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Phase Changes in Crystalline and Glassy-Crystalline Cyclohexanol*[1]

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It has been known that cyclohexanol has low-temperature form (crystal-II) and high-temperature form (crystal-I) and that the supercooled crystal-I shows in its heat capacity curve an anomalous jump resembled to that associated with glass transition. In order to clarify whether this anomaly arises from relaxation phenomenon or not, we have reinvestigated the heat capacity of this substance from 14°K to 320°K and obtained the values of 8827 J/mol, 265.31°K, 1782 J/mol and 299.09°K for heat of transition, transition point, heat of fusion and melting point respectively. Comparing the ideal gas entropy of cyclohexanol calculated from thermal data and that from statistical-mechanical data, we have estimated that the residual entropy of the crystal-II is of zero and that the potential barrier of internal rotation of *OH* group is 7.0 kJ/mol. From these results, the residual entropy of the supercooled crystal-I amounts to 4.72 J/(mol deg K). We have discussed the glass transition of this crystal and proposed a new term **glassy crystal.** We have also studied the heat capacity of metastable phase (crystal-III) and obtained the results 244.8°K and 8640 J/mol for transition point and heat of transition. The residual entropy of the crystal-III has determined to be zero.

Thermal study of cyclohexanol crystal from liquid hydrogen temperature was first carried out by Kelley.[1] He drew main two conclusions. First, this substance had two crystalline phases, the high-temperature phase (crystal-I) and the low-temperature one (crystal-II).*[2] The crystal-I was found to be supercooled easily and the heat capacity curve of the supercooled phase showed anomalous jump closely resembled to that associated with the glass transition of a supercooled liquid. Second, the supercooled crystal-I and the crystal-II had the same value of entropy at 0°K within the experimental error. In other words, the anomalous jump of the heat capacity curve of the supercooled crystal-I was considered to be second order transition in the sense of thermodynamics. Thereafter, Ôtsubo and Sugawara[2] reinvestigated this anomaly of the heat capacity under the various annealing conditions and concluded that this anomaly was looked upon as a relaxation phenomenon associated with the glass transition. This stands in contrast to the conclusion by Kelley that the supercooled crystal-I is in the internal equilibrium state. However, they have given no discussion about the residual entropy which is a kind of measure for the degree of internal equilibrium. We have accordingly reinvestigated the low-temperature heat capacities of various crystalline phases accurately and also studied the kinetics of the relaxation in order to clarify the problem that the glass transition characteristic to amorphous state takes place also in the crystalline state in the sense of relaxation phenomenon. If this glass transition phenomenon is a real relaxation effect, the second conclusion of Kelley is contradicting to the fact of zero residual entropy. As to the substances which have been hitherto known to show the anomalous jump of the heat capacity similar to the glass transition in the crystalline state there are only *cis*-1,2-dimethylcyclohexane[3] and the molecular compound

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*[1] Read before the 20th Annual Meeting of the Chemical Society of Japan (1967), Tokyo and partially presented at the symposium on New Investigations in Thermodynamics, Thermochemistry and Transport Properties (1967), Heidelberg.

[1] K. K. Kelley, *J. Am. Chem. Soc.*, **51**, 1400 (1929).

*[2] Following Smyth, Ôtsubo and Sugawara designated this modification as form-III and metastable one as form-II. We changed, however, this nomenclature as described in the text, since the metastable crystal-III in the text has lower transition point as described later.

[2] A. Ôtsubo and T. Sugawara, *Sci. Rep. Res. Inst. Tohoku Univ.*, **A7**, 583 (1955).

[3] H. M. Huffman, S. S. Todd and G. D. Oliver, *J. Am. Chem. Soc.*, **71**, 584 (1949).

between 2,3-dimethylbutane and 2,2-dimethylbutane.[4] It should be noted here that both of these substances and cyclohexanol belong to the so-called plastic crystals defined by Timmermans.[5] Aside from this problem, Ôtsubo and Sugawara also reported the occurrence of three kinds of metastable intermediate phases in the course of irreversible transformation from the supercooled crystal-I to the crystal-II. In the present study we have also studied the metastable crystalline phase (crystal-III) and the thermodynamic stability-relationship of the crystal-I, II and III were further determined in terms of Gibbs energy. On the basis of the data of the heat capacities, the vapor pressure and of the heat of vaporrization which were previously reported in this laboratory,[6] the residual entropies of the crystal-I, II and III have been determined by comparing the experimentally obtained entropies of ideal gas state with that calculated by statistical-mechanical method. The potential barrier of the internal rotation of *OH* group has been also estimated.

Experimental

Material. Commercial " Special-grade " cyclohexanol (Nakarai Chemicals) was fractionally distilled twice and further purified through vacuum distillation (10^{-3} mmHg) with baked calcium oxide. The calorimetric determination of the melting point (see below) revealed that the impurities in the sample were found to 0.025 mol% assuming no formation of a solid solution. Only a kind of impurity, presumably cyclohexanone, was detected by gas chromatography (Shimadzu Gas Chromatograph model GC-1B equipped with hydrogen flame ionization detector) and this impurity was calculated to be 0.02 mol% from the peak area of the chromatogram.

Apparatus. The heat capacity of cyclohexanol was measured between 14 and 320°K by the low-temperature adiabatic calorimeter with platinum resistance thermometer. The details of the apparatus, procedure, temperature scale and accuracy were previously described.[7] The purified sample was transferred into the cell of the calorimeter (whose capacity is about 30 cc) by vacuum distillation. The weight of the sample employed was 27.548 g and 1.3×10^{-4} mol of helium gas for heat exchange was introduced (about 1 atm in a room temperature).

For the preliminary study of the occurrence and the thermal properties of metastable crystalline phases, differential thermal analysis was carried out. The apparatus was previously reported[8] also.

The infrared spectra were obtained by a Nihon Bunko Co. Double-beam Spectrometer (model DS-402G) between 600 cm^{-1} and 4000 cm^{-1} and by a Hitachi Co. Spectrometer (model No. FIS-001) between 200 cm^{-1} and 600 cm^{-1}. In the measurement above 400 cm^{-1}, the sample which was the same as that used in the measurements of the heat capacity was put between the polished plates of KBr single crystal. Because of the high hygroscopy of this substance, the preparation of this sample was carried out in the dry nitrogen atmosphere.

Experimental Results

Studies of the Polymorphism of Cyclohexanol with Differential Thermal Analysis (D.T.A.). D.T.A. curves under various conditions are shown in Fig. 1. Run-1 is a cooling curve with the rate of −1.5°K/min. The peak at about 299°K corresponds to the freezing point of the crystal-I. Even with the more rapid cooling rate, the freezing point was observed always at the same point and supercooling of the liquid state has never been observed. On the other hand the crystal-I is easily supercooled and shows no remarkable anomaly due to the transition to other crystalline phase. However, irregular small anomalies seemingly due to the sluggish transitions from the supercooled crystal-I to other phases were observed below 200°K (see curve Run-1), so the glass transition[*3] (the jump of the heat capacity of the crystal-1) was not clearly found. Run-2 shows a heating curve with the rate of about 1°K/min after the crystal-I was supercooled to about 80°K with cooling rate of −10°K/min. The anomaly due to the glass transition reported by Kelley and by Ôtsubo and Sugawara was observed about 150°K,

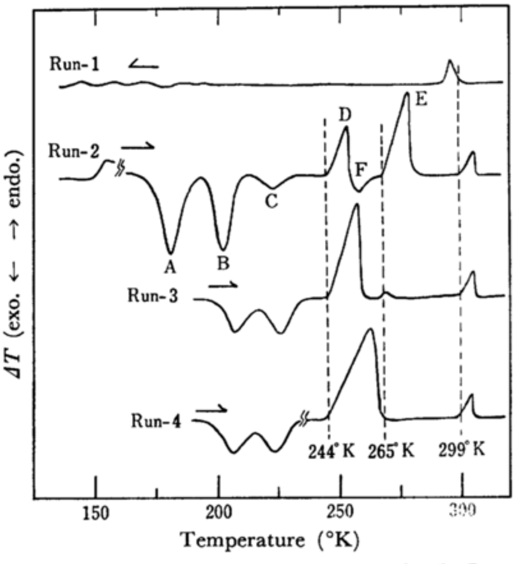

Fig. 1. D. T. A. curves of cyclohexanol. In Run-2 the mark ≀ shows the change of the sensitivity and in Run-4 the change of heating rate, respectively.

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

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

[6] I. Nitta and S. Seki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **69**, 141 (1948).

[7] H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

[8] H. Suga, H. Chihara and S. Seki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **82**, 24 (1961).

[*3] As is described below, it has been confirmed that the anomalous jump of the heat capacity of the supercooled crystal-I at about 150°K is attributable to a relaxation phenomenon. Accordingly we call this anomaly as a glass transition in spite of the phenomenon observed in the crystalline state.

TABLE 1. SELECTED VALUES OF THE MOLAR HEAT CAPACITIES OF CYCLOHEXANOL

Mol wt = 100.163 0°C = 273.15°K

$T_{av.}$ (°K)	$\Delta H/\Delta T$ (J/mol degK)	ΔT (°K)
	Series 1	
	(Supercooled crystal-I)	
14.916	7.578	1.6084
16.558	9.326	1.6267
18.213	11.187	1.6023
19.904	12.965	1.7088
21.495	14.543	1.4181
23.161	16.325	1.8821
25.091	18.113	1.9276
26.924	19.869	1.7382
28.597	21.332	1.6031
30.309	22.946	1.8196
32.071	24.561	1.6902
33.717	26.064	1.5872
35.446	27.486	1.8534
37.255	28.862	1.7542
51.306	37.591	2.1472
53.406	38.645	2.0435
55.416	39.857	1.9787
57.367	41.063	1.9201
59.267	42.078	1.8718
61.114	43.246	1.8230
63.209	44.510	2.3645
65.372	45.690	1.9598
67.313	46.653	1.9190
69.216	47.594	1.8810
71.861	48.880	1.8261
75.483	50.813	1.8315
79.112	52.591	1.7729
82.604	54.455	1.7187
87.691	57.055	1.6499
90.954	58.568	1.6135
94.148	60.175	1.5789
96.873	61.421	1.7412
100.350	63.159	1.7724
103.900	65.041	1.8145
107.493	66.866	1.7766
111.010	68.669	1.7393
114.494	70.696	1.7783
118.019	72.449	1.7437
121.590	74.284	1.7878
124.109	76.065	1.7533
127.636	78.256	1.8403
131.342	80.186	1.8475
135.172	83.158	1.8891
139.106	86.239	1.9361
141.079	87.930	1.9095
143.059	90.652	1.8689
144.951	93.635	1.8277
146.873	97.632	1.9164
148.705	115.91	1.7476
150.416	118.70	1.6743
152.087	119.16	1.6684
153.753	119.54	1.6628

$T_{av.}$ (°K)	$\Delta H/\Delta T$ (J/mol degK)	ΔT (°K)
	Series 2	
	(Supercooled crystal-I)	
37.026	29.014	2.3613
39.313	30.741	2.2118
41.392	32.153	1.9372
43.291	33.402	1.8525
45.168	34.528	1.8925
47.236	35.766	2.2414
49.432	37.044	2.1495
51.543	38.235	2.0702
156.090	120.72	2.3207
158.404	121.78	2.3020
160.748	123.31	2.2757
	Series 3	
	(Supercooled crystal-I)	
248.488	153.20	1.8406
250.481	154.27	2.1467
252.619	155.77	2.1282
254.701	157.24	2.0350
256.728	158.52	2.0197
258.742	159.89	2.0085
260.743	161.27	1.9920
262.728	162.65	1.9779
	Series 4	
	(Supercooled crystal-I annealed at T°K)*	
	(T°K = 144°K)	
144.394	90.283	1.8524
146.178	93.063	1.8120
147.911	97.441	1.8865
149.590	119.15	1.9756
151.317	120.83	1.9515
153.268	120.52	1.9510
155.216	120.87	1.9449
	(T°K = 141°K)	
141.719	87.267	1.8660
143.544	89.041	1.8480
145.276	95.250	1.7557
147.127	95.018	2.0922
148.865	114.16	1.8436
150.525	123.02	1.8440
152.382	120.47	1.8693
	(T°K = 137°K)	
137.924	84.885	0.3728
138.982	85.240	1.7463
140.767	86.605	1.8520
142.744	88.690	2.1733
144.816	91.651	2.1225
146.770	97.375	2.0355
148.569	109.31	1.8839
150.280	120.92	1.7493
152.187	120.36	2.0691
154.253	120.55	2.0634

(TABLE 1 continued)

$T_{av.}$ (°K)	$\Delta H/\Delta T$ (J/mol degK)	ΔT (°K)
	(T°K=133°K)	
134.745	82.760	2.2073
137.267	84.584	2.8462
140.066	86.901	2.7911
142.766	90.620	2.7101
145.339	97.136	2.5833
147.897	98.798	2.5475
151.268	119.16	4.4685
	Series 5	
	(Crystal-II)	
73.503	47.243	1.6829
76.823	48.800	1.6353
80.133	50.440	1.6459
83.379	52.073	1.6009
86.675	53.630	1.6497
90.037	55.118	1.6780
92.735	56.287	1.6719
96.633	57.834	1.9157
100.459	59.553	1.8779
104.178	61.106	1.8387
107.833	62.536	1.8262
111.417	64.209	1.7666
114.938	65.544	1.7751
118.449	67.007	1.7434
121.942	68.625	1.7887
125.563	69.900	1.7440
129.143	71.305	1.7944
132.827	72.930	1.8447
136.624	74.581	1.9013
140.403	76.239	1.8707
144.388	77.767	1.9386
148.084	79.298	1.9013
151.860	80.888	1.8728
155.582	82.387	1.8474
159.251	83.947	1.8215
162.940	85.345	1.8434
166.736	86.923	1.9084
171.779	89.121	1.8806
175.285	90.978	1.7977
178.978	92.850	1.8499
182.857	94.497	1.9704
186.760	96.506	1.9411
190.618	98.270	1.9151
194.432	99.823	1.8931
198.419	101.74	2.0188
202.429	103.78	1.9891
206.380	105.54	1.9633
210.284	107.33	1.9384
214.747	109.28	2.0613
221.066	112.26	2.0211
225.083	114.39	1.9941
229.056	116.56	1.9619
233.019	118.82	2.0492
237.092	120.68	2.0236
241.105	123.22	1.9927
245.110	125.82	2.0816
249.879	129.04	2.0410
253.926	131.90	2.0069
257.929	135.03	1.9718
261.832	138.79	1.9321
263.714	148.93	1.8351
265.004	449.49	0.7436
	Transition	
	(Crystal-I)	
267.788	165.97	1.8132
267.790	165.68	2.0040
269.787	167.06	1.9892
273.833	170.35	2.1563
278.534	174.13	2.0957
282.696	177.41	2.0649
286.790	181.52	2.0289
290.794	185.54	1.9880
294.742	189.78	1.9501
296.671	195.77	1.9043
297.887	288.86	0.5282
	(Fusion)	
300.058	213.41	0.1369
301.989	215.24	1.9455
303.830	217.67	1.9155
305.790	219.91	1.8889
307.669	221.50	1.8753
308.457	221.92	2.0810
310.791	223.74	2.5816
313.565	226.77	2.9658
316.509	230.62	2.9196
	Series 6	
	(Crystal-III)	
14.844	4.341	1.9244
17.071	6.249	2.3073
19.156	7.998	1.8017
20.815	9.620	1.5063
22.339	11.136	1.5150
23.778	12.556	1.3458
25.553	14.236	2.1957
27.619	16.194	1.9259
29.457	17.903	1.7403
31.274	19.536	1.8838
33.086	21.205	1.7384
35.028	22.885	2.1405
37.093	24.536	1.9896
39.019	26.067	1.8683
40.841	27.323	1.7736
42.927	28.779	2.4012
45.262	30.314	2.2654
47.471	31.708	2.1533
49.710	33.022	2.3241
51.961	34.347	2.1767
54.099	35.593	2.0963

(Table 1 continued)

$T_{av.}$ (°K)	$\Delta H/\Delta T$ (J/mol degK)	ΔT (°K)
56.163	36.744	2.0282
58.162	37.852	1.9667
60.100	39.017	1.9108
61.989	40.086	1.8618
63.831	41.096	1.8178
65.628	42.080	1.7762
67.439	43.018	1.8401
69.268	43.612	1.8111
70.555	44.177	1.4909
74.568	46.128	2.1469
78.946	48.195	2.3940
83.717	50.444	2.2983
88.232	52.562	2.2182
92.605	54.433	2.1535
96.858	56.106	2.0987
101.001	58.018	2.0427
105.045	59.723	1.9986
108.936	61.175	2.2266
113.354	63.014	2.1850
117.907	64.914	2.2901
122.432	66.841	2.2369
126.849	68.850	2.1863
131.181	70.588	2.1449
135.431	72.362	2.1051
139.603	74.186	2.0674
143.763	76.047	2.1497
148.026	77.858	2.1137
151.011	78.893	2.3922
155.765	80.794	2.3695
160.502	82.676	2.4450
165.153	84.465	2.2702
169.654	86.568	2.2323
174.087	88.491	2.1980
178.988	90.714	2.5178
186.433	94.168	2.4298
191.301	96.300	2.4105
196.492	98.328	0.5804
200.173	99.732	2.2459
204.737	101.95	2.3919
209.423	104.22	2.3118
216.660	108.07	2.4669
221.437	110.59	2.3454
228.856	115.46	2.4593
231.308	116.34	2.4438
	Series 7	
	(Crystal-III)	
237.258	120.590	1.6191
237.943	121.578	1.4400
238.832	121.100	1.6145
241.400	151.820	1.2001

* These specimens were anneald for 25 hr at respective temperatures. In the calculation of the heat capacities, anomalous temperature drift due to the stabilization (relaxation) is treated as if it were arizen from thermal leakages.

and there exist the exothermic irreversible transitions at about 180°K, 200°K, 220°K and 254°K (in Fig. 1, the peaks A, B, C and F, respectively) and the endothermic transitions at 244°K and at 265°K (peaks D and E, respectively). Ôtsubo and Sugawara studied these phase transformations by X-ray analysis in parallel with the thermal studies and concluded that peak A corresponded to the irreversible transition from the supercooled crystal-I to the metastable intermediate mixed crystalline phases and that peak B corresponded to the transition from these metastable phases to other metastable crystalline (crystal-III) or to low temperature form (crystal-II). But they did not find the existence of the peak C. The peaks D and E correspond to the transitions from the metastable crystal-III to the crystal-I and that from the crystal-II to the crystal-I, respectively. The exothermic anomaly F is probably the irreversible transition from the crystal-I occurred by III-I transition to the crystal-II. For the purpose of the measurement of the heat capacity of the metastable phase crystal-III, the condition of preparing the pure crystal-III was investigated by D. T. A. and the typical results are indicated by Runs 3 and 4. Run-3 is a heating curve of the supercooled crystal-I with the rate of about 1.1°K/min followed after rapid cooling from 280°K to 190°K with cooling rate of about −10°K/min. There exists a very small peak due to II-I transition at 265°K. But if one increase the heating rate from 1.1°K/min to 2.5°K/min at 235°K after the same cooling and heating operations as Run-3, the peak at 265°K is scarcely found as shown in Run-4. This fact may be explained in such a way that in Run-3 small peak of II-I transition appears because of the formation of the crystal-II between 244°K and 265°K due to the irreversible transition from I to II, although the almost pure metastable crystal-III is produced at 235°K. While in Run-4, it is considered that a detectable amount of the crystal-II was not produced on account of the rapid heating. For the measurement of the heat capacity of crystal-III, we prepared this modification by cooling the sample after stopping Run-3 around at 235°K.

Measurement of the Heat Capacities. The molar heat capacities are listed in Table 1 and plotted in Fig. 2, where are shown the data of Kelley and those of Ôtsubo and Sugawara for reference. Kelley's data agree well with our data for crystal-II between 14 and 65°K. They deviate, however, from −1.2 to −3% in the ranges between 65 and 170°K, from +1 to +5% between 180 and 230°K and more than 10% between 240 and 260°K, respectively.

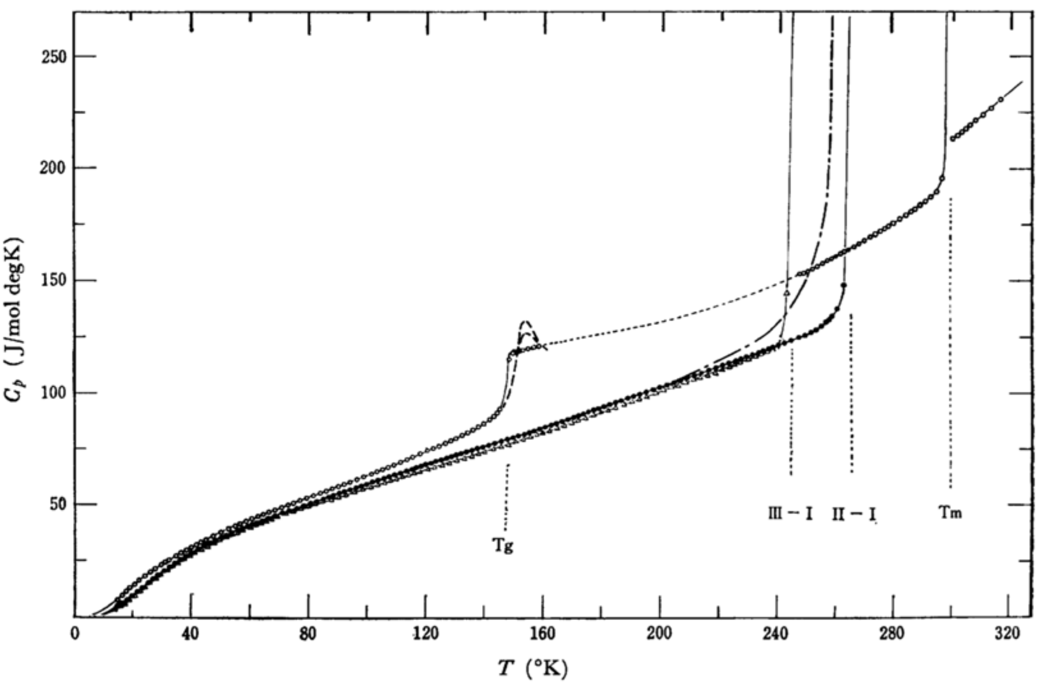

Fig. 2. The molar heat capacities of cyclohexanol.

—○— supercooled crystal-I, crystal-I and liquid

—●— crystal-II

—△— crystal-III

------ estimated heat capacity curve of supercooled crystal-I

——— Ôtsubo and Sugawara's data near T_g

—-—- Kelley's data of crystal-II

For the crystal-I or the supercooled crystal-I, the smoothed values of his experiment agree fairly well with our data except for the region between 130 and 150°K, where the deviation is approximately +2%. Kelley's data for the crystal-II in the temperature region between 65 and 170°K coincide rather with the data of the crystal-III in the present measurement. Comparison with the data of Ôtsubo and Sugawara was not done because they did not give any numerical values. The heat capacities of the supercooled crystal-I below 160°K have been measured after the specimen was chilled with cooling rate of about −6°K/min from room temperatures and the heat capacities between 245 and 265°K have been measured after the specimen was slowly chilled with a cooling rate of −0.5°K/min from 310°K (liquid state) to 245°K. Crystal-II has been prepared as follows: The crystal-I supercooled below the glass transition temperature was heated up to about 255°K and slowly cooled from this temperature to about 240°K in 13 hr. The crystal-III (metastable phase) has been prepared after the condition investigated by D.T.A. as described above. In the course of the measurement of the heat capacities of this metastable phase, no remarkable irreversible transition to other phase was observed.

Thermal Data Associated with the Phase Transitions. The equilibrium temperatures during the fusion process are listed in Table 2. The temperatures of transitions are shown in Table 3 with those of Ôtsubo and Sugawara. The transition temperature of the crystal-III to the crystal-I could not be determined from the measurement of the heat capacity due to the sluggish irreversible transition from the crystal-I to the crystal-II, so we listed the value determined by D.T.A. Table 4, 5 and 6 summarize the data for the heat of transitions and of fusion together with the data of Kelley and of Ôtsubo *et al.* for comparison. As shown in Table 4 the heat of transition from the crystal-III to the crystal-I was

TABLE 2. THE EQUILIBRIUM TEMPERATURES DURING FUSION PROCESS

Fraction melted (%)	Temperature (°K)
25.01	298.729
34.11	298.790
43.46	298.833
52.97	298.864
62.54	298.889
82.37	298.929
92.08	298.946

Melting point of pure cyclohexanol under 1 atm pressure; 299.09±0.03°K, Mol% of impurity; 0.025%

Table 3. THE TEMPEPATURES OF TRANSITIONS AND FUSION UNDER THE SATURATED VAPOR PRESSURE

Phase change	This research	Kelley	Ôtsubo *et al.*
II—I	265.50±0.01	263.5	266
III—I	244.8 ±0.1		243
I—liquid	299.05±0.03*	297.0	298

* Corrected for pressure variation by using Clausius-Clapeyron's equation. Data of the volume increases on melting and on transition were taken from Ref. 19 and Ref. 6.

Table 4. MOLAR HEAT OF TRANSITION FROM THE CRYSTAL-II TO CRYSTAL-I (unit; kJ/mol)

Temp. interval (°K)	Heat input	$\int C_p dT$	ΔH_t
260.817—271.077	10.9783	2.1563	8.823
259.555—268.181	10.5836	1.7527	8.830
		Mean	8.827±0.01
	Data by Kelley		8.201
	Data by Ôtsubo *et al.*		8.699

Table 5. MOLAR HEAT OF TRANSITION FROM THE CRYSTAL-III TO THE CRYSTAL-I (unit; kJ/mol)

Temp. interval (°K)	Heat input	$\int C_p dT$	ΔH_t
240.736—268.613	13.7693	5.8289	8.664
236.448—270.639	15.7898	7.0403	8.754
237.222—271.427	15.5911	7.0816	8.513
234.863—270.502	15.9060	7.2818	8.624
		Mean	8.64±0.1
	Data by Ôtubo *et al.*		8.4—8.8

Table 6. MOLAR HEAT OF FUSION (unit; kJ/mol)

Temp. interval (°K)	Heat input	$\int C_p dT$	ΔH
294.916—300.773	3.2816	1.4952	1.786
293.254—302.425	4.1349	2.3533	1.782
294.306—302.185	3.8112	2.0296	1.782
		Mean	1.783±0.002
	Data by Kelley		1.699
	Data by Ôtsubo *et al.*		1.70

obtained by measuring the enthalpy difference between the crystal-I above 265°K and the crystal-II, because of the instability of the crystal-I below 265°K.

The Entropy of Cyclohexanol in the Ideal Gas State from the Thermal Data. The molar entropy of cyclohexanol in the ideal gas state at 280°K is calculated by a third-law path *via* II–I transition and summarized in Table 7. The contribution below 14°K is determined by means of the Debye theory with 125°K for Θ_D and assuming 6 degrees of freedom. The data of the heat of sublimation and the vapor pressure were reported previously.⁶⁾ Due to the lack of the critical data or the virial coefficients of this material, the magnitude of the gas imperfection correction was estimated from the critical data of *n*-propanol, phenol and cyclohexane by using the Berthelot equation. The correction is, however, negligibly small due to the low vapor pressure at 280°K (0.149 mmHg).⁶⁾

Table 7. THE ENTROPY IN THE IDEAL GAS STATE FROM THERMAL DATA

Temp. (°K)	Contribution	ΔS (J/mol degK)
0—13.75	Debye extrapolation	1.30±0.08
13.75—265.51	$\int C_p(\mathrm{II}) d\ln T$	141.55±0.43
265.51	Transition (8827/265.51)	33.25±0.04
		176.10±0.55
265.51—280	$\int C_p(\mathrm{I}) d\ln T$	9.01±0.03
280	Sublimation ($6.075\times10^4/280$)	217.0±1.0
280	Compression to 1 atm	−70.97±0.02
280	Correction to ideal gas	0.00±0.00
		331.1±1.6

The Entropy from Statistical Data and Residual Entropy of the Crystal-II. The Raman effect of this material was reported by Neelakantan⁹⁾ from 300 cm^{-1} to 4000 cm^{-1}. But a normal coordinate analysis was not carried out. Since the far-infrared spectra of this material have not been reported, we measured the infrared spectra down to 200 cm^{-1}. They are summarized in Table 8. The frequencies of the normal modes were estimated by comparison with those of cyclohexane which were assigned by Takahashi *et al.*¹⁰⁾ These are listed in Table 9. Measurements in the region from 200 cm^{-1} to 300 cm^{-1} were not reliable on account of the noise effect, so we considered that the weak absorptions at 220 cm^{-1} and 240 cm^{-1} corresponded to the normal mode of cyclohexane at 248 cm^{-1} which is of doubly degenerated skeletal vibration. Taking 1.54, 1.09, 1.43 and 0.96 Å for the *C–C*, *C–H*, *O–C* and *O–H* bond distances respectively and 109° for both of

Table 8. OBSERVED FREQUENCIES OF IR SPECTRUM (unit; cm^{-1})

220 w, 240 w, 279 vw, 338 m, 395 m, 406 w, 454 w, 481 m, 556 m, 650 s(b), 786 m, 832 w, 843 m, 860 w, 888 m, 924 w, 970 s, 1025 m, 1033 w, 1070 s, 1138 m, 1172 m. (higher frequencies are omitted.)

s; strong, m; medium, w; weak, v; very, b; broad

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9) P. Neelakantan, *Proc. Indian Acad. Sci.*, **A57** (**2**), 94 (1963).

10) H. Takahashi, T. Shimanouchi, K. Fukushima and T. Miyazawa, *J. Mol. Spectry.*, **13**, 43 (1964).

TABLE 9. ESTIMATION OF THE FREQUENCIES OF NORMAL MODES OF CYCLOHEXANOL BY COMPARING WITH THOSE OF CYCLOHEXANE

vib.	frequencies estimated	vib.	freq. of cyclohexane
220 240	C-C-C bend.+torsion	248×2	C-C-C bend.+torsion
338	C-C-C bend.+torsion	381	C-C-C bend.+torsion
395 406	C-C-C bend.+torsion	423×2	C-C-C bend.+torsion
454 481 556	C-C-C bend. (2) or C-C-C bend. (1)	522	C-C-C bend.
650	O-H out of plane vib.		
786 832 843 860 888 924 970 1025 1033 1048	C-C str. (6) or CH_2 rock. (3) or C-O str. (1)	802 862×2 (778) (923) 1031×2	C-C str. C-C str. CH_2 rock. (calc.) C-C str.
1200×9	CH_2 twist (5) and CH_2 rock. (2) and H-C-O bend. (1) and C-O-H bend. (1)		
1400×10	CH_2 wag. (5) and CH_2 scis. (5)		
3000×12	C-H str. (11) and O-H str. (1)		

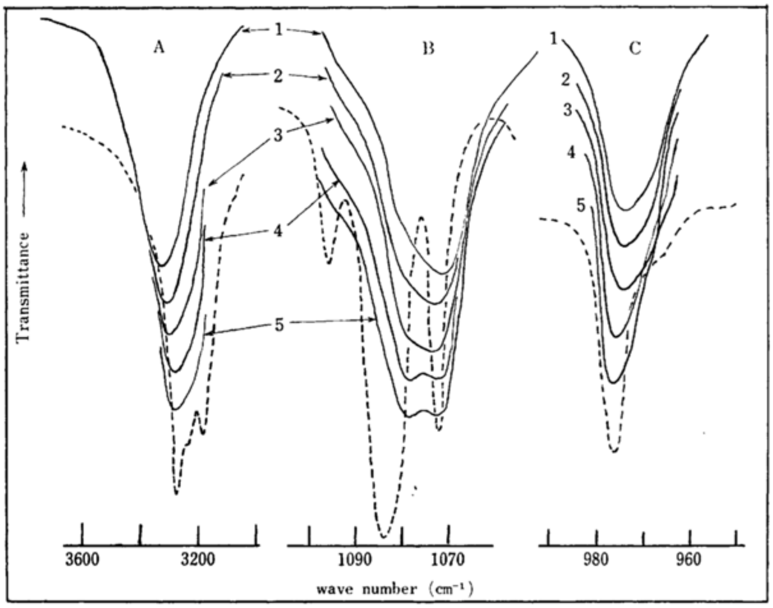

Fig. 3. Temperature dependence of the IR absorption. Full line for the crystal-I and the supercooled crystal-I.
Broken line for the crystal-III (at about 240°K)
A O-H stretching band
B C-O stretching band of equatorial form
C C-O stretching band of axial form
Crystal-I: 1, 301°K; 2, 276°K
Supercooled crystal-I: 3, 239°K; 4, 178°K; 5, 118°K

C-C-X (*X-H, C* or *O*) and *C-O-H* bond angles, one obtaines 3.63×10^{-113} g^3cm^6 for the product of three principal moments of inertia. This value is for the chair form with mean value of those for the axial (polar) and the equatorial conformations. The energy difference between the axial and the equatorial conformers was reported by Masschelein[11] as 1.57 ±0.21 kJ/mol from the temperature dependence of the intensity of infrared absorptions. The mixing entropy of both conformers was calculated by using this value. The value of this entropy amount is, however, somewhat ambiguous, since the result of our reinvestigation on the intensity of infrared absorption at low temperatures shows a little difference from that measured by Masschelein[*4] (Fig. 3). Here, we have employed the value of the energy differences in the crystalline state in place of that in the gaseous state. As the mixing entropy is not so sensitive to the change of this value as far as the energy difference is smaller than $\boldsymbol{RT}$, the error due to this ambiguity may be small. The entropy of internal rotation of *OH* group is left unknown and this value was determined so that the third-law entropy coincided with the statistical one. As shown in Table 10, it was found to be 6.9±2.9 J/(mol degK). Assuming the three-fold symmetry for hindering potential, the barrier height for internal rotation was then determined as 7.0 kJ/mol using the Pitzer and Gwinn table.[12] The value seems to be reasonable compared with those obtained for some aliphatic alcohols, *i.e.*, 3.3 kJ/mol for ethanol and 4.5 kJ/mol for methanol. These results constitute reasonably a third-law verification of the crystal-II. That is, we can safely conclude that the residual entropy of crystal-II is equal to zero.

TABLE 10. THE ENTROPY OF GASEOUS STATE FROM STATISTICAL DATA (unit; J/mol degK)

Translation	164.97
Rotation	113.61±0.08
Vibration	40.23±1.2
Mixing isomers	5.34±0.05
Internal rot. of *OH* group	6.9 ±(2.9)
	331.1 ±1.3

TABLE 11. THE THIRD LAW ENTROPY OF THE CPYSTAL-I AT 265.51°K *via* III-I TRANSITION

Temperature (°K)	Contribution	ΔS (J/mol degK)
0—13.75	Debye extrapolation	1.22±0.07
13.75—244.8	$\int C_p(\mathrm{III})\mathrm{d}\ln T$	127.04±0.38
244.8	Transition(8638/244.8)	35.29±0.4
244.8—265.51	$\int C_p(\mathrm{I})\mathrm{d}\ln T$	12.78±0.04
		176.33±0.8

TABLE 12. THE DIFFERENCE OF ENTROPY OF THE SUPERCOOLED CRYSTAL-I AT 0°K AND THE CRYSTAL-I AT 265.51°K

Temp. (°K)	Contribution	ΔS(J/mol degK)
0—13.75	Debye extrapolation	2.28±0.12
13.75—161.5	$\int C_p(\mathrm{I})\mathrm{d}\ln T$	100.28±0.30
161.5—245.5	$\int C_p(\mathrm{I})\mathrm{d}\ln T$*	56.47±0.51
245.5—265.51	$\int C_p(\mathrm{I})\mathrm{d}\ln T$	12.35±0.04
		171.4 ±1.0

* Calculated from Eqs. (1) and (2).

Residual Entropies of Respective Phases. Calculations of the differences of entropies between that of the crystal-I at 265.51°K and those of the supercooled crystal-I, the crystal-II and the crystal-III at 0°K are shown in Table 11, 7 and 12, respectively. Since the supercooled crystal-I is unstable between 160 and 240°K, the heat capacity in this temperature region in Table 12 was calculated by using the following interpolation equations [unit; J/(mol degK)]:

$$C_p = 75.421 + 0.29368\mathrm{T} \quad (160\text{—}217°\mathrm{K}) \qquad (1)$$

and

$$C_p = 47.340 + 0.42290\mathrm{T} \quad (217\text{—}240°\mathrm{K}) \qquad (2)$$

These equations are derived based on our data and Kelley's value at 217°K and the error in determining the entropy is estimated to be ±0.5 J/(mol degK) in this temperature range. The contributions below 14°K were determined by using the Debye functions taking 102.3° and 127.6° for the Θ_D of the supercooled crystal-I and the crystal-III respectively. Comparison of Table 10, 6 and 11 shows that the residual entropy of the supercooled crystal-I amounts to 4.72±1.6 J/(mol degK) and that of the crystal-III −0.23±1.3 J/(mol degK). Accordingly, we may conclude that the crystal-III has actually no residual entropy. It may be noted that the crystal-III is in internal equilibrium notwithstanding that it is a metastable phase.

Finally based on the above data, the thermodynamic functions are calculated and these are listed in Table 13. Gibbs energies relationship of respective phases are shown in Fig. 4.

Discussion

Frozen-in State. What kind of degree of freedom would be involved in the relaxation process of the supercooled crystal-I is an interesting problem. In the ordinary glassy substances, they are usually

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[11] W. Masschelein, *ibid.*, **10**, 161 (1961).

[*4] Masschelein calculated the energy difference from the temperature dependence of the intensity of the bands at 1070 cm^{-1} and 970 cm^{-1} which were estimated to be those of the C–O stretching vibration of equatorial and axial forms, respectively. These absorption bands in the spectra of his measurement, however, did not show any such a splitting observed by us.

[12] K. S. Pitzer and W. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

TABLE 13. THERMODYNAMIC FUNCTIONS OF CYCLOHEXANOL
unit; J/(mol degK)

T(°K)	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
		(Crystal-II)		
5	(0.1912)	(0.0637)	(0.0478)	(0.0159)
10	(1.512)	(0.5093)	(0.3838)	(0.1256)
20	9.22	3.551	2.646	0.9045
30	19.13	9.180	6.502	2.678
40	27.84	15.93	10.80	5.134
50	34.73	22.91	14.92	7.986
60	40.85	29.78	18.74	11.04
70	46.02	36.49	22.28	14.21
80	50.49	42.92	25.52	17.40
90	55.10	49.14	28.56	20.58
100	59.35	55.17	31.43	23.74
110	63.60	61.02	34.15	26.87
120	67.79	66.73	36.78	29.95
130	71.67	72.32	39.32	33.00
140	76.02	77.79	41.79	36.00
150	80.10	83.17	44.20	38.97
160	84.22	88.47	46.58	41.90
170	88.38	93.70	48.91	44.79
180	93.18	98.89	51.24	47.66
190	97.89	104.05	53.57	50.48
200	102.54	109.19	55.90	53.29
210	107.18	114.56	58.23	56.33
220	111.78	119.40	60.56	58.84
230	117.03	124.48	62.90	61.58
240	122.57	129.58	65.27	64.31
250	129.22	134.71	67.69	67.02
260	136.93	139.92	70.20	69.72
265.51		Transition		
		(Crystal-I)		
270	167.40	178.89	105.90	72.92
280	175.16	185.12	108.23	76.89
290	184.55	191.42	110.70	80.72
299.09		Fusion		
		(Liquid)		
300	213.60	203.87	119.33	84.54
310	223.40	211.74	122.53	89.21
		(Crystal-III) $S_0^\circ=0$ $H_0^\circ(\mathrm{III})-H_0^\circ(\mathrm{II})=70.2$ J/mol		
5	(0.1676)	(0.0559)	(0.0444)	(0.0115)
10	(1.276)	(0.4743)	(0.3579)	(0.1164)
20	8.821	3.430	2.526	0.9045
30	18.37	8.847	6.441	2.435
40	26.75	15.33	10.37	4.962
50	33.18	22.02	14.32	7.706
60	38.93	28.58	17.94	10.64
70	44.13	34.99	21.37	13.62
80	48.70	41.18	24.49	16.69
90	53.32	47.18	27.44	19.74
100	57.56	53.02	30.24	22.78
110	61.67	58.70	32.92	25.78

TABLE 13 (continued)

T(°K)	$C_p°$	$S°$	$(H°-H_0°)/T$	$-(G°-H_0°)/T$
120	65.81	64.24	35.48	28.78
130	70.16	69.69	37.99	31.70
140	74.35	75.04	40.43	34.61
150	78.70	80.32	42.84	37.48
160	82.40	85.51	45.20	40.31
170	86.69	90.64	47.51	43.13
180	91.18	95.72	49.81	45.91
190	95.70	100.77	52.11	48.66
200	99.72	105.78	54.39	51.39
210	104.56	110.76	56.66	54.10
220	109.84	115.74	58.95	56.79
230	115.63	120.75	61.29	59.46
240	122.91	125.80	63.68	62.11

(Supercooled crystal-I)

$S_0°=4.72$ J/mol degK $H_0°(\mathrm{I})-H_0(\mathrm{II})=4570$ J/mol

T(°K)	$C_p°$	$S°$	$(H°-H_0°)/T$	$-(G°-H_0°)/T$
5	(0.348)	(4.48)	(0.0870)	(4.75)
10	(2.716)	(5.64)	(0.692)	(4.95)
20	13.06	10.56	4.198	6.36
30	22.67	17.72	8.790	8.93
40	31.21	25.45	13.37	12.09
50	37.32	33.10	17.57	15.53
60	42.67	40.38	21.31	19.07
70	47.91	47.36	24.75	22.61
80	53.08	54.10	27.97	26.13
90	58.15	60.64	31.04	29.60
100	63.00	67.02	33.99	33.03
110	68.19	73.26	36.86	36.40
120	73.56	79.43	39.70	39.73
130	79.63	85.55	42.53	43.02
140	86.84	91.70	45.42	46.28
150	118.72	98.37	48.85	49.52
160	122.28	106.14	53.32	52.82
170	125.35	113.65	57.47	56.18
180	128.28	121.36	61.33	60.03
190	131.22	127.91	64.93	62.98
200	134.16	134.72	68.32	66.41
210	137.09	141.33	71.52	69.81
220	140.38	147.78	74.57	73.21
230	144.61	154.01	77.52	76.49
240	148.84	160.25	80.41	79.85
250	154.08	166.54	83.24	83.30
260	160.68	172.70	86.09	87.00

represented by a kind of quasi-particle "hole"[13,14] conventionally. Because the crystal-I has positional order (face-centered cubic),[15,16] the degree of freedom frozen in the glass transition of this crystal are expected as follows:

(a) Orientation of overall molecule,
(b) Number of the hydrogen bonds in the crystal,
(c) Orientation of OH group around a C–O bond,
(d) Tautomerism between the axial and the equatorial forms,
(e) Number of the defect.

We shall first discuss the contributions from the intramolecular terms (c) and (d). If it is assumed that the energy difference between the axial and the equatorial forms at T_g is equal to the value which

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13) N. Hirai and H. Eyring, *J. Polymer Sci.*, **37**, 51 (1959).
14) B. Wunderlich, *ibid.*, **Pt. C, No. 6**, 137 (1963).
15) T. Oda, *X-rays*, **4**, 2 (1945).
16) T. Oda, *ibid.*, **5**, 26 (1948).

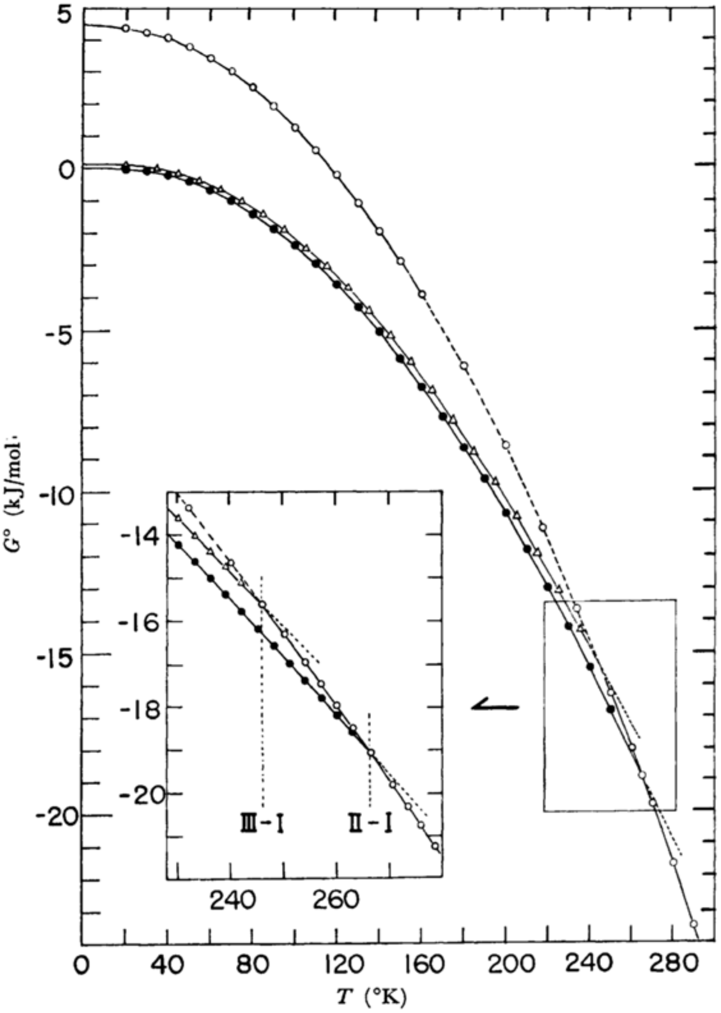

Fig. 4. Gibbs energies of respective phases.
—○— crystal-I and supercooled crystal-I
—●— crystal-II
—△— crystal-III

was reported by Masschelein and that this degree of freedom is frozen at T_g, the contribution of the mixing entropy of these tautomers to the residual entropy amounts to 4.5 J/(mol degK). This value seems to be large compared with the residual entropy (4.7 J/(mol degK)) and it may be considered that the energy difference will increase at low temperature. Focussing our attention to the intensity of the absorption of bands at 1070 cm^{-1} and at 970 cm^{-1} whose intensities had been studied by Masschelein, we reinvestigated the infra-red spectrum of supercooled crystal-I at low temperatures. The results are given in Fig. 3, where is also shown the temperature dependence of the *OH* stretching band. Maschelein assigned the bands at 1070 cm^{-1} and at 970 cm^{-1} to *C–O* stretching vibration of the equatorial and the axial forms, assuming these bands were single. However both of them are apparently composed of a pair of bands respectively and the individual bands of each pair show remarkable temperature dependence. Since it is very difficult to separate accurately the piled bands in two parts, we did not analyze the intensities of these bands quantitatively. From the fact that the bands do not change between 150°K and 80°K, it may be concluded that the degree of freedom of the tautomerism is frozen below T_g.

As to the contribution to the residual entropy of the orientation of the *OH* group for the rotation around a *C–O* bond, it should be also small. The quantitative discussion about it is, however, difficult at the present stage of our knowledge. If one attributes the residual entropy only to these intra molecular degrees of freedom ((c) and (d)), the jump of the heat capacity at T_g can not be explained, because these degrees of freedom offer the Schottky heat capacity which is very small compared with the actual jump of the heat capacity at T_g.

We discuss now about the effects of (a) and (b). Meakins[17] and Corfield and Davies[18] have studied the dielectric dispersion of the crystal-I and also of supercooled one. Comparing with the results of cyclohexanone and chlorocyclohexane,[*5] they concluded that the chains of hydrogen bonds are formed in this cyclohexanol crystal. If one extraporated the $\log(f_{max})$ *vs.* $1/T$ plots to low-temperature, the $1/f_{max}$ becomes from 1 sec to 1 hr at T_g, where the f_{max} indicated the frequency of maximum dispersion. Although these behaviors are also known in the ordinary glassy materials, this result shows that the orientation of the overall molecule is frozen at T_g. The careful examination of the possibility of the point defects in this crystal, as well as other plastic crystals by Staveley *et al.*,[19] has given no definite conclusion about the numbers of defects in these crystals. Accordingly, the role of the defects to the glass transition are still in question. In conclusion, we may only say that the residual entropy of the supercooled crystal-I may arise from frozen-in state partly of reorientational, and partly of conformational freedoms of the molecule in the lattice. The supercooled crystal-I below T_g is considered as a kind of new state of aggregation of pure material in the sense that the crystalline material has glass transition point and we should like to propose a term **glassy crystal** to this phase.

Debye Temperature. Debye temperatures of the supercooled crystal-I and the crystal-II are shown in Fig. 5. These calculations are based on the method of Wulff.[20] In Fig. 5, (1) and (2) are obtained by assuming 6 degrees of freedom. Debye temperatures due to 3 degrees of translational freedom are plotted in (3) and (4), where 3 degrees of torsional freedom are represented by a kind of Einstein function, whose average frequency is determined by a trial and error method. The lowering of the Debye temperature of the supercooled crystal-I above 90°K shows the existence of some configurational degrees of freedom which contribute to the heat capacity. Recently, Green and Scheie[21] determined the Debye temperature of the crystal-I between −40°C and 20°C from the study of the velocity of ultrasonic wave in the crystal. The result agrees fairly well with that of present low-temperature study. They have also reported that the velocity of ultrasonic wave in the crystal-III is larger than that in the crystal-II. This result is consistent with present result that the heat capacity of the crystal-III is smaller than that of the crystal-II.

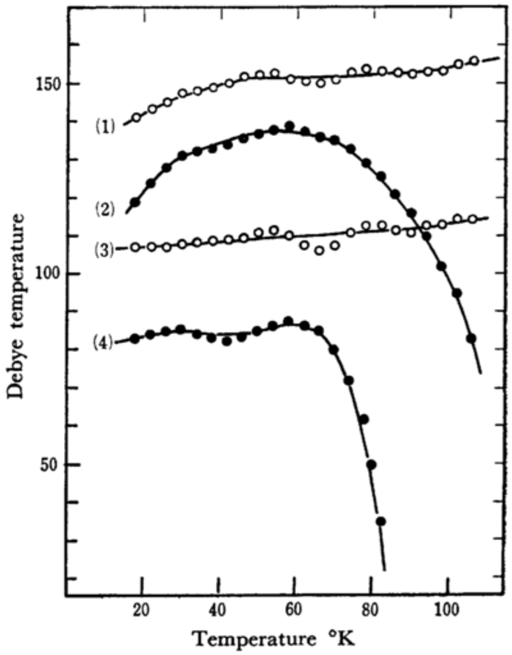

Fig. 5. Debye temperature of the supercooled crystal-I and the crystal-II.

(1)	Crystal-II	6 degrees of freedom
(2)	Supercooled crystal-I	6 degrees of freedom
(3)	Crystal-II	3 degrees of freedom, $\omega = 103$ cm^{-1}
(4)	Supercooled crystal-I	3 degrees of freedom, $\omega = 97$ cm^{-1}

Here, ω represents the frequency of the torsional vibration of overall molecule.

Relaxation Phenomenon of the Supercooled Crystal-I. We have investigated the relaxation phenomena of the supercooled crystal-I below T_g with annealing treatment under different conditions. Figure 6 shows the contribution to the enthalpy from the degrees of freedom of configurations and conformations; in other words, the contributions from the intermolecular potential energy and intramolecular one. We call these terms conventionally configurational enthalpy. The experimental procedure for obtaining the configurational enthalpy $\Delta H_{\text{conf.}}$ is as follows: for instance, the difference of the total enthalpy between 155°K and 141°K is experimentally determined from the adiabatically supplied electric energies which is necessary to raise the temperature of the supercooled crystal-I from 141°K to 155°K. The increment of the kinetic energy and the energy of expansion due to the lattice vibration and internal vibration between 141°K and 155°K is calculated from the estimated heat capacity of vibrations that is represented by the following equation,

$$C_p\ (\text{vib.}) = 22.81 + 0.41256T\ \ (\text{J/mol degK}). \quad (3)$$

This equation was determined so that the Debye

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[17] R. J. Meakins, *Trans. Faraday Soc.*, **58**, 1962 (1962).

[18] G. Corfield and M. Davies, *ibid.*, **60** (**Pt. 1**), 10 (1964).

[*5] They are also plastic crystals.

[19] L. A. K. Staveley, P. F. Higgins and J. J. Virden, *J. Chem. Soc.* (*Suppl.* 1), **1964**, 5762.

[20] C. A. Wulff, *J. Chem. Phys.*, **39**, 1227 (1963).

[21] J. R. Green and C. E. Scheie, *J. Phys. Chem. Solids*, **28**, 383 (1967).

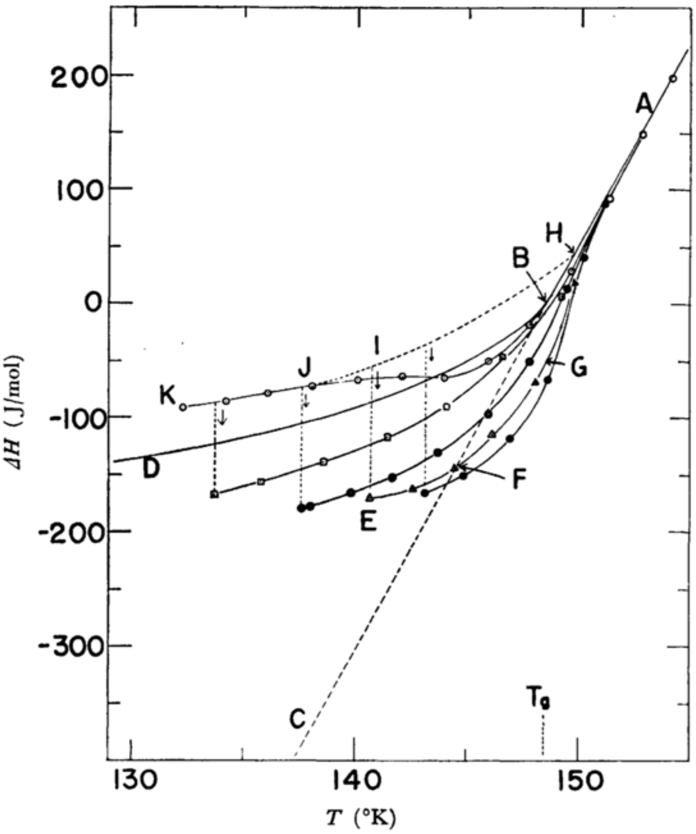

Fig. 6. Configurational enthalpy *vs.* temperature curves.

temperature calculated from above equation maintained nearly the same value as one at 90°K. The difference of the configurational enthalpy $\Delta H_{\mathrm{conf.}}$ is determined by subtracting the increment of the kinetic energy from the total increment of enthalpy. Since the details about the origin of the anomalous heat capacity (C_p(obs)—C_p(vib)) is not known, it has some uncertainty whether this anomalous heat capacity is completely attributed to the degree of freedom of the configuration. Instead of this method, the $\Delta H_{\mathrm{conf.}}$ is also calculable by the integration of the (C_p(obs)—C_p(vib)). In Fig. 6, curve A–B–C shows the estimated equilibrium curve assuming that the equilibrium heat capacity below T_g is represented by Eq. (1). A–B–D is obtained from the experimental heat capacity data (Table 1). In the measurement of the heat capacity of the supercooled crystal-I below T_g, the anomalous temperature drift due to the stabilization is treated as if the drift were arisen from thermal leakages.[*6] This procedure below T_g provides the heat capacity eliminating the effect of relaxation. In other words, this heat capacity corresponds to the value for infinitely rapid measurement. If one takes this effect into consideration, the heat capacity curve shows a hump at T_g as shown by the data of Ôtsubo *et al.*, in Fig. 2. Accordingly, A–B–D shows the enthalpy changes for infinitely rapid heating. Other curves were determined from electric energy supplied under adiabatic condition. K–J–B–A shows the enthalpy increment when heated with the rate of about 1.5°K/hr as soon as cooled down to 130°K with the cooling rate of −6°K/min. The dotted line H–I–K is estimated curve for the cooling rate of −6°K/min. Annealing experiments were made at 144°K, 141°K, 137°K and 133°K for 25 hr, respectively, after cooling to these temperatures with cooling rate of −6°K/min from the liquid state at 300°K. For example, the enthalpy at 141°K changes from I to E in 25 hr and then traces the curve E–F–G upon heating. Assuming the exponential decay of enthalpy during the annealing period, the time constants (in hours) were calculated and summarized in Table 14. Here, it is assumed that the enthalpy at time zero lies on the curve A–H–I–J–K and on the curve A–B–C after infinite time. The Arrhenius plot of log τ against $1/T$ deviated from a straight line as shown in Fig. 7. The activation

TABLE 14. THE TIME CONSTANTS OF THE RELAXATION OF THE CONFIGURATIONAL ENTHALPY

Temperature (°K)	144	141	137	133
Time const. (hr)	11.9	32.3	60.4	125

[*6] See Ref. 7.

energy calculated from the nearly straight portion of this curve is of 28.8 kJ/mol. As is well known, the relaxation time of dielectric or viscoelastic relaxation of supercooled liquid near T_g deviates from Arrhenius equation and is represented by the equation $\tau = \tau_0 \exp(E/(T-T_2))$, where T_2 is the temperature at which the relaxation time becomes infinite. But in these experiments, the deviation of the plot in Fig. 7 from the Arrhenius equation is the inverse to the deviation of the type of above equation. The origin of this result is apparently considered to be experimental error due to the incompleteness of adiabatic condition. But as shown in Fig. 7, the extent of this error is too small to change the behavior of the result. Another origin may be the ambiguity of the estimation of equilibrium curve (A–B–C). Assumption of exponential decay is also considered to be the possible source of the result. But if this result is accurate, it is seemingly explained by assuming the co-existence of different relaxation processes having respective characteristic time constants. The observed temperature drifts due to the stabilization also support this assumption. In general, the frozen-in state whose enthalpy is larger than that of equilibrium state should show the exothermic stabilization. Accordingly, behaviors of stabilization at all the points which are above the equilibrium curve (A–B–C) in Fig. 6 should be exothermic. But in this experiments, all the annealed specimen, *i.e.* at the points of ⊡, ◎, ● and ◬ in Fig. 6 showed net endothermic stabilization. This fact can be explained as follows: Although some degrees of freedom are frozen-in in this state, some other degrees of freedom which have shorter time-constant are already in equilibrium. So, when the temperature is raised up, the endothermic relaxation due to the degree of freedom having shorter relaxation time contributes largely to the stabilization.

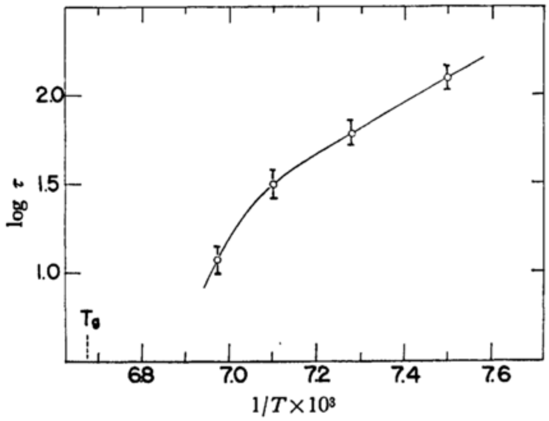

Fig. 7. log τ *vs.* $1/T$ curve.
In this figure, $\overset{\top}{\underset{\perp}{\circ}}$ shows the limit of the experimentanl error due to incompleteness of adiabatic condition.

T_2-Temperature. Gibbs and Adam[22] proposed a theory to solve the so-called Kauzmann's paradox[23] and the existence of a temperature denoted by T_2 where the relaxation time becomes infinite and the configurational entropy would vanish only if one supercooled a liquid infinitely slowly. Assuming that the heat capacity of the equilibrium state of glassy state corresponds to the extraporation of the heat capacity above T_g (Eq. (1)), we determined T_2 of the supercooled crystal-I to be 128°K. It is known that the ratio of T_g and T_2 of ordinary glassy substance is about 1.3, whereas the value amounts to 1.18 in this crystal.

Summary

(1) The heat capacities of cyclohexanol have been determined from 14°K to 320°K. The temperatures and the heats of transitions and of fusion for respective modifications were determined and the following results were obtained: *i.e.*, 265.50°K and 8827 J/mol for the phase transition of crystal-II—I, 244.8°K and 8638 J/mol for crystal-III—I and 299.05°K and 1782 J/mol for crystal-I—liquid.

(2) Comparing the entropy of ideal gas state calculated from thermal data with that from statistical-mechanical method, we have estimated that the residual entropy of the crystal-II is equal to zero and that the potential barrier of the internal rotation of *OH* group amounts to about 7.0 kJ/mol.

(3) Based on the estimation that the crystal-II has no residual entropy, the residual entropies of the supercooled crystal-I and of the crystal-III were determined. The residual entropy of the supercooled crystal-I amounted to 4.72 J/(mol degK) whereas that of the crystal-III was found to be zero within the experimental error.

(4) The Gibbs energies of the supercooled crystal-I, the crystal-II and of the crystal-III were calculated. From these results as well as that of the residual entropy, we can conclude that the crystal-III is of metastable but in the internal equilibrium state.

(5) It was confirmed that the anomalous jump of the heat capacity of the supercooled crystal-I at T_g ($\approx$150°K) arises from relaxation phenomena and the time constants in the relaxation process in enthalpy were determined.

(6) The origin of the residual entropy of the supercooled crystal-I was discussed and we proposed a new term **glassy crystal** for a crystalline material having glass transition temperature.

(7) Debye temperatures for the crystal-I and the crystal-II, and T_2 temperature were determined.

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[22] J. H. Gibbs and G. Adam, *J. Chem. Phys.*, **43**, 139 (1965).

[23] W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).