ORDERING PROCESSES IN SOME DISORDERED SYSTEMS*

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Abstract - Modern development of the low-temperature adiabatic calorimeter mekes it possible to detect slight spontaneous temperature changes due to freezing of some of the degrees of freedom of a system. Measurements of the rate of the temperature drift as well as the residual entropy of the system are used for thermal characterization of the non-equilibrium nature of the state of the system. The glassy states observed in this way are classified according to the type of disorder that is brought into the non-equilibrium state and to the stability of the phase that produces the glassy state. A phase transition observed recently in hexagonal ice crystals is discussed with respect to its kinetic features as well as its historical background. An important difference between the glassy states realized in the metastable and the stable phases is discussed from the view-point of Kauzmann's paradox.

INTRODUCTION

Disorder prevails in various condensed phases of matter (1, 2). Modern material science started with the study of crystals which have the highest degree of spatial order in nature, and recently shifted its center of interest to encompass various disordered systems; meso-phases like orientationally disordered crystals or liquid crystals, isotropic liquids and so on. If such a disordered system is cooled, in principle one of the following two things can happen. The disorder either remains, so that there would still be disorder at the lowest temperature, or disappears if the system undergoes a phase change into an ordered state. For example, a liquid as representative of the disordered system becomes usually an ordered crystal through the freezing point. Sometimes a liquid crystallizes into a disordered crystal and the crystal may have to pass through more than one transition before realizing a completely ordered state. Phase transition in crystals have been one of the main subjects of heat-capacity calorimetry. Many advances have been established in the interdisciplinary field of phase transitions and critical phenomena (3).

If the cooling rate is high enough to prevent crystallization, the liquid can keep its undercooled form and finally goes over to glassy state. The entropy associated with the dis-order of the liquid can be removed to some extent during this kind of ordering process. Thermodynamic study of the glassy state was initiated by the pioneering work of Gibson and Giauque (4). They found that the glassy state obtained by undercooling of liquid glycerol shows a glass transition and has residual entropy. These two features have been used for the thermodynamic characterization of the glassy state. Nowadays, it is widely agreed that these phenomena arise from the rapidity of the cooling process as compared with the rate of structural change in the undercooled liquid. The glass-transition temperature is looked upon as the temperature at which the disorder of the liquid is frozen on cooling on the laboratory time scale. Thus, the glass transition is caused by a relaxational effect, through which some processes in the disordered system occur too slowly at low temperatures to permit thermodynamic equilibrium to be established in all degrees of freedom during a finite time. The present article gives a historical survey and describes some recent studies of the order-ing processes in several disordered systems that have been undertaken by the chemical thermo-dynamic group of Osaka University.

FREEZING-IN PROCESS IN A METASTABLE UNDERCOOLED PHASE

The freezing process of orientational disorder in crystals was first studied on cyclohexanol crystals by dielectric loss measurements with a rather uncommon technique. When a dielectric with a polar group is placed in an alternating electric field, it absorbs energy from the field, the amount of which is proportional to the dielectric loss ε'' of the material, to the square of the strength, and to the frequency of the field. The absorbed energy is converted

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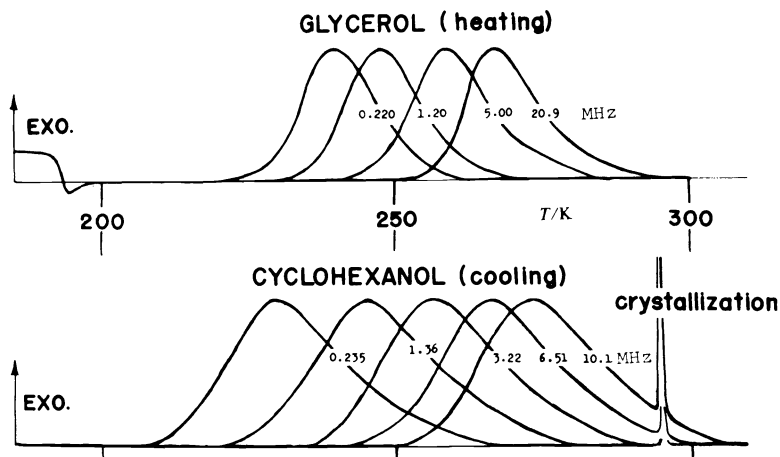
Fig. 1.   DTA curves of glycerol and cyclohexanol under alternating
electric field.

ultimately into thermal energy, being a typical irreversible process. This suggested the
possibility of measuring the dielectric loss factor by temperature measurement. In fact we
have abserved this effect by using a differential thermal analysis technique (5).
Electrodes for applying the field are a pair of aluminum foils attached to the outer surface
of a glass tube, in which the specimen is held. The electrodes are electrically insulated
by a thin sheet of polyethylene from a copper block, into which the sample tube and a
reference tube are inserted.

When we applied this technique to the study of molecular motion in undercooled liquid
glycerol and the undercooled high-temperature phase of crystalline cyclohexanol, we en-
countered an unexpected result as shown in Fig. 1. The upper curve is for glycerol.
Glycerol has its melting point at 291 K, but the liquid can easily undercool. No peak due
to the melting does appear in the curve. An exothermic broad peak due to the dielectric
loss appears in the undercooled liquid, at a temperature depending on the applied frequency.
A small anomaly around 180 K is due to the glass transition and the temperature corresponds
approximately to 10^3 s for the dielectric relaxation time of glycerol. This value
corresponds to the proposal by Kauzmann (6) in defining the glass-transition temperature.
The lower curve is for cyclohexanol. Liquid cyclohexanol crystallizes into a fcc lattice at
299 K, in spite of ·the fact that the molecule itself has only a mirror symmetry at most.
This indicates the highly disordered nature of the orientational degrees of freedom of the
constituent molecules. This feature is reflected in the fact that the peak due to the
crystallization is superposed on the high-temperature side of the dielectric loss peak
without breaking the continuity of the latter. The high-temperature phase has a transition
temperature at 265 K, but can easily undercool. Again, there appears a dielectric loss peak
in the undercooled high-temperature phase. A small anomaly essentially similar to the glass
transition of glycerol was found to occur at 150 K, which is not shown in the figure. The
temperature again corresponds to 10^3 s for the dielectric relaxation time in the undercooled
phase. When these observations were made, their interpretation was by no means clear.

Two years later we made heat capacity measurements (7) on the crystal. Figure 2 shows the
heat capacity data of the low-temperature crystal(II), the high-temperature crystal(I), the
undercooled crystal I and the liquid. From a comparison of the calorimetric and spectro-
scopic entropies of gaseous cyclohexanol, crystal II was found to obey the third law of
thermodynamics. In addition to crystals I and II, there exists a metastable crystal III, and
this crystal III, like II, becomes perfectly ordered at 0 K. However, a loop calculation of
entropy change along the crystal II, II-I transition, crystal I and the undercooled crystal
I showed that the undercooled crystal I retained entropy of 4.72 $JK^{-1} mol^{-1}$ at 0 K. The
amount far exceeds the experimental uncertainties. This kind of experiment was first done
by Kelley (8), but he concluded that the undercooled crystal I approaches zero entropy at 0
K. Also, he did not mention any relaxational nature of the heat-capacity anomaly observed
around 150 K. Figure 3 shows the enthalpy relaxation phenomena observed for the undercooled
crystal I below the "glass transition" temperature T_g. The dotted line ABC is an assumed
equilibrium curve obtained by extrapolating the enthalpy-temperature curve from above T_g.
The enthalpy curve of a rapidly cooled specimen is shown by the broken line AHK. The
enthalpy relaxation, the rate of which is observed by the rate of spontaneous temperature
increase or decrease under adiabatic conditions, was observed at several temperatures below
T_g. For example, the configurational enthalpy at 141 K changed from point I to E during 25
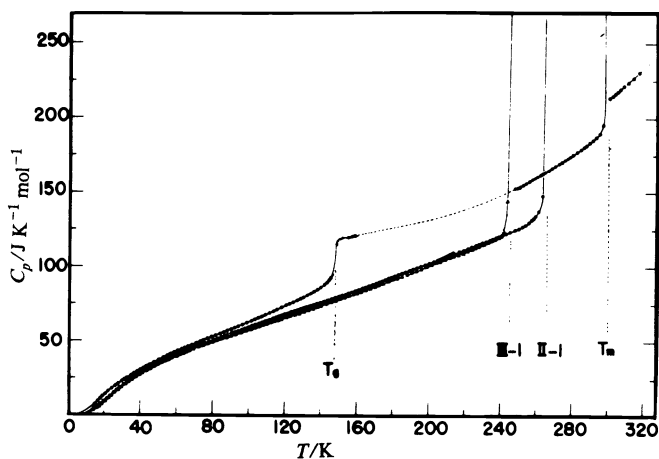
Fig. 2. Heat capacity of cyclohexanol.

h and then traced the curve EFG upon heating. Assuming an exponential approach towards the equilibrium value during the quasi-isothermal annealing process, the relaxation time τ was calculated as a function of temperature.

The heat capacity jump together with the relaxational nature as well as the existence of the residual entropy of the undercooled crystal I are characteristic properties of glass. On the other hand, such properties of the crystal as its sharp melting point and its ability to give an X-ray Laue photograph are typical of a crystal. We proposed the name "glassy crystal" for the orientationally frozen crystalline state realized below T_g, from the view-point that this is a new kind of state of aggregation of molecules. The discovery of many examples (9) of glassy crystal and of glassy liquid crystal (10), the latter being considered as the frozen-in disordered state of the counterpart of the dual nature of disorder existing in liquids, led us to conclude that the ordinary glass transition is just one example of a class of glass transition occurring widely in nature.

The discovery of glassy crystals immediately suggested the possible existence of several glass transition phenomena for differently disordered phases of one and the same substance. Actually clear evidence for this was obtained for cyclohexene (11). Two kinds of glassy crystal, one derived from crystal I and the other from a metastable crystal III, were obtain- ed in addition to the glass given by the undercooled liquid. The values of the glass transition temperature do not differ greatly. The other interesting example was provided by ethanol (12). Since the heat capacity measurements by Gibson et al. (13), this compound has been accepted for about 50 years as one of the typical low-molecular-weight materials which form a glassy state from the undercooled liquid. However, our DTA measurements showed that an extremely rapid cooling (more than 50 K min^{-1}) of liquid is required to realize the glassy state. If the cooling rate is moderate (1$\sim$2 K min^{-1}), a metastable crystal II is formed first and then goes over to a glassy crystal II . The heat capacities of these forms as well as of the stable crystal I were measured and the results are shown in Fig. 4. The corresponding entropy diagram is given in Fig. 5. It is interesting to note that the glass tran- sitions for undercooled phases of liquid and orientationally disordered crystals take place at essentially the same temperature. This observation suggests the importance of the role of reorientational motion (6) in determining the relaxational nature of the configurational change in the vitrification process of the liquid. Also, it is worth noting that the heat capacities reported previously for the "under- cooled liquid" by three groups (13,14,15) agree well with those for the metastable crystal II . It would appear that all the previous workers in the last 60 years have realized the glassy crystalline state in their calorimetric cell.
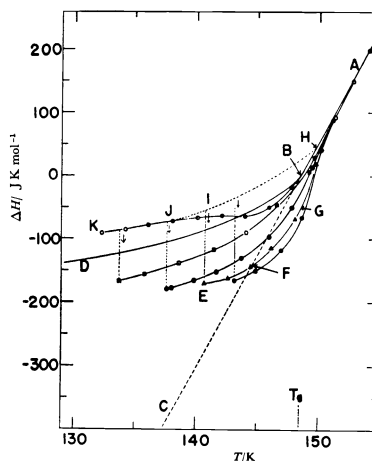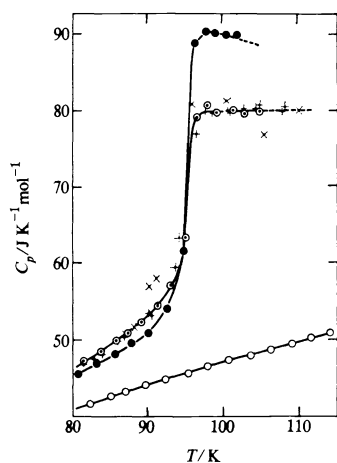

Fig. 3. Enthalpy relaxation of cyclohexanol.

Fig. 4. Heat capacities of ● , glassy liquid;
⊙ glassy crystal-Ⅱ ; and ○ , crystal-I of
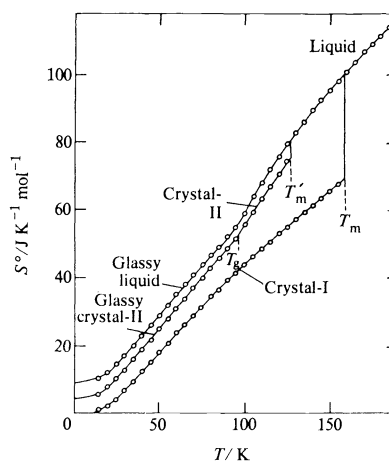ethanol. The literature values are shown by
× (Parks) and by + (Kelley).

Fig. 5. Entropy diagram of ethanol.

FREEZING-IN PROCESS IN STABLE CRYSTALLINE PHASES

We now extend the concept of the glassy state so that the glass transition is regarded as the boundary between dynamic and static disorder regardless of the nature of the disorder. We can then expect that the glass transition could take place not only in a metastable under-cooled state but also in a stable crystalline state. The freezing phenomenon was observed experimentally in $SnCl_2 \cdot 2H_2O$ crystal (16) for the first time. The crystal provides one example of a "two-dimensional" ice crystal (17). A relaxational heat-capacity anomaly observed below a critically divergent heat-capacity peak was interpreted as the freezing-in process of the proton system in the hydrogen-bonded network at the low-temperature stage of further development of an ordering process, after realizing long-range order at T_c. Here, some recent topics associated with stable crystals will be summarized briefly.

Nitrite disorder
Thallium nitrite crystallizes in the CsCl-type structure at room temperature. The V-shaped NO_2^- ion must be in an orientationally disordered state in the crystal in view of the octa-hedral symmetry of the anion site. On cooling the crystal, a phase transition was observed to occur at 282 K as shown in Fig. 6 (18). The associated entropy change is 23.6 $JK^{-1} mol^{-1}$ and the crystal seems to settle into an ordered phase. A small heat-capacity anomaly with relaxational nature similar to the glass transition was observed around 60 K. Exothermic temperature drifts were observed below this temperature which were then followed by endo-thermic ones on further heating. This is just the enthalpy relaxation which accompanies the usual glass transition. Associated with this relaxational heat-capacity anomaly, dielectric dispersion was found between 80 and 180 K in the frequency range of 200 Hz and 100 kHz. The magnitude of the dielectric dispersion suggests that reorientational motion of dipolar NO_2^- ions is responsible for the relaxation. The dielectric relaxation time extrapolated from these data becomes 10^3 s at 60 K. The value is approximately the time scale of a single heat-capacity determination. The Arrhenius plot of the relaxation time data obtained by the calorimetric and the dielectric measurements is shown in Fig. 7. Both sets of data lie on the same straight line, whose slope gives 19.5 $kJ mol^{-1}$ for the activation enthalpy. These experimental findings suggest that the low-temperature phase of $TlNO_2$ still has some orientational degree of freedom and the orientational disorder is frozen-in around 60 K.

Extensive orientational disorder was inferred in the high-temperature cubic phase. Based on the entropic and packing considerations, a disorder model was proposed in which there are two different sets of orientation of NO_2^- ions with the O-O axis parallel to [111] and [110] axes in the cubic lattice. There are four of the [111] axis in the lattice. Each of them has three associated orientations because the body-diagonal is a three-fold rotation axis. In total, there are $3 \times 4 = 12$ equivalent orientations. Similarly, there are $6 \times 2 = 12$
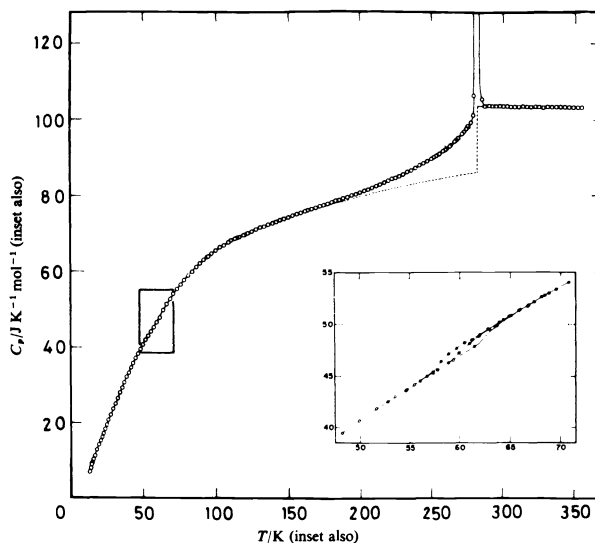
Fig. 6. Heat capacity of crystalline $TlNO_2$.

additional stable orientations for the O-O axis parallel to [110]. This model gives $R \ln 24$ for the orientational entropy. A model of orientational disorder of NO_2^- ion in the cubic phase is shown in Fig. 8. Associated with the highly disordered nature, the cubic phase shows high plasticity and high electric conductivity (19) characteristic of the plastic crystal (20) of organic origin. Most of the entropy arising from the orientational disorder is removed by the phase transition into orthorhombic phase (19), but still the low-temperature phase possesses some residual orientational disorder. On further cooling, the disorder becomes frozen on the way to reach a hypothetical ordered phase.

A similar phase transition was found in crystalline $CsNO_2$ by Mraw and Staveley (21) on cooling the room-temperature CsCl modification. The lower limit of their measurements was 77 K and we expected another phase transition or glass transition depending on the rate of reorientational motion of NO_2^- ion. The symmetry of the low-temperature phase (22) requires that orientational disorder of NO_2^- ions still persists in this phase, since the phase belongs to the rhombohedral system and the O-O axis of NO_2^- ion is expected to align parallel to the trigonal axis from the packing consideration.

Actually, a relaxational heat-capacity anomaly was observed to exist around 42 K by a careful calorimetric study with a specially designed cryostat that can maintain cryogenic temperatures for a long time (23). Again, a similar dielectric relaxation was observed in dielectric measurements. The calorimetric and dielectric relaxation times data fall on the
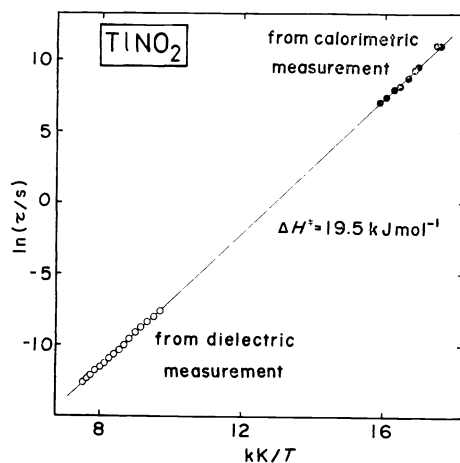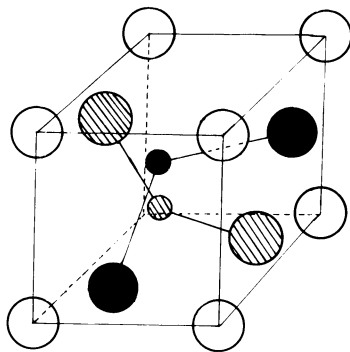

Fig. 7. Arrhenius plot of relaxation times of $TlNO_2$.

Fig. 8. A model of orientational disorder
in cubic TlNO$_2$.

same straight line. We conclude that the same mechanism is involved in both of the relax-
ation phenomena and the orientational motion of NO$_2^-$ ion is responsible for the relaxation
as in the case of TlNO$_2$. These cases should be similar to the head-to-tail orientational
freezing phenomenon of CO crystal (24).

Ice disorder
The disorder in ice has been one of the most important unresolved problems among others in
relation to the third law of thermodynamics. The story started when Giauque and Stout (25)
found the residual entropy of 3.44 JK^{-1} mol^{-1} in hexagonal ice, which is the most stable
form of ice at atmospheric pressure. Soon after, Pauling (26) gave an interpretation of
this entropy by assuming a completely disordered pattern of proton location in accordance
with the Bernal-Fowler ice rules (27). Figure 9 (left) shows a snapshot of an ice crystal
with a disordered proton configuration satisfying these rules. There are enormous numbers
of such kind of proton configuration. The large dielectric constant of ice crsytals origi-
nates from the dynamic nature of this disorder. Here, the disorder can be considered either
as a positional problem in the number of different ways in which protons can be located in
double-minimum positions in the hydrogen bonds, or alternatively as an orientational problem
in the number of different ways in which water dipoles can be directed into six possible
orientations (2). Neutron diffraction experiments by Peterson and Levy (28) confirmed the
disordered structure, which is known as a half-hydrogen model (Fig. 9 right). Bernal and
Fowler stated that " ...in that case ice would be crystalline only in the position of its
molecules but glass-like in their orientation." We feel some hesitation, however, in using
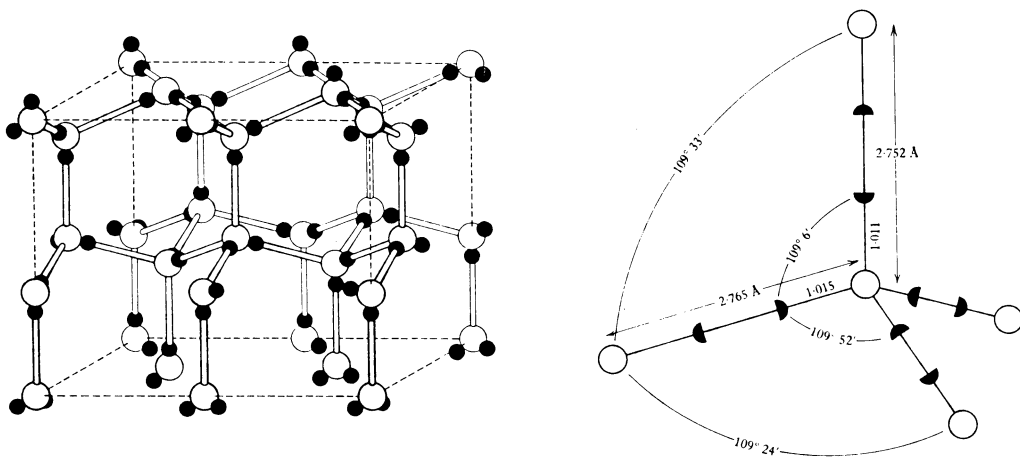

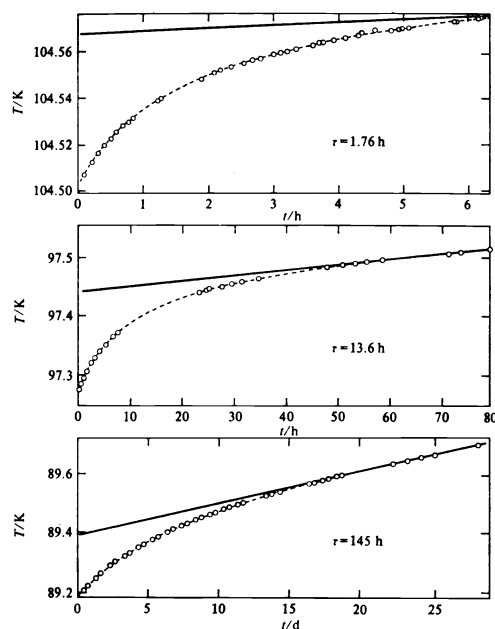
Fig. 9. Structure of hexagonal ice.

Fig. 10.   Three typical runs of the
annealing experiment of ice.

the term glass-like until we know the dynamical situation of the proton system.

The presence of the residual entropy means lack of thermal equilibrium in the crystal below a certain temperature. In fact, we have observed relaxational heat-capacity anomalies around 100 K for ordinary ice (29) and around 115 K for heavy ice (30), and studied the kinetics of associated enthalpy relaxation by subjecting the ice specimen to rapid cooling and long annealing in an adiabatic calorimeter. Figure 10 shows three typical runs of the temperature rise due to the enthalpy relaxation around 90 K. The straight line in the figure refers to the temperature drift due to heat leakage arising from incomplete adiabatic conditions. These studies resulted in a recognition of the relaxational behavior as a kind of glass transition in the stable crystal, replacing the earlier controversial interpretation of the corresponding anomalies in dielectric properties as due to the onset of a ferroelectric phase transition (31). The data on the relaxation time of the ice crystals are summarized in Table 1. Since the data coincide approximately to the extrapolated values of dielectric relaxation times, we imagine that the same mechanism is operative for the calorimetric and dielectric relaxations.

To what state does the thermal relaxation take place ? The degeneracy of various proton configurations will be removed by the intermolecular dipolar and quadrupolar interactions in the ice lattice. In terms of multipole interactions, Campbell and others (32) found significant differences among the energies of various proton configurations, and this must affect the thermodynamic properties of the crystal at a temperature around 100 K. Pitzer and Polissar (33) proposed the existence of an order-disorder transition between a polar ordered

TABLE 1.—RESULTS FOR THE ANNEALING EXPERIMENTS OF ICE CRYSTALS; T_a IS THE ANNEALING TEMPERATURE, t_a THE ANNEALING TIME, AND τ THE RELAXATION TIME.

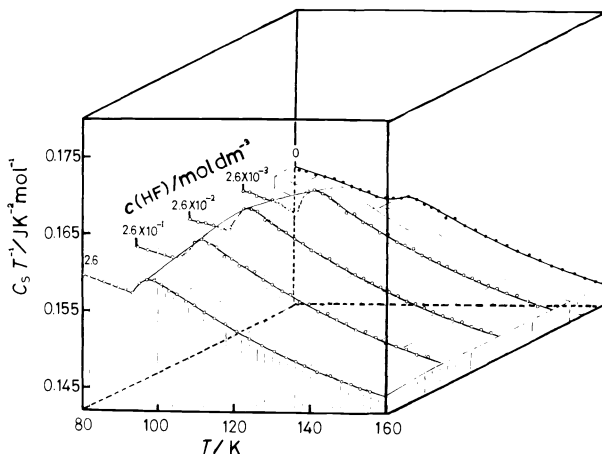| ordinary ice			heavy ice		
T_a/K	t_a/h	τ/h	T_a/K	t_a/h	τ/h
89.4	624	145	110.0	166	44.8
94.4	71	20.0	112.9	92	17.2
97.4	55	13.6	113.5	68	12.2
99.4	45	10.4	117.9	31	6.50
102.5	9	3.82	120.9	28	4.63
104.5	7	1.76	122.1	9	1.97
107.6	2	1.01			

Fig. 11. Heat capacities of HF-doped ices.

structure and the disordered structure at about 60 K by using the mean field theory. Comparing the entropy changes associated with the excess heat capacities of the quenched and the annealed specimens, the actual freezing of the proton systems is considered to occur at the very initial stage of the proton ordering (short-range order) which would lead to the hypothetical ordered state. Simple extrapolation of the relaxation time data to 60 K reveals that a geological time scale is required to realize the ordered state in the ice crystal.

There is other evidence against the existence of a hypothetical phase transition in ice. Barns *et al.* (34) first assumed a hypothetical ordered structure. After randomizing the proton configuration by computer simulation, subject to appropriate rules, they recalculated the energy of the new configuration. Since the average energy of the disordered configurations was always lower than that of the initially assumed ordered structure, they concluded that the disordered structure is favoured energetically as well as entropically in the ice crystal in the whole temperature region. This conclusion has an important consequence in relation to the third law of thermodynamics, on which our experimental thermodynamics is based.

Following the proposal by Onsager (35), we have made use of the heat capacity measurements on HF-doped ice crystal (36). Doping with this impurity is believed to introduce Bjerrum L defects into the lattice. This defect, being essentially a hydrogen bond that lacks a proton, is expected to participate in an essential way in the proton ordering. According to Jaccard (37), the energy of the L-defect liberation at 218 K is less than $1 \ kJ \ mol^{-1}$. The heat capacity measurements actually revealed positive effect of HF-doping in increasing the heat capacity anomaly and hence in realizing a more ordered state, as shown in Fig. 11. In this figure, the ordinate is taken as C_p/T for clearer appreciation of the anomaly. As the concentration of HF is increased, the excess heat capacity becomes more prominent and tends to occur at lower temperatures. The largest effect of doping is observed at the HF concentration $2.6 \times 10^{-2} \ mol \ dm^{-3}$. The effect of HF is clearer when the relaxation times of this specimen and of a pure specimen are compared at the same temperature. The relaxation time for the doped specimen becomes shorter by a factor of 30 at 90 K, but this is not enough to induce an apparent phase transition.

When we doped an ice sample with a small amount of KOH, a drastic change was observed in its thermal behaviour (38). A calorimetric cell containing a $0.1 \ mol \ dm^{-3}$ KOH solution was cooled down to 50 K and the heat-capacity measurements were started. When the tempera-
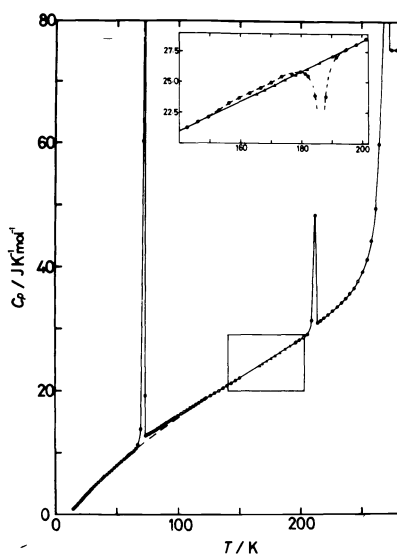

Fig. 12. Heat capacity of KOH-doped ice.

ture exceeded 60 K, a measurable heat evolution was observed. The calorimeter was kept around 65 K, where the rate of temperature rise was the largest. After about one week, when the exothermic effect had ceased, the calorimetric system was cooled down to 13 K and the heat-capacity measurements were restarted. As shown in Fig. 12, three anomalies were observed at 72, 208, and 273 K, respectively. The second anomaly corresponds to the eutectic point of the ice and hydrated KOH, and the third to the melting point of the impure ice. The heat-capacity peak observed at 72 K is due to the phase transition and is essentially isothermal. The excess heat capacities of the doped ice over those of pure ice extend to as high as 40 K above the transition temperature. It is this high-temperature tail of the excess heat capacities that we have observed partly as the relaxational heat-capacity anomalies in pure ice owing to the prolonged relaxation time. The entropy of transition is $2.32 \ JK^{-1} \ mol^{-1}$. Thus the phase transition removes a substantial fraction of the configu- rational entropy that the ice crystal posesses at higher temperatures.

The phase transition can be induced at the same temperature by KOH at the amount-of-substance fractions of 2×10^{-4} and 2×10^{-5}. These experimental observations led us to conclude that the phase transition is an intrinsic equilibrium property of hexagonal ice which has so far escaped observation for kinetic reasons, and has now emerged under the catalytic action of KOH. In a perfect ice crystal, proton rearrangement can only be accomplished by infringing the ice rules. A real crystal will contain many kinds of lattice defects which facilitate such rearrangement. An impurity such as KOH presumably acts as a catalyst by increasing the number of defects and by lowering the activation enthalpy for the proton movement.

Kawada (39) studied the dielectric properties of several doped ices and found the phase transition at 70 K in KOH-doped specimens. The temperature of the dielectric transition agrees well with the present observation. Minagawa (40) recalculated the lattice energy of an ice crystal based on a revised electrostatic model in conjunction with the latest dielectric data, and concluded that a first-order phase transition takes place at 73 K. The ice problem seems to have reached a new stage at which we can carry out studies on our laboratory time scale to clarify many questions that might be raised by many scientists. The role of cations as a catalyst, and the significance of the difference between the residual entropy and the observed entropy of transition are among the many interesting problems which remain to be clarified.

CONCLUDING REMARKS

An important consequence of the observation of glass transitions in stable crystals is that there arises no problem of Kauzmann's paradox (6) on this occasion. The paradox consists of the observation that if the equilibrium entropy of a liquid is extrapolated through the glass transition then a value of S for the glass is ultimately obtained which is lower than the corresponding value for the crystal. The same is true for the glass-transition phenomenon observed for the undercooled high-temperature mesophase. Two kinds of time-dependent phenomena will be observed in principle; one is the relaxation for "structural change" toward a metastable equilibrium state and the other the kinetic effect of crystallization or transformation into the most stable crystal. For the stable crystal, the latter problem does not arise. The substance in the non-equilibrium state will not be induced to crsytallize or transform. The only thing that can happen on aging the non-equilibrium crystal is to realize a more ordered state with respect to the degree of freedom frozen below the glass-transition temperature. The origin of the variety of the glassy states has been discussed (16) in terms of the transition temperature and the temperature dependence of the molecular relaxation time by use of the concept of Deborah number (41). Several studies along these lines finally led us to disclose an ordering phenomenon in an ordinary ice crystal. A time-dependent phenome- non sometimes correlates strongly with time-independent static properties. The theory of the phase transitions has been confined mainly to the static aspect of the properties of matter.

Eisenberg and Kauzmann (42) proposed three structures for ice depending on the time-scale of the experimental observation, an instantaneous structure or I-structure, a vibrationally- averaged structure or V-structure, and a diffusionally-averaged structure or D-structure. They considered various experimental techniques that give information about the respective structures. All the processes occurring in nature derive from this kind of time-dependent effect. Nature is essentially in movement. We must consider the stability and non-equi- librium nature of a system with respect to all the degrees of freedom that it possesses.

Among the various relevant techniques, the adiabatic calorimetry is suitable for the study of molecular motion with a long relaxation time. The relaxation time that can be covered by this method ranges from 10^3 s to an infinitely long time, depending on the patience of the experimentalist and on the quality of the calorimeter. Thus, adiabatic calorimetry can become a powerful tool in the field of an extreme science of super-long time.

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