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Calorimetric Study of the Glassy State. IV. Heat Capacities of Glassy Water and Cubic Ice

Masayasu SUGISAKI, Hiroshi SUGA and Syûzô SEKI

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

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By making use of the vapor-condensation type calorimeter, the heat capacity measurements of amorphous, cubic and hexagonal ices were made between 20°K and 250°K. The glass transition phenomenon was found near 135°K with the sudden change of the heat capacity amounting to 35 J/(mol°K). The drastic crystallization with the exothermic effect which amounts to 1.64 kJ/mol was then followed at this temperature. The transformation of the cubic crystal to the hexagonal one was confirmed to occur in the temperature region from 160 to 210°K and to proceed in two steps with the activation energies of 21.3 and 44.7 kJ/mol, respectively. The amount of the exothermic effect accompanying this transformation was found to be about 160 J/mol.

In the previous paper,[1] we have reported the construction of the novel type of calorimeter for studying a glassy state and the experimental data on the glassy state of methanol. In the present paper we should like to report our results of investigation on water.

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[1] M. Sugisaki, H. Suga and S. Seki, This Bulletin, **41**, 2586 (1968).

Since the work by Burton and Oliver[2] in 1935, it has been reported by many workers[2-12] that so-called amorphous state of water may be obtained when the water vapor is condensed onto the chilled substrate below about 140°K. In 1952 Pryde and Jones[4] have first tried to find out the glass transition phenomenon of the amorphous state deposited on a chilled substrate, and several such trials have been followed by many other workers. They are, for example, Ghormley (1956),[5] de Nordwall and Staveley (1956),[6] and McMillan and Los (1965).[12] Nevertheless, there had been no successful work before the study with a differential thermal analysis method by McMillan and Los who have found an endothermic effect at 139°K just below a crystallization temperature for an amorphous ice. Furthermore, many other workers have reported by use of the X-ray or electron diffraction methods that the amorphous ice crystallizes into a cubic form when it is heated up to about 140°K, and that the cubic ice transforms into the hexagonal one very sluggishly and irreversibly around 200°K.[7-11,13] McMillan and Los have also found that this transformation is accompanied with the exothermic effect. Although there have been thus accumulated considerable number of data on the glassy state of this material, it may be said that there is no quantitative and conclusive evidence about the presence of the glassy state of water.

In the present investigation, we have tried to perform the quantitative heat-capacity measurements of the amorphous, cubic and hexagonal ices, and further to obtain some thermodynamical data of the glass transition phenomenon of the amorphous ice, of its crystallization effect and further of the phase transformation of the cubic form to the hexagonal one.

Experimental

Apparatus. An adiabatic Nernst-type calorimeter with a cell for condensing a sample vapor as an amorphous state was used. The detailed structure of the calorimeter and of the experimental procedures were already reported in the previous paper.[1]

Purification of Water. The water treated by ion-exchange resin was distilled under atmospheric pressure, and then this product was distilled twice in high vacuum (10^{-6} mmHg). After the final product was degassed very carefully by repeating melting and freezing of the sample under high vacuum (10^{-6} mmHg), the sample was condensed into the calorimeter in high vacuum (10^{-6} mmHg) as an amorphous state at about 120°K.

Preparation of the Vitreous Water. Four kinds of sample of water were vitrified by condensing their vapor into the calorimeter cell in quite a same fashion as reported in the previous paper.[1] During the vitrification, the temperature of the sample cell was kept first between 103°K and 106°K [sample (1)] and between 120 and 123°K in the other three cases of sample [(2), (3) and (4)]. The filling tube was kept around 300°K in each case for all samples. The rate of condensation and the total amount of the sample used for the measurements are given in Table 1.

Experimental Results

Heat Treatment Adopted for the Heat-capacity Measurement. *Sample (1).* The measurements of heat capacities of the glassy state were made in the region between 118 and 136°K covering the glass transition temperature, through which some exothermic effect was always traced above 115°K. The drastic crystallization was observed at about 135°K which is just above the glass transition point.

TABLE 1. VITRIFICATION CONDITION AND SOME EXPERIMENTAL DATA ON GLASSY WATER

Number of sample	Rate of condensation (g/hr)	Total amount of sample (g)	Heat of crystallization (kJ/mol)		ΔC_P at T_g (J/mol°K)	Amorphous part of sample (%)
1	0.032	0.6054	1.64	±0.05	35	100(assumed)
2*	0.033	0.5897	1.46		29	89.0
3**	0.024	0.6959	1.06		19	64.6
4***	0.030	0.7745	0.85		11	49.0

* Annealed at 128°K for 4 hr.
** Annealed at 128°K for 16 hr.
*** Annealed at 128°K for 13 hr.

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2) E. F. Burton and W. F. Oliver, *Proc. Roy. Soc.*, **A153**, 166 (1935).

3) L. Staronka, *Roczniki Chem.*, **19**, 201 (1939).

4) J. A. Pryde and G. O. Jones, *Nature*, **170**, 685 (1952).

5) J. A. Ghormley, *J. Chem. Phys.*, **25**, 599 (1956).

6) H. J. de Nordwall and L. A. K. Staveley, *Trans. Faraday Soc.*, **52**, 1061 (1956).

7) M. Blackman and N. D. Linsgarten, *Proc. Roy. Soc.*, **A239**, 93 (1957); N. D. Linsgarten and M. Blackman, *Nature*, **178**, 39 (1956).

8) F. V. Shallcross and G. B. Carpenter, *J. Chem. Phys.*, **26**, 782 (1957).

9) J. G. Dowell and A. P. Linfret, *Nature*, **188**, 1144 (1960).

10) K. Shimaoka, *J. Phys. Soc. Japan*, **15**, 106 (1960).

11) R. H. Beaumont, H. Chihara and J. A. Morrison, *J. Chem. Phys.*, **34**, 1456 (1961).

12) J. A. McMillan and S. C. Los, *Nature*, **206**, 806 (1965).

13) H. Konig, Nachr. Akad. Wiss. Göttingen, No. 1, 1 (1942); *Z. Krist.*, **105**, 279 (1943).

Sample (2). The measurements for the glassy state were made in the region from 118 to 136°K including the glass transition temperature. In this case the exothermic effect was observed above 123°K. The drastic crystallization was observed at about 135°K. After the crystallization was over this sample was chilled down to 110°K and measurements were carried out again from 180 to 237°K. The appreciable exothermic effect accompanying the phase transition was observed between 180 and 210°K. After the previous series of measurement was completed, this sample was chilled down once more to 180°K and the measurements were made from 180 to 225°K for the hexagonal phase.

Sample (3). Prior to the measurement of the glassy state, the sample was annealed at 128°K for 12 hr. The measurements of the glassy state were made from 20 to 135°K. After the crystallization was performed, this sample was chilled down to 20°K, and the measurements were made again from 20 to 240°K, an appreciable exothermic effect being also observed between 160 and 210°K during this series of measurement. This sample was again chilled down to 60°K and the measurements were carried out from 60 to 240°K.

Sample (4). After the measurement on the glassy state between 60 and 125°K was over, the sample was annealed at 128°K for 12 hr, and then for this annealed sample the measurements were made between 120 and 135°K in which the drastic crystallization was observed at about 135°K. After the completion of this crystallization, the sample was chilled down to 60°K and the measurements were repeated from 60 to 240°K.

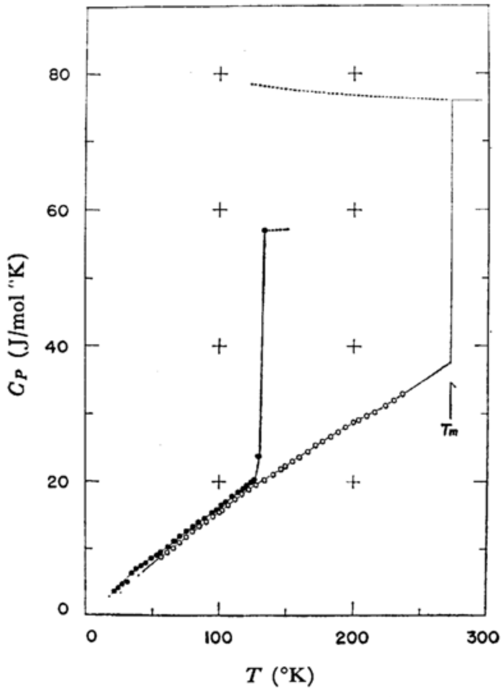

Fig. 1. Heat capacity curve of water.
● Amorphous ○ Hexagonal ice

Determination of a Number of Mole of the Sample. A total amount of the sample, which was condensed into the calorimeter cell for the heat-capacity measurement, was determined first by measuring the weight of the sample collected into the glass tube equipped outside the calorimeter. However, the heat capacities of the hexagonal ice calculated based on this value of the number of mole were smaller than those of Giauque's data[14] by 10%. This seems to be due to the fact that some amount of water were condensed in the filling tube situated out of the sample

TABLE 2. HEAT CAPACITY OF WATER (HEXAGONAL ICE) IN J/(mol °K)

T (°K)	C_P	T (°K)	C_P
Sample (3)		Sample (4)	
56.02	9.058	59.29	9.473
61.13	9.761	63.46	10.13
65.69	10.49	68.05	10.50
70.28	11.30	72.68	11.27
75.20	12.05	77.25	12.37
80.01	12.73	82.30	12.77
85.00	13.98	87.60	14.50
89.70	14.64	92.72	14.62
95.15	15.28	97.58	14.95
99.90	15.98	97.79	14.97
102.10	15.83	102.55	15.55
107.22	16.53	107.36	16.44
112.17	17.41	112.24	17.45
117.20	18.22	116.98	17.99
122.32	18.77	121.57	19.02
127.95	19.52	126.06	19.32
134.04	20.28	130.67	19.74
140.00	20.98	135.42	20.58
145.81	21.87	140.06	21.47
149.26	22.18	144.67	21.45
154.93	23.04	136.89	20.86
160.48	23.61	141.56	21.21
165.93	24.39	146.15	21.94
171.54	25.35	150.66	22.20
177.27	25.95	155.09	22.36
182.97	26.63	159.67	23.48
188.58	27.31	165.44	23.81
194.10	28.11	170.73	24.93
199.53	29.54	175.37	25.71
203.78	29.02	181.01	26.29
210.18	30.46	186.57	26.88
216.49	30.59	192.04	28.07
		197.44	28.82
		202.77	29.45
		208.03	30.20
		213.09	30.85

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14) W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.*, **58**, 1144 (1936).

cell, because the sample in the filling tube does not take part in the heat-capacity measurement, so the number of mole of the sample in the cell was over-estimated than the true value. In this respect, the number of mole of the sample was determined by fitting our values of hexagonal ice to those of Giauque's data between 100 and 140°K.

The accuracy of our calorimeter was checked already in the case of methanol, and so this method of determination may be reasonable and satisfactory for the present purpose. So that, in place of the value determined by direct measurement of the weight of the sample collected into the glass tube, the number of mole based on the Giauque's data was adopted in the following.

Table 3. Heat capacity of water (glass and supercooled liquid) in J/(mol°K)

T (°K)	C_P	T (°K)	C_P
		76.05	12.68
Sample (1)		80.80	13.30
118.82	19.42	85.27	14.47
120.21	19.63	89.74	14.86
122.23	20.17	94.23	15.28
124.21	20.64	98.57	15.75
126.17	21.12	102.75	16.50
128.11	21.45	104.94	16.97
130.01	21.89	109.77	17.67
131.88	23.37	114.46	18.35
133.58	57.30	118.20	18.90
135.86	46.47	121.01	19.39
		123.79	19.94
Sample (2)		126.56	20.72
118.05	19.20	129.34	23.74
119.90	19.72	131.97	32.36
121.81	20.21	134.67	38.47
123.72	20.49		
125.61	20.83	Sample (4)	
127.48	21.38	79.98	13.71
129.35	21.78	84.23	14.29
131.23	25.44	88.51	14.78
133.19	35.42	92.93	15.27
135.50	50.04	97.50	15.88
		101.91	16.63
Sample (3)		106.49	17.19
21.75	3.644	111.25	18.17
24.73	3.957	115.88	19.09
27.75	4.061	120.38	19.88
31.10	4.685		
34.53	6.378	Series after annealing at 128°K for 12 hr	
38.10	7.002		
41.70	7.393	119.95	19.30
45.40	7.653	122.16	19.93
49.33	8.590	124.35	20.33
53.56	9.032	126.52	21.17
57.83	9.501	128.69	22.31
58.04	9.527	130.90	24.49
62.22	10.26	132.73	28.14
66.59	11.24	134.18	31.51
71.24	11.92		

Results of Heat-capacity Measurement. *Hexagonal Ice.* The results for the samples (3)

Table 4. Heat capacity of water (cubic ice) in J/(mol°K)

T (°K)	C_P	T (°K)	C_P
		170.40	24.18
Sample (2)		176.11	25.25
182.56	24.73	181.79	26.32
187.11	25.71	187.47	26.94
191.64	25.80	193.15	25.25
196.19	24.05	198.82	26.60
200.59	27.40	204.24	29.13
204.87	29.25	210.08	30.12
209.08	30.04	216.36	30.85
213.26	30.07	222.55	31.81
217.39	30.44		
221.48	31.19	Sample (4)	
		60.14	9.496
Sample (3)		64.62	10.41
21.62	1.275	69.14	11.02
24.08	3.019	73.72	12.12
26.64	3.462	78.21	12.35
29.79	4.139	82.68	13.15
33.45	5.076	87.47	13.94
37.24	5.805	92.56	14.34
41.00	6.716	97.44	14.95
44.83	7.106	97.72	14.95
48.82	8.069	102.76	15.58
53.10	8.434	107.77	16.51
57.63	8.980	112.61	17.47
58.98	9.397	117.32	18.22
63.25	10.26	121.90	18.85
67.54	11.04	126.10	19.48
72.10	11.66	126.62	19.74
76.86	12.21	130.92	20.02
81.57	13.38	131.43	20.00
86.02	14.03	135.64	20.84
90.51	14.58	136.17	20.98
95.08	15.16	140.26	21.40
99.49	15.54	144.82	22.29
103.75	16.16	149.30	22.62
108.11	17.02	153.72	22.97
109.94	17.36	156.21	23.53
114.64	18.27	162.22	23.32
119.20	19.13	168.17	24.04
123.69	19.65	174.03	24.40
128.33	20.20	179.82	25.03
133.07	20.85	185.51	26.10
137.70	21.55	191.14	26.80
142.28	22.18	196.77	25.57
146.77	22.65	202.24	28.91
151.18	23.48	208.07	29.77
155.79	23.64	214.34	30.83
159.67	23.01	220.52	31.34
164.57	23.69		

and (4) are given in Table 2 and are represented by the hollow circles in Fig. 1. The deviation of the values around the smoothed curve is within 3% in the vicinity of the boiling point of liquid nitrogen and within 1% around 200°K.

Glass and Supercooled Liquid. The results for the samples (1), (2), (3) and (4) are all given in Table 3. The temperature-dependence of the heat capacity in the vicinity of the glass transition point is drawn for each case of the samples in Fig. 2. Amongst the filled circles given in Fig. 1 the values on the sample (1) are plotted around T_g and those of the sample (3) for the temperature region below 80°K. As is seen in these figures the amorphous solid of water obtained by the method of vapor condensation was found to show a glass transition phenomenon at about 135°K. On further heating the drastic crystallization was found to occur just above the glass transition point. The jump of heat capacity at the glass transition point and the total amount of the exothermic effect accompanying the crystallization are given in Table 1.

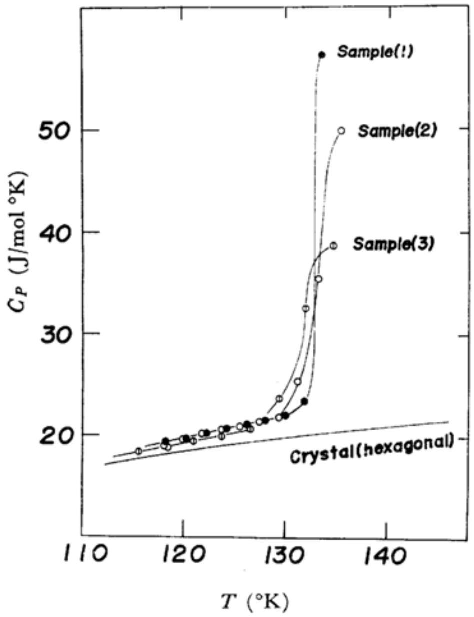

Fig. 2. Heat capacity curve of water near the glass transition temperature.

Cubic Ice. The results for the samples (2), (3) and (4) are given in Table 4, and are illustrated in Figs. 3 and 4 in comparison with those of the hexagonal ice. The total exothermic effect was observed in the temperature region from 160 to 210°K, and in particular we can recognize the remarkably anomalous region of heat capacities between 190 and 210°K. The corresponding enthalpy amount of this exothermic effect was estimated between 160 and 210°K for each sample as is given in Table 5.

TABLE 5. TOTAL AMOUNT OF EXOTHERMIC EFFECT ACCOMPANYING IRREVERSIBLE TRANSFORMATION OF THE CUBIC ICE TO THE HEXAGONAL ONE

Number of sample	$-\Delta H$ (J/mol)	
2	158.9	±15
3	164.4	
4	159.5	

Discussion

Realization of Glassy State. From the results of our heat-capacity measurement, it is quite clear that the amorphous water condensed

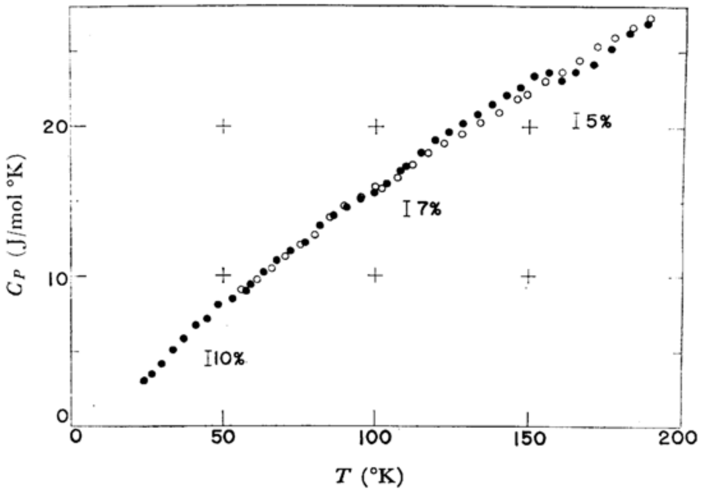

Fig. 3. Heat capacity of ice. The filled circle represents the cubic ice and the hollow circle the hexagonal one.

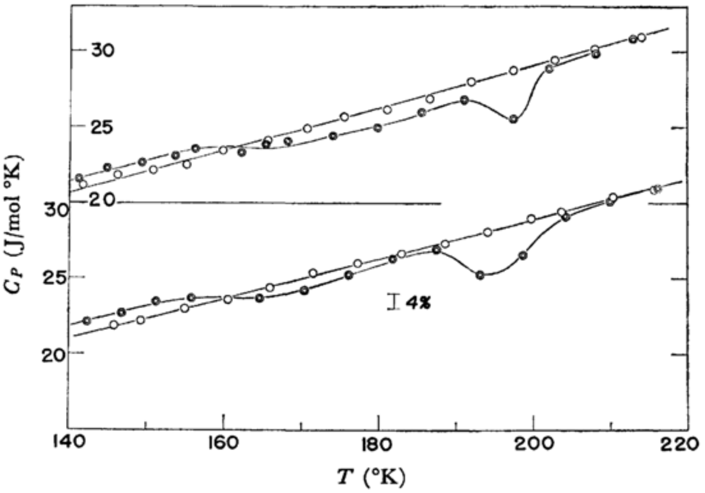

Fig. 4. Heat capacity of ice near the transformation temperature. The lower figure is results for the sample (3) and the upper for the sample (4).
◎ Cubic ○ Hexagonal

from the vapor onto the substrate chilled below 135°K shows a glass transition phenomenon. This fact shows that the condensed amorphous water exists in the glassy state below 135°K. This new finding of the glass transition phenomenon gives a definite resolution to the question whether the non-crystalline solid obtained by the vapor-condensation method is really a glass or not.

It is to be noted that the jump height of heat capacity at the glass transition point, and the heat of crystallization have different four values from sample to sample (see Table 1). This fact suggests that each of samples contains a few amount of a crystalline part. This crystalline part of the sample is considered to appear during the process of annealing. This is evidenced by the fact that the exothermic effect was observed even after the annealing at 128°K for 16 hr, and that the heat of crystallization gets smaller as the time of duration for annealing is longer (see Table 1), and further that the heat capacity curves of two series do not agree with each other in the case of the sample (4), as is shown in Fig. 5, where one series of measurements is made prior to annealing and the other after annealing at 128°K for 13 hr.

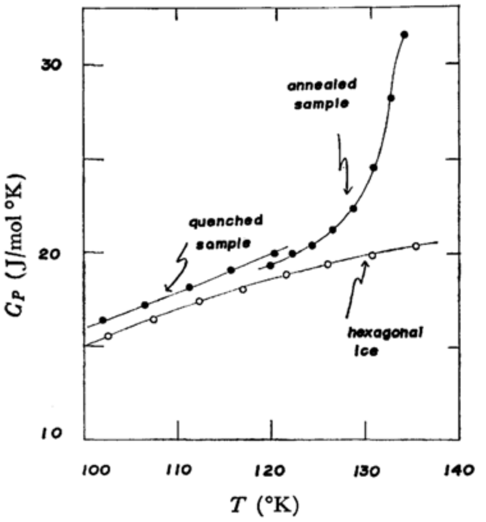

Fig. 5. Heat capacity of the glassy state of water.

In the case of sample (1), the jump height of heat capacity ΔC_P at T_g is of the highest value among all samples (see Table 1 and Fig. 2). The heat capacity just above T_g of this sample is, however, appreciably smaller than that of the supercooled liquid at the same temperature assumed by the extrapolation of the heat capacity of the liquid above the melting point. This fact is, at the first glance, considered to be due to the existence of crystalline part in the vitreous sample. This interpretation seems, however, to be inadequate because of some thermodynamical contradiction as will be described below. If C_P values of the supercooled liquid are assumed to be extended like a dotted line in Fig. 1, the corresponding enthalpy curve of the supercooled liquid comes out to be drawn in Fig. 6. At first sight of this figure it is shortly understood that the curve of the supercooled liquid intersects that of the crystal far above 135°K($=T_g$). This circumstance is evidently incompatible with the fact that the crystallization is necessarily accompanied by the exothermic effect. Consequently, it turns out to be inappropriate to assume that the C_P values of the supercooled liquid is equal to those obtained with extrapolating the C_P values of the liquid above the melting point.

Now, water has been known as a typical anomalous liquid. For example, its C_V values are much higher than those of other normal liquids composed of triatomic molecules. In order to interpret the remarkably abnormal physical properties, Eucken[15] has proposed that water is an equilibrating mixture of several kinds of associated species (*e. g.*, H_2O, $(H_2O)_2$, $(H_2O)_4$ and $(H_2O)_8$), and that the anomalous large value of heat capacity is caused by the dissociation of the associated species with the rise of temperature. Recently, Wada[16] has calculated the heat capacity of water reduced to a normal liquid assuming the existence of two states in water such as icy and packed states. According to his calculation, the C_P value of water reduced to the normal liquid is smaller than that of crystal at 0°C. Although his result does not directly stand for our present results, the hypothetical C_P value of water consisting of exclusively monomer molecules might be smaller than the observed one. Based on this consideration, it seems to be supported that the vitreous water obtained in the present work (in particular sample (1)), may be nearly 100 per cent amorphous state.

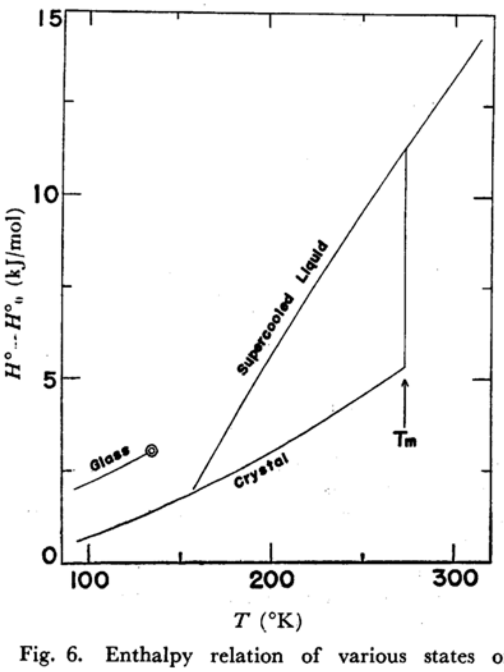

Fig. 6. Enthalpy relation of various states of water.

Appearance of the Cubic Ice and Its Transformation into the Hexagonal Ice. During past many years, a great deal of investigations[7-11,13] have been reported concerning the appearance of the cubic ice and its transformation to the hexagonal ice. As the results of these studies it is now well known that the cubic form of ice can be obtained either as a product of crystallization of amorphous ice or as a kind of high pressure form. In this section, we should like to concern only with the cubic ice prepared by the former method.

Up to the present, the existence of sluggish and irreversible transformation of the cubic ice to the hexagonal one has been observed by several workers. There has been, however, no quantitative experiment on the sample at the thermodynamically equilibrium state, so there remains still a confusion about the temperature interval of the appearance of the cubic ice, and also a more important problem whether the cubic ice is more stable than the hexagonal ice or not in the lower temperature region.

According to our present heat capacity measurements, the cubic ice transforms sluggishly and irreversibly into the hexagonal ice with an appreciable exothermic effect between 160 and 210°K The average total amount of the exothermic enthalpy change, 160 J/mol, is close to the value, 150 J/mol, previously reported by McMillan and Los. This agreement seems, however, to be fortuitous, because their experiment was of dynamical nature and their results were based on the Ghormley's value (1.26 kJ/mol)[5] for the heat of crystallization which does not agree with our present data (1.64 kJ/mol).

As is well known, the hexagonal ice has a center of symmetry in the direction vertical to *c*-axis and a mirror of symmetry in the direction parallel to this axis with regard to the conformation of oxygen atoms in the lattice. On the other hand the cubic ice has the center of symmetry in these two directions, *i. e.*, a diamond structure.

The enthalpy change of the transformation amounting to about 160 J/mol, which is obtained in the present experiment, is considered to be due to the difference of the lattice energy between these two structures. Such an exothermic phenomenon seems to be concordant with the result calculated by Bjerrum[17] *i. e.*, the hexagonal ice is more stable than the cubic ice with regard to its lattice energy.

Now, the kinetics of this transformation has been studied by several previous workers who have interpreted this phenomenon in terms of the activation energy.[12,18] McMillan and Los have reported that this irreversible transformation may be characterized by the activation energy of about 7.4 kcal/mol, which is calculated based on the X-ray data by Dowell and Rinfret.[9] On the other hand Nozik and Kaplan,[18] by use of the Mössbauer resonance method for the ice doped with ferrous ion, have reported that the transformation occurs at least in two stages with a certain intermediate

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[15] A. Eucken, Nachricht. Akad. Wiss. Göttingen, Math. Physik Klasse S. 38 (1946).

[16] G. Wada, This Bulletin, **34**, 955 (1961).

[17] N. Bjerrum, *Kgl Danskab. Selskab. Math-fys. Medd,* **27**, 1 (1951); *Science*, **115**, 385 (1952).

[18] A. J. Nozik and M. Kaplan, *Chem. Phys. Letters,* **1**, 391 (1967).

state, and that the activation energy for the process of the cubic-to-intermediate comes to about 29 kcal/mol.

We have also estimated the activation energy for this irreversible phenomenon from the results of heat-capacity measurement. When the cubic ice transforms into the hexagonal one with the exothermic effect, the temperature of the sample rises spontaneously if an adiabatic condition is well maintained. Concerning this phenomenon, the following equations were assumed to hold,

$$\dot{T} = (\Delta H/C_P)\cdot\dot{x} = 1/\tau(\Delta H/C_P)\cdot x,$$
$$\dot{x} = (1/\tau)\cdot x \qquad \tau \propto \exp(E/\boldsymbol{R}T)$$

here $\dot{T}$ is the time-derivative of the temperature of the sample, C_P the heat capacity of the sample including the sample-container, ΔH enthalpy change accompanying the cubic-hexagonal phase transition, $\dot{x}$ the time-derivative of the mole number of the cubic ice, τ the relaxation time characteristic of this phenomenon, x the mole number of the cubic ice, E the activation energy for this rate process. The values of $\dot{T}$, C_P, ΔH, and x are all obtained as a function of the temperature from the results of heat capacity measurement, so τ is easily calculated for all temperatures. The obtained relation between log τ and $1/T$ is drawn in Fig. 7. From this figure we see that this rate process may be separated into two processes, one of which is characterized with the activation energy of about 5 kcal/mol, the other with the activation energy of about 11 kcal/mol. The fact that this phenomenon occurs in two stages in our study is quite concordant with the results by Nozik and Kaplan, but the values of the activation energy are different from each other. Taking into consideration the difference that our experiments are based on the pure ice, whereas Nozik and Kaplan's works are based on the frozen solution, it is not quite clear to what extent such a comparison is plausible.

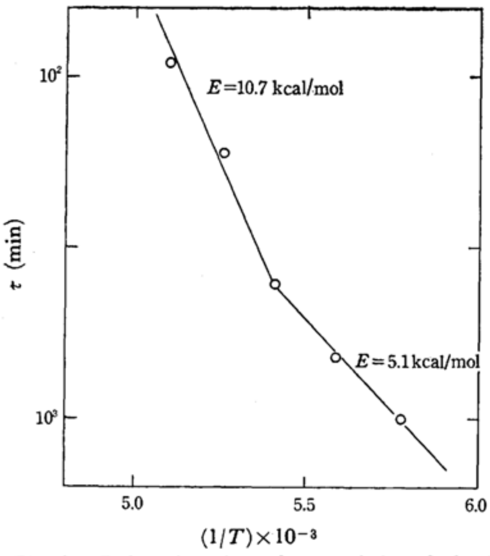

Fig. 7. Relaxation time characteristic of the irreversible transformation of cubic to hexagonal ice.

It is to be noted here that the activation energy of about 11 kcal/mol concerning the higher-temperature process is concordant with the result of Dowell and Rinfrĕt. As their experiment was carried out with the X-ray analysis method, it may be possible that they have observed mainly the higher-temperature process for which the rate of transformation is pretty high.

Definition of the Glassy State. As to the difinition of the glassy state, no unequivocal conclusion has been given hitherto, so there has been still a few confusions concerning the usage of the term "glassy state."[19] This seems to be due to the fact that the past definitions of the glassy state are almost concerned with the chemical composition of the glass or with the methods of obtaining the glassy state.

Commonly, a glassy state has been considered to be equivalent to a non-crystalline or amorphous solid obtained by supercooling the liquid. However, the non-crystalline solid can be obtained also by using other rather uncommon methods, such as vapor condensation, neutron bombardment, and others. Such a non-crystalline solid has been observed to crystallize on heating. For this kind of solid, the glass transition phenomenon has not ever been verified. As far as the glass transition phenomena are not observed, we may feel a certain hesitation to call this non-crystalline solid as a glass. However, our previous finding of the glass transition phenomena of methanol[1] and the same result for water prepared by the vapor condensation method in the present study afford the conclusion that the non-crystalline solids of these materials prepared by this uncommon method must be called as a glass. On the basis of our new observation we may propose a more general properties of the glassy state as follows: (a) The glassy state must be distinguished from other states only by the fact that the thermodynamically equilibrium state is never attained. (b) The glassy state must show the glass transition phenomenon which characterizes the boundary between

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[19] D. R. Secrist and J. D. Mackenzie, "Modern Aspect of the Vitreous State," Vol. 3, ed. by J. D. Mackenzie, Butterworths Scientific Publication, Ltd., London (1964), Chapter 6.

Note added in proof: Quite recently J. A. Ghormley [*J. Chem. Phys.*, **48**, 503 (1968)] has re-investigated the glass transition phenomenon of water by use of the method of thermal analysis and suspected the observation of T_g by J. A. McMillan and S. C. Los cited in this text. I. Yannas has pointed out also the elusive nature of the glass transition point of water and estimated the glass transition point of water to be 127±4°K indirectly by the extrapolation of T_g for glycerol with the increase of water content [*Science*, **160**, 298 (1968)].

the glassy and the supercooled liquid states. (c) The glassy state is established irrespective of either the method of preparation or the chemical composition of the material.

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