two modifications. Attempts were made to assign the diffraction lines to either α or β modification by comparing the members of the series of the diffraction patterns. The results are summarized in Table II.

Although some of the lines ascribed to the β modification coincide with the lines of the α modification or with the lines of the anhydrous crystal, there exist lines essentially attributable to the β modification. The time change of the intensities also supports this view. The patterns of Fig. 6b and its succeeding changes can not be obtained by a mere superposition of the diffractions from the α-hydrate and those from the β-hydrate. In fact, the intensities of lines belonging to various crystalline forms show intricate changes, for example, (1) 24.1* line first becomes stronger with time, (2) 13.4 and 15.4 are both characteristic to the α-hydrate but their recovery in the intensity is not proportional with each other; the recovery is first more rapid in 15.4 line than 13.4 line, and then the recovery of 13.4 line predominates again, and (3) five lines between 28 and 31 do not change their intensities in a regular, simple way.

It was first supposed that the sample chilled from above the transition temperature might be a mixture of the α and the β modifications, and that the transition might be observed as the decrease in intensity of the characteristic lines of the β form accompanied with the increase in the intensities of lines of the α form by equal fractions. If so, it should be possible to determine the rate of transformation at a supercooled condition which is itself a rare experimental information. Instead, it has become very plausible that the transition is essentially of gradual nature: a structure does not abruptly transform itself into another but there is a continuous series of structures between the β and the α modifications.

This is an analogous situation to the order-disorder transitions in such respect that there are an infinite number of phases between two extreme phases**. But a difference from the order-disorder transition is that nothing like the order parameter may be introduced and that every step of the transition probably corresponds to an ordered state because no regular, proportional change in the diffraction intensities with time was observed in contrast to the case of order-disorder transitions, in which it is possible to calculate the order parameters from the monotonous change of a superstructure-line intensity with temperature[8]. In the case of order-disorder transitions, a unit cell within a crystal has only statistical significance in the sense that a particular unit cell has not necessarily the structure identical with the neighboring unit cell. In the present case of the transition in $K_2HgCl_4 \cdot H_2O$, every unit cell is considered to have the identical structure which gradually changes with time. This type of transition may be termed a slow "Martensite transition" which does not accompany nucleation-and-growth[9].

The determination of the precise structure of the β modification*** seems to be very difficult because the unit cell is relatively large, being

$$a=16.51\text{Å},\ b=23.26\text{Å},\ \text{and}\ c=8.89\text{Å}$$

and containing 16 formula units of $K_2HgCl_4 \cdot H_2O$. This cell is four times as large as the unit cell in the α modification[4] owing to the appearance of the line ($2\theta=11.75°$) which may be indexed as inhibited ($1\,{}^1/_2\,0$) on the basis of the structure of the α form.

Rehydration of Anhydrous Crystals

$K_2HgCl_4 \cdot H_2O$ was dehydrated in the apparatus of the differential thermal

* 2θ value (twice the diffraction angle).

** It may not be immediately evident that the transition at 114°C from the α to the β form is of the same nature as that from the β to the α form occuring at room temperature. But there is no reason, at present, to believe otherwise.

8) Y. Saito, *X-sen*, 7, 9 (1952); Z. W. Wilchinsky, *J. Appl. Phys.*, 15, 806 (1944).

9) M. Cohen, "Phase Transformations in Solids", John Wiley & Sons, Inc., New York (1958), p. 588.

*** Kiriyama and Ibamoto[10] reported the structure of the high-temperature form of $K_2HgCl_4 \cdot H_2O$ by use of a high-temperature camera after prolonged heat-treatment at high temperature. Their experimental condition was very different from the present one. There are some discrepancies between their results and the results of the current investigation; for instance, the 11.75 line is missing from their X-ray photographs and therefore the unit cell dimentions are also different from those described here.

10) R. Kiriyama and H. Ibamoto, This Bulletin, 27, 317 (1954).

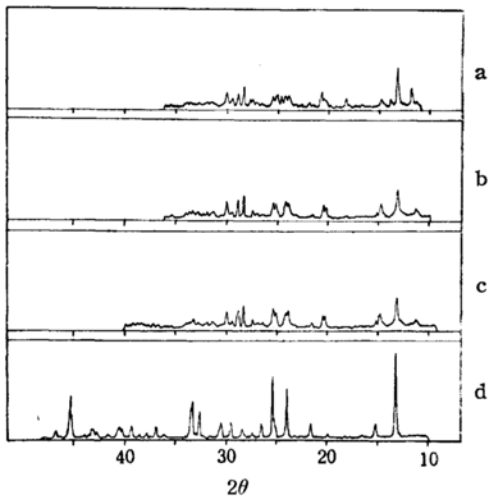

Fig. 7. Change of X-ray diffraction patterns due to rehydration of anhydrous crystal at room temperature; (a) Anhydrous phase, (b) after standing for 60 min. in the open air, (c) after 140 min. (d) after 30 hr. (α-modification of the hydrate).

analysis and it was immediately transferred to the goniometer of the Norelco X-ray diffractometer. It was observed that rehydration occurred in the open air at room temperature, at a measurable rate. This series of diffraction patterns, which is a cinematogram of the rehydration reaction, is reproduced in Fig. 7. It took about 30 hr. at about 30°C for the complete rehydration. This is a comparatively rapid rate of rehydration and therefore it is confirmed that the measurements of the dehydration pressures of the crystalline hydrate correspond to the equilibrium property of the system.

Summary

The dehydration pressures of the crystalline $K_2HgCl_4 \cdot H_2O$ are measured and given by $\log P = 8.538 - (2161/T)$ with P expressed in mmHg. No thermal hysteresis effect was observed. Production and some experiments for partly amorphous hydrate are briefly discussed. A consideration of the entropy of dehydration led to the conclusion that the dehydration is zeolitic. The differential thermal analysis revealed that there is a non-dehydrating transition at 114°C and that the dehydration occurs at 123°C. Infrared spectra of the solids showed that the 6-micron band of water persisted between 114 and 123°C. The X-ray study of the transition at the supercooled condition showed that this is a transition quite different in nature from those of ordinary nucleation-and-growth mechanism. The rehydration of dehydrated crystals was followed by the X-ray diffraction method and found to be relatively rapid at room temperature.

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Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka