Thermodynamic study of ice and clathrate hydrates*

Hiroshi Suga, Takasuke Matsuo and Osamu Yamamuro

Department of Chemistry and Microcalorimetry Research Center, Faculty of
Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract – Although glass transition phenomenon has been believed to occur in
an undercooled liquid, evidence has accumulated in recent years to indicate
that some orientationally disordered crystals also exhibit behavior which is
phenomenologically similar to the glass. The freezing-in disordered states of
orientational degree of freedom, keeping the translational symmetry with re-
spect to the center of mass, are designated as glassy crystals. The existence
of glassy crystals requires an extension of the concept of glass transition.
Ice and clathrate hydrates turned out to belong to one category of glassy
crystals in which the reorientational motions of molecules freeze out owing to
prolonged relaxation time before the samples reach their hypothetical transi-
tion temperatures on cooling. Particular impurity incorporated into their
lattices was found to relax locally the ice rules which severely constrain the
reorientational motion in these hydrogen-bonded systems. This article reviews
the discovery of orientational ordering processes in ice and clathrate hydrates
doped with small amounts of alkali hydroxides. Both of them have similar
geometrical arrangements of the hydrogen-bonded networks with orientational
disorder of water molecules at high temperature. The ordering transition
removes substantially the entropy corresponding to the disorder and thus con-
firms the validity of the third law of thermodynamics. The apparent deviation
of these crystals from the law is merely due to a limited time of our laborato-
ry experiment.

INTRODUCTION

Our planet is covered by a great amount of water and ice (ref. 1). The ocean alone is
estimated to contain 10^{21} kg of water. Ice exists mainly in the polar areas. The
Antarctic Continent is covered by about 10^{19} kg of ice and snow. One tenth of this
quantity exist sporadically in Greenland and various glaciers all over the world. The
study on structures and properties of water and ice is undoubtedly one important subject
of physics and chemistry for its own interest and also from the viewpoint of proper
utilization of valuable natural resources. The word crystal originates from the Greek
"Krustallos" which means ice. Ice has been regarded from the ancient time as one of
typical crystalline materials surrounding us. In spite of this fact, ice has long been
known to deviate from the third law of thermodynamics (ref. 2) which a pure crystalline
substance should obey.

From the structural point, ice is composed entirely of O–H···O hydrogen bonding. Each
water molecule in ice can be regarded as forming a tetrahedron with an oxygen atom at
its center, with a hydrogen atom at each of two of the four tetrahedral positions, and
with a lone pair of electrons at each of the two remaining tetrahedral positions. The
spatial arrangement of the oxygen atoms in hexagonal ice is the same as that of the
tridymite form of silica. Thus the geometrical requirements imposed on proton donors
and acceptors for the formation of hydrogen bonding is ideally realized in the ice
crystal. The O···O distance in ordinary ice is 276 pm and this distance provides a
double minimum potential for the hydrogen atom in the hydrogen bond. Many interesting
properties of the hydrogen-bonded crystal arise from this disordered nature of hydrogen
atoms with respect to its position, or alternatively orientational disorder of water
molecule. Thus various types of phase transition due to order-disorder process of
hydrogen atoms have been studied so far in many hydrogen-bonded systems. This was

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typically observed in KH_2PO_4 (ferroelectric) (ref. 3), $K_4Fe(CN)_6 \cdot 3H_2O$ (ferroelectric) (ref. 4), $Cu(HCOO)_2 \cdot 4H_2O$ (antiferroelectric) (ref. 5), and $NH_4H_2PO_4$ (antiferroelectric) (ref. 6). Some crystals exhibit first-order transitions associated with the order-disorder processes, some second-order transitions. The phase transitions are accompanied by crystal symmetry changes as described by the Landau theory. An exception is $SnCl_2 \cdot 2H_2O$ crystal (ref. 7), in which the order-disorder process is accompanied by heat capacity divergence around the critical temperature without any crystallographic symmetry change (ref. 8). An important question that had been raised was why the disorder in ice crystal could not be removed by a phase transition. Any heat capacity anomalies that could be ascribed to a phase transition had not been observed.

Similar situation occurs in clathrate hydrates (ref. 9) which are also found in nature in a large quantity. The clathrate hydrates seem like ice and exist in many ocean sediments or land deep below permanently frozen ground, permafrost. We may extract energy by decomposing the seemingly ice crystals when the next energy crisis visits us in a future. On the other hand, the green-house effect due to increased carbon dioxide in air will accelerate decomposition of these natural gas hydrates and the delivered gases like CH_4 or C_2H_6 enhance the green-house effect further. Thus the study of clathrate hydrates is important again not only as a basic science but also as an urgent subject of the environmental science.

The clathrate hydrates are composed of two kinds of molecules, the host and guest molecules (ref. 10). The host lattice formed by water molecules through hydrogen-bonding formation can accommodate various guest molecules of suitable size and shape in well-defined polyhedral cages. There exist two kinds of orientational disorder for the host and polyatomic guest molecules. The geometrical arrangements of hydrogen bonds in the clathrate hydrates are not much different from that of ice crystals. Again, any indication of the heat-capacity anomaly due to a possible ordering transition of the host water molecules has not been observed in spite of endeavor by many scientists (ref. 11). The absence of ordering transition in ice and clathrate hydrates limited the validity of the third law of thermodynamics. It is the purpose of this article to describe briefly our discovery of order-disorder transitions revealed calorimetrically in these hydrogen-bonded systems.

EXPERIMENTAL

Among many experimental techniques for detecting transitions in condensed systems, adiabatic calorimetry is one of the powerful method in that it provides information on the entropic aspect of a system in addition to heat-capacity anomaly as an indication of the transition. Entropy can be correlated with the nature of relevant disorder of the system. The adiabatic calorimeter has long been improved to a highly sophisticated level since the era of Nernst, and has a long-term stability of the adiabatic condition and high resolution of the temperature measurement. This is particularly profitable for the study of phase transition and glass transition phenomena. We have developed essentially two types of adiabatic low-temperature calorimeters. One is for use under atmospheric pressure (ref. 12) and the other under high pressure up to 0.25 GPa (ref. 13). Both of them are operated in a discontinuous heating mode in which the measurement proceeds as successive of energizing and equilibration periods.

In the equilibration period, the temperature drift rate due to residual heat leakage is of the order of several mK h^{-1} in most of the temperature range. Any temperature drift rate exceeding this magnitude is an indication of relaxation of the sample from a frozen-in nonequilibrium to equilibrium state with respect to some degree of freedom of the constituent molecules (ref. 14). The continued measurement of the calorimetric temperature as a function of time gives the basic data from which the relaxation time of the relevant motion can be calculated. The heat effect thus determined is directly related to the entropy production which characterizes the irreversible change. Thus an adiabatic calorimeter can work as a time-domain spectrometer in the range of 0.1 ks ~ 1 Ms while being engaged in the heat capacity determination (ref. 15). The calorimetric temperature is measured by an Fe-Rh resistance thermometer in conjunction with an ac double bridge. The input energy is determined using a digital multimeter. All the operations are computerized with a preset program so that the heat capacity is calculated immediately after a cycle of measurement is finished. This automation has removed human factors from the time-consumed and laborious measurement, and is indispensable for the study of relaxation phenomena which often last for days or months.

RESULTS AND DISCUSSION

Hexagonal ice

The experimental values of residual entropy of ordinary and heavy ices have been shown that the hydrogen atoms lie closer to one oxygen atom than to the other in the hydrogen bond, each oxygen atom having two hydrogen atoms near it, about 100 pm away, and two at a larger distance of about 176 pm. This asymmetric structure of the hydrogen bond in hexagonal ice has been verified by neutron diffraction. The rules that govern this disordered structure keeping neutral species all the times are called "ice conditions" (ref. 16). The disorder is dynamic even though the ice conditions severely restrict the reorientational motion of the water molecules. This is evidenced by their high dielectric constants near their melting temperatures. The value of dielectric constant of hexagonal ice I_h as high as 100 arises from the orientation polarization of water molecules which are able to respond to an external ac field. This is shown schematically in Fig. 1. As the temperature is lowered, the dielectric relaxation time becomes progressively longer, and finally an ice specimen reaches a temperature at which the molecules are not able to respond anymore to the sinusoidal change of the electric field. The relaxation time determined by the dielectric dispersion at 120 K is of the order of 10^2 s. The orientational disorder remains down to lower temperatures (ref. 17). In fact, our heat-capacity remeasurement (ref. 18) has clearly shown a glass transition in pure ice specimen. A small heat-capacity jump accompanied by systematic spontaneous temperature drift rates was found around 100 K at which the dielectric relaxation time was roughly 10^4 s. This is the time scale of a single heat-capacity determination. In this way, the dielectric dispersion phenomenon is correlated closely with the freezing-in process of the orientational disorder.
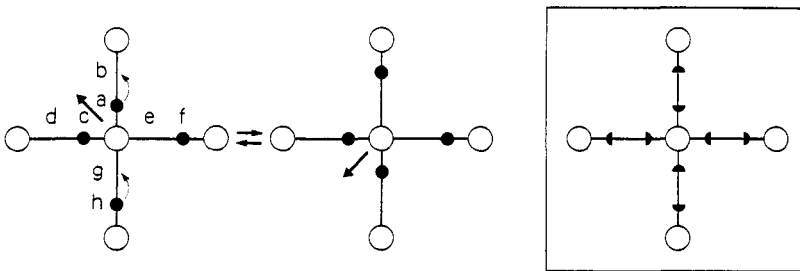

Fig. 1. Instantaneous configuration and its temporal change of ice represented schematically in two dimensions. The right is the time-averaged statistical structure.

Ida *et al.* (ref. 19) have found that the dielectric dispersion shifted to lower temperatures if an ice specimen was doped with some kinds of impurity. This evidences the acceleration effect of impurity incorporated into the ice lattice on the mobility of water reorientation. Molecular mechanism of this effect may be that the dopant breaks locally the ice conditions which impose severe cooperativity on the motion of water molecules as a whole. In fact, Onsager (ref. 20) had proposed that the possible order-disorder transition in ice should be tested for on an impure sample. Among other things, alkali hydroxides showed the most significant effect in shortening the relaxation time. This impurity was expected hopefully to reveal the ordering transition in ice crystal. As an example, the results of our heat capacity measurement on ices doped with KOH in three kinds of concentration are summarized in Fig. 2 In each measurement, the sample was annealed at around 65 K for three days. The subsequent measurement exhibited a long-sought-for heat capacity peak at 72 K (ref. 21). The transition temperature is independent of the kind of alkali ion and the amount of dopant, but the corresponding entropy change depended on the concentration of the dopant. The maximum entropy change 2.33 $JK^{-1}mol^{-1}$ was obtained for the sample doped with 1.9×10^{-3} mole fraction of KOH. Thus the transition removed the substantial part of the residual entropy. The extra peak around 210 K for the most heavily doped sample was due to eutectic melting of ice and $KOH \cdot 4H_2O$. It is worthy to note that the calorimetric measurement enables us to determine the slight solubility of impurity in the main component of the solid solution. It is this limited solubility of KOH which hinders the crystal to complete the transformation into the ordered phase.
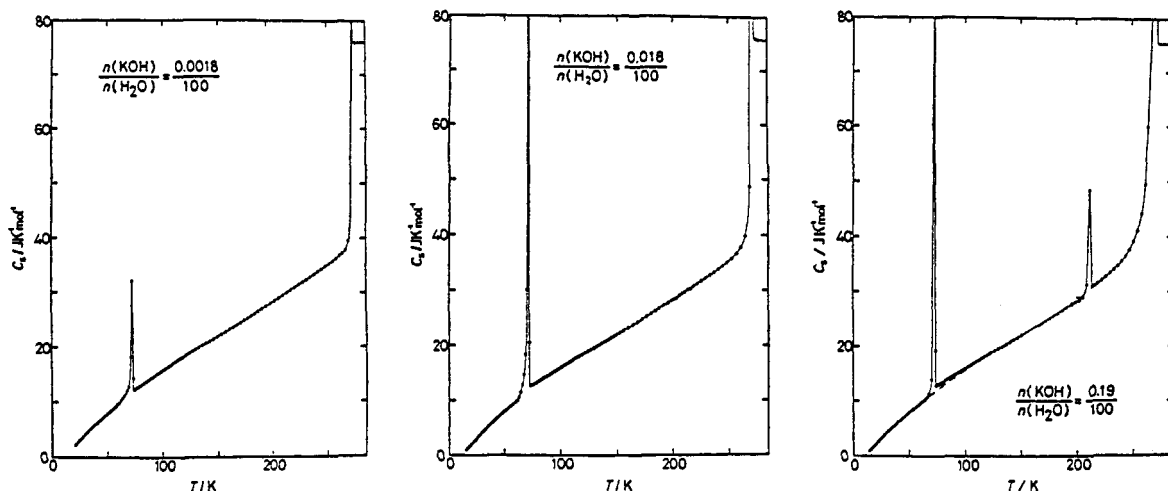
Fig. 2. Heat capacities of ice I_h doped with KOH in mole fraction of (left) 1.8×10^{-5}, (center) 1.8×10^{-4}, and (right) 1.9×10^{-3}.

Kawada (ref. 22) has measured recently the dielectric dispersion of ice I_h and found that the relaxation time of a KOH-doped specimen is shortened by a factor of 10^8 at 90 K than that of pure specimen. The activation energy was also reduced. This drastic change of relaxation time by dopant enabled us to realize the ordered ice in laboratory, instead of a geological time scale required for the pure specimen.

Neutron diffraction experiments (ref. 23, 24) have shown that the low temperature phase has the space group of $Cmc2_1$ and is polar along the original c-axis. This is consistent with the suggestion by Kauzmann (ref. 17) that the most symmetrical arrangements of hydrogen atoms in ice result in very large dipole moments along the unique axis of hexagonal lattice. Since the most symmetrical arrangements are also usually energetically the most stable, we should expect that at low temperature phase the ice crystal should become ferroelectric. Unfortunately, however, the extremely long relaxation time prevents experimental confirmation of the ferroelectric behavior in the ordered phase. The low-temperature ordered phase was designated as ice XI (ref. 25). A high-pressure adiabatic calorimeter using helium gas as a pressure-transmitting medium was applied to the I_h-XI phase transition (ref. 26). The results are summarized in Fig. 3.
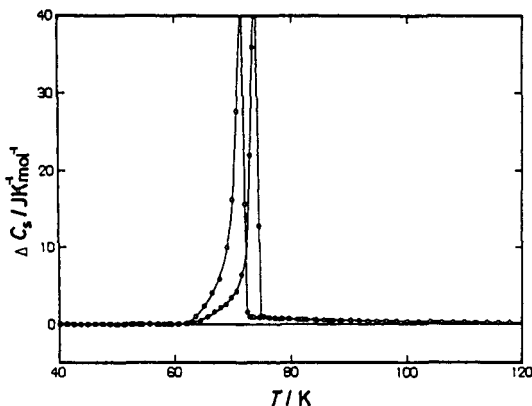

Fig. 3. Excess heat capacity of ice I_h due to ordering transition measured at 0.1 MPa($\circ$) and 159 MPa($\bullet$).

The transition temperature increases by 2.4 K by the application of 159 MPa, so that $dT_{trs}/dp = (0.015 \pm 0.001)$ KMPa^{-1}. Inserting this value to the Clausius-Clapeyron's equation, we obtain the volume change associated with the transition as $\Delta_{trs}V = (0.051 \pm 0.003)$ cm^{3}mol^{-1}. Ordering of the water molecules is thus accompanied by a relatively small volume change. This is generally true for the ordering transitions of high-pressure modifications of ice. Both the III-IX and VII-VIII transitions studied so far have small values of dT_{trs}/dp, reflecting the slight volume changes compared to rather large entropy changes.

Cubic ice

Cubic ice I_c exists also in nature (ref. 27) and is one modification of ice at atmospheric pressure. Ice I_c can be produced in laboratory by raising the temperature of amorphous ice (ref. 28) or any high-pressure forms (ref. 29) existing metastably at 77 K up to about 140 K. The crystals obtained by both processes transform irreversibly to ice I_h around 160~170 K on further warming. Owing to its metastability relative to I_h, cubic ice can not have citizenship in the p-T phase diagram of H_2O. Ice I_c is structurally similar to ice I_h, with an almost identical arrangement of the nearest neighbors, and by reason of symmetry is fully disordered with respect to the hydrogen atoms in the hydrogen bond. The spatial arrangement of the oxygen atoms is the same as that of diamond or the cristobalite form of silica. It is interesting therefore to examine whether the glass transition due to freezing of water reorientation can be found in ice I_c and whether the alkali hydroxides work to release the freezing as in the case of ice I_h.

In order to obtain the calorimetric specimen of ice I_c in a large quantity, the high pressure method was employed. Pure and KOH-doped water were pressurized by helium gas to 250 MPa at 300 K, cooled down to 77 K, returned to atmospheric pressure, and heated up to 150 K. Results of the heat capacity measurements as well as the corresponding temperature drift rates are summarized in Fig. 4, along with those of I_h (ref. 30). Here the heat capacity is converted to encraty (C_p/T) so that small heat capacity anomaly can be magnified in the plot. Spontaneous exothermic drifts followed by endothermic ones characteristic of the glass transition were observed around 140 K at which a small jump of heat capacity occurred. The anomaly increased with an annealing carried out just below the glass transition temperature. Thus the freezing out of water reorientational motion in I_c takes place about 30 K higher than that of I_h. The characteristic time for the enthalpy relaxation can be deduced by analyzing the data with approximation of exponential approach toward the equilibrium state. The relaxation time data thus obtained are plotted in an Arrhenius form giving a straight line. The activation energy is 38.0 kJmol^{-1} and is higher than that of pure ice I_h, 22 kJmol^{-1}. The doping effect of KOH was not signicant as that of ice I_h. The dopant did not induce a nexpected ordering transition but only lowered the glass transition temperature by about 30 K. The initial concentration of KOH in aqueous solution was 1.8×10^{-3} mole fraction. The dopant was probably rejected out of the sample by pressurizing. Ionic impurities are known to segregate from the

Fig. 4. (upper) Encraty(C_p/T) and (lower) spontaneous temperature drift rate of ice I_c. $\circ\, I_c$ cooled at 0.8 Kmin^{-1}, $\triangle\, I_c$ annealed at 133 K for 21 h, $+\, I_h$ cooled at 0.6 Kmin^{-1}.

high-pressure forms of ice and this provides one of the best methods for purification of water. An aerosol method (ref. 31), in which KOH aqueous solution is atomized ultrasonically to form micro-droplets and condensed on a cryoplate, will be an appropriate candidate to prepare the doped I_c specimen. This has not been done yet. Theoretically, the ordering transition in cubic ice is expected to occur at 60 K (ref. 32).
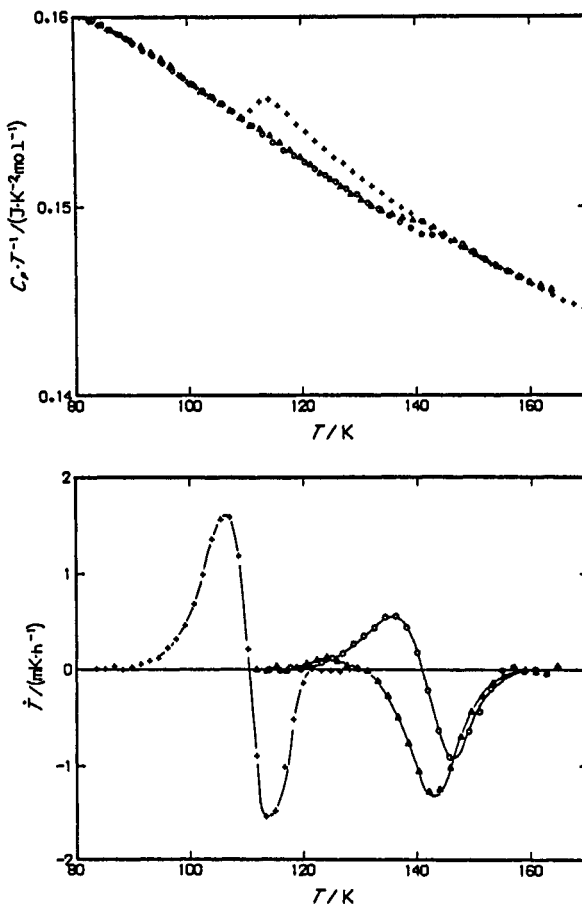
Tetrahydrofuran (THF) clathrate hydrate

Clathrate hydrates are one kind of clathrate compounds generically termed. They constitute a class of solids in which small molecules of suitable size and shape are enclathrated in almost spherical cavities in ice-like lattices made up of hydrogen-bonded water molecules. Two types of widely known clathrate hydrates are schematically drawn in Fig. 5. In both of the clathrate hydrates, the interaction between the host water and guest molecules is so weak that the host lattice can be regarded as one of ice polymorphs. There are two kinds of disorder in the clathrate hydrates encaging polyatomic guest species. The host lattice built up of the hydrogen bonds has orientational disorder similar to ice I_h. The guest molecules are also orientationally disordered inside the cages. This double disorder is a special feature of the clathrate hydrates and its ordering phenomena are one of the most interesting thema of clathrate-hydrate research. Dynamical aspects of the constituent molecules have been studied extensively by Davidson *et al.* (ref. 33) by using NMR and dielectric methods. For the clathrate hydrates including polar guest molecules, they found two kinds of dielectric dispersion. One occurring around 160 K at 1 kHz is due to freezing out of reorientational motions of water molecules. The other occurring at cryogenic temperatures is due to freezing out of the guest motions. The maximum dielectric loss occurs around 12 K for trimethylene oxide, 20 K for acetone, and 21 K for THF measured at 1 kHz, respectively. These molecules form the structure II hydrate and are encaged only in the larger 16-hedral cages. There are 136 water molecules in the unit cell. The ideal formula for the full occupation of the structure II hydrates is therefore G·17H$_2$O, where G is the guest species.
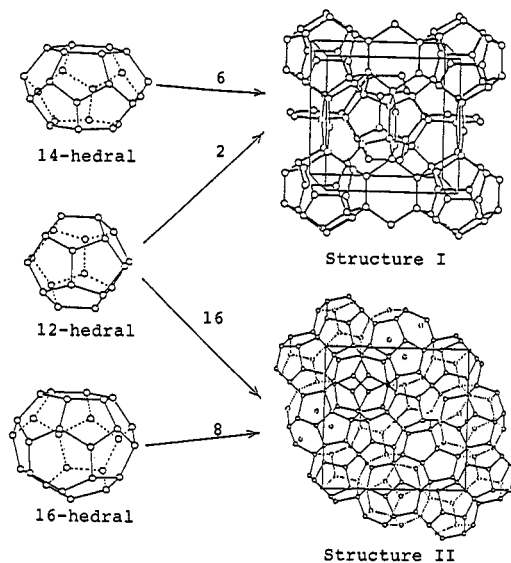

Fig. 5. Crystal structures of type-I and -II clathrate hydrates composed of three kinds of Archimedes' polyhedra.

THF hydrate undergoes congruent melting (ref. 34). Therefore an aqueous solution of THF in almost ideal composition is kept around 0 °C in situ in a calorimetric cell to form easily a specimen for the measurement (ref. 35). The results of heat capacity measurement are given in Fig. 6. A glass transition was observed around 85 K with a small heat-capacity jump of relaxational nature. The data agrees closely with those reported by White and MacLean (ref. 36) who have, however, not mentioned the existence of the anomalous behavior. The enthalpy relaxation time is 3.85 ks at 80.8 K and agrees with the extrapolation of the dielectric relaxation time data reported by Davidson et al. (ref. 34) in an Arrhenius plot. The activation energy for the water reorientation is 19.4 kJmol^{-1} which is slightly lower than that of ice I_h.

Doping effect of KOH on the enhanced mobility was tested again. Actually the specimen of THF hydrate doped with 1.8×10^{-4} mole fraction of KOH showed a first-order phase transition at 61.9 K (ref. 37). These results are summarized in Fig. 7. In this case, the transition takes place rapidly without any sluggish nature as in the case of ice I_h. The associated entropy change is 42.6 JK^{-1}mol^{-1} for THF·16.64H$_2$O or 2.56 JK^{-1}mol^{-1} for mole of H$_2$O. The latter value is close to that of ice I_h. The excess heat capacity over an appropriately estimated baseline has a long tail above the transition temperature, indicating the persistence of short-range ordering effect. The high-temperature tail of the excess heat capacity agrees well with that of pure specimen. Configurational entropy of disordered hydrogen atoms in clathrate hydrates has not been determined experimentally. However, the Pauling value $R\ln(3/2)=3.37$ JK^{-1}mol^{-1} should give a good estimate in view of the local similarity of the hydrogen-bond networks of ice I_h and the clathrate hydrates.
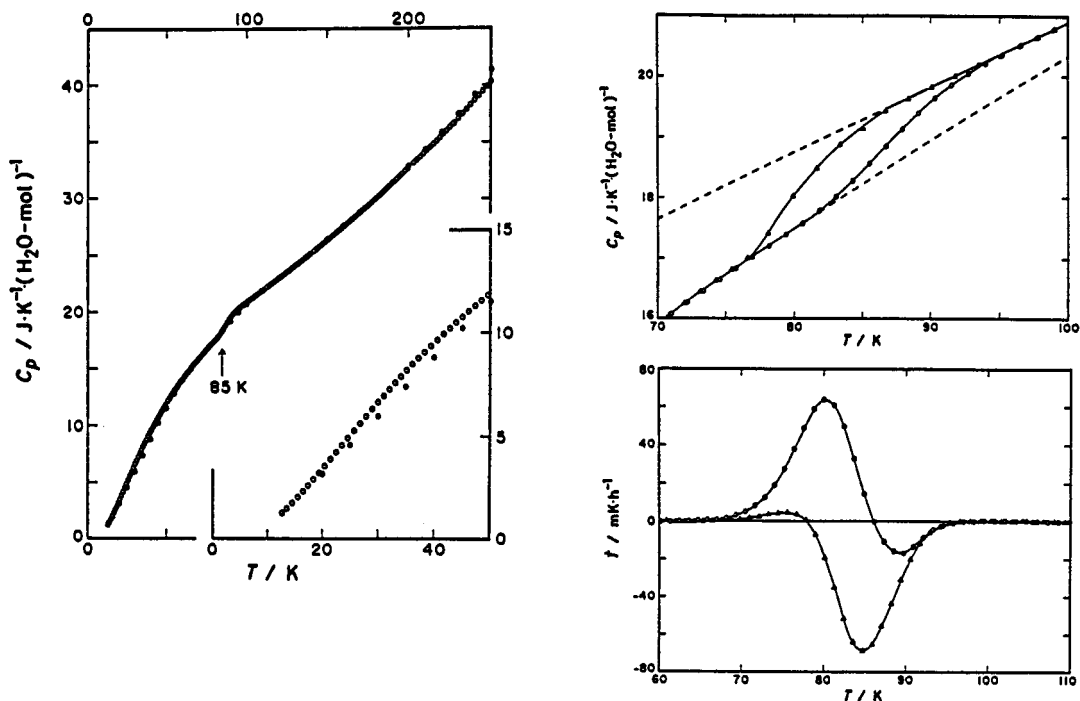
Fig. 6. (left) Molar heat capacity of THF·16.64H$_2$O crystal. (right) Heat capacity jump and spontaneous temperature drift rate of THF·16.64H$_2$O crystal.
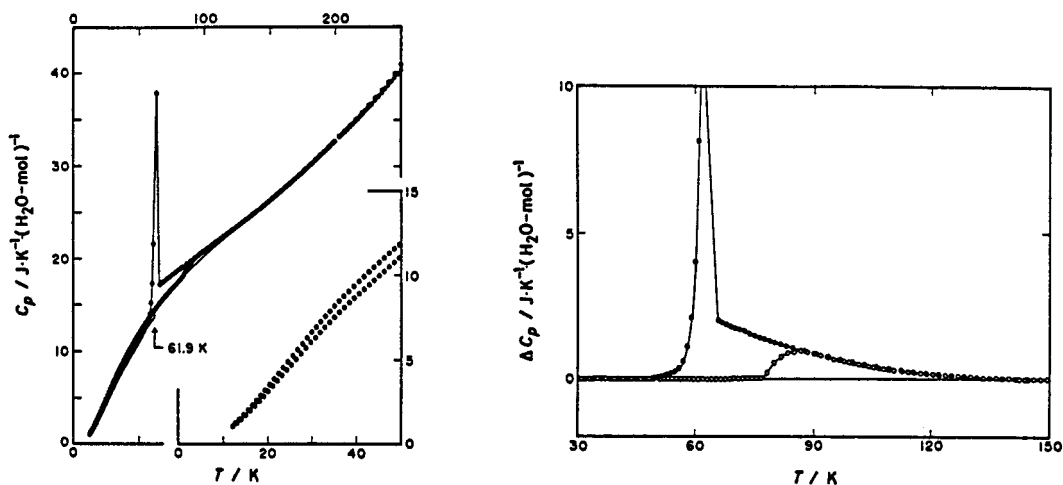

Fig. 7. (left) Molar heat capacity of THF·16.64H$_2$O crystal doped with KOH of 1.8x10^{-4} mole fraction. (right) Excess heat capacity of KOH-doped THF hydrate crystal showing a significant persistence of short-range ordering effect.

Thus the transition removed a substantial fraction of disorder due to the water molecules. A dielectric measurement (ref. 38) of pure and KOH-doped THF hydrates showed that the guest molecules ordered concomitantly at the phase transition. The audio-frequency dielectric constant below the transition temperature is practically identical to ε_∞ of the crystal. One might imagine that the guest molecules could still rotate in the clathrate cavity even when the water molecules forming the cavity wall were ordered in the low-temperature phase. It may be that the ordering of water dipoles produces a strong electric field at the guest site which gives a preferred orientation to the dipolar guest molecule. The alignments of the guest molecules in the low-temperature phase will depend on the manner by which the water dipoles order. The clathrate hydrate including argon molecule (ref. 39) as the guest does not show any anomalous behavior of the heat capacity. KOH dopant incorporated in the mole fraction of 1.8x10^{-3} does not induce the ordering transition but does exhibit only a glass transition around 55 K. In

passing, this hydrate crystal represents a model substance of "particle in a potential box" and the heat capacity contribution from rattling motion of the guest molecule in each cage can be analyzed in terms of Pöschl-Teller potential function.   In this way, the dipole-dipole interaction among all the dipolar species will play an important role in the appearance of the phase transition of the clathrate hydrates.

Acetone clathrate hydrate

Acetone molecules are enclathrated in the 16-hedral cages of the structure II host lattice as in the case of THF hydrate.   The acetone molecule has a larger van der Waals diameter of 630 pm and dipole moment of 9.6×10^{-30} Cm than the corresponding quantities 590 pm and 5.4×10^{-30} Cm of the THF molecule.   This situation provides us a good system on which to investigate the effect of nature of guest molecule on the static and dynamic properties of clathrate hydrates.   Acetone-water binary system has an incongruent-type phase diagram with stoichiometric composition around $C_3H_6O \cdot 17H_2O$.   Temperatures of the peritectic and eutectic melting are reported to be 253 K and 176 K, respectively.   When the aqueous solution with the stoichiometric composition was cooled, ice formed first around 267 K and the acetone hydrate was formed below 253 K through the reaction between the ice and the remaining acetone-rich solution.   Thus the mixture was annealed at several temperatures below the peritectic point for about one month until the completion of the clathrate formation was indicated by the gradual ceasing of the exothermic effect due to the heat of the peritectic reaction.
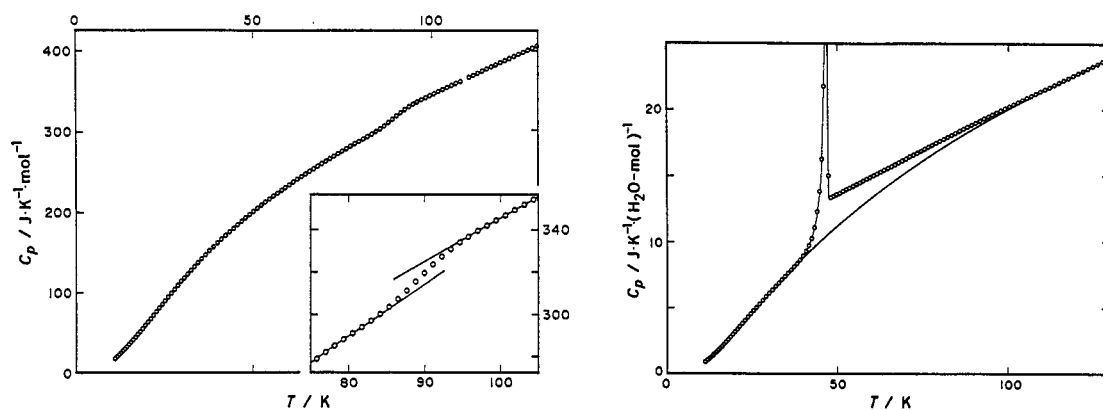

Fig. 8.   (left) Molar heat capacity of $C_3H_6O \cdot 17.00H_2O$.   (right) Molar heat capacity of $C_3H_6O \cdot 16.97H_2O$ doped with KOH of 1.8×10^{-4} mole fraction.

Figure 8 shows the molar heat capacity of acetone hydrate based on 1 mole water for the pure and KOH-doped specimens (ref. 40).   No phase transition was observed in the temperature range but a glass transition with a heat-capacity jump of 12 $JK^{-1}mol^{-1}$ appeared in the pure specimen.   The enthalpy relaxation times are 23.4 ks at 80.2 K, 0.51 ks at 92.3 K, and fall closely on the extrapolation of the dielectric relaxation times.   The activation energy is 21.2 $kJmol^{-1}$.   These data are consistent with the statement (ref. 33) that the dielectric relaxation time is not much influenced by the polarity of the guest species.   For the specimen doped with KOH in the mole fraction of 1.8×10^{-4}, a first-order phase transition appeared at 46.6 K.   Again, the doping effect of KOH on releasing the freezing process is significant.   The short-range order persisting above the transition temperature is also noticeable.   The corresponding entropy change is 42.1 $JK^{-1}mol^{-1}$ for $C_3H_6O \cdot 16.97H_2O$ or 2.48$JK^{-1}mol^{-1}$ for 1 mole H_2O basis.   One unexpected thing is that the transition temperature of acetone hydrate is lower than that of THF hydrate, in spite of the fact that the dipole moment is 1.8 times larger than that of the THF molecule.   If the dipolar interactions among the guest-host and guest-guest molecules are crucial, and the crystal structure of the low-temperature phase is the same in both clathrate hydrates, one might expect a higher transition temperature for the acetone hydrate.   We must consider, therefore, different sources of the intermolecular interactions other than the dipole-dipole energy in seeking factors that stabilize the low-temperature phase.   One factor would be a possible formation of hydrogen bond between the guest and host molecules.   We have no reason to expect the same ordered structure of the low-temperature phase.   Therefore,

neutron diffraction experiments of these hydrate crystals including the position of hydrogen (deuterium) atoms play a key role in understanding the unexpected behavior. A preliminary experiment on a fully deuterated THF clathrate hydrate showed that the low-temperature diffraction peaks were too broad to be suitable for the structure determination. This may be due to severe strain or deformation of the lattice caused by the phase transition. The diffraction peaks of the high-temperature phase were sharp enough to determine the disordered structure and the result will be reported in due time.

Role of dopant

At first glance of Fig. 2, one may argue that the 72 K peak is associated with a transition of KOH or its hydrate species, because the magnitude of the excess peak increases with the increased amount of dopant. This argument is, however, disproved clearly by the entropy consideration. The entropy of transition becomes of the order of 1000 $JK^{-1}mol^{-1}$ on the basis of KOH mole. In condensed systems, it is not possible to imagine any disordering process with an entropy change which exceeds much that corresponding to the vaporization ($\sim$100 $JK^{-1}mol^{-1}$). Therefore the role of dopant is to accelerate the reorientational motion of the water molecules and to reveal its intrinsic order-disorder transition which has been concealed for the kinetic reason for a long time.

As has been stated earlier, the relaxation time of ice I_h decreases by a factor of 10^8 at 90 K on doping of KOH. This shortening effect made it possible to realize the ordering process in ice within a reasonable time. The acceleration effect is more significant in the case of the clathrate hydrates. For the THF hydrate, the reduction factor is 10^{10} and for the acetone hydrate 10^{12} at 70 K. In each case, the dopant shortens the relaxation time and reduces the activation energy.

It is worthy to consider here the molecular mechanism of the dramatic acceleration effect of KOH dopant on the water reorientational motion in these systems (ref. 41). Examination of an ideally hydrogen-bonded networks in ice shows that reorientation of the water dipole in any manner that remains the hydrogen bonding with the intact unit of H_2O is not possible without the cooperation of neighboring molecules, as has been pointed out by Debye. The most plausible mechanism proposed to account for a possible reorientation is that of Bjerrum (ref. 42). A fluctuational misorientation of a water molecule about one of its hydrogen bonds results in the formation of a pair of two defect bonds, a D(doppel) bond bearing two protons and an L(leer) bond bearing none. Once formed, the pair may separate by successive reorientations of the neighboring water molecules. The process of diffusion of these orientational defects makes it possible to reorient the water molecules with less activation energy than that of the pure ice, owing to the temporary break of the highly cooperative chain process. The hydroxyl ion of KOH can replace the water molecule in the lattice and introduces necessarily an ionized vertex together with an orientational L defect. The negatively charged ion attracts more easily neighboring protons than in the case of neutral species, and re-duces effectively the activation energy for the diffusion of the defect.

It is also probable that the charged hydroxyl group disturbs the ice lattice severely and has a great effect on the mobility of protons or water reorientation. We cannot rule out, however, an important polarization effect of alkali ions which may find a low energy interstitial binding sites (ref. 43) near the center of the puckered hexagons of hexagonal ice. Thus the role of dopant is to release the hydrogen-bonded system from the kinetically immobilized state to the equilibrium state and to reveal the intrinsic property. The dopant acts like a sort of catalysis and we shall need a new definition to denote the process; perhaps doping chemistry.

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