BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1960—1972(1972)

Calorimetric Study of the Glassy State. VII. Phase Changes between the Crystalline Phases of Cycloheptanol with Various Degrees of Stability

Keiichiro Adachi, Hiroshi Suga, and Syûzô Seki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan

(Received November 8, 1971)

The heat capacities of 8 kinds of stable and meta-stable crystalline phases including the glassy crystal of cycloheptanol were measured at temperatures from 13 to 300 K. The crystalline phases have been named crystals I, II, II′, III, III′, III″, I_β, and glassy crystal. Transition temperatures between crystals II and I, III and II, II′ and II, III′ and III, III″ and III were determined to be 258.45, 227.26, 172.23, 152.30, and 128.2 K, respectively. The melting point and glass transition point of the glassy crystal were determined to be 280.30 and 140 K, respectively. The heats of transition between crystals II and I, III and II, III′ and III and the heat of melting were determined to be 876, 554, 58.1, and 1604 $\mathrm{J\,mol^{-1}}$, respectively. The residual entropy of the glassy crystal was found to be 0.7 $\mathrm{J K^{-1} mol^{-1}}$ assuming that of crystal III′ to be zero. The stabilization phenomenon in the glassy crystalline state was also studied from the measurements of enthalpy relaxation. The stability of the various phases was determined by calculating their free energies. The degree of freedom which is frozen in the glassy crystalline state was discussed from molecular viewpoints. Classification of various phase transitions found in this material was also made from the viewpoint of thermodynamical stability.

In general the glassy state results from an elongation of a relaxation time by cooling a material which is in a supercooled metastable state. Thus, the glassy state is looked upon as a non-equilibrium state in a thermodynamic sense.[1] We measured the heat capacities of the quenched high-temperature crystalline phases of cyclohexanol and 2,3-dimethylbutane and concluded that these crystalline phases have definite residual entropies at 0 K and exhibit glass transition phenomena characteristic of non-equilibrium glassy states.[2,3,4] We proposed the term "*glassy crystal*" for defining the glassy crystalline state as the non-equilibrium frozen-in state of crystals which have glass transition points. The present paper describes the results of measurements of heat capacity for cycloheptanol expected to form the glassy crystal from a preliminary study of the differential thermal analyses (DTA).

In previous studies,[2,3] we attempted to explain the residual entropies in terms of the degrees of freedom frozen-in below the glass transition points and proposed two possible explanations, the orientational degree of freedom of the molecules and the conformational one. However, the residual entropies were so small that they were accounted for only by taking into consideration the conformational degree of freedom frozen below the glass transition point. An important feature of the present investigation may be found in the fact that the molecule of cycloheptanol can be expected to have more kinds of possible conformations than that of cyclohexanol or 2,3-dimethylbutane. We can expect 42 kinds of distinguishable conformations for this molecule. Although we do not know much about the energy difference between these conformers, we can expect the conformational degree of freedom to contribute greatly to the residual entropy of the glassy crystal of this material, if the conformational degree of freedom is frozen at or below the glass transition point.

The influence of the complicated molecular structure on the behaviors of phase transitions is also of interest. Various metastable phases were found and some thermodynamic functions were determined for them.[2,3,4] In the present study we have also found the occurrence of 8 kinds of stable and metastable crystalline phases from DTA measurement and clarified the relation of

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

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

[3] *Idem, ibid.*, **43**, 1916 (1970).

[4] *Idem, ibid.*, **44**, 77 (1971).

the instability by measuring their heat capacities.

It is well-known that the glassy state is not a completely frozen-in state but is stabilized very gradually into an equilibrium state. In this respect we measured the enthalpy relaxation time of the stabilization process.

We also measured the Raman and IR spectra in order to analyze the magnitude of the heat capacities. From the results the magnitude of heat capacity due to internal vibrations was calculated and that due to the change of the configuration of molecules was estimated. Variation in the magnitude of heat capacity caused by annealing in the glassy crystalline state was also examined.

Experimental

Material. The sample employed was synthesized by reducing cycloheptanone prepared by the reaction of cyclohexanone with diazomethane. The equations of the chemical reactions are as follows.

$$C_6H_{10}O + CH_2N_2 \longrightarrow C_7H_{12}O$$
$$C_7H_{12}O + LiAlH_4 \longrightarrow C_7H_{13}OH.$$

Cycloheptanone was synthesized by adding 550 g of nitrosomethylurethane little by little with violent stirring into a mixture of 400 g of cyclohexanone, 2 *l* of ethylether and 1200 g of 50% KOH aqueous solution. The temperature of the reacting system was regulated to 10±5°C. It took about 6 hr to complete the reaction. Fractional distillation of the reaction product yielded about 200 m*l* of pure cycloheptanone. Hydrogenation of the cycloheptanone was carried out with the aid of $LiAlH_4$ in an ethylether solution by the usual method. The reaction product was then purified by repeating fractional distillation. About 50 m*l* of the purified cycloheptanol was obtained. In order to remove the trace of water, vacuum distillation was craried out over baked CaO. The absolute purity of the sample was finally determined to be 99.932% from the equilibrium temperatures in the melting process.

Apparatus. The measurement of the heat capacity was made with an adiabatic calorimeter.[5] The cryostat was reconstructed in such a way that liquid nitrogen could be introduced into the inside of the inner jacket when the sample was required to be quenched. The platinum resistance thermometer was calibrated after the completion of investigation by comparison with the laboratory standard thermometer which had been calibrated at the US National Bureau of Standards. The deviation of the temperature scale was, however, too small to cause any error in spite of severe thermal treatment. The sample cell contained 26.774 g of the sample as well as a small amount of helium gas for heat exchange medium (1 atm at room temperature).

The Raman spectra were obtained with a Nihon Bunko Co. Raman spectrometer model R 1000 and the IR spectra with a Nihon Bunko Co. Double beam spectrometer model DS 402 G. The apparatus for DTA was reported previously.[6]

Results

DTA. Thermal behaviors were studied preliminarily by means of DTA before the precise measurements of heat capacity. The results are shown in Fig. 1. Run 1 is the cooling curve measured at a rate of about −1.5 K/min. A sharp exothermic peak due to abrupt crystallization was observed at 267 K followed by a phase transition at about 245 K. A small exothermic anomaly was observed at about 165 K on further cooling. Run 2 is the heating curve measured after the specimen had been slowly cooled down to 80 K from 280 K. The heating rate was about 2 K/min. A small and broad anomaly with two shoulders was observed at about 170 K and peaks due to a phase transition and melting followed at 259 and 278 K, respectively. We named the phases as follows, table between 259 and 278 K, Crystal I; between 170 and 259 K, Crystal II; below 170 K, Crystal II′. The heating curve taken after crystal II had been rapidly chilled at a rate of about 4 K/sec by steeping the DTA sample container in liquid nitrogen is shown in Run 3. The DTA curve taken after crystal I had been chilled rapidly by the same procedure is shown in Run 4. When the specimen in the liquid state was chilled at the same cooling rate, nearly the same DTA diagram as for Run 3 was obtained. In Run 4 an anomaly resembling that for glass transition was observed at 140 K. This is considered to be the glass transition. We thus called the phase below 140 K the glassy crystal. On further heating, an exothermic transition followed around 167 K. We named the phase between 140 and 160 K Crystal I_α and that established by the transition around 167 K Crystal I_β. A phase change took place from crystal I_β to another unknown phase at 197 K. A small exothermic anomaly was recognized around 190 K. The phase to which crystal I_β was transformed at 197 K was unstable and irreversibly transformed into the more stable one at about 210 K. A new peak appeared at 239 K which was not observed in Run 2. Above 250 K, nearly the same thermogram as in Run 2 was obtained. We named the phase with transition point at about 239 K Crystal III. In order to obtain crystal III as a pure

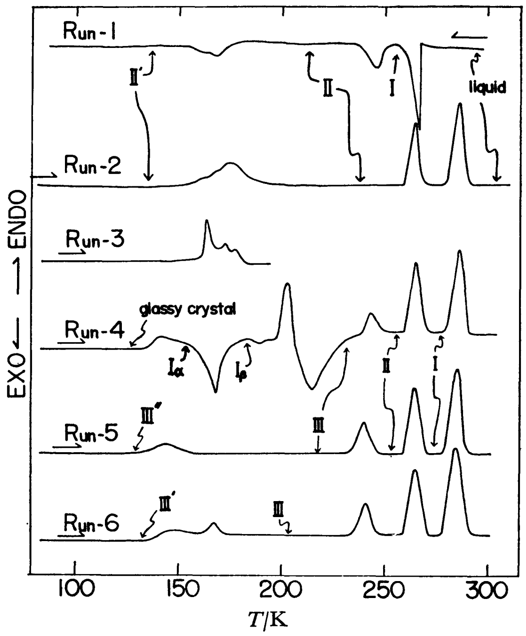

Fig. 1. DTA curves of cycloheptanol.

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

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

phase, crystal II was annealed at dry ice temperature for 3 days. Run 5 is a heating curve taken after the annealing. A small and broad anomaly was observed around 130 K. The peak at about 240 K is slightly larger than the one in Run 4. Since no peak due to the transition from crystal II′ to crystal II appeared at 170 K, it was concluded that crystal III had been established in pure state by the annealing. By annealing at 140±3 K for 5 days, crystal III changed to another phase, the DTA thermogram for which is represented by Run 6. However, when crystal III was annealed at 115—125 K for 5 days, nearly the same thermogram as in Run 5 was obtained. The phases appearing at the lowest temperature in Runs 5 and 6 were named Crystals III′ and III″, respectively.

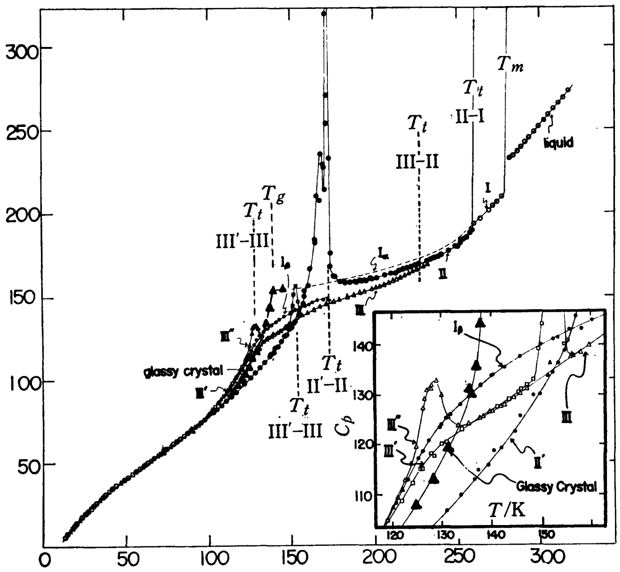

Fig. 2. Heat capacities of cycloheptanol

▲: crystals I, I_α, and glassy crystal
●: crystals II and II
△: crystals III and III″
□: crystal III′
○: crystal I_β

Heat Capacity Measurements. Selected values of the heat capacity data are listed in Table 1; a complete set of the heat capacity data is preserved by the Chemical Society of Japan.[7] These heat capacity data are plotted against temperature in Fig. 2. In Series 1, the heat capacities were measured after the liquid specimen at room temperature had been chilled at a rate of about −50 K/min (Series 1). Under these conditions, it was expected from DTA that crystal I would be supercooled and the glassy crystalline state established below 140 K. The data listed in Series 2 and 2′ were taken before measurement of the enthalpy relaxation in annealing treatment, *i.e.* determination of the points D and E shown in Fig. 8. In Series 1, 2, and 2′, the heat evolution or absorption due to a stabilization effect near T_g was subtracted by correction of temperature drift. In the II′—II transition temperature region (Series 3′, 3″) the heat capacity changed slightly with thermal history. Measurements were carried out after the following thermal histories. In Series 3′ crystal II was cooled down to 100 K at the rate of −6 K/min and then annealed for 18 hr at 138 K. In Series 3″ the specimen was annealed for 12 hr at 156 K after cooling. Measurements for the supercooled crystal II in the temperature region 200—215 K were somewhat difficult on account of the exo-thermic transition from this phase to crystal III. Crystal III (Series 4) was prepared under the same conditions as for DTA (Run 5, Fig. 1). When it was annealed at 140 K for 3 days, it was transformed irreversibly into another phase which showed a phase transition to crystal III at 152.3 K. We named this phase crystal III′ (Run 6, Fig. 1). At the ordinary cooling rate (−1 K/min), crystal III was supercooled easily with no III′—III transition. The heat capacity curve of the supercooled crystal III showed a small anomaly at about 128 K. We named the supercooled phase below 128 K crystal III″ (Run 6 Fig. 1). The results for crystal III′ and crystal III″ are listed in Series 5 and 6, respectively. Crystl I (Series 9) was prepared from the results of DTA (Run 4, Fig. 1). The results for crystal III′ and crystal III″ are listed in Series 5 and 6 respectively. Crystal I_β (Series 9) was prepared from the results of DTA (Run 4, Fig. 1). Measurements for I_β were carried out after the phase had been annealed at 123 K for 15 hr (Series 9′). The aim of these measurements was to check a possible relaxation phenomenon of I_β having different thermal histories. However, no such effect was observed.

Determination of the Transition Points and the Heats and Entropies of Transition. *(1) II—I Transition*: The transition point was determined to be 258.45 K from the heat capacity measurement. Determination of the heat of transition was carried out for three series of independent measurement. As is shown in Table 2, the values obtained in experiments 1 and 3 were smaller than those of experiment 2. The deviation is beyond experimental error. This might have been caused by the thermal history of crystal II. In Expts. 1 and 3, measurements were carried out for crystal II (fresh sample produced by cooling crystal I to about 245 K), whereas in Expt. 2 crystal II prepared from crystal III was employed. It was expected that a small amount of crystal I was included in crystal II in Expts. 1 and 3 and caused a decrease in the magnitude of the heat of transition. Accordingly the values from Expts. 1 and 3 were abandoned and those from Expt. 2 were taken for calculation of the thermodynamic variables.

(2) II′—II Transition: Figure 2 indicates that, the heat capacity curve in this transition region has two maxima at 167.88 and 172.33 K, respectively, of which the latter is taken as the true transition point. Since the transition takes place over a wide temperature range, it is difficult to determine the exact heat of transition owing to the difficulty in estimation of the

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[7] The complete data of the heat capacity are kept as Document No. 7207 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance ¥700 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

Table 1. The molar heat capacities of cycloheptanol
Mol. wt. = 114.189 0°C = 273.15K

$T_{\mathrm{av.}}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K	$T_{\mathrm{av.}}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K	$T_{\mathrm{av.}}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K
Series 1			Series 2[a]			Series 3		
(Quenched glassy crystal)			(Annealed glassy crystal)			(Crystals II′ and II)		
13.955	6.964	1.82	13.804	6.561	1.43	13.993	6.722	2.54
17.920	11.156	2.47	16.473	9.589	1.94	18.393	11.304	2.25
21.725	15.520	2.43	19.782	13.902	2.41	22.181	15.628	2.03
14.161	6.902	2.20	14.405	7.285	1.72	25.784	19.562	1.90
18.146	11.418	1.79	17.815	11.088	1.61	29.783	25.739	1.89
22.375	16.209	2.62	20.590	14.165	1.52	33.481	26.903	1.77
26.786	20.659	1.96	23.201	17.150	1.24	37.468	30.712	2.01
31.082	25.001	2.10	26.062	20.207	1.54	41.408	31.876	2.15
35.066	28.831	2.28	29.352	23.414	1.65	45.444	37.045	1.94
39.279	32.537	1.99	32.574	26.579	1.87	49.334	39.941	2.16
43.322	35.326	2.39	36.029	29.709	1.64	53.467	43.054	2.00
47.819	39.028	2.15	39.926	32.951	1.99	57.628	46.095	2.49
52.104	42.133	2.36	44.344	36.405	1.91	60.456	48.065	2.39
56.622	45.396	2.19	49.075	39.941	2.30	65.056	51.426	2.24
61.054	48.624	2.04	53.815	43.429	2.34	69.398	54.352	2.12
65.213	51.665	2.34	58.307	46.696	2.17	73.541	57.120	2.03
98.889	76.866	2.07	63.322	50.398	2.06	78.469	60.916	1.92
102.982	80.317	2.01	67.022	52.906	1.77	83.631	64.929	2.66
119.422	97.747	2.39	70.634	55.358	2.03	88.812	68.946	2.55
134.369	131.393	1.94	74.602	58.114	1.94	93.792	72.691	2.47
138.134	144.337	1.81	78.770	61.223	2.10	98.604	76.355	2.39
141.602	153.050	1.73	82.886	64.490	2.03	104.600	81.263	3.15
145.058	155.541	1.71	87.175	67.893	2.15	110.764	87.179	2.99
			91.577	71.126	2.42	116.612	92.936	2.85
124.930	109.693	1.67						
128.302	117.025	1.59	Series 2′[b]			112.794	88.724	3.27
132.553	126.825	2.02	(Annealed glassy crystal)			121.472	97.295	4.59
						128.199	103.872	2.91
78.727	61.197	1.44	13.977	6.557	2.28	133.991	109.825	2.79
82.136	63.931	1.78	21.621	15.295	2.93	139.515	115.720	2.69
86.726	67.509	2.18	26.815	20.766	2.75	144.802	122.556	2.58
91.008	71.211	2.09	31.604	25.444	2.16	149.934	130.092	2.47
95.135	73.757	2.03	35.627	29.244	1.85	154.803	138.720	2.35
			39.359	32.507	2.18			
59.132	44.538	1.84	43.506	34.861	2.03	140.423	118.897	2.73
63.328	50.322	2.15	48.274	38.994	2.43	145.768	125.729	2.61
67.995	53.537	2.02	53.145	42.922	2.21	151.398	133.713	3.40
74.748	58.224	2.33	57.714	46.266	2.67			
79.209	61.508	2.18	62.849	50.027	2.49	191.381	159.247	2.94
101.084	78.687	1.72	70.948	55.606	2.24	197.986	159.985	4.39
104.958	81.950	2.65	76.133	59.188	1.63	206.737	162.305	3.34
108.888	87.384	2.57	91.867	71.313	1.65			
115.177	92.864	2.43	97.496	75.711	3.15	244.267	176.695	4.03
119.954	99.854	2.30	109.590	86.445	2.85	252.206	182.516	3.94
124.470	107.493	2.19	114.266	91.444	2.74			
128.758	116.602	2.06	119.879	98.784	3.11	189.474	157.396	2.97
131.821	125.482	1.97				195.379	158.650	2.94
136.903	143.753	2.17	119.428	97.589	3.14	201.251	160.531	2.91
139.869	152.402	1.25	125.474	108.047	2.92			
			131.512	119.451	3.52	214.743	164.966	2.29
			143.235	152.074	1.71	219.667	166.574	2.27

TABLE 1 (Continued)
Mol. wt. = 114.189 0°C = 273.15K

$T_{av.}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K
224.195	167.721	2.26
231.237	169.769	2.19
235.576	171.765	2.16
239.868	174.072	2.14
Series 3′ (II′–II transition)		
157.396	149.979	3.12
164.762	181.075	2.35
169.729	226.453	2.27
171.854	269.793	1.97
172.974	167.713	4.28
179.510	158.343	2.96
185.474	157.993	2.96
Series 3″ (II′–II transition region)		
155.758	135.833	2.38
160.330	156.398	2.15
164.405	183.045	1.91
167.882	234.778	1.60
170.610	213.245	0.65
171.702	318.968	0.45
172.976	232.292	0.88
175.240	161.960	1.86
Series 4 (Crystal III)		
208.655	157.686	2.33
213.282	159.759	2.30
218.546	162.028	2.29
223.089	164.374	2.26
227.587	166.463	2.24
232.038	168.711	2.22
178.713	147.267	4.85
187.570	149.796	4.78
195.473	152.389	4.71
202.488	154.918	3.10
210.570	158.479	3.04
156.103	138.136	3.70
163.428	141.518	3.62
170.592	144.981	3.55
177.648	146.883	3.51
178.713	147.267	4.85
187.570	149.796	4.78
195.473	152.389	4.70
202.488	154.918	3.10
210.570	158.479	3.04
Series 5 (Crystal III′)		
13.881	6.643	2.24
17.551	10.771	1.92
20.757	14.490	1.73
24.595	18.621	2.45
28.884	23.069	2.30
33.158	27.133	2.23
37.453	31.061	2.35
41.809	34.597	2.08
45.890	37.727	2.19
50.054	40.832	2.00
54.826	44.381	2.45
59.529	47.818	2.28
62.345	49.857	2.18
66.558	52.872	2.06
71.080	55.955	2.32
75.558	59.048	2.18
80.208	62.604	2.08
85.387	67.087	3.21
93.140	73.604	2.99
98.977	79.280	2.83
103.525	84.671	2.79
108.780	91.107	2.55
113.749	97.892	2.42
119.046	105.040	3.45
124.101	112.205	2.19
128.398	117.750	2.11
133.799	123.047	2.86
138.796	129.615	2.31
143.433	129.235	2.31
125.516	115.144	2.19
129.804	120.057	2.11
134.482	123.767	3.08
140.888	127.555	3.66
125.230	113.604	2.18
129.506	119.033	2.10
Series 5′ (II′–III transition region)		
145.354	130.395	1.72
148.326	132.881	0.85
150.359	144.183	1.07
152.426	155.933	1.01
154.522	140.477	1.08
157.762	138.801	1.80
Series 6 (Crystal III″)		
15.859	8.773	2.53
19.700	13.133	1.71
23.660	17.572	2.20
27.508	21.538	2.14
31.545	25.517	2.30
35.722	29.432	1.96
39.924	33.023	2.09
43.862	36.094	1.89
47.876	39.152	2.00
52.012	42.359	2.46
57.753	45.255	2.33
59.361	47.652	2.28
63.754	50.893	2.14
68.020	53.874	2.22
72.360	56.911	2.12
76.742	60.067	2.35
81.668	64.178	3.52
86.440	72.328	1.99
91.062	71.817	2.38
96.301	76.401	3.40
102.918	83.110	3.19
108.629	89.815	2.01
105.933	86.633	2.78
112.660	94.992	2.60
120.149	107.599	2.38
124.785	119.622	2.20
128.014	131.790	2.06
133.243	123.767	2.14
137.515	125.362	2.12
141.736	127.559	2.09
146.919	131.167	2.04
138.181	125.576	1.94
142.352	127.892	2.51
121.078	109.612	2.15
126.233	127.218	1.93
109.648	90.928	1.98
115.693	99.470	2.39
122.022	110.772	3.32
127.828	131.244	1.96
132.438	132.344	2.91
Series 7 (Crystal-I)		
259.534	192.462	1.40
265.674	197.908	2.68

Table 1 (Continued)
Mol. wt. = 114.189 0°C = 273.15K

$T_{av.}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K	$T_{av.}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K	$T_{av.}$ / K	$\Delta H/\Delta T$ / JK^{-1} mol^{-1}	ΔT / K
270.958	203.218	2.62	17.559	10.763	1.83	120.837	107.787	2.74
276.139	208.788	2.57	21.080	14.800	2.19	125.482	117.306	2.15
			25.181	19.255	2.06	129.784	123.575	2.13
276.689	210.545	1.74	28.910	22.971	1.92	133.977	128.190	2.07
			33.211	27.065	2.19	138.066	132.058	2.02
			37.318	30.801	2.21			
	Series 8		41.693	34.362	2.55	153.570	141.625	2.32
	(Liquid)		46.477	37.962	2.28	158.202	143.639	2.29
			52.009	42.235	2.45	162.799	145.715	2.26
283.167	233.064	2.44	56.698	45.575	2.27	169.097	147.156	3.37
285.471	235.589	2.39	59.029	47.328	2.71			
290.211	241.035	2.36	64.836	51.494	2.05			
295.444	247.142	3.46	68.817	54.211	1.95		Series 9′	
			72.619	57.307	1.87			
298.265	250.256	3.05	76.862	59.901	2.18	114.059	94.050	1.82
304.377	257.417	3.18	81.109	63.270	2.08	117.624	100.067	1.74
310.344	264.176	2.91	85.183	66.456	2.00	121.023	107.032	1.67
316.075	271.098	2.85	89.424	69.812	1.87	124.057	113.788	1.19
			93.601	73.066	2.14	126.379	118.637	1.15
			97.807	76.504	2.07	136.207	130.305	6.02
	Series 9		101.872	80.300	1.99	142.739	135.453	2.34
	(Crystal I$_\beta$)		107.227	85.115	2.84	150.160	140.012	2.27
			111.912	91.627	2.04	152.432	141.202	2.26
14.001	6.871	1.82	116.596	99.206	1.93			

a) Annealed at 130.7 K for 75 hr
b) Annealed at 133.2 K for 68 hr

'normal' heat capacity. We thus calculated only the difference of enthalpy between crystal II′ at 162.5 K and crystal II at 176.5 K as given in Table 2.

(3) III—II Transition: The transition point could not be determined on account of the superheating effect of crystal III above the transition point. Thus the determination was carried out by measuring the magnitude of the temperature drift which was brought about by a spontaneous heat evolution or absorption due to the transition between crystals II and III. For this purpose a mixture of crystals II and III in the ratio about 1 : 1 was used since the rate of transition is expected to be maximum at this ratio where the best sensitivity is expected for the measurement. The temperature dependence of the drift for this specimen was measured at the temperature region 215—240 K and the transition point was determined as shown in

Table 2. Transition points, heats of transition, and transition entropies

II—I Transition T_t = 258.45K

Enthalpy of transition

		T_i / K	T_f / K	$\Delta_t H$ / Jmol^{-1}
Expt	1	252.606	261.592	827.3
Expt	2	252.103	260.307	875.5
Expt	3	249.892	260.228	849.3

$\Delta_t S$ = 3.39 JK^{-1}mol^{-1}

III—II Transition T_t = 227.26K

Enthalpy of transition

		T_i / K	T_f / K	$\Delta_t H$ / Jmol^{-1}
Expt	1	230.127	239.667	551.3
Expt	2	226.236	239.911	555.8
			mean	554±2

$\Delta_t S$ = 2.44 JK^{-1}mol^{-1}

III′—III Transition T_t = 152.30K

Enthalpy of transition = 58.07 Jmol^{-1}

$\Delta_t S$ = 0.381 JK^{-1}mol^{-1}

II′—II Transition T_t = 172.23K

Enthalpy difference between 162.500 and 176.500K

Expt	1		2919 Jmol^{-1}
Expt	2		2930 Jmol^{-1}
		mean	2925 Jmol^{-1}

Melting T_m = 280.30K

Heat of melting

		T_i / K	T_f / K	ΔH_m / Jmol^{-1}
Expt	1	276.622	281.958	1606.9
Expt	2	276.571	282.239	1598.5
Expt	3	275.829	282.276	1606.4
			mean	1604±3

$\Delta_m S$ = 5.72 JK^{-1}mol^{-1}

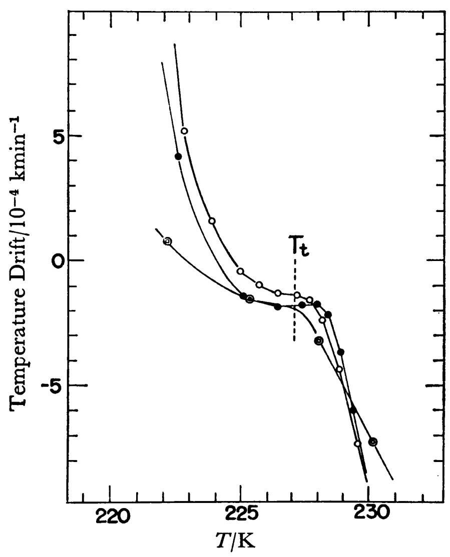


Fig. 3. Determination of the transition point between the crystal-II and III.

Fig. 3. The heat of transition was measured twice and the results are shown in Table 2. The values from Expt. 1 were determined by measuring the enthalpy difference between superheated crystal III (at 230.1 K) and crystal II at 239.7 K, since we did not know the superheating effect at that stage. The measurement in Expt. 2 was carried out between 226 and 240 K.

(4) III′—III Transition: The transition point was determined to be the temperature at which the heat capacity curve reaches a maximum value. Although this curve has a shape similar to that of second order phase transition, it took more than one hour to attain equilibrium after heating was over. The heat and entropy of transition are given in Table 2.

(5) III″—III Transition: The transition is considered to be that of higher order judging from the shape of the heat capacity curve. In contrast to the III′—III transition, equilibrium temperature was attained in a few minutes. As in the case of the II—II′ transition, estimation of contribution from the lattice part was difficult and no accurate determination of the entropy of transition could be made. The transition point was determined to be 128.2 K from the heat capacity curve.

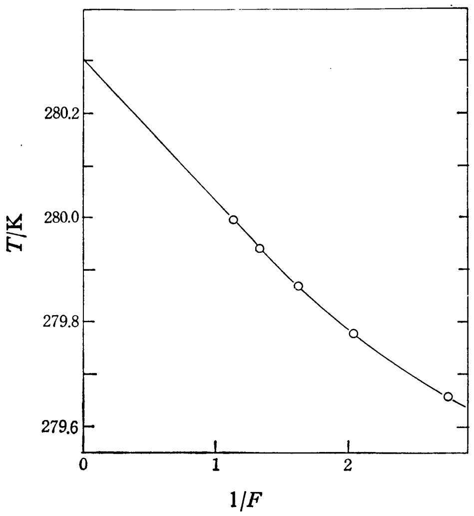


Fig. 4. Melting curve for cycloheptaol

(6) Melting Process: The data of fractional melting are plotted in Fig. 4. The melting point and the content of impurities which do not form solid solution with crystal I were determined from the curve. The melting point is the value obtained under the pressure of about 1 atm since the calorimeter cell contained helium gas. The difference between this and the triple point cannot be calculated since the data of the volume change at the melting is not available. The purity of the specimen was found to be 99.932%. The value of the enthalpy of melting is given in Table 2.

Estimation of the Heat Capacity of Crystal I_α Between 140 and 258 K. The heat capacity of crystal I_α (supercooled crystal I) between the temperature region 145—258 K could not be measured on account of its instability. Thus it was estimated in such a way that the difference of the enthalpy between 145 and 258 K agrees with that determined experimentally. The result is given in Fig. 2 by dashed line. Between 228 and 258 K, the heat capacity curve of crystal I is estimated to be parallel to that of crystal II and represented as follows.

$$C_p(\mathrm{I}) = C_p(\mathrm{II}) + 4.30. \qquad (1)$$

Between 145 and 288 K, the interpolation equation is estimated to be;

$$C_p(\mathrm{I}_\alpha) = 180.35 - 0.45888T + 1.8769 \times 10^{-3}T^2. \qquad (2)$$

By these equations the enthalpy of crystal I_α at 144.097 K is calculated to be 9036 J mol^{-1}. Here the enthalpy of crystal III′ at 0 K was taken as the reference point of enthalpy. The value obtained by direct measurement was 9010 J mol^{-1} which is in good agreement with that calculated by Eqs. 1 and 2. The procedure of the direct measurement was reported previously.[3]

Estimation of the Heat of Transition Between Crystal I and the Unidentified Phase. From DTA, it was found that crystal I_α is transformed into an unidentified phase at 197 K. We attempted to calculate the heat of transition for this phase change assuming that the unidentified phase was either crystal I or crystal II. For this purpose it is necessary to determine the enthalpies for crystals I_α, I_β, and II at 197 K. The values for crystals I_α and II were calculated to be 17.35 and 16.71 kJ mol^{-1}, respectively, from the above data. The value for crystal I_β was determined directly[3] at 163.9 K to be 11.48 kJ mol^{-1}. The value at 197 K was then calculated to be 16.49 kJ mol^{-1} by means of the following equation which was estimated to be between 165 and 197 K as

$$C_p = 0.291T + 99. \qquad (3)$$

The heat of transition is thus determined to be either 0.86±0.05 or 0.22±0.05 kJ mol^{-1} by assuming that the unidentified phase is either crystal I_α or crystal II. It is reasonable, however, to consider the value of transition between I_β and the unidentified phase to be close to that of the II—I transition (0.875 kJ mol^{-1}) from a comparison of the peak areas of DTA thermogram (Run 4, Fig. 1). Accordingly, we estimated that the phase into which crystal I_β is transformed would be

Table 3. Calculation of third law entropies.

1) The third law entropy of crystal I at 258.45 K *via* III′—III, III—II, and II—I transition

Temperature	Contribution	ΔS / $\mathrm{JK^{-1}mol^{-1}}$
0 — 12.5	Debye extrapolation $\theta_D = 112.9$	1.73
12.5—152.30	$\int C_p(\mathrm{III'})\, d\ln T$	114.04
152.30	Transition $\left(\frac{58.07}{152.30}\right)$	0.38
	$\sum$ =	116.15
152.30—227.26	$\int C_p(\mathrm{III})\, d\ln T$	60.08
227.26	Transition $\left(\frac{554}{227.3}\right)$	2.44
	$\sum$ =	178.67
227.26—258.45	$\int C_p(\mathrm{II})\, d\ln T$	22.70
258.45	Transition $\left(\frac{875.5}{258.45}\right)$	3.39
	$\sum$ =	204.76

2) The third law entropy of crystal I_α at 258.45K *via* crystal I.

0 — 13.5	Debye extrapolation $\theta_D = 112.7$	2.17
13.5 — 145.5	$\int C_p(\text{Glassy cryst.})\, d\ln T$	107.07
145.5 —258.45	$\int C_p(\mathrm{I}_\alpha)\, d\ln T$	94.82
	$\sum$ =	204.06

a) Equations 18 and 19 were used for the calculation.

3) The third law entropy of crystal II at 227.26K *via* crystal II′

Temperature	Contribution	ΔS
0 — 13.5	Debye extrapolation $\theta_D = 114.2$	2.09
13.5 — 162.5	$\int C_p(\mathrm{II'})\, d\ln T$	118.65
162.5 — 177.5	Transition region	18.15
177.5 —227.26	$\int C_p(\mathrm{II})\, d\ln T$	39.97
	$\sum$ =	178.86

4) The third law entropy of crystal III at 152.30K

Temperature	Contribution	ΔS
0 — 13.5	Debye extrapolation	2.31
13.5 —152.30	$\int C_p(\mathrm{III''})\, d\ln T$	114.41
	$\sum$ =	116.41

5) Zero-point entropy calculated by assuming that of crystal III′ to be zero.

Glassy crystal	0.70
Crystal II′	−0.19
Crystal III″	−0.26

crystal I_α and the heat of transition between the phases 860±50 J $\mathrm{mol^{-1}}$.

Residual Entropies of Various Phases. Assuming the entropy of crystal III′ at 0 K to be zero, we calculated the zero-point entropies for various other phases. The calculation for glassy crystal and crystal I_β are based on the above estimations. The results are given in Table 3. Below 13 K, the entropy changes were calculated with use of the Debye equation assuming 6 degrees of freedom. The Debye temperatures are given in Table 3. The residual entropy determined for glassy crystalline state amounts to 0.70 $\mathrm{JK^{-1}mol^{-1}}$, whereas the zero point entropies of other phases can be considered to be zero within experimental error.

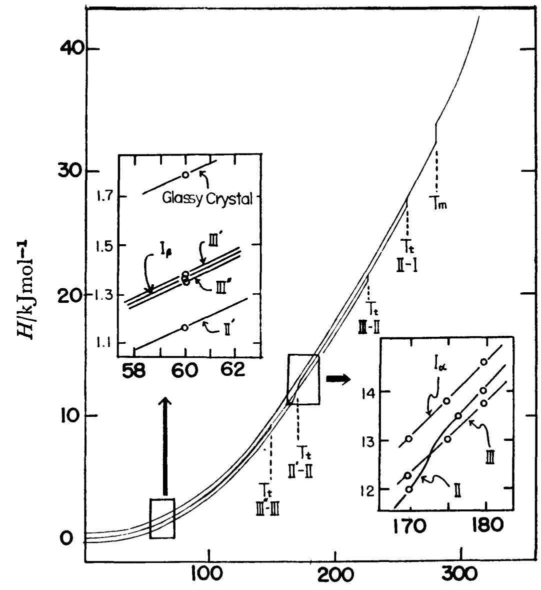


Fig. 5. Enthalpy curves of cycloheptanol.

Thermodynamic Functions of Various Phases. The thermodynamic functions derived from the data are given in Table 4 and the enthalpies in Fig. 5. The enthalpy curves are close to each other on account of small heats of transition. The entropy curves behave in a similar way. The relative Gibbs energies as well as the relative enthalpies of each phase with reference to crystals III′ and III are plotted in Figs. 6 and 7 for comparison of the stabilities of various phases. We see in Fig. 6, that crystal II′ is more stable than crystal III′ below 150 K. Thus the phase transformation from crystal III′ or III″ to crystal II′ should take place by annealing crystal III′ or III″ below 150 K. However, annealing of crystal III′ for 6 days at 140 K gave no such an effect by DTA study. The enthalpies of crystals II and III become equal at about 170 K

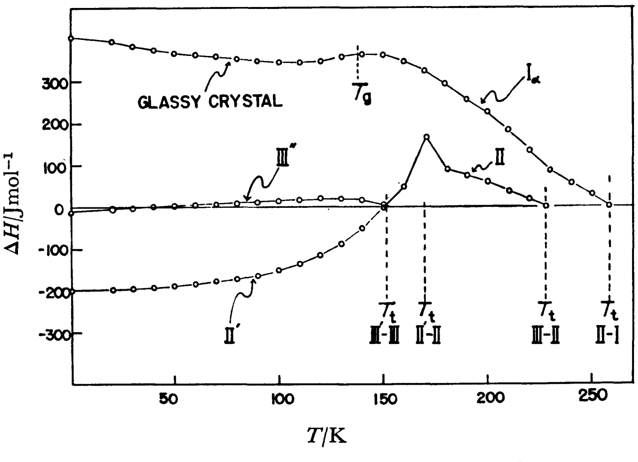


Fig. 6. Difference in Gibbs energy between the crystal-III' and the other various phases.

TABLE 4. THERMODYNAMIC FUNCTIONS OF CYCLOHEPTANOL

T K	C_p° JK^{-1}mol^{-1}	$S^\circ-S_0^\circ$ JK^{-1}mol^{-1}	$[H^\circ-H_0^\circ]/T$ JK^{-1}mol^{-1}	$-[G^\circ-H_0^\circ]/T$ JK^{-1}mol^{-1}
		(Crystal III′)		
10	(2.67)	(0.898)	(0.6730)	(0.2250)
20	13.66	5.951	4.304	1.647
30	24.18	13.524	9.213	4.310
40	33.04	21.74	14.105	7.635
50	40.80	29.96	18.676	11.284
60	48.22	38.06	22.985	15.075
70	55.23	46.02	27.09	18.93
80	62.60	53.86	31.06	22.80
90	70.82	61.70	35.01	26.69
100	80.39	69.64	39.05	30.59
110	92.65	77.86	43.35	34.51
120	106.38	86.50	48.03	38.48
130	119.58	95.56	53.05	42.52
140	127.18	104.73	58.09	46.64
150	141.41	113.73	62.91	50.82
		Transition 152.30K		
		(Crystal III)		
160	139.97	122.94	67.90	55.04
170	144.63	131.58	72.29	59.29
180	147.60	139.93	76.39	63.53
190	150.57	147.99	80.22	67.77
200	154.08	155.80	83.82	71.98
210	158.23	163.42	87.26	76.16
220	162.82	170.88	90.59	80.29
		Transition 227.26K		
		(Crystal II)		
230	169.71	180.69	96.27	84.42
240	174.05	188.00	99.41	88.59
250	180.60	195.23	102.52	92.71
		Transition 258.45K		
		(Crystal I)		
260	192.83	205.88	109.07	96.82
270	202.20	213.33	112.34	100.99
280	213.13	220.87	115.78	105.10
		Fusion 280.30K		
290	240.83	234.83	125.37	109.46
300	252.35	243.18	129.41	113.77
310	264.02	251.65	133.56	118.09

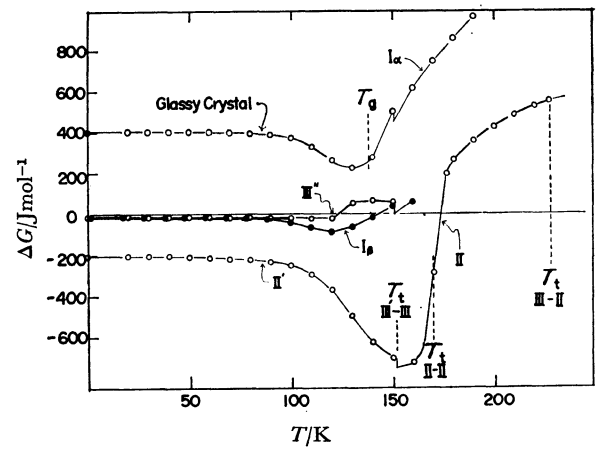


Fig. 7. Difference in enthalpy between the crystal-III' and the other various phases.

as shown in Fig. 7. The irreversible phase change might take place at this temperature, with neither heat evolution nor heat absorption. It was found, however, that the annealing of crystal II at about 170 K (II′—II transition region) for several days caused no phase change in crystal III. The Gibbs energy of crystal III″ is slightly smaller than that of crystal III′. This might be due to experimental error.

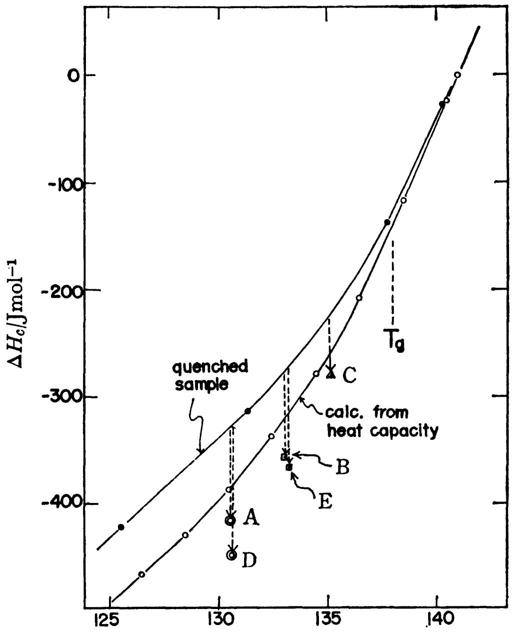


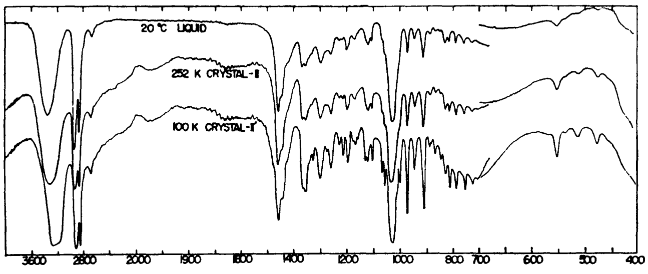
Fig. 8. Decrease of the configurational enthalpy of the glassy crystal by annealing treatment.

Relaxation Phenomenon of Enthalpy. The relaxation of the enthalpy of the glassy crystalline state was investigated by annealing for 20 hr at 130.6, 133.0, and 135.2 K. The values of the enthalpy decrease during the treatments are given by points A, B, and C in Fig. 8 where the ordinate indicates the configurational enthalpy for the sake of convenience. The method of calculation of the configurational enthalpy has been given.[2,3] For the calculation it was necessary to estimate the heat capacity due to lattice and internal vibrations. This is difficult on account of the gradual increase of the heat capacity curve below T_g (Fig. 2), but it was estimated by the equation

$$C(\text{vib}) = 0.7197T + 4.62. \tag{4}$$

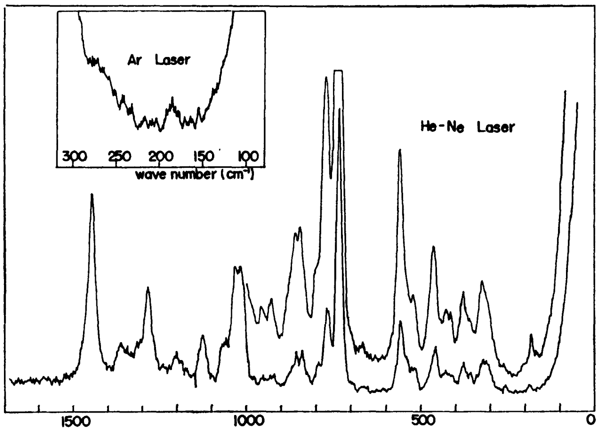
Point D represents the value of the enthalpy after annealing for 75 hr at 130.7±0.5 K and point E stands for the value after the annealing for 68 hr at 133.3 K. From the results, the conventional relaxation times were calculated to be 24 hr at 130.7 K on the assumption that the enthalpy decreased exponentially. This might not be correct since it was found that the relaxation in the glassy crystalline state of 2,3-dimethylbutane is not the genuine exponential type.[3] Thus the present data of the relaxation time give only approximate values of the time constant.

Measurements of Raman and IR Spectra. In order to estimate the contribution of internal vibrations to heat capacities, the Raman and IR spectra were



Wave number (cm^{-1})

Fig. 9. Infrared spectra of cycloheptanol.



Wave number (cm^{-1})

Fig. 10. Raman spectra of cycloheptanol.

measured in liquid state. The observed Raman and IR spectra are shown in Figs. 9 and 10, respectively. The frequencies of bands are as follows;

Raman: 179, 255, 295, 319, 355, 372, 410, 420, 456,
516, 553, 661, 725, 764, 790, 835, 853, 922,
IR: 455, 474, 512, 535, 552, 570, 725, 730, 760,
790, 816, 813, 850, cm^{-1}.

Since the band at 179 cm^{-1} was observed by using both a He–Ne laser and an Ar laser as a light source, it was not a noise accompanied by a He–Ne laser. The weak infrared bands at 474, 535, and 570 cm^{-1} were assigned to combination bands, *i.e.* $179+295=474$, $179+355=534$, and $255+319=574$. From the results, the frequencies of the normal modes were estimated. Among the possible 60 modes, the following 37 modes are assigned empirically (Table 5). The remaining 23 modes are assigned to the CH_2 rocking ($\times 6$) and skeletal modes ($\times 17$). Since the molecule of cycloheptane belongs to a symmetry group of C_s or C_2,[8] it is expected that it has at most only a mirror plane for a symmetry element and that all of the modes are not degenerate and active both in the IR and Raman spectra. We therefore adopted the following 15 bands; 179, 255, 295, 319, 355, 372, 410, 421, 456, 516, 553, 661, 725, 764, and 790 cm^{-1} as the normal modes which are not degenerate. There still remain 8 modes. Since it is known empirically that the CH_2 rocking modes have frequency below 1100 cm^{-1}, we assumed 4 modes with an average frequency of 900 cm^{-1} and other 4 modes with one of 1100 cm^{-1}. Since the heat capacity due to the mode whose frequency is greater than 800 cm^{-1} is small below 200 K, ambiguity in the estimation causes no trouble.

TABLE 5.

Assignment	Wave number	Number of modes
OH stretching	3500	$\times 1$
OH bending	1300	$\times 1$
OH bending	725	$\times 1$
CH stretching	3000	$\times 13$
CH_2 scissors	1450	$\times 6$
CH_2 wagging	1300	$\times 6$
CH_2 twist	1300	$\times 6$
CH bending	1300	$\times 2$
CO stretching	1030	$\times 1$

Discussion

Residual Entropy. We have used a term "glassy crystal" for the phase which was established below 140 K by rapid cooling of crystal I. The residual entropy of this crystalline phase amounted to 0.7 $Jmol^{-1}K^{-1}$. This is too small to claim that the phase has a residual entropy because its magnitude is the same order as that of the experimental error. However, we can give several reasons for assuming that the phase should be in a glassy crystalline state. First, it is possible that the value we obtained for the residual entropy is not correct, since it was determined on the assumption that crystal III′ has no residual entropy. It is necessary to determine the absolute value of the entropy from a comparison of the entropy in the gaseous state determined by thermal method with that determined from spectroscopic data. Second, the stabilization phenomenon characteristic of glassy state was actually observed in this phase. Thus it can be concluded that the phase is in a non-equilibrium state. Third, if crystal II′ is taken as the reference state with no residual entropy (Table 3 and Fig. 6), the value of the residual entropy increases to 0.9 $Jmol^{-1}K^{-1}$. This value is slightly larger than the limit of experimental error (0.6 J $mol^{-1}K^{-1}$) and might indicate the presence of the residual entropy. Fourth, the shapes of the heat capacity curve and the DTA diagram closely resemble those of known glassy crystals.[2,3,4] The empirical rule for the glassy crystals states that the ratio of T_g and T_2 is nearly constant (1.15—1.20).[3] Here T_2 is the temperature defined by Gibbs and DiMarzio,[9] at wihch the configurational entropy of supercooled liquid vanishes. By means of the rule we attempted to estimate the true value of the residual entropy of the glassy crystalline state. The value of a ratio between T_g and T_2 is related to a residual entropy S_0 by the following equation.

$$\Delta C_p \ln (T_g/T_2) = S_0. \tag{5}$$

Here ΔC_p is the jump of the heat capacity at the glass

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[8] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537, (1961).

[9] J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).

transition point. Since the value of T_g/T_2 is known to be 1.15—1.20 for the glassy crystals and the ΔC_p for the present glassy crystal amounts to about 30 JK^{-1}mol^{-1}, the value of S_0 is determined to be 5.0 JK^{-1}mol^{-1} from the equation. If this is correct, all the other phases also have a residual entropy of about 5 JK^{-1}mol^{-1}. We therefore consider that the residual entropy of glassy crystal is not so large as compared with 5 JK^{-1}mol^{-1}. The order of magnitude seems to be too small since this molecule has the following conformations.

If one assumes a chair form, there are seven distinguishable conformations with respect to the carbon atom on which a hydroxyl group is bonded. Furthermore, there are two positions to locate the hydroxyl group on the carbon atom *i.e.* an equatorial position and an axial one. Thus we can anticipate at least 14 conformations. If the position of a hydrogen atom of the hydroxyl group is considered with respect to its internal rotation, the number of conformations may increase further by a factor of three *i.e.* 42 kinds of conformations. The value of $R\ln(14)$ and/or $R\ln(42)$ amount to 22 and/or 31 JK^{-1}mol^{-1} respectively. Here R reprensents the gas constant. Although we do not know the energy difference between the conformations, we can expect that the configurational degree of freedom will contribute greatly if they are frozen at the glass transition point. Thus it seems to be reasonable to consider that not all of these conformational degrees of freedom are frozen at the T_g. It is suggested that some motional degrees of freedom exist even below T_g. This might be explained in terms of interconversions between the molecules with various conformations in the glassy crystalline state.

The Plastic Crystalline State. Since the value of the entropy of melting is 5.72 JK^{-1}mol^{-1}, crystal I is considered to be plastic. The sum of the values of the entropy of melting and those of I—II transition amounts to 11.6 JK^{-1}mol^{-1}. Since this is still smaller than that of the Timmermans criterion,[9] crystals II and III might also be considered to be plastic. This is supported further by the motional narrowing phenomenon of the NMR spectra for these phases and the magnitude of the heat capacities. We see in Fig. 2 that the supercooled states of crystals II and III show no anomaly similar to that in glass transition in their heat capacity curves. In contrast to the glassy crystal, the high degree of configurational degrees of freedom for crystals II and III give rise to the λ-type phase transitions as shown in Fig. 2. We suggested that crystals II and III have residual entropy and these phases are also looked upon as frozen-in states at low temperatures. However, since no glass transition phenomenon could be observed for the crystals down to the lowest temperature, we are not convinced that we can call them glassy crystals. We might say that plastic crystals such as II or III do not always show the glass transition when they are cooled down without irreversible transformation into other more stable phases. In order to solve the so-called Kauzmann paradox,[1] Gibbs and DiMarzio postulated that a supercooled liquid will show the second order phase transition with infinitely slow cooling rate.[9,11] If we adopt this point of view for crystal I and cool it down very slowly below T_g, this phase might also have a second order phase transition similar to that of crystal II or III as far as the internal equilibrium is maintained below 140 K.

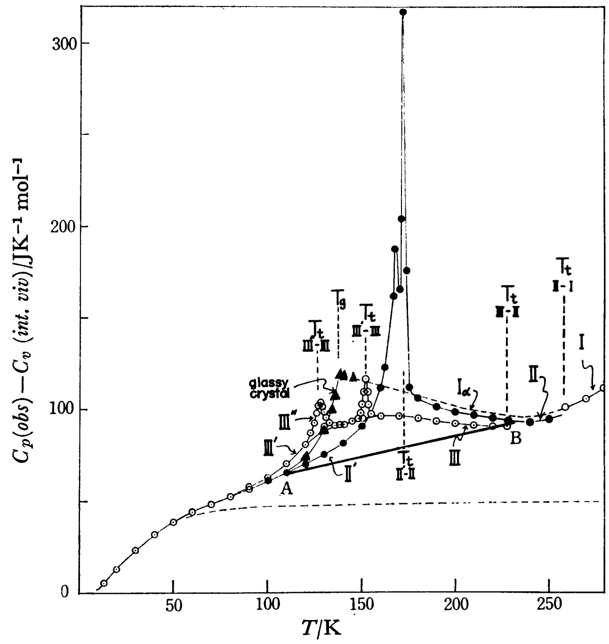

Fig. 11. Plot of C_p(obs)–C_v(internal vib.).

Analysis of Heat Capacities. From the data of Raman and IR spectra, the magnitude of contribution of internal vibrations to the heat capacity was calculated. The value was then subtracted from the observed total heat capacities. The result is shown in Fig. 11. The dashed line represents the heat capacity due to the lattice vibration calculated by using the Debye model with 6 degrees of freedom. The difference between the plotted value of (C_p(obs)—C_v(int)) and the value of the dashed line is explained as the sum of anomalous heat capacity C(an) and (C_p—C_v). The C(an) becomes noticeable above around 70 K and amounts to about 50 JK^{-1}mol^{-1} around 200 K for all the phases. This is considered to be another evidence for these phases to be plastic crystals which are generally known to have a large heat capacity whose magnitude can not be explained in terms of only a contribution of vibrations and (C_p—C_v). It is known that the material belonging to the plastic crystals has first order phase transition point in its crystalline state and that the entropy of transition is much larger than that of melting. On the contrary, the entropy of transition of cycloheptanol does not amount to such a large value and the magnitude of the heat capacity of the low temperature form (crystal III) is too large to be explained only from vibrational contribution. This should indicate the evidence of continuous ordering of the molecular orientation and conformations with decreasing temperature. Although the magnitude of

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

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

the C(an) is not explained from the molecular motions, we might expect that the changes of configurations and conformations cause this effect.

II—II′ Transition. The difficulty of determining the entropy change for II—II′ transition has been already pointed out. As is shown in Fig. 11, the heat capacity due to the change of configuration does not vanish at temperatures far above the transition point. We calculated the entropy of transition assuming that the "normal" heat capacity is given by the straight line A—B. The procedure is based on an assumption that the configurational heat capacity can be separated into two parts *i.e.* the configurational heat capacity accompanied by the phase transition and that independent of the transition. The entropy of transition thus determined amounted to 17.2 $\mathrm{J mol^{-1} K^{-1}}$ (Rln 7.9).

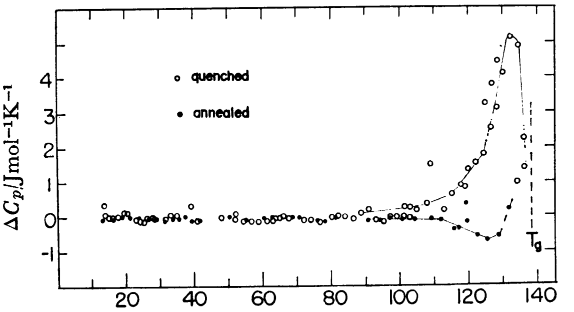

Fig. 12. The deviation of the heat capacities of the quenched glassy crystal and annealed one from the smoothed values.

Difference Between the Heat Capacity of Annealed Glassy Crystal and the Quenched One. The heat capacity of the glassy crystalline state was measured with the specimens which was annealed below T_g and then quenched. The aim of this measurement is to detect the difference in heat capacities of specimens. The difference is shown in Fig. 12. Hardly any difference can be seen below 100 K. However above this temperature it becomes noticeable with a maximum value of 5 $\mathrm{JK^{-1}mol^{-1}}$ around 130 K. As a possible explanation, an experimental error might be considered at first since the heat evolution or absorption due to the stablilization effect disturbed the measurements of the heat capacity around 130 K. However, the observed temperature drift due to this effect was not so large as to account for the actual difference at least below 130 K. Thus the fact can be ascribed to the variation of the configurational heat capacity caused by annealing since the anomalous heat capacity was recognized in the glassy crystalline state above 70 K as is seen in Fig. 11. Existence of the degree of freedom not frozen below the glass transition point was confirmed in the glassy crystalline state of cyclohexanol and 2,3-dimethylbutane in the study of broad line NMR and dielectric loss. The decrement of the anomalous heat capacity in the glassy crystalline state caused by annealing can be explained in terms of the variation of the shape and size of the potential energy curves for various conformations caused by annealing.

Crystal I_β. Run-4 in Fig. 1 shows that crystal I_α is transformed into a meta-stable phase around 170 K. Similar phenomena of the supercooled plastic crystals transformed into other meta-stable phases just above their glass transition points were also observed for cyclohexanol[2)] and 2,3-dimethylbutane.[3)] The heat capacity curve of crystal I_β showed an anomalous increase around 130 K. However, this is not as steep as in the case of glass transition (Fig. 2). The heat capacity curve of the meta-stable phase of 2,3-dimethylbutane also shows a similar hump. The residual entropy of crystal I_β was calculated to be -1.0 ± 1 $\mathrm{JK^{-1}mol^{-1}}$ based on the above assumption. On the other hand, the residual entropy of the meta-stable phase of 2,3-dimethylbutane was found to be 2.7 $\mathrm{JK^{-1}mol^{-1}}$. In order to see whether this meta-stable phase can be considered as a glassy crystal or not below the temperature at which the anomaly was observed, we measured the heat capacity of crystal I_β in two series subjected to different thermal histories. No change was detected in the magnitude of the heat capacity due to the difference in thermal history. Thus the anomalous increase of the heat capacity can not be attributed to the relaxation phenomenon. It would be noted that this phase does not show any phase transition as in the case of crystal II or III. We may regard this phase as a plastic crystal above 140 K from the magnitude of its heat capacity.

Phase Transition Between Phases with Various Degrees of Stability. In general the degree of stability of a material system can be classified into three steps, *i.e.* stable, meta-stable, and non-equilibrium states. A stable state is the state in which free energy is at its absolute minimum. The meta-stable state is the state in which free energy is at the minimum, but not absolute minimum. The two states are, however, classified as thermodynamically equilibrium states. On the other hand, non-equilibrium state is the state at which free energy is not in its minimum. From this point of view, the phase changes which occur in cycloheptanol can be classified into five groups as shown in Table 6.

TABLE 6. CLASSIFICATION OF PHASE TRANSITIONS FROM THE STANDPOINT OF THERMODYNAMICAL STABILITIES

Type	Stability relation	Example
	Irreversible Transitions	
(1)	non-equilibrium→metastable	Glassy crystal $\rightarrow I_\alpha$
(2)	metastable→metastable or stable	$I_\alpha \rightarrow I_\beta$ $I_\alpha \rightarrow$ II II→III
	Reversible Transitions	
(3)	metastable⇌metastable	III″⇌III III′⇌III $I_\beta \rightleftharpoons I_\alpha$
(4)	stable⇌metastable	II′⇌II
(5)	stable⇌stable	III⇌II II⇌I I⇌liquid

(1) includes phase changes between non-equilibrium and meta-stable states. A typical example might be the so-called glass transition, although this is a kind of relaxation phenomenon and not a "phase transition" in a strict sense. In cycloheptanol, the glass transition

between glassy crystal and crystal I_α corresponds to this group. Since the state of glassy crystal changes gradually and continuously with time, the transition is regarded to be irreversible.

(2) includes irreversible transitions between a meta-stable and a stable state or between one meta-stable and another meta-stable phase. These phase transitions are considered to be exo-thermic peaks of the thermogram of DTA (Run 4, Fig. 1).

(3), (4), and (5) include various kinds of reversible phase changes. An example of group (3) can, however, be classified into group (1), since crystals III′, III″, and I_β can be in a non-equilibrium state with residual entropy. At the present stage of investigation, however these phases may be regarded as meta-stable since no thermal histories were detected. The example in (4) might be peculiar in the sense that we can follow the phase transition from each side of the starting phase. Usually we know only the examples from right to left with exothermic effect.

In the previous papers,[2,3,4] we have reported that various kinds of supercooled plastic crystals are transformed stepwise into more stable states. The phenomenon is known as "Ostwald's law of stage" (or step rule). Transitions of this type are those between the discrete states in the phase space and the transitions proceed at the boundary of the phases. There also exists a transition which occurs continuously between the different states in the phase space. This phase change takes place homogeneously. When it happens to occur irreversibly, then one of two phases between which the transition proceeds should be invariably in a non-equilibrium state. Cycloheptanol shows both these trends depending on the thermal histories, and provides good examples for a study of phase changes from thermodynamic or statistical-mechanical as well as kinetic aspects.

Summary

(1) The heat capacities of cycloheptanol were measured from 13 to 300 K. It was found that there exist 8 crystalline phases *i.e.* Crystals I, II, II′, III, III′, III″, I_β, and glassy crystal.

(2) The transition points for transitions II—I, III—II, II′—II, III′—III, and III″—III were determined to be 258.45, 227.26, 127.23, 152.30, and 128.2 K, respectively. Melting point and the glass transition point of glassy crystal were also determined to be 280.30 and 240 K, respectively.

(3) Heats of transition for transitions II—I, III—II, and III′—III and the heat of melting were determined to be 876, 554, 58.1, and 1604 $\mathrm{J mol^{-1}}$, respectively. The entropies of transition corresponding to these phase changes were calculated to be 3.39, 2.44, 0.38, and 5.72 $\mathrm{JK^{-1} mol^{-1}}$, respectively.

(4) The residual entropies were also determined for glassy crystal, crystals II and III″ to be 0.70, −0.19, and −0.26 $\mathrm{JK^{-1} mol^{-1}}$, respectively, assuming that crystal III′ has no residual entropy.

(5) The free energies and enthalpies of the various crystalline phases were calculated, the instability being determined by comparison of their free energies. It was concluded that crystal II′ was most stable in the temperature region below 170 K, III between 170 and 227.26 K, II between 227.26 and 258.45 K and I between 258.45 and 280.30 K.

(6) Relaxation of the enthalpy in the glassy crystalline state was studied and the relaxation time was determined to be about 24 hr at 133.3 K.

(7) The degree of freedom frozen in the glassy crystalline state was discussed from the viewpoint of conformations of the molecule.

(8) The heat capacities due to internal vibrations were calculated from the data of IR and Raman spectra and the magnitude of heat capacities in the various phases were discussed.

(9) Various kinds of phase transitions found in cycloheptanol were classified from the viewpoint of thermodynamical stabilities.

The authors wish to thank Mr. Shinichi Ishikawa and Mr. Mitsuo Ohama for the measurements of infrared and Raman spectra.