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Calorimetric Study of the Glassy State. VI. Phase Changes in Crystalline and Glassy-Crystalline 2,3-Dimethylbutane

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2,3-Dimethylbutane has two crystalline phases, high temperature form (crystal-I) and low temperature form (crystal-II). On account of the supercooling effect of crystal-I, its *glassy crystalline* state (non-equilibrium frozen-in state) is established below T_g (76 K) by rapid cooling. The heat capacities for various phases were determined from 13 to 300 K from principal interest in the thermodynamic properties of the glassy crystal. The transition temperature from crystal-II to crystal-I and melting point were determined to be 136.02 K and 145.05 K, respectively. The heats of transition and of fusion were determined to be 6427 J mol^{-1} and 788 J mol^{-1}, respectively. From these data, the residual entropy and T_2 temperature were determined to be 7.4 JK^{-1} mol^{-1} and 65 K, respectively. We also calculated the ratio of T_g to T_2 for several glassy crystals known hitherto, which amounts to 1.15—1.20. The stabilization effect was studied by the measurement of the change of the configurational enthalpy in the glassy crystalline state. Also, we discovered a new meta-stable intermediate phase (crystal-III) in the course of irreversible transition from the supercooled crystal-I to crystal-II. The thermal properties of this phase were also studied and its residual entropy was determined to be 2.7 JK^{-1} mol^{-1}.

Although the glass transition phenomenon is generally considered to be characteristic of the supercooled liquid state, it is known that the supercooled crystalline state of some materials also shows a similar behavior.[1–3] We studied the heat capacities of cyclohexanol and concluded that the anomalous jump of the heat capacity curve of the supercooled high-temperature form is attributed to the glass transition phenomenon. We have proposed a new term "*Glassy Crystal*" for the frozen-in state of the supercooled crystalline phase which has glass transition point. We would like to present the results of heat capacity measurements on the glassy crystalline state of 2,3-dimethylbutane as well as on various other stable phases and also on a metastable phase of this material. The thermal study of this substance has already been carried out by Douslin and Huffman.[4] They revealed that it has two crystalline phases, a high-temperature form (crystal-I) and a low-temperature form (crystal-II). The easy supercooling effect of the high-temperature form with rapid cooling has been confirmed in the study of nuclear magnetic resonance by Segall and Aston.[5] The thermal data of the supercooled crystal-I, however, were not given by Douslin and Huffman. In this article we report on the residual entropy of the glassy crystal as well as the T_2 temperature which was defined by Gibbs and Adam.[6] The relaxation phenomenon of the enthalpy was observed below glass transition temperature by annealing. An attempt has been also made to clarify the temperature dependence of the relaxation time. Furthermore, in the course of the irreversible transition from the supercooled crystal-I to crystal-II, we have discovered a metastable intermediate phase (crystal-III). Based on the heat capacity data of the crystal-III, the heat of transition from crystal-III to the supercooled crystal-I and the residual entropy of crystal-III have also been estimated.

Experimental

Material. The material was a mixture of two parts which had different purity. About 60 cc of 2,3-dimethylbutane (Tokyo Kagaku Seiki Co., Ltd. standard material 99.0%) was washed with concentrated sulfuric acid (including a small amount of potassium chromate) for ten hours at room temperatures to remove olefins involved. After this treatment the specimen was separated from the sulfuric acid solution by vacuum distillation and finally fractionally distilled. About 30 cc of the middle fraction of the distillate was obtained ——(A). On the other hand, 40 cc of the specimen which was claimed to have near 99.9% purity (Tokyo Kagaku Seiki Co., Ltd.) was purified by vacuum distillation at −70°C and about 20 cc of the middle fraction was obtained ——(B). The fractions (A) and (B) were mixed and the mixture was further distilled in a vacuum at −70°C. The purified specimen was introduced into the sample container for heat capacity measurements by vacuum distillation. The sample which had the same purity as that for heat capacity measurements was used for differential thermal analysis. The purity determined from equilibrium temperatures during fusion process was found to be 99.87% as will be described below.

Apparatus. The heat capacity was measured by a Nernst type adiabatic calorimeter with a platinum resistance thermometer. The details of the apparatus were reported previously.[7,8] The weight of the specimen employed in the measurement was 19.844 g (about 30 cc) after the correction for buoyancy due to air. A small amount of helium gas (0.2—0.5 cc at room temperature and 1 atm) was added as a heat exchange medium. After the sample and helium gas were introduced into the container, the filling tube (copper capillary) was pinched off and shielded with a soft solder. The apparatus for the differential thermal analysis has also been reported.[9]

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1) K. Adachi, H. Suga, and S. Seki, This Bulletin, **41**, 1073 (1968).

2) H. M. Huffman, S. S. Todd, and G. D. Oliver, *J. Amer. Chem. Soc.*, **71**, 584 (1949).

3) J. G. Aston, H. Segall, and N. Fuscheillo, *J. Chem. Phys.*, **24**, 1061 (1956).

4) D. R. Douslin and H. M. Huffman, *J. Amer. Chem. Soc.*, **68**, 1704 (1946).

5) H. Segall and J. G. Aston, *J. Chem. Phys.*, **23**, 528 (1955).

6) J. H. Gibbs and G. Adam, *ibid.*, **43**, 139 (1965).

7) T. Matsuo, H. Suga, and S. Seki, Reported at The 3rd Japanese Calorimetry Conference 1967.

8) H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

9) H. Suga, H. Chihara, and S. Seki, *Nippon Kagaku Zasshi*, **82**, 24 (1961).

Experimental Results

Differential Thermal Analysis (DTA). For the preliminary study of thermal behaviors of this material, differential thermal analyses have been carried out. The results are shown in Fig. 1. Run-1 is for a cooling curve with a rate about -1.4 K min^{-1}. The liquid state is supercooled to about 128 K where a sharp exothermic peak due to an abrupt crystallization has been observed. No remarkable thermal anomalies have been observed on further cooling. On account of noise effects and of a slow cooling rate between 80 K and 60 K, a reliable DTA curve has not been obtained. When the temperature was raised rapidly as soon as the sharp exothermic peak was observed at about 128 K in Run-1, only a peak due to the fusion effect was observed at about 145 K. This is shown by the curve for Run-2. From these DTA curves, it was confirmed that the high-temperature form (crystal-1) is easily supercooled. Run-3 is of a heating curve after slow cooling down to 65 K with a similar condition for Run-1. The heating rate of Run-3 is of about 1 K min^{-1}. It is seen that the supercooled crystal-I exhibits an anomaly resembling glass transition at about 78 K. The anomaly has been attributed to the glass transition phenomenon. An exothermic change was successively observed at about 89 K where the supercooled crystal-I was irreversibly transformed into another crystalline phase. We designate this crystalline phase as crystal-III, although we have not confirmed by X-ray analysis whether it is a pure single phase or a mixture of several modifications. After the formation of crystal-III, a gradual heat evolution was observed between 95 K and 105 K. It is considered that a part of crystal-III was transformed into a low temperature form (crystal-II) irreversibly in this temperature region. At about 107 K, the phase transition from crystal-III to an unknown crystalline phase was observed. This unknown phase is, however, unstable and irreversibly transformed to another crystalline phase. The resulting crystalline phase is evidently a stable modification below 136 K as shown by Run-4. Here Run-4 is for the heating curve determined after Run-3 has been stopped at about 125 K and cooled to a lower temperature. We designate this stable phase as crystal-II. Crystal-II was then transformed to crystal-I at 136 K, followed by the fusion of crystal-I at about 145 K. In this case we have always observed a small anomaly at about 135 K just before the II-I transition point in Fig. 1, and the anomaly is rather exaggerated. Occurrence of this anomalous hump$^{10)}$ was influenced by previous

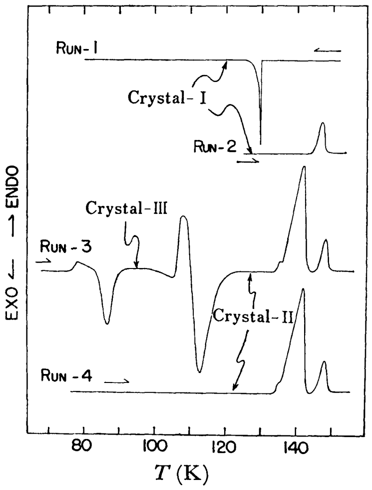

Fig. 1. DTA curves of 2,3-dimethylbutane.

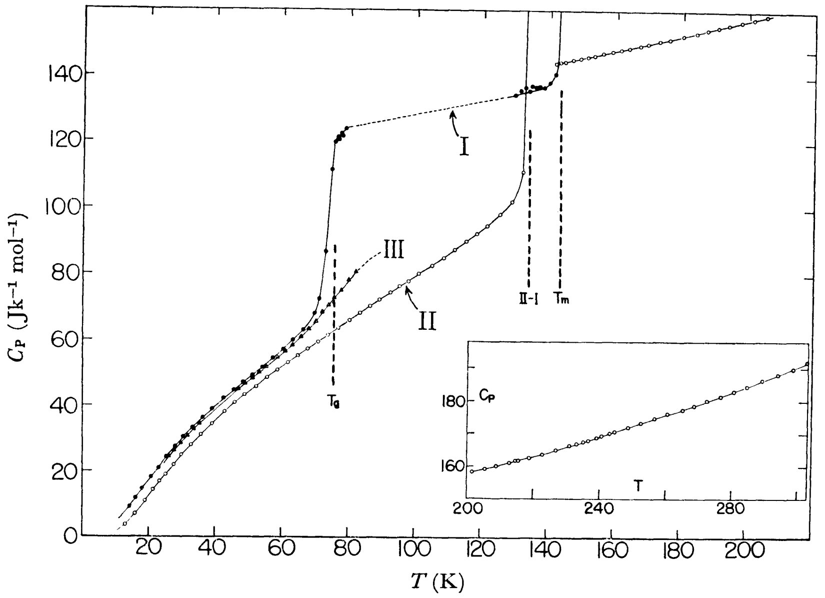

Fig. 2. The heat capacity curves of 2,3-dimethylbutane.
● the crystal-I, the supercooled crystal-I and the glassy crystal
○ the crystal-II (below 136 K) and the liquid (above 136 K)
△ the crystal-III

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10) After the experiment was over, more clear and doubly separated peaks were observed by use of a new type DTA apparatus constructed in our laboratory. The details will be reported elsewhere.

TABLE 1. MOLAR HEAT CAPACITIES OF 2,3-DIMETHYLBUTANE

Mol wt=86.179 0°C=273.15K

$T_{\mathrm{av.}}$ K	$\Delta H/\Delta T$ $\mathrm{JK^{-1}mol^{-1}}$	ΔT K	$T_{\mathrm{av.}}$ K	$\Delta H/\Delta T$ $\mathrm{JK^{-1}mol^{-1}}$	ΔT K
Series 1					
(Glassy crystal and Supercooled crystal-I)					
14.481	9.420	1.62	16.259	11.817	1.92
18.444	14.826	2.45	20.972	18.374	2.61
23.381	21.623	2.20	25.681	24.567	2.40
27.949	27.368	2.13	30.596	30.443	3.16
33.584	33.678	2.82	36.281	36.423	2.58
39.313	39.268	3.48	42.662	42.234	3.21
45.764	44.861	3.00	48.673	47.289	2.82
51.429	49.595	2.69	54.404	51.975	3.26
57.589	54.706	3.10	60.635	57.447	2.96
63.570	60.269	2.83	66.638	63.509	3.16
69.823	68.428	2.98	72.813	78.974	2.69
75.198	98.343	1.98	76.849	117.104	1.74
78.547	125.021	1.65			
Series 2					
(Glassy crystal and Supercooled crystal-I)					
71.507	72.651	1.81	73.397	86.856	1.98
74.905	111.857	1.04	75.918	120.114	0.99
76.900	121.025	0.98	77.876	122.50	0.97
Series 3					
(Supercooled crystal-I)					
76.755	121.151	0.85	77.472	122.940	0.56
Series 4					
(Crystal-III)					
50.368	47.832	2.10	55.354	51.823	2.55
60.269	55.727	2.37	64.882	60.156	2.28
69.190	64.925	2.07	73.218	69.611	1.96
77.248	74.961	2.29	81.691	81.723	2.14
83.871	84.698	2.08			
Series 5					
(Crystal-III)					
26.399	24.485	1.11	27.988	26.300	2.05
29.946	28.532	1.87	31.886	30.708	2.01
33.824	32.827	1.87	35.634	34.725	1.75
47.239	45.191	1.75	51.319	48.561	2.08
55.342	51.792	1.95	59.124	54.745	1.84
63.566	58.697	2.30	67.997	64.017	2.14
72.153	69.016	2.01	76.075	73.267	1.91
80.018	79.013	2.25	82.254	82.122	2.18
Series 6					
(Crystal-II)					
13.033	3.865	3.24	16.061	6.966	2.82
18.989	10.566	3.04	21.662	14.062	2.30
23.607	16.616	1.58	25.445	18.982	2.09
27.769	21.962	2.56	30.170	24.854	2.25
32.944	28.033	3.30	36.056	31.398	2.92
39.372	34.699	3.71	42.911	37.975	3.37
46.151	40.775	3.12	49.170	43.324	2.92
52.366	45.890	3.47	55.742	48.500	3.28
58.948	50.932	3.13	62.009	53.295	2.99
64.940	55.471	2.88	67.936	57.568	3.12
70.996	59.696	3.01	73.958	61.707	2.92
77.067	63.926	3.30	80.324	66.310	3.21
83.483	68.534	3.10	86.546	70.744	3.02
89.534	72.707	2.95	92.458	74.562	2.89
95.323	76.420	2.74	98.134	78.253	2.78
101.344	80.333	3.64	104.939	82.752	3.55
108.451	85.240	3.47	111.888	87.751	3.40
115.248	90.157	3.33	118.542	92.571	3.26
121.402	95.416	3.54	125.444	98.430	3.46
128.855	102.503	3.36	132.188	111.636	3.30
134.814	216.86	1.95			
Series 7					
(Crystal-I)					
138.319	137.20	1.61	139.847	138.68	1.45
141.283	142.27	1.42			
Series 8					
(Supercooled crystal-I and Crystal-I)					
133.939	136.11	0.98	134.919	137.02	0.98
136.071	137.35	1.32	137.394	137.54	1.32
Series 9					
(Supercooled crystal-I)					
129.809	134.38	1.28	131.353	136.11	1.80
133.147	137.05	1.79	134.935	137.28	1.79
Series 10					
(Supercooled liquid and Liquid)					
141.900	144.02	0.86	142.908	144.40	1.15
144.630	144.77	2.29	146.915	145.31	2.28
149.192	145.73	2.27			
Series 11					
(Liquid)					
153.254	146.73	2.59	155.836	147.31	2.58
158.409	147.82	2.57	160.974	148.53	2.56
163.531	149.05	2.55	166.078	149.64	2.54
169.373	150.37	4.05	172.656	151.01	2.52
175.926	151.82	4.02	179.932	152.80	3.99
183.915	153.74	3.97			
Series 12					
(Liquid)					
187.462	154.61	3.95	190.662	155.39	2.45
193.843	156.21	3.91	197.730	157.14	3.89
201.617	158.20	3.87	205.474	159.15	3.85
208.595	159.98	2.39			
Series 13					
(Liquid)					
212.836	161.12	2.60	214.304	161.86	0.34
215.509	161.86	2.07	218.606	162.69	4.12
222.719	163.73	4.10	226.806	165.08	4.07
230.910	166.34	4.14	234.989	167.57	4.02
238.997	168.76	3.99	242.977	170.09	3.97
Series 14					
(Liquid)					
233.074	166.96	2.57	236.407	167.96	4.10
240.497	169.31	4.08	244.560	170.74	4.04
248.592	171.96	4.02	252.599	173.36	3.99
256.583	174.66	3.98	260.543	176.07	3.94
264.510	177.42	3.99	268.452	178.85	3.89
272.332	180.20	3.87	276.656	181.65	4.78
280.527	183.07	2.96	284.372	184.52	4.73
289.071	186.33	4.67	298.723	188.10	4.63
298.340	189.75	4.60	302.921	191.52	4.56

thermal history and may be attributed to the effect of impurities.

Measurement of Heat Capacity. The results of the heat capacities are listed in Table 1 and heat capacity curves are shown in Fig. 2, where direct results of the measured heat capacities are given by $\Delta H/\Delta T$, that is, an increment of the molar enthalpy divided by the corresponding temperature increment. Series-1 shows the heat capacities of the glassy crystalline state of crystal-I which has been established by supercooling the specimen with an average cooling rate of -2 K min^{-1} from 150 K to 75 K. In series-1 and series-2, the average heating rates were about 10 K/hr and 4 K/hr, respectively, in the glass transition region. The glass transition temperature was determined to be about 75 K from series-1 and 76 K from series-2. As is well known, it is considered that the discrepancy resulted from the difference in heating rates.[11,12] Series-2 also shows the heat capacity of the glassy crystalline state of crystal-I after supercooling with a cooling rate about -2 K min^{-1}. In the glass transition region, the measurements were disturbed by heat evolution due to the relaxation of enthalpy. This phenomenon was observed from 55 K and gradually increased up to 72 K. This heat evolution due to relaxation effect was removed by treating it as if it had arisen from heat inflow due to an incompleteness of adiabatic conditions. In other words, these relaxation effects were subtracted by the correction of a temperature drift in the computation of the heat capacities.[13] If we treat the heat due to the relaxation effect in this way, the calculated values of the heat capacities correspond to those of constant configuration; *i. e.* those measured with an infinitely rapid heating rate. The data of supercooled crystal-I which were obtained successively after the annealing experiments (described later) are shown in series-3. The aim of the measurements of this series was to see whether the irreversible transition from the glassy crystal to another phase had occurred or not during the course of annealing. Series-4 and series-5 give the selected values for crystal-III. The condition for establishing this phase is determined on the basis of the DTA measurements. Series-6 shows the heat capacities for crystal-II. The heat capacities of crystal-I and supercooled crystal-I are given in series-7,8 and 9. The heat capacities of supercooled crystal-I were measured after the specimen was slowly cooled (about -1 K min^{-1}) to about 133 K. However, below 133 K, the irreversible transition from supercooled crystal-I to the low temperature phase occurred gradually before the adiabatic condition for measurement was established. On account of this instability, the heat capacities of supercooled crystal-I between 80 K and 130 K could not be measured. The heat capacities of the liquid state are given in series-10—14. Heat capacities measured in this investigation have been compared with the data of Douslin and Huffman.[4] The deviation is found to be about $\pm 0.5\%$ below 20 K, whereas the data agree quite well within 0.1% between 25 K and 100 K for crystal-II. However, near transition temperature (136 K), our results are larger than those of Douslin and Huffman. The deviation between 110 K and 120 K is from 0.3% to 1% and between 120 K and 130 K about 2%. The deviation near the transition point might be due to impurity. In the region from 136 K to 220 K, the data of Douslin and Huffman is about 0.2% smaller and in the region from 220 K to 300 K, about 0.5% smaller.

Table 2. Equilibrium temperatures during fusion process

Fraction melted F (%)	$1/F$	Temperature (K)
46.8	2.137	144.488
58.7	1.704	144.578
71.2	1.404	144.646
84.1	1.189	144.702
97.1	1.030	144.752

Melting point of pure 2,3-Dimethylbutane 145.04± 0.01K
Mol % of impurity 0.13%

Table 3. Molar heat of fusion

	ΔH/J mol^{-1}
1st experiment	794.3
2nd experiment	793.1
mean	793.7±1.0

Table 4. Molar heat of transition

	ΔH/KJ mol^{-1}
1st experiment	6.423
2nd experiment	6.428
3rd experiment	6.430
mean	6.425±0.01

Molar Heats of Transition and Fusion. Equilibrium temperatures during fusion process and the molar heats of fusion and transition are given in Tables 2, 3, and 4, respectively. As shown in Table 2, the impurities in the specimen are determined to be 0.13% from the fractional melting data assuming no formation of solid solution. Compared with the data of Douslin and Huffman[4] both the melting point and the transition point of this study are somewhat lower. The values of the heat of fusion and the heat of transition are also smaller than those of Douslin and Huffman. A part of the disagreement may be attributed to the effect of the impurity. Another origin of the discrepancy may be attributed to the ambiguity in the estimation of the normal heat capacity curve. For the determination of the standard entropy, however, an error due to this ambiguity is small enough because the error of the entropy change at the transition point is corrected by heat capacity due to pre-transition. The increment of the molar entropy from 120 K (below transition point) to 150 K (above melting point) is compared with the value calculated from the data of Douslin and Huffman. The difference of these values is only 0.4 J K^{-1} mol^{-1}. Therefore the molar entropy may not be affected severely by the impurity of about 0.1% involved in the present specimen.

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11) B. Wunderlich, *J. Polymer Sci.*, **C 6**, 137 (1963).
12) J. A. McMillan, *J. Chem. Phys.*, **42**, 3497 (1965).
13) For temperature drift, see Ref. 8.

Estimation of the Heat Capacity of Supercooled Crystal-I between 80 K and 130 K. The heat capacity of supercooled crystal-I between 80 K and 130 K is estimated to be

$$C_p = 0.18571\mathrm{T} + 111.143\,\mathrm{JK^{-1}\,mol^{-1}} \qquad (1)$$

which corresponds to the straight line obtained by connecting the values of the heat capacities at 80 and 130 K as shown in Fig. 2 (dotted line). Based on this interpolation equation, the molar enthalpy of supercooled crystal-I was calculated. Here, we have taken the value of the enthalpy of crystal-II at 0 K as 0 for the standard point of the enthalpy of this material. This value is compared with the directly determined value of the molar enthalpy of supercooled crystal-I at 77.72 K. Direct determination of the molar enthalpy of crystal-I was made as follows. If the temperature of glassy-crystal-I be raised up a little above T_g, say 77.7 K, a spontaneous exothermic transition takes place to another metastable phase which is finally transformed into the most stable crystal-II. If an adiabatic condition of the calorimeter cell is maintained during the irreversible changes, the molar enthalpy of supercooled crystal-I at 77.7 K can be determined by measuring the temperature at which the irreversible transitions terminate, since the enthalpy of crystal-II at this temperature is already known. In the actual measurement, an excess electric energy was supplied to terminate the phase change more rapidly. Assuming a complete adiabaticity, the calculation was made as follows.

$$H_{\mathrm{I}}(77.720) = H_{\mathrm{II}}(125.984) + \int_{77.720}^{125.984} C_p(\text{empty cell})dT$$
$$- \sum(\text{supplied electric energy}) \qquad (2)$$

Here, $H_{\mathrm{I}}(77.720)$ and $H_{\mathrm{II}}(125.984)$ are the enthalpies of supercooled crystal-I at 77.720 K and of crystal-II at 125.984 K, at which the irreversible transition ends completely under a specified condition for energy supply. Thus the enthalpy of supercooled crystal-I at 77.720 K was determined to be 6084.8 Jmol^{-1}. Calculation from the integration of Eq. (1) gives, on the other hand, 6211.1 Jmol^{-1}. For this discrepancy, the following three possibilities are considered; 1) True heat capacity curve of supercooled crystal-I is located above the estimated one. 2) The actual glassy crystal contains some amounts of the crystal-II phase due to insufficient cooling rate in the preparation of glassy crystal. 3) Experimental error due to the incompleteness of adiabatic conditions. In the calculation of various thermodynamic functions, the mean value 6150±70 Jmol^{-1} has been employed.

The Residual Entropy of the Glassy Crystalline State. By comparison of the gaseous entropy determined from thermal data with that computed from spectroscopic data, it was concluded by Scott *et al.* that the crystal-II has no residual entropy at 0 K.[14] Based on this result the residual entropy of the glassy-crystalline state at 0 K has been determined by a well defined method. Contributions below 13 K have been determined from extrapolated heat capacities assuming the Debye theory. The Debye temperatures were taken to be 129.44 K and 101.35 K for crystal-II and the glassy crystal-I, respectively, by assuming 6 degrees of freedom. The increment of the entropy of the supercooled crystal-I between 80 and 136 K was calculated by using Eq. (1) with a slight correction (0.6 JK^{-1} mol^{-1}) due to the uncertainty of this equation as described above. The calculation is shown in Table 5 and the residual entropy of the glassy crystal is determined to be 7.4±1.3 J K^{-1} mol^{-1}.

TABLE 5. THE THIRD LAW ENTROPY OF CRYSTAL-I AT 136.02 K *via* II-I TRANSITION AND *via* GLASSY CRYSTALLINE STATE

Temperature (K)	Contribution	ΔS (JK^{-1} mol^{-1})
via II-I transition		
0— 12.5	Debye extrapolation	1.16
12.5—136.02	$\int C_p$(II) dln$T$	98.22
136.02	Transition (6427/136.02)	47.25
		146.63
via glassy crystalline state		
0— 13.5	Debye extrapolation	2.92
13.5— 80.0	$\int C_p$ (Glassy cryst.) dln$T$	66.35
80.0—136.02	$\int C_p$ (I) dln$T$+0.6[a]	70.0
		139.27

a) Equation(1) is used for C_p(I) and 0.6 JK^{-1} mol^{-1} is added after integration for correction.

Crystal-III. On account of intricate irreversible transitions, the heat capacity of crystal-III between 80 K and 107 K and the heat of transition which occurs at 107 K from crystal-III to other unknown phase could not be measured. The molar enthalpy of the crystal-III at about 80 K has been measured by the same procedure as that employed in the determination of the enthalpy of supercooled crystal-I. The procedure gives 4990±40 J mol^{-1} at 78.39 K. Using this value, we have attempted to estimate the heat of transition at 107 K. We assumed that the unknown crystalline phase into which crystal-III is transformed at 107 K is supercooled crystal-I. The heat capacity of crystal-III between 80 K and 107 K is estimated by the extrapolation equation which is represented by

$$C_p = 0.782\mathrm{T} + 16.3\,\mathrm{JK^{-1}\,mol^{-1}} \qquad (3)$$

From these assumptions, the heat of transition from crystal-III to supercooled crystal-I has been calculated to be 2370 J mol^{-1}.

The residual entropy of crystal-III which amounted to 2.7 JK^{-1} mol^{-1} was calculated from the heat of transition determined above and the estimated heat capacity equations 1 and 3. The calculation is given

TABLE 6. THE THIRD LAW ENTROPY OF CRYSTAL-I AT 136.02K *via* III-I TRANSITION

Temperature (K)	Contribution	ΔS (JK^{-1} mol^{-1})
0— 24.5	Debye extrapolation	10.81
24.5— 82.0	$\int C_p$ (III) dln$T$	54.72
82.0—107	$\int C_p$ (III) dln$T$	23.8
107	Transition (2373/107)	22.2
107 —136.02	$\int C_p$ (I) dln$T$	32.4
		143.9

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[14] D. W. Scott, J. P. McCullough, K. D. Williamson, and G. Waddington, *J. Amer. Chem. Soc.*, **73**, 1707 (1951).

in Table 6 where contributions to the entropy below about 25 K has been estimated by using the Debye function with the value of 107.6 K for θ_D and by assuming 6 degrees of freedom. There appears an anomalous swelling in the heat capacity curve around 70 K. At this temperature range, a fairly long time was required to attain thermal equilibrium (about 25 min). Above 75 K, gradual heat liberation due to the irreversible transition to crystal-II was observed.

Thermodynamic Functions. Thermodynamic functions for the three crystalline phases and for the liquid phase are all listed in Table 7. The molar enthalpies and the molar entropies of respective phases are plotted in Figs. 3 and 4.

Relaxation of Enthalpy below the Glass-Transition Point. It is well known that the configurational degrees of freedom of the glass-forming materials are virtually frozen below T_g on account of the long relaxation time. However, if the temperature is regulated to be constant below glass transition point, the configurational

TABLE 7. THERMODYNAMIC FUNCTIONS OF 2,3-DIMETHYLBUTANE (unit: $\mathrm{JK^{-1}mol^{-1}}$)

T(K)	$C_p°$	$S°$	$(H°-H_0°)/T$	$-(G°-H_0°)/T$
		(Crystal-II)		
5	(0.224)	(0.0747)	(0.0569)	(0.0187)
10	(1.787)	(0.5976)	(0.4481)	(0.1495)
20	11.89	4.457	3.303	1.154
30	24.65	11.73	8.327	3.404
40	35.31	20.34	13.79	6.549
50	44.03	29.18	18.79	10.39
60	51.73	37.89	23.81	14.08
70	59.02	46.43	28.33	18.10
80	66.07	54.77	32.60	22.17
90	73.02	62.96	36.71	26.25
100	79.44	70.99	40.66	30.33
110	86.30	78.88	44.49	34.39
120	94.01	86.70	48.29	38.41
130	103.18	94.58	52.15	42.43
136.02		Transition		
		(Crystal-I)		
140	137.72	151.08	103.29	47.49
145.04		Fusion		
		(Liquid)		
150	145.92	166.81	110.69	56.12
160	148.16	176.30	112.97	63.33
170	150.43	185.35	115.11	70.24
180	152.81	194.01	117.11	76.90
190	155.22	202.34	119.06	83.28
200	157.73	210.37	120.94	89.43
210	160.23	218.12	122.76	95.36
220	163.03	225.64	124.52	101.12
230	165.98	232.95	126.26	106.69
240	169.09	240.08	127.98	112.10
250	172.39	247.05	129.69	117.36
260	175.83	253.88	131.40	122.48
270	179.32	260.58	133.11	127.47
280	182.91	267.16	134.82	132.34
290	186.61	273.65	136.54	137.11
300	190.40	280.03	138.27	141.76

T(K)	$C_p°$	$S°-S_0°$ (g)	$(H°-H_0°$ (g))/T	$-(G°-H_0°$ (g))/T
		(Glassy crystal and Supercooled crystal-I)		
5	(0.4669)	(0.1557)	(0.1167)	(7.6)
10	(3.637)	(1.234)	(0.9238)	(7.7)
20	17.01	7.71	5.54	9.6
30	29.75	17.10	11.56	12.9
40	39.91	27.10	17.42	17.1
50	48.40	36.93	22.78	21.5
60	56.84	46.49	27.71	26.2
70	68.88	56.03	32.63	30.8
80	126.00	69.27	41.32	35.4
90	(127.9)	(84.3)	(50.9)	(40.8)
100	(129.7)	(98.0)	(58.8)	(46.6)
110	(131.6)	(110.5)	(65.5)	(52.4)
120	(133.4)	(122.2)	(71.1)	(58.5)
130	(135.3)	(133.3)	(76.1)	(64.3)

T(K)	$C_p°$	$S°-S_0°$ (III)	$(H°-\mathrm{H}_0°$ (III))/T	$-(G°-H°$ (III))/$T°$
		(Crystal-III)		
5	(0.3906)	(0.1302)	(0.0977)	(2.7)
10	(3.073)	(1.037)	(0.7768)	(3.0)
20	(16.27)	(6.90)	(5.00)	(4.6)
30	28.60	15.94	10.91	7.7
40	39.00	25.64	16.68	11.6
50	47.48	35.28	22.01	16.0
60	55.53	44.66	26.93	20.5
70	65.87	53.95	31.71	25.0
80	78.85	63.55	37.74	28.6

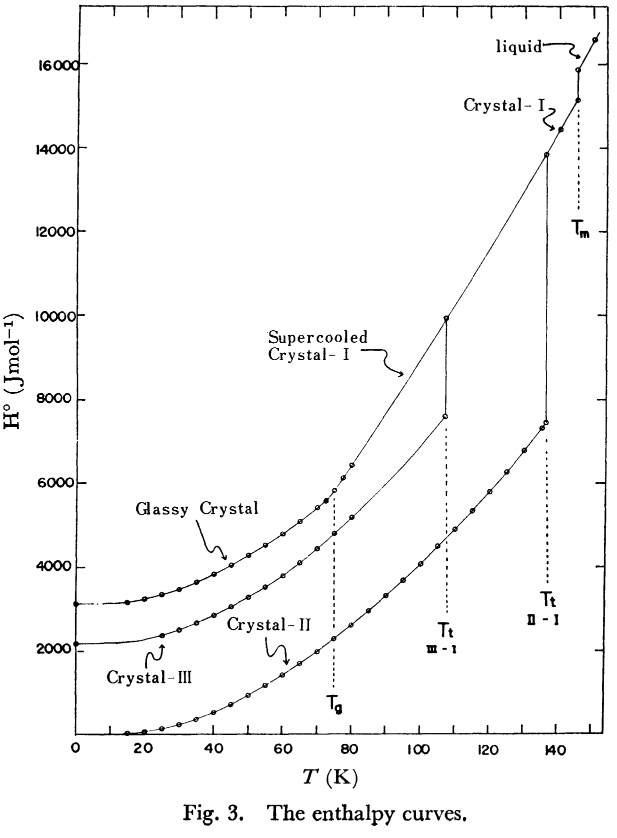

Fig. 3. The enthalpy curves.

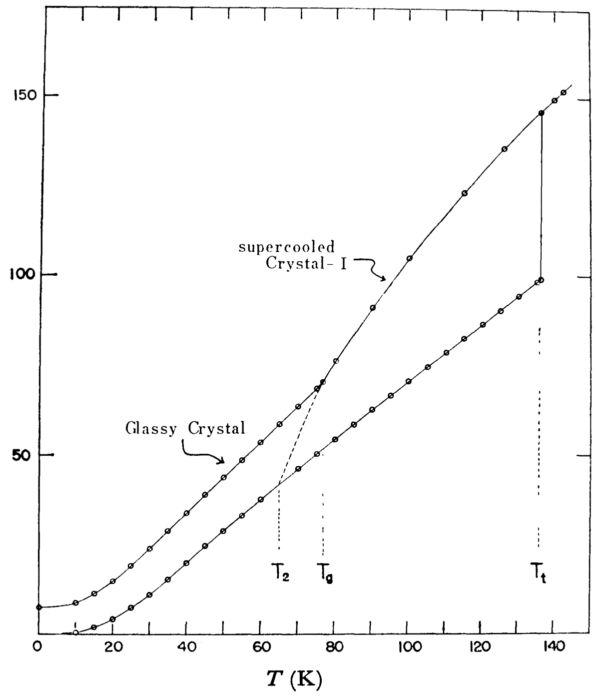

Fig. 4. The entropy curves.

enthalpy returns gradually to the equilibrium value from that of non-equilibrium frozen state.[15] We have revealed previously[1] that a similar behavior to ordinary glass is observed in the glassy crystalline state of cyclohexanol. The relaxation process for the glassy crystal of 2,3-dimethylbutane was investigated in the same way below T_g by annealing. The experiments were carried out as follows. Crystal-I was supercooled with the cooling rate of about -2 K min^{-1}. Cooling was stopped at a definite temperature below T_g and the temperature was regulated to maintain constant value for at least 20 hr. These studies were carried out at 60.7, 65.1, 69.7 and 72.0 K and the temperatures were regulated in the range of ± 0.3 K. After annealing for 20 hr, the temperature of the specimen was raised by supplying electric energy under adiabatic conditions to a temperature where an internal equilibrium was established, say 76 K. From the supplied energy, the difference in the enthalpies between the annealed glassy crystal at the initial temperature T_i and the supercooled crystal-I at T_f (about 76 K) was determined. Of course a part of the supplied electric energy is used to change the enthalpy of some degrees of freedom which is not frozen at the T_g. Thus, the enthalpy change due to this kind of degree of freedom (increment of the energy of vibrations or so) was subtracted from the total change of enthalpy in order to see directly the change of the configurational enthalpy. The heat capacity due to the vibrations (C_p(vib)) was estimated by the following equation between 60 and 80 K.

$$C_p(\text{vib}) = 0.9200\text{T} + 1.72 \text{ JK}^{-1}\text{mol}^{-1} \qquad (4)$$

The change of the configurational ΔH_c is given by

$$\Delta H_c = \Delta H - \int_{T_i}^{T_f} C_p(\text{vib})\text{d}T \text{ Jmol}^{-1} \qquad (5)$$

where T_i and T_f were defined above and ΔH is the electric energy supplied per mol. The calculated values of ΔH_c are modified so that the final temperature T_f is 76.40 K by using the measured heat capacities near T_g. We take T_f=76.40 K as the reference point for ΔH_c=0. The results are shown in Fig. 5 and Table 8. During the course of annealing, the rates of the

Table 8. Relaxation of the configurational enthalpy of the glassy crystal

	T_i(K)	T_f(K)	ΔH	ΔH(vib)	ΔH_c
1	69.669	76.425	671.7	465.6	206.0
2	65.138	76.346	913.7	748.7	165.0
3	60.692	76.327	1146.8	1012.3	134.4
4	72.028	76.328	493.4	300.9	192.6

The unit of ΔH is Jmol^{-1}. ΔH represents the supplied energy to raise the temperature from T_i where the specimen was annealed to T_f. ΔH(vib) indicates $\int_{T_i}^{T_f} C_p(\text{vib})\text{d}T$. C_p(vib) is given by Eq. (3). ΔH_c represents the difference of the configurational enthalpy, *i.e.* $\Delta H - \Delta H$ (vib).

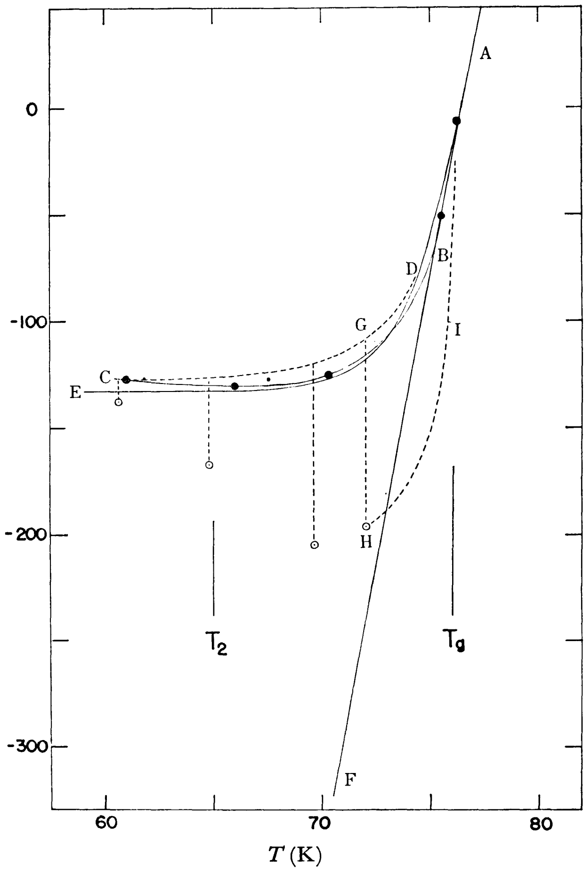

Fig. 5. The relaxation effect of the configurational enthalpy.
A-B-F Equilibrium curve calculated from Eq. (1).
A-B-C Change of the configurational enthalpy of the glassy crystal when it was heated with the rate of 4 K/hr after cooled down to about 50 K with the rate of -2 K/min.
A-D-G-C Estimated value of the enthalpy after cooling with the rate of -2 K/min.
G-H The point G shows the value of H_c just after the crystal-I was chilled to 72 K. After the annealing period of 20 hr the enthalpy changes to the point H.
H-I-A Estimated change of the configurational enthalpy when the specimen is heated from H with the rate of about 10 K/hr.

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[15] R. O. Davies and G. O. Jones, Advances in Phys., **2**, 370 (1953).

Table 9. The rate of change of configurational enthalpy

Annealed at							
72.0K		69.7K		65.2K		60.7K	
Time	$-\dot{H}_c$	Time	$-\dot{H}_c$	Time	$-\dot{H}_c$	Time	$-\dot{H}_c$
0.53	54.4	1.33	27.9	1.33	9.99	0.83	3.25
0.66	48.0	3.09	14.2	4.58	3.20	2.17	2.35
2.58	14.5	4.33	10.4	5.50	4.32	5.00	1.74
5.42	7.50	5.58	8.22	18.75	1.94	6.25	1.58
8.42	4.07	7.00	6.86	19.50	2.16	11.17	1.22
10.66	3.43	9.09	5.09			14.25	1.04
20.00	1.29	15.09	3.88			17.25	1.35
		17.83	2.87			19.92	0.81
		19.83	2.22				

(time unit: hr; $-\dot{H}_c$: $10^{-2}J$ mol^{-1}min^{-1})

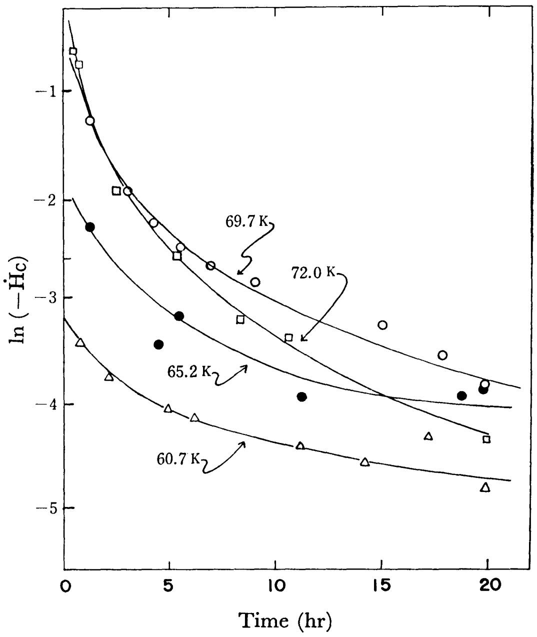

Fig. 6. Curves of the rate of the enthalpy change at various temperatures below T_g.

heat evolution due to the reversion of the enthalpy to the equilibrium state were determined from the rate of spontaneous temperature rise under the temporarily adjusted adiabatic conditions. The rates of the enthalpy change at various temperatures were calculated from these measurements and are shown in Fig. 6. and Table 9.

Discussion

Residual Entropy and Frozen-in State. Crystal-I of this material belongs to the so-called "plastic crystal" named by Timmermans.[16] It is known that in the plastic crystalline phase, the constituent molecules change their orientations rather rapidly at their lattice points. The self-diffusion phenomenon is also observed in many plastic crystals just below their melting points.[17,18] The second moment of NMR absorption line for crystal-I was reported to be 0.7 gauss^2 at about 140 K.[19] This may be explained also as a result of the rapid motion of molecules in the plastic crystal phase. It was also reported that the broadening of the line width of NMR spectrum was observed in the supercooled crystal-I at about 85 K, about 10 K higher than T_g (=76 K).[5] This behavior resembles that of ordinary glasses.[20] On the other hand, we have observed the relaxation effect of the configurational enthalpy below T_g where the relaxation time turns out to be 20 hr or more. These facts indicate that the probability of reorientation of molecules becomes smaller at lower temperatures due to the existence of hindering potential. At a temperature around 10 K higher than T_g, the frequency of the reorientation is estimated to be of the order of 10^3 times per second from the NMR data. Below T_g, on the other hand, the relaxation time becomes longer than the experimental time scale for heat capacity measurement, resulting in an establishment of non-equilibrium state. Therefore, it is expected that the main origin of the residual entropy can be attributed to the randomness of the orientation of molecules. If one calculates from the residual entropy the average number of configurational states permitted for a molecule in the glassy crystalline state by using the relation $S_0 = \boldsymbol{R}\ln W$, W amounts to 2.4 ± 0.3. Here, S_0, $\boldsymbol{R}$ and W are the residual entropy, the gas constant and the number of states, respectively. Unfortunately, the crystal structure of crystal–I is unknown and quantitative treatment for the orientational degree of freedom is impossible at the present stage. We should like to discuss, however, its contribution to the residual entropy briefly. If we assume the face-centered or body-centered lattice[21] for crystal-I and the center of gravity of the molecule located at the lattice point, it is plausible that the orientation of the molecular axis is directed to one of the three axis of the cubic cell with respect to their elongated sphere shape of a molecule. Here, the molecular axis is taken as the line parallel to the C–C bond connecting two $(CH_3)_2CH$-groups. There remains further the degree of freedom of the rotation of a whole molecule around this axis. The possible number of orientations permitted for this degree of freedom may be 4, at least even the conformation of the molecule being fixed. Thus, it may be concluded that at the limit of the most random state, the molecule will have about 12 kinds of orientations (3×4). In other word, the configurational entropy due to the orientational degree of freedom may be $\boldsymbol{R}\ln 12$ (21 JK^{-1} mol^{-1}) at high temperature. Comparing this value with the residual entropy ($\boldsymbol{R}\ln 2.4$), it may be said that the ordering of orientation should take place with the decrease of temperature. Furthermore, we may take into consideration the contribution of

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[16] J. Timmermans, *J. Phys. Chem. Solids*, **18**, 1 (1961).

[17] H. Suga, M. Sugisaki, and S. Seki, *Mol. Cryst.*, **1**, 377 (1966).

[18] C. P. Smyth, *J. Phys. Chem. Solids*, **18**, 40 (1961).

[19] R. G. Eades, G. P. Jones, J. P. Llewellyn, and K. W. Terry, *Proc. Phys. Soc.*, **91**, 124 (1967).

[20] for example, K. Luszczynski, J. A. E. Kail, and J. G. Powles, *ibid.*, **75**, 243 (1960).

[21] W. J. Dunning, *J. Phys. Chem. Solids*, **18**, 21 (1967).

the molecular conformations to residual entropy. It is possible for the molecule of 2,3-dimethylbutane to have two different conformations by internal rotation,[22] *i.e.* one *trans*-form and two identical *gauche*-forms. The energy difference between them in the liquid state has been reported from the studies of the infrared and Raman spectra and from the absorption of sound wave. Szasz and Sheppard[23] proposed two possibilities for the energy difference between two conformations in the liquid state, *i.e.* either less than 100 cal/mol or very high value from the temperature dependence of the Raman spectra, based on the fact that no measureable intensity changes were observed in the spectra investigated at various temperatures. Brown and Sheppard studied further the IR and Raman spectra of the crystalline state and concluded the existence of only the *trans*-form.[24] They reported, however, that crystallization took place by raising the temperature of the "*glassy state*."[25] They also reported that the spectrum in the "*glassy state*" closely resembled that in the liquid state. Accordingly, supercooled crystal-I is considered to be composed of a mixture of the *trans*-form and the *gauche*-form with the ratio of about one to two. On the other hand, Chen and Petrauskas determined the energy difference between two conformations to be 4.0 KJ mol^{-1} from their study of the absorption of the hypersonic sound wave in the liquid state.[26] The energy difference in the gaseous state was estimated to be 6.7 KJ mol^{-1} by Pitzer.[27] Scott *et al.* concluded, however, that it was very small (less than 100 cal mol^{-1}) from studies of the heat capacity and the entropy in the gaseous state.[14] We have reinvestigated the infrared spectrum of the glassy crystal at 40 ± 30 K and found that the spectrum was nearly the same as that of the liquid.[28] The study has been carried out in the region of 1050—800 cm^{-1}. If we assume that the mixing ratio of the isomers is frozen at the glass transition point and that the energy difference is 100 cal mol^{-1}, the contribution of this degree of freedom to the residual entropy amounts to 8.6 JK^{-1} mol^{-1}. Here, the *gauche* form is taken as the higher energy species. This value exceeds the actual value of the residual entropy. Thus, we understand from spectroscopic experiments that most of the residual entropy can be attributed to the randomness in the conformation of molecules. That the residual entropy can be explained only by the freezing of conformational degree of freedom was already observed in the case of the glassy crystalline state of cyclohexanol.[1] This seemingly strange result can be explained if we assume that the conformational degree of freedom is strongly coupled with the orientational degree. It should be noted that if the conformation be independent of the neighboring molecules, its contribution to heat capacity should be Schottky-type and may be much smaller than the actual jump of the heat capacity at T_g which is caused by the release from frozen-in state.

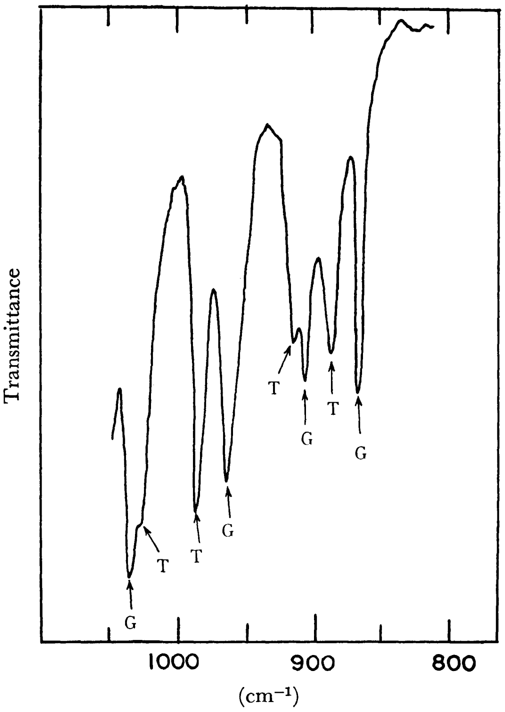

Fig. 7. Infrared spectra in the glassy crystalline state of 2,3-dimethylbutane.
T; the absorption band due to the *trans*-form.
G; the absorption band due to the *gauche*-form.

T_2 *Temperature.* In order to explain Kauzmann's paradox,[29] Gibbs and Adam have proposed an equation for the temperature dependence of the relaxation time in terms of the configurational entropy of the supercooled liquid.[6] The theory predicts that the relaxation time of viscoelastic properties becomes infinite at a temperature (T_2) where the configurational entropy disappears. T_2 temperature is determined from the equation described below by assuming that the equilibrium heat capacity is given by the extrapolation of the heat capacity curve above T_g.

$$S_0^\circ = \int_{T_2}^{T_g}[C_p(\mathrm{eq})-C_p(\mathrm{gl})]\mathrm{d}\ln T, \tag{6}$$

where S_0°, C_p(eq) and C_p(gl) are the residual entropy, the heat capacity of the supercooled crystal-I and that of the glassy crystal, respectively. Here, Eq. (1) extrapolated to lower temperature is used for C_p(eq). T_2 Temperature determined in this way amounts to 65.0 ± 0.7 K. It is known empirically that for ordinary amorphous glass, the ratio of T_g to T_2 is about 1.3.

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[22] R. I. Podlovchenko, L. M. Sverdlov, and M. M. Sushchinskii, *Optics. Spectr.*, **6**, 96 (1959).

[23] G. J. Szasz and N. Sheppard, *J. Chem. Phys.*, **17**, 93 (1949).

[24] J. K. Brown and N. Sheppard, *ibid.*, **19**, 976 (1951).

[25] They decribed it as a "*glassy state*". It is, however, incorrect, because they did not find any glass transition point. This "*glassy state*" may be the supercooled crystal-I and the crystal (in their notation) is presumably crystal-II.

[26] J. H. Chen and A. A. Petrauskas, *ibid.*, **30**, 304 (1959).

[27] K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

[28] The results are shown in Fig. 7. Almost the same spectra were observed in liquid state. Podlovchenko *et al.* concluded from calculation of the normal modes of vibration that these bands are attributed to those of *trans*-isomer and *gauche*-isomer as shown in Fig. 7. Since the specimen sealed in a polyethylene container was used, transmittance was rather bad. Accordingly, the intensity of each band is not very reliable.

[29] W. Kauzmann, *Chem. Pev.*, **43**, 219 (1948).

Table 10. Values of ΔC_p, S_0, and T_g/T_2 for glassy crystals

	T_g(K)	ΔC_p	S_0	T_g/T_2
2,3-Dimethylbutane	76	51	7.4	1.17
Cyclohexanol[a]	150	24	4.7	1.18
cis-1,2-Dimethylcyclohexane[b]	94	54	8.6	1.15
Molecular compound[c] of 2,3-Dimethylbutane and 2,2-Dimethylbutane	69	56	10.0	1.19

The unit of ΔC_p and S_0; JK^{-1} mol^{-1}

a) From Ref. 1.

b) Calculated from Ref. 2.

c) Calculated from Ref. 3

For the glassy crystals including some other examples known hitherto the ratio T_g/T_2 amounts to about 1.15—1.20 as shown in Table 10. Angell discussed the value of T_g/T_2 for ordinary glass[30] and considered the glass having the value of $T_g/T_2=1$ to be an ideal glass. The small value of T_g/T_2 for glassy crystal may be explained from the fact that glassy crystal has higher positional order than ordinary glass. It is interesting to compare the glassy crystal of 2,3-dimethylbutane with the glassy state of 2-methylbutane (isopentane), the study of which was reported previously.[31] The values of T_g/T_2, ΔC_p and $S_0{}^\circ$ of 2-methylbutane amount to 1.30, 52 JK^{-1}mol^{-1} and 14.1 JK^{-1} mol^{-1}, respectively. Although their structures differ slightly the difference between their residual entropies, 6.7 JK^{-1} mol^{-1}, seems to be attributable to the entropy of positional disorder of the glassy state of isopentane. The glassy crystal is considered to be positionally ideal glass from Angell's viewpoint.

Relaxation of Enthalpy. If one assumes an exponential decay for the change of configurational enthalpy in the period of annealing below T_g, it may be represented by the equation

$$\Delta H_c(t) = \Delta H_c(0) \exp(-t/\tau). \tag{7}$$

Here, ΔH_c is the difference between configurational enthalpy of frozen state and that of equilibrium state and τ the time constant. Differentiation of Eq. (7) with time gives

$$\log(-\dot{H}_c) = -t/\tau + \text{constant}, \tag{8}$$

where $\dot{H}_c$ represents dH_c/dt. The experimental result shown in Fig. 6, however, do not fit such a type of linear equation. From this figure, we recognize immediately that the rate of the enthalpy relaxation is more rapid at the initial stage than the corresponding exponential decay with a nearly equal time constant. This may be explained in two different ways. If one assumes the existence of different relaxation processes with different relaxation times, the results shown in Fig. 6 can be explained. For example, if there exist two relaxation processes, the equation will be given by

$$\Delta H_c(t) = \Delta H_1 \exp(-t/\tau_1) + \Delta H_2 \exp(-t/\tau_2). \tag{9}$$

Co-existence of two relaxation processes has been demonstrated experimentally by Macedo and Napolitano[32,33] for boro-silicate glass. Another explanation is given by considering that the time constant is not only a function of temperature but also of the thermodynamic variables of the glassy state. Gibbs and Adam considered that the mechanical relaxation time in the supercooled liquid depends on the configurational entropy as well as on the temperature.[6] We have examined the applicability of their theory to the relaxation of the configurational enthalpy. The $\dot{H}_c(t)$ at time t is given by

$$-\dot{H}_c(t) = \overline{W}(T)H_c(t). \tag{10}$$

Here, $\overline{W}(T)$ is the transition probability of the region in which molecules (or segments) change their configuration co-operatively. $\overline{W}(T)$ is given by

$$\overline{W}(T) = \bar{A} \exp(C/TS_c). \tag{11}$$

Here, $\bar{A}$ and C are constants and S_c the configurational entropy. From Eq. (10) and (11), we obtain

$$\log(-\dot{H}_c/\Delta H_c) = -C/(2.30TS_c) \tag{12}$$

From the data of annealing at 69.7 K and 72.0 K, the values of $\log(-\dot{H}_c/\Delta H_c)$ are plotted against $1/S_c$ in Fig. 8. The values of S_c at various time values are determined by the equation

$$S_c(t) = S_c(0) - \int_0^t (\dot{H}_c/T)\mathrm{d}t + \Delta S_{irr}. \tag{13}$$

Here, $S_c(0)$ is equal to the residual entropy and ΔS_{irr} is, the irreversible entropy production.[15] The latter is however, too small (less than 1% of the integral term) and can be neglected. As is seen in Fig. 8, the agreement between theory and experiment is roughly established. From the slopes, the value of the constant C in Eq. (12) is determined to be about 9.9 KJ mol^{-1} for 69.7 K and 9.1 KJ mol^{-1} for 72.0 K. In the Gibbs-Adam theory, constant C is related to the number of

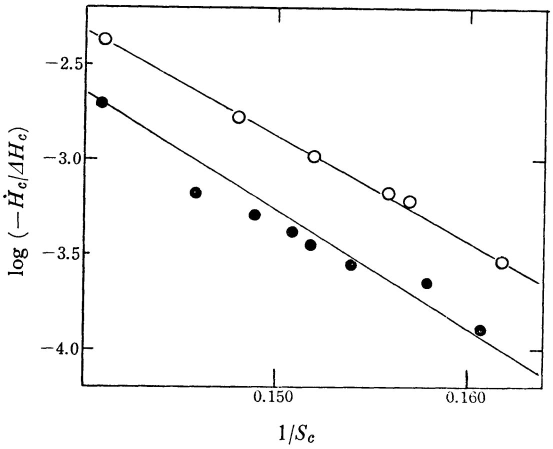

Fig. 8. The plot of ln $(-\dot{H}_c/\Delta H_c)$ *vs.* $1/S_c$.

○ calculated from the data of annealing experiment at 72.0 K

● calculated from the data at 69.7 K

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[30] C. A. Angell, *J. Amer. Ceram. Soc.*, **51**, 117 (1968).

[31] M. Sugisaki, K. Adachi, H. Suga, and S. Seki, This Bulletin, **41**, 593 (1968).

[32] P. B. Macedo and A. Napolitano, *J. Res. Natl. Bur. Std.* (U. S. A.), **71A**, 231 (1967).

[33] A. Napolitano and P. B. Macedo, *ibid.*, **72A**, 425 (1968).

molecules or segments Z^* in a minimum cooperative region by the equation

$$C = \Delta\mu S_c Z^*/\boldsymbol{R}, \qquad (14)$$

where $\Delta\mu$ is the activation free energy per mole and $\boldsymbol{R}$ the gas constant. We have assumed for a moment that the value of $\Delta\mu$ is equal to the difference between the Gibbs free energies of crystal-I just below melting point and of the glassy crystal at 70 K. It turns out to be 1.5 KJ mol^{-1}. This assessment on $\Delta\mu$ is rather small judging from the fact that the apparent activation energy for the rotational diffusion of molecule in the plastic crystals is known to be about 8 KJ mol^{-1}.[34] Therefore, we take 1.5—8 KJ mol^{-1} for the value of $\Delta\mu$ and determined the value of S_cZ^* to be 10—55 JK^{-1} mol^{-1} by putting 9.9 KJ mol^{-1} for the value of C. Taking the residual entropy (=7.4 JK^{-1} mol^{-1}) for S_c, Z^* is calculated to be 1—7. It may be noted that the relaxation effect was still observed below T_2 temperature as shown in Fig. 5. This fact does not contradict the Gibbs-Adam theory because the glassy crystalline state prepared in this way has a finite value of S_c.

The Heat Capacity Below T_g. As shown in Fig. 2, the heat capacity of the glassy crystal is anomalously large at low temperature compared with that of crystal-II. The frequency spectrum of lattice vibration for the glassy crystalline state seems to be of interest. The data of C_v (the heat capacity at constant volume) is necessary, but as the expansion coefficient and compressibility of this material are unknown at low temperature, it is impossible to know the C_p-C_v. Based upon the theory of Hovi[35] and Pautano, we have tried to find out the difference in the spectra of the glassy crystal and crystal-II from the difference of their heat capacity. Here, it is assumed that the C_p-C_v of each state are equal and all the vibrations are harmonic. According to the notation by Hovi and Pautano, the equations are given by

$$\boldsymbol{A}\cdot\boldsymbol{X}_1 = \boldsymbol{C}_1 \text{ and} \qquad (15)$$

$$\boldsymbol{A}\cdot\boldsymbol{X}_2 = \boldsymbol{C}_2, \qquad (16)$$

where $\boldsymbol{X}_1$ and $\boldsymbol{C}_1$ are the column vectors representing the magnitude of the histogram of the spectrum and that representing the heat capacities for the glassy crystal, respectively, and $\boldsymbol{X}_2$ and $\boldsymbol{C}_2$ are those for cystal-II. The difference between Eqs. (15) and (16) is given by

$$\boldsymbol{A}\cdot\Delta\boldsymbol{X} = \Delta\boldsymbol{C},$$

where $\Delta\boldsymbol{X}$ is $\boldsymbol{X}_1-\boldsymbol{X}_2$ and $\Delta\boldsymbol{C}$ is $\boldsymbol{C}_1-\boldsymbol{C}_2$. In the region from 0 to 30 cm^{-1}, the frequency spectrum is assumed to follow the Debye model. The cut-off frequency is then taken as 130 cm^{-1} judging from the Debye temperature 130 K (=90 cm^{-1}) for crystal-II. The region from 30 to 130 cm^{-1} is devided into five sections with equal width of 20 cm^{-1}. The values of the specific heat at 14, 17, 20, 25, 30 and 40 K are employed for ΔC in Eq. (14). The result is shown in Fig. 9. The positive value of the spectrum below 30 cm^{-1} can be explained by the lower density of the glassy crystal compared with that of crystal-II. Unfortunately, the data of the density of this material at low temperature is not available at present. It is known, however, that the large increase of the molar volume is associated with the transition from the low-temperature phase to the plastic phase, so the lower density of the glassy crystal may be the case. The large negative spectrum at 80 cm^{-1} suggests that a sharp peak (the vibrational mode —) exists in the spectrum of crystal-II whereas the spectrum is smoothed out in the glassy crystalline state. Dean[36] has shown this feature of the smoothing out effect of the spectrum of the perfect crystal by introducing a glass-like disorder.

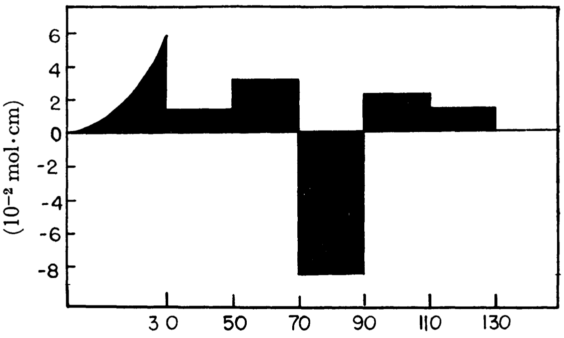

Fig. 9. The difference in the frequency spectrum of the lattice vibration between the glassy crystal and the crystal-II.

The Entropy of Transition. Guthrie and McCullough discussed the transition entropy ΔS_t from the low temperature form to the plastic phase for various materials by considering molecular symmetry and symmetry of the crystal lattice of the plastic phases.[37] They interpreted ΔS_t from the viewpoint of the randomness of orientation and of the conformation of molecules. However, we can expect the contribution of entropy of the lattice vibration to be not negligible because the large change of the frequency spectrum is expected on account of softness of the plastic phase. It is considered that ΔS_t is the sum of ΔS_{or}, ΔS_c and ΔS_{vib}, where ΔS_{or} is the difference of entropy due to orientational change, ΔS_c that due to conformational change of the molecule and ΔS_{vib} that due to the change in lattice vibration. We calculated ΔS_{vib} for the 2,3-dimethylbutane from the difference in the spectrum of vibration which is given in Fig. 9. It amounts to 12.8 JK^{-1} mol^{-1} assuming the spectrum of the glassy crystalline state is retained even at transition temperature. ΔS_{or} and ΔS_c have been estimated to be 21 ($\simeq\boldsymbol{R}\ln 12$) and 9 ($\simeq\boldsymbol{R}\ln 3$) J K^{-1} mol^{-1}, respectively at the most random state (see page 85). Their sum becomes 43 JK^{-1} mol^{-1} which is comparable with the experimental value of ΔS_t (=47.25 JK^{-1} mol^{-1}).

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[34] A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses," J. Wiley and Sons, Inc., New York (1968), p. 106—121.

[35] V. Hovi and Y. Pautano, *Ann. Acad. Sci. Fenn.* **Ser. A, 6**, 1, (1960).

[36] P. Dean, *Proc. Phys. Soc.*, **84**, 727 (1960).

[37] G. B. Guthrie and J. P. McCullough, *J. Phys. Chem. Solids*, **18**, 53 (1961).

[38] J. R. Green and C. E. Sheie, *ibid.*, **28**, 383 (1967).

The agreement will be improved if we take account of the variation of the frequency spectra (Fig. 9) at a higher temperature. The data[38] of the elastic constant measured with high frequency ultrasonic wave for the plastic phase of the cyclohexanol will be helpful for this consideration. The Debye temperature calculated is 60 K around 265 K whereas the Debye temperature in the glassy crystalline state (at 50 K) has been determined to be about 90 K from thermal data.[1] If the effect is taken into account, the value of ΔS_{vib} becomes larger and a better agreement is obtained between experimental and calculated ΔS_t. We would like to point out that the contribution of ΔS_{vib} is not negligible for the explanation of the content of ΔS_t.

Crystal-III. It has been revealed that the residual entropy of crystal-III is determined to be 2.7 JK^{-1} mol^{-1} and that there exists an anomalous hump in the heat capacity curve around 70 K. From these facts, there is the possibility that the state of crystal-III below 70 K is also glassy crystalline. This can not be confirmed, however, as the relaxation phenomenon has not yet been observed.