BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3020—3031 (1973)

Calorimetric Study of the Glassy State. VIII. Heat Capacity and Relaxational Phenomena of Isopropylbenzene

Koji KISHIMOTO, Hiroshi SUGA, and Syûzô SEKI
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received June 25, 1973)

The heat capacities of isopropylbenzene were measured with an adiabatic calorimeter for the crystal from 14 to 177.13 K (T_m), for the glassy state from 14 to around 126 K (glass transition temperature: T_g) and for the liquid from T_g to 313 K, with a sample of 99.93% purity. The heat and entropy of fusion were found to be 7326 J mol^{-1} and 41.36 J K^{-1} mol^{-1}, respectively. Based on these data, a set of thermodynamic functions are tabulated at rounded temperatures. In addition to the primary glass transition phenomenon, a secondary enthalpy relaxation as well as a step-like heat capacity anomaly was observed at around 70 K. These facts were discussed in correlation with the β-relaxation already observed by dielectric measurement. Configurational entropies of the supercooled liquid and of the glassy state were calculated to investigate a relation with relaxational properties. The agreement is found between the temperatures where catastrophe occurs in viscosity (T_0), and where the configurational entropy vanishes (T_2). Finally, a kind of heat capacity break observed in the liquid state is discussed against the view that this behavior is compatible with a third-order thermodynamic transition.

Recently a considerable number of papers on the glassy state have been accumulated and the concept of "*glassy state*" as a kind of state of matter is getting familiar to the wider circle of investigators. Nevertheless, rather scanty are quantitative treatments to describe this state from the thermodynamic point of view and further to clarify a relationship between dynamical and static properties. One of the purposes of this study is to elucidate a correlation between such dynamical properties as viscosity and relaxation time, and the static ones such as heat capacity, *etc*. In answer to this subject, Adam and Gibbs[1] proposed a description of the relaxation time, τ, in terms of the configurational entropy, S_c. The relation proposed by them is as follows:

$$\tau = A \exp (C/TS_c), \tag{1}$$

where A and C are constants. It was reported that this equation conformed well to the experimental results.[2,3]

As is well known, relaxations found below the glass transition temperature, T_g, are usually designated as

---

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

[2] S. S. Chang and A. B. Bestul, *ibid.*, **56**, 503 (1972).

[3] J. Greet and D. Turnbull, *ibid.*, **47**, 2185 (1967).

β-relaxation, γ-relaxation, *etc.* in their order of appearance with decreasing temperature. β-relaxation phenomena are frequently observed by mechanical,[4] dielectric and/or nuclear magnetic resonance[5] methods not only for polymers but also for low molecular weight compounds. It is widely believed that heat capacity is not seriously affected by the molecular motions giving rise to these mechanical or dielectric relaxations. We have examined the possible observation by precise calorimetry in the present investigation. On the other hand, several workers have suggested a possible existence of a phase change in a liquid state. In 1953 Moore *et al.*[6] found the discontinuities in the several physical properties such as heat capacity, vapor pressure, density, compressibility, and viscosity in the liquid alkanes. Davies *et al.*[7] pointed out that the discontinuities in viscosity in the liquid states should correspond to thermodynamic transitions of the third order in the sense of Ehrenfest. The verification of the validity of their discussions on the nature of the transition is another principal object of the present investigation.

Experimental

Material. About 40 cm^3 of isopropylbenzene (Tokyo Kagaku Seiki Co. Ltd., claimed purity better than 99.9%) was first purified by molecular sieve (Linde 4A) under vacuum to remove low molecular weight impurities, and subjected to vacuum distillation. The purified sample of 24.997 g of the middle fraction of the distillate was introduced into a container for the heat capacity measurements by vacuum distillation. Helium exchange gas to aid heat transfer in the container was not used. But, no difficulty in establishments of thermal equilibrium was encountered except for the glass transition and the melting temperature ranges. The analysis of the fractional melting process of the sample, as will be described later, indicated the impurity content of 0.07 mol%.

Apparatus. The measurement of heat capacity of isopropylbenzene was carried out by using an adiabatic calorimeter which had been constructed already in this laboratory.[8] A capsule-type platinum resistance thermometer used for the measurement was already calibrated in our laboratory by comparison with the laboratory standard thermometer which had been calibrated at the US National Bureau of Standards according to the International Practical Temperature Scale (1948) above 90 K and the provisional NBS scale below 90 K.

Results

DTA. As a preliminary study of the thermal properties of this material, the differential thermal analysis (DTA) was performed. The results are shown in Fig. 1. Run-1 is for a cooling with a rate of about -0.7 K/min. In Run-1 a sharp exothermic peak was observed at 102 K following after a slight and gradual shift in the base line around 130 K. This sharp exothermic peak is attributed to the formation of cracks in the sample when the sample vitrifies. The evolution of heat is accompanied with sounding and flashing of visible light. The details of this phenomenon will be published elsewhere.[9] Run-2 is the subsequent heating (heating rate: 1.8 K/min). Only a peak due to the glass transition was observed at 130 K. Run-3 shows the heating curve of the sample which is subjected to annealing at 150 K for over two hours. The endothermic peak at 176 K was attributed to the fusion of the crystalline phase.

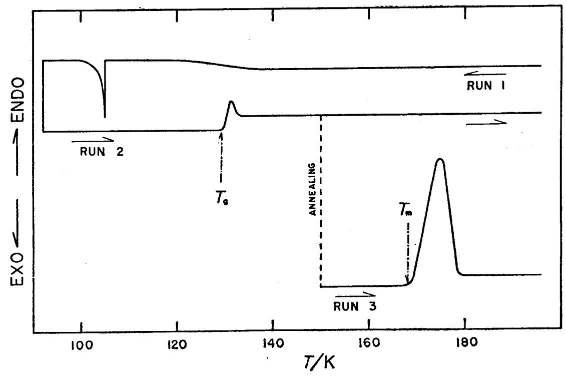

Fig. 1. DTA curves of isopropylbenzene.

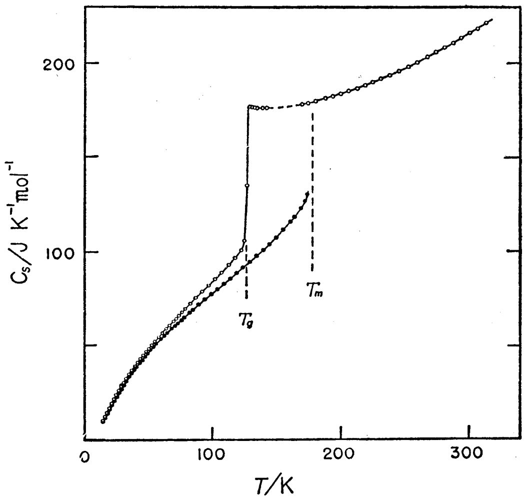

Fig. 2. Heat capacities of isopropylbenzene.
●: Crystalline phase,
○: Glassy, supercooled liquid and liquid phases.

Heat Capacity Measurements. The heat capacity data for isopropylbenzene are listed in Table 1 and are depicted in Fig. 2. These series are numbered chronologically so that the thermal history may be followed. Estimation of the vaporization correction was performed by use of the equation given by Hoge.[10] With the aid of the data on the vapor pressure[11] and the specific volume,[12] the correction on the heat capacities

---

4) Y. Ishida, *J. Polymer Sci.*, **A-27**, 1835 (1969).

5) W. P. Slichter, *J. Chem. Educ.*, **47**, 193 (1970).

6) R. J. Moore, P. Gibbs, and H. Eyring, *J. Phys. Chem.*, **57**, 172 (1953).

7) D. B. Davies and A. J. Matheson, *J. Chem. Phys.*, **45**, 1000 (1966).

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

9) To be published in *J. Non-Cryst. Solids*.

10) H. J. Hoge, "Precision Measurement and Calibration, selected NBS Papers on Heat," ed. by D. C. Ginnings (1970).

11) R. C. Wilhoit and B. J. Zwolinski, "Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds," Thermodynamic Research Center Department of Chemistry, Texas A & M University, College Station, Texas 77843 (1971).

12) A. J. Barlow, J. Lamb and A. J. Matheson, *Proc. Roy. Soc., Ser. A*, **292**, 322 (1966).

Table 1. The molar heat capacities of isopropylbenzene
Mol. wt. = 120.20 0 °C = 273.15 K

T_{av} / K	$\Delta H/\Delta T$ / J K^{-1} mol^{-1}	ΔT / K
(crystalline state)		
Series 10		
14.54	9.718	1.356
16.16	11.618	1.868
18.06	13.931	1.926
19.99	16.277	1.918
21.80	18.552	1.704
23.53	20.658	1.736
25.37	22.836	1.934
27.21	25.014	1.742
28.97	27.005	1.780
30.83	29.034	1.952
32.92	31.285	2.213
35.04	33.569	2.029
37.00	35.363	1.895
38.87	37.084	1.839
40.91	38.892	2.228
43.07	40.777	2.094
Series 20		
47.06	43.838	2.288
50.53	46.552	2.386
52.85	48.279	2.259
55.14	49.899	2.346
57.43	51.626	2.235
59.73	53.231	2.387
62.07	54.914	2.302
64.44	56.622	2.435
66.83	58.138	2.364
69.16	59.630	2.297
Series 11		
72.68	61.921	2.379
75.17	63.464	2.599
77.73	65.003	2.524
Series 9		
79.36	66.066	2.654
81.90	67.763	2.430
84.31	69.239	2.388
86.67	70.692	2.334
101.09	78.847	2.499
103.57	80.121	2.465
106.01	81.545	2.417
108.50	83.016	2.569
111.05	84.449	2.530
Series 8		
88.85	71.985	2.336
91.17	73.303	2.290
93.61	74.740	2.602
96.19	75.957	2.552
98.73	77.496	2.519
Series 12		
113.36	85.767	2.511
115.85	87.147	2.473
118.41	88.700	2.641
121.03	90.089	2.604
123.61	91.676	2.563
126.16	93.239	2.525
128.66	94.672	2.491
131.25	96.134	2.684
133.92	97.851	2.644
136.54	99.567	2.607
139.13	101.159	2.573
141.69	102.602	2.541
Series 13		
144.00	104.145	2.617
146.60	105.968	2.586
149.17	107.655	2.550
151.82	109.492	2.759
154.56	111.723	2.716
157.40	113.777	2.956
160.32	116.003	2.901
163.36	118.393	3.168
168.56	122.928	3.068
171.60	126.722	2.999
(supercooled liquid and glassy states)		
Series 5		
14.53	10.363	1.334
16.00	12.286	1.592
17.69	14.551	1.760
19.44	16.821	1.749
21.29	19.321	1.938
23.09	21.711	1.664
24.86	23.942	1.861
26.73	26.241	1.887
28.54	28.356	1.722
30.35	30.376	1.899
32.38	32.675	2.170
34.47	34.930	1.998
36.70	37.065	2.463
39.07	39.253	2.283
41.28	41.224	2.138
43.36	42.979	2.022
45.55	44.831	2.362
Series 18		
45.35	44.579	2.312
47.60	46.400	2.187
49.85	48.201	2.307
52.09	49.899	2.185
54.35	51.518	2.337
56.65	53.270	2.255
58.86	54.895	2.186
61.08	56.666	2.253
63.29	58.413	2.162
65.56	60.229	2.375
67.88	61.961	2.268
70.14	63.370	2.253
72.31	64.876	2.089
74.49	66.452	2.284
76.86	68.209	2.444
Series 6		
69.31	62.796	1.857
71.44	64.277	2.413
73.82	65.950	2.347
76.14	67.609	2.279
78.65	69.658	2.761
81.37	71.615	2.680
84.01	73.543	2.594
Series 4		
80.23	70.773	2.252
82.45	72.456	2.198
84.62	74.053	2.149
86.79	75.601	2.184
89.13	77.183	2.497
91.61	78.756	2.458
94.14	80.347	2.613
96.73	82.025	2.559
99.26	83.742	2.508
101.75	85.372	2.461
104.30	87.036	2.634
106.91	88.897	2.581
Series 7		
105.12	87.627	2.398
107.50	89.325	2.359
109.93	91.056	2.500
112.41	92.946	2.463
114.87	94.773	2.428
117.30	96.663	2.382
119.70	98.803	2.339
122.09	100.87	2.299
124.45	105.79	2.222

Table 1. (Continued)

T_{av} / K	$\Delta H/\Delta T$ / J K^{-1}mol^{-1}	ΔT / K	T_{av} / K	$\Delta H/\Delta T$ / J K^{-1}mol^{-1}	ΔT / K	T_{av} / K	$\Delta H/\Delta T$ / J K^{-1}mol^{-1}	ΔT / K
126.60	135.17	1.865	182.77	180.41	2.892	241.41	194.75	3.553
128.30	176.86	1.534	185.65	180.87	2.871	244.96	195.95	3.534
130.03	176.61	1.926				248.63	197.01	3.807
131.96	176.34	1.927		Series 1		252.28	198.21	3.496
134.08	176.31	2.309				255.76	199.54	3.479
136.38	176.61	2.306	187.49	181.35	2.919	259.23	200.59	3.453
138.22	176.27	2.620	190.40	181.63	2.912	260.35	200.99	3.452
140.84	176.12	2.614	193.30	182.34	2.896	263.79	202.27	3.435
			196.19	182.99	2.882	267.22	203.38	3.418
	Series 16		199.25	183.52	3.227	270.62	204.76	3.398
			202.47	184.31	3.224	274.02	206.04	3.386
129.82	177.49	2.077	205.70	185.10	3.240	277.39	207.12	3.364
131.90	176.36	2.083	208.93	185.70	3.211	280.79	208.55	3.427
135.33	176.33	2.597	212.18	186.62	3.298	284.30	209.88	3.599
138.97	176.34	4.771	215.47	187.52	3.285			
141.48	176.15	2.511	218.75	188.14	3.268		Series 3	
			222.03	189.21	3.298			
	(supercooled liquid and liquid states)					287.41	211.07	3.268
				Series 2		290.67	212.43	3.252
						293.92	213.61	3.234
	Series 14		217.81	187.98	3.544	297.14	214.84	3.218
			221.21	189.01	3.252	300.35	216.26	3.196
169.16	178.27	2.250	224.45	189.94	3.229	303.54	217.62	3.178
171.60	178.56	2.626	227.67	190.81	3.218	306.71	218.62	3.166
174.22	179.11	2.613	230.88	191.70	3.197	309.86	220.11	3.145
176.98	179.36	2.909	234.27	192.77	3.587	313.14	221.61	3.410
179.88	179.80	2.894	237.85	193.52	3.575			

was assessed to be less than 0.004% at the highest temperature of the measurements. This figure is within an experimental error of our apparatus. As a consequence, the measured heat capacities are regarded as ones under saturated pressure, C_s. The curvature correction is not taken into consideration.

The glassy state of the specimen was established by cooling the supercooled liquid sample to the liquid nitrogen temperature with a rate of −0.7 K/min in the glass transition region. In order to measure the heat capacities of the supercooled liquid just below the melting point and also just above T_g, we have prepared the sample by two different ways. The supercooled liquid obtained by raising temperature just above T_g was observed to crystallize around 145 K. The measurement on the supercooled liquid in the range from T_g to 141 K was performed in this manner. The measurement from 169 K to the melting point was made for the liquid cooled down to the temperatures not below 165 K to avoid the crystallization during measurements.

The crystalline phase was obtained from the supercooled liquid which had been prepared by heating the glassy state above T_g. The crystal was usually annealed at around 165 K to ensure the completion of the crystallization. No evidence for the existence of a metastable crystalline phase was found from the pursuit of spontaneous temperature rise of the sample during the crystallization process.

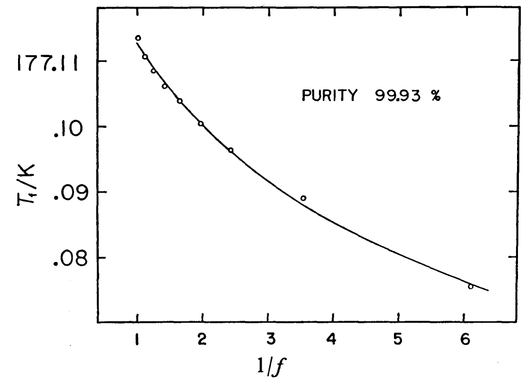

Fig. 3. Melting curve for isopropylbenzene
Open circle: experimental values,
Solid line: theoretical curve.

Determination of the Purity. To determine the melting point and the purity of the present material, a fractional melting experiment was carried out. In Fig. 3 the reciprocal of the fraction of the sample melted, 1/*f*, is plotted against the equilibrium final temperature, T_f, of each energy input. As ample time was required for the establishment of thermal equilibrium during the melting process, the extrapolated value of the temperature to the time being infinite at each input was used as T_f. These values are given in Table 2. It is apparent that T_f *versus* 1/*f* plot does not yield a straight line. Therefore, White-

Table 2. The equilibrium temperatures during fusion process

Fraction melted (f)	$1/f$	T_f/K
0.1639	6.103	177.0755
0.2827	3.537	177.0890
0.4127	2.423	177.0964
0.5102	1.960	177.1004
0.6079	1.645	177.1028
0.7052	1.418	177.1061
0.8026	1.246	177.1084
0.8985	1.113	177.1106
0.9933	1.007	177.1135

The melting point of pure isopropylbenzene = 177.13 K
Mol% of impurity = 0.07%

Taylor-Rossini's method[13,14] which treats impurities as solid-insoluble and liquid-soluble is not applicable. Then, we adopted Mastrangelo-Dornte's method[15] in which they derive a solid solutions treatment for calorimetric melting point data. The equation derived by them is as follows:

$$T_f = T^* - \frac{R(T^*)^2}{\Delta H_F} \frac{X_2}{\frac{K}{1-K}+f}, \qquad (2)$$

where T^* is the triple point of a hypothetical 100% pure material whose heat of fusion is ΔH_F, R the gas constant and X_2 a mole fraction of the impurity whose distribution between the solid and liquid phases is expressed by K. For the determination of K, T^* and X_2 the method of least squares was applied. From this treatment X_2 and T^* are determined to be 0.7×10^{-3} and 177.13 K, respectively. The solid curve in Fig. 3 is the theoretical curve of Eq. (2) with the value of 0.2128 for K. As is seen, data fit this theoretical curve fairly well.

The heat of fusion was measured twice and the values of the molar heat of fusion are given in Table 3.

Table 3. The molar heat of fusion

	ΔH / kJ mol^{-1}
Experiment 1	7.325
Experiment 2	7.326
Mean value	7.326

Estimation of the Heat Capacity for the Supercooled Liquid. Since the heat capacity of the supercooled liquid between 142 and 169 K could not be measured as a result of interference from the crystallization, it was estimated by graphical interpolation of the measured heat capacity data of the supercooled liquid below T_m and just above T_g. A dashed curve in Fig. 2 represents the interpolated heat capacity. The errors arising from arbitrariness in this interpolation are at most 0.2% of C_s of the supercooled liquid. Adequacy of the interpolation as well as the absence of crystal or crystallite in the actual specimen in the glassy state obtained was confirmed by comparing the enthalpy of the supercooled liquid at 142.74 K obtained from the direct measurement with that calculated by use of the interpolated heat capacity. The former is 13.33 kJ mol^{-1} and the latter is 13.34 kJ mol^{-1}. Reference 16 illustrates the procedure of the direct measurement.

Table 4. The third law entropy of liquid at 177.13 K

via crystal

Temperature	Contribution	ΔS/J K^{-1} mol^{-1}
0 —14.0	Effective frequency spectra	4.00±0.05
14.0—177.13	$\int C_s(\text{cry.})\,d\ln T$	131.56±0.13
177.13	Transition $\left(\frac{7326}{177.13}\right)$	41.36±0.04
		176.92±0.22

via glassy state

Temperature	Contribution	ΔS/J K^{-1} mol^{-1}
0 —14.0	Effective frequency spectra	4.17±0.06
14.0—126	$\int C_s(\text{glass})\,d\ln T$	107.79±0.11
126—177.13	$\int C_s(\text{supercooled liq.})\,d\ln T$	52.95±0.05
		164.90±0.22

Residual Entropy of Glassy State. The entropy of the crystal at 0 K was concluded to obey the third law of thermodynamics by comparison of the gaseous entropy determined from thermal data with that computed from the calculated data, as described later. Based on this result the residual entropy of the glassy phase was calculated by a well-defined method which is given in Table 4. Contributions from entropy below 14 K for the crystalline and the glassy phases were determined by adopting the method of effective frequency distribution[17] with some modification. The necessary preset-parameters in this modified method include the two Debye and the Einstein cut-off frequencies. After the conversion of the measured heat capacity C_p into C_v with the aid of the Nernst-Lindemann[18] equation, the effective frequency distributions were determined for several sets of these preset-parameters by using about 20 values for C_v between 14 and 50 K. Fig. 4(A) shows the frequency distributions which reproduce best the heat capacity for the crystalline state of isopropylbenzene and Fig. 4 (B) for the glassy state. The values of entropy below 14 K used in order to assess the residual entropy and to derive the thermodynamic functions of the glassy, crystalline and

---

13) W. P. White, *J. Phys. Chem.*, **24**, 393 (1920).

14) W. J. Taylor and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **32**, 197 (1944).

15) S. V. R. Mastrangelo and R. W. Dornte, *J. Amer. Chem. Soc.*, **77**, 6200 (1955).

16) K. Adachi, H. Suga, and S. Seki, This Bulletin, **44**, 78 (1971).

17) M. Sorai and S. Seki, *J. Phys. Soc. Japan*, **32**, 382 (1972).

18) "Handbuch der Experimentalphysik, Band 8, 1. Teil, Energie und Wärmeinhalt" ed. by A. Eucken, Akademische Verlargsgesellschaft M. B. H., Leipzig (1929).

TABLE 5. THERMODYNAMIC FUNCTIONS OF ISOPROPYLBENZENE

$\frac{T}{\mathrm{K}}$	$\frac{C_s^\circ}{\mathrm{J\,K^{-}\,mol^{-1}}}$	$\frac{S_s^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{(H^\circ-H_0^\circ)/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-(G^\circ-H_0^\circ)/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$
(crystalline phase)				
10	(4.60)	(1.76)	(1.28)	(0.48)
20	16.26	8.39	5.77	2.63
30	28.12	17.28	11.29	6.00
40	38.09	26.79	16.79	10.00
50	46.12	36.17	21.87	14.30
60	53.46	45.24	26.53	18.71
70	60.18	53.99	30.87	23.13
80	66.49	62.44	34.92	27.52
90	72.62	70.63	38.78	31.86
100	78.20	78.58	42.44	36.13
110	83.86	86.29	45.95	40.34
120	89.62	93.84	49.35	44.49
130	95.48	101.24	52.67	48.57
140	101.64	108.54	55.95	52.59
150	108.31	115.77	59.21	56.56
160	115.75	123.00	62.51	60.49
170	124.54	130.26	65.88	64.38
(glassy state)				
10	(4.83)	(13.81)	(349.89)	(−336.08)
20	17.60	20.94	180.46	−159.52
30	30.01	30.51	128.31	−97.80
40	40.08	40.59	105.06	−64.46
50	48.30	50.44	92.90	−42.46
60	55.92	59.92	86.10	−26.18
70	63.27	69.09	82.32	−13.23
80	70.66	78.01	80.39	−2.38
90	77.76	86.75	79.71	7.04
100	84.21	95.28	79.84	15.44
110	91.16	103.62	80.54	23.08
120	99.03	111.88	81.74	30.14
(liquid state)				
130	176.62	122.11	85.34	36.77
140	176.23	135.18	91.84	43.34
150	(176.47)	147.34	97.47	49.87
160	(177.21)	158.75	102.43	56.32
170	177.38	169.53	106.86	62.67
180	179.90	179.77	110.87	68.89
190	181.74	189.54	114.55	74.99
200	183.78	198.91	117.96	80.95
210	186.10	207.93	121.15	86.78
220	188.69	216.65	124.16	92.49
230	191.48	225.10	127.03	98.07
240	194.37	233.31	129.77	103.54
250	197.47	241.31	132.42	108.89
260	200.88	249.12	134.98	114.13
270	204.49	256.77	137.49	119.27
280	208.22	264.27	139.95	124.32
290	212.14	271.64	142.37	129.27
300	216.15	278.90	144.76	134.14
310	220.16	286.06	147.13	138.92
298.15	215.40	277.57	144.21	133.36

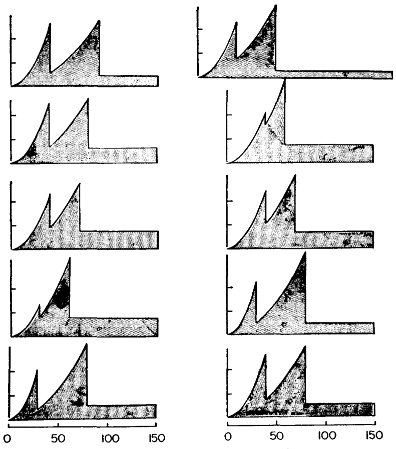

Fig. 4. Frequency distribution spectra determined from the heat capacities below 50 K,
(A) for the crystalline state,
(B) for the glassy state.

liquid phases were obtained by averaging the values of entropy which were calculated based on each lattice frequency spectrum shown in Fig. 4. The residual entropy of the glassy state turns out to be 12.0± 0.5 J K^{-1} mol^{-1}.

Thermodynamic Functions. Thermodynamic functions for the crystalline, glassy and liquid states were derived from the smoothed heat capacity data based on the values listed in Tables 3 and 4, and were all tabulated in Table 5. In the derivation of these values, the crystalline phase at 0 K was taken as a reference state.

Verification of the Third Law for the Crystalline Phase. The calorimetric entropy of isopropylbenzene as an ideal gas at 298.15 K was determined and given in Table 6, together with the values for the heat of vaporization,[19] the critical temperature and pressure.[20] The values of the spectroscopic entropy calculated by Taylor *et al.*[21] for isopropylbenzene, *n*-propylbenzene and *n*-butylbenzene in their ideal gas states

Table 6. The third law entropy at 298.15 K of isopropylbenzene in ideal gas state

Contribution	S/J K^{-1} mol^{-1}
Effective frequency distribution (0—14 K)	4.00
Heat capacity measurement (14—298.15 K)	273.62
Vaporization at 298.15 K	151.40
Gas imperfection correction	0.013
Compression to 1 atm	−42.50
	386.53

Table 7. Molar entropy of ideal gas at 298.15 K

	Third law entropy (S/J K^{-1} mol^{-1})	Calculated entropy (S/J K^{-1} mol^{-1})	δ
Isopropylbenzene	386.53	388.57	−0.528
n-Propylbenzene	397.86[a]	400.66	−0.704
n-Butylbenzene	437.86[a]	439.49	−0.372

a) J. F. Messerly, S. S. Todd, and H. L. Finke, *J. Phys. Chem.*, **69**, 4304 (1965).

are compared with the calorimetric ones in Table where δ means $[S(\text{calorimetric})-S(\text{calculated})]/S(\text{calorimetric})\times 100$. The calculated values for these benzene derivatives show systematically positive deviations from the calorimetric ones. These discrepancies seem to exceed the estimated inaccuracies of respective experiments. In view of the approximate method adopted in calculating the spectroscopic entropies, however, it seems plausible to conclude that the third law of thermodynamics is applicable to the crystalline phase of isopropylbenzene rather than to assume a possible existence of randomness at zero Kelvin.

β-Relaxational Phenomenon. In the preceding series[22] of papers we concerned ourselves exclusively with the relaxational effect of primary glass transition phenomena. Glassy state or glassy-crystalline state is a non-equilibrium state and tends to be stabilized by releasing its excess enthalpy toward an equilibrium state. The practical observation of the enthalpy relaxation phenomena is usually limited within a temperature interval of 10—30 K below T_g, owing to the elongation of relaxation time.

During the course of heat capacity measurement in the glassy state, we encountered unusual temperature drifts and a step-like heat capacity increment at around 70 K, far below the primary glass transition temperature. Figure 5 shows the change of the temperature drifts in series 6. Slight exothermic drifts revealed themselves at around 50 K and gradually increased up to about 70 K. On the contrary, above 70 K endothermic drifts were observed and disappeared gradually at higher temperatures. This variation of the temperature drifts is quite similar to that observed in the usual glass transition region. The magnitude of the drifts

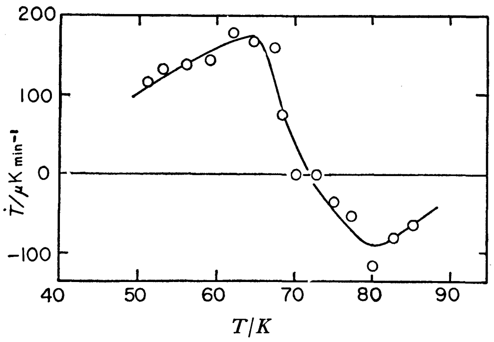

Fig. 5. Temperature-drift change around T_β.

---

[19] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa. (1953).

[20] K. A. Kobe and R. E. Lynn, Jr., *Chem. Rev.*, **52**, 117 (1953).

[21] W. P. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **37**, 95 (1946).

[22] K. Adachi, H. Suga, and S. Seki, This Bulletin, **45**, 1960 (1972); *Idem*, *ibid.*, **43**, 1916 (1970); M. Sugisaki, K. Adachi, H. Suga, and S. Seki, *ibid.*, **41**, 593 (1968).

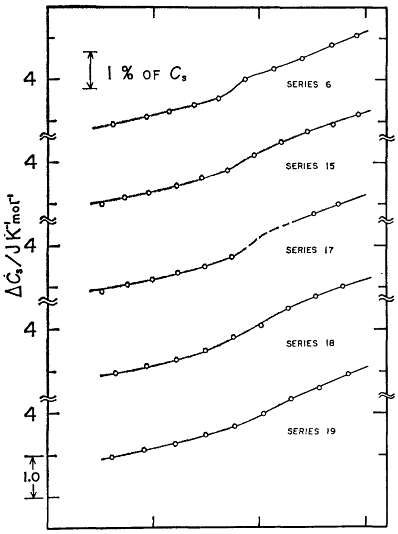

Fig. 6. Excess heat capacity of the glassy phase over the crystalline phase around T_β.

Table 8. Excess heat capacity of the glassy over the crystalline phase

T/K	ΔC_s/J K^{-1} mol^{-1}	T/K	ΔC_s/J K^{-1} mol^{-1}
Series 6		Series 18	
66.22	2.92	66.39	2.95
69.31	3.10	69.33	3.12
71.44	3.22	72.16	3.26
73.82	3.39	74.89	3.48
76.14	3.54	77.52	3.81
78.65	4.00	80.12	4.07
81.37	4.25	82.69	4.48
84.01	4.51	85.29	4.77
86.79	4.84	87.81	5.00
89.13	5.06		
Series 15		Series 19	
65.10	2.99	66.04	2.95
67.25	3.14	69.12	3.11
69.52	3.24	72.09	3.24
72.17	3.42	74.94	3.47
74.55	3.62	77.69	3.67
76.99	3.78	80.36	3.96
79.49	4.16	82.95	4.31
82.04	4.48	85.62	4.56
84.52	4.75	88.37	4.92
86.93	4.91		
89.30	5.17		
Series 17			
65.08	2.88		
67.49	3.06		
69.86	3.17		
72.30	3.34		
74.83	3.48		
77.39	3.71		
85.09	4.75		
87.43	4.98		

Table 9. Thermal history of each run

Series number	Cooling rate around T_g (K/min)	Cooling rate around 70 K (K/min)
6	0.7	2
15	4	0.3
17	3	0.9
18	1	0.5
19	2	3

in this case is far smaller than that around T_g, but larger than that due to a heat leak to or from the calorimetric cell arising from the incompleteness of adiabatic conditions.

Heat capacity measurements for the glassy state in this region were performed several times under different conditions. The C_s values of the glassy state subtracted by those of the crystalline phase were depicted in Fig. 6 for each run and tabulated in Table 8. One can find the abrupt increase in the heat capacity at around 80 K which has a resemblance to that at an ordinary glass transition point. For each series, the specimen was cooled from temperatures far above the melting point down to the liquid nitrogen temperature and then cooled further to around 50 K except for series 6 by use of liquid hydrogen or solid nitrogen as a refrigerant. The thermal history for each series is listed in Table 9. In series 6, the specimen in the glassy state was allowed to stand at the liquid nitrogen temperature for one night prior to being cooled down to 14 K. The thermal drifts were already mentioned for this series (Fig. 5). In the case of series 15, exothermic drifts change into endothermic ones at around 72 K. In series 17, the changeover of the drifts occurs at 78 K. In series 18 the specimen was annealed for 15 days at the liquid nitrogen temperature. In this case only endothermic drifts appeared in the temperature range from 55 to 80 K. The temperature drifts in series 19 were almost the same as in series 18. As is shown in this figure, the hystereses in the heat capacity due to the different thermal histories were perceptible, which reminds us of glass transition phenomena.

The temperature drifts similar to those in the primary glass transition region and the abrupt increase in C_s seem to support the view that a β-transition exists around 70—80 K.

Discussion

β-Relaxation. Johari *et al.*[23] found the β-relaxation for isopropylbenzene by means of dielectric measurements and showed that the Arrhenius plot of the frequency of maximum loss $f_{\max}$ against $1/T$ gives a straight line with an activation energy of 8 kcal/mol. Using their data, we extrapolated this Arrhenius plot and determined the temperature at which $f_{\max}$ becomes equal to 10^{-3} Hz to be 76 K.

The calorimetric β-transition temperature, T_β, of

---

[23] G. P. Johari and M. Goldstein, *J. Chem. Phys.*, **53**, 2372 (1970).

about 80 K, is in agreement with that inferred from the dielectric measurement. However, the behavior of the thermal drifts in the β-transition region was not interpreted in terms of cooling rates around T_g, and T_β, respectively.

This failure in explanation may be attributed to the small magnitude of the observable temperature drifts which are apt to be significantly influenced by the incomplete adiabatic conditions. The other explanation may be that we could not quench the specimen instantly from the temperature above T_g to far below T_β because at least a few hours were compelled to be consumed under our experimental conditions. As a result the cooling rate could not be varied definitely from run to run. This makes a possible correlation between the cooling rates around both T_g and T_β and the behavior of the temperature drifts difficult to be clarified.

Goldstein[24] proposed that β-relaxation is intrinsic to the glassy state and arising from such degrees of freedom whose freezing out is responsible for the main glass transition. To explain β-relaxation on the basis of the earlier description given by Orowan[25] for viscous flow as an activated process, he put an additional hypothesis to Orowan's picture. The hypothesis is that the packing of molecules in an amorphous state is always such as to give rise to a distribution of barrier height against molecular motions responsible for viscous flow. The existence of lower barriers makes some molecular motions possible to be excited even at temperatures where viscous flow can no longer occur at a detectable rate. When these modes of motion become frozen-in, the β-relaxation would be observed.

However, this hypothesis alone can not account for a question why a maximum of dielectric loss or an abrupt change in heat capacity does appear. The existence of β-relaxation will lead to a hump or a shoulder in relaxation spectra in a shorter time-region than that responsible for the main glass transition, though the broadening out of relaxation spectra can be interpreted by cooperative molecular motions as well as by the distribution of potential barrier heights. If a hump or a shoulder does not exist in the spectra, a maximum of dielectric loss or an abrupt increase in heat capacity below T_g will not be expected and only a continuous loss will appear. In Goldstein's picture there is no reason for the existence of a hump (*i.e.*, the existence of many barriers with the same heights in a particular range). However, by taking into account molecular rearrangements involving defects or holes as a hypothesis in addition to Goldstein's description, the above question can be explained. Around holes less cooperative molecular motions should occur in a shorter time than those in other normal parts. Such molecular motions are expected to be responsible for a hump in the spectra and consequently related to β-relaxation.

Relation between Relaxation Time and Configurational Entropy. The validity of the Adam-Gibbs equation (Eq. (1)) was examined along the following line. Viscosity, η, in a supercooled liquid region is given by the Fulcher-Tammann-Hesse equation

$$\ln \eta = A' + B'/(T-T_0), \tag{2}$$

where A', B' and T_0 are constants. η is also related to τ by the equation

$$\eta = G_\infty \tau, \tag{3}$$

where G_∞ is the limiting high frequency shear modulus. If Eq. (1) holds, combination of Eqs. (1) and (3) yields

$$\ln \eta = \ln G_\infty + \ln A + \frac{C}{TS_c}. \tag{4}$$

The temperature dependence of G_∞ is given by the following equation[26]

$$G_\infty = G_0 + \frac{B''}{T - T_0'},$$

where G_0 is the rigidity modulus at the temperature T_0', and B'' a constant. On the other hand, τ and η usually vary exponentially with temperature. Therefore, the temperature dependence of G_∞ may be neglected compared with those of τ and η, and comparing Eq. (2) with Eq. (4), one is led to a conclusion that the quantity TS_c is proportional to $T-T_0$ and S_c must vanish at T_0 as far as the approximation adopted above is correct. The temperature at which the configurational entropy vanishes is designated as T_2. Experimentally, T_2 temperature is determined from the intersection of the extrapolated entropy curve of a supercooled liquid (curve *c–d* in Fig. 7) and the entropy curve (*a–g*) which is obtained by subtracting the residual entropy (segment *e–a* of the ordinate) from the entropy curve for the glassy state (*e–f*). Curve *a–g* is corresponding to the entropy curve of a hypothetical phonon system in the glassy state. However, estimation of the entropy of the hypothetical phonon system of this ideal glass by the method described above is not accurate. If the temperature of supercooled liquid is lowered along the equilibrium curve *d–c*, volume contraction takes place mainly by virtue of the change in the configura-

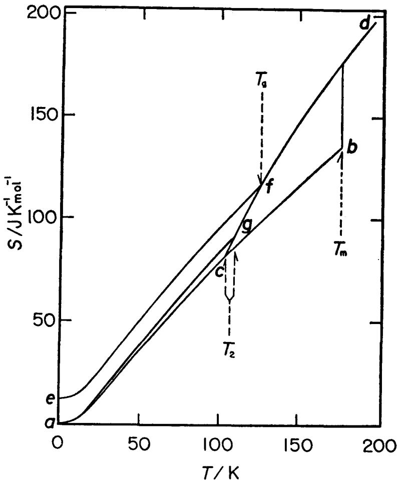

Fig. 7. Entropy diagram of isopropylbenzene.

---

[24] M. Goldstein, *J. Chem. Phys.*, **51**, 3728 (1969).

[25] E. Orowan, "Creep in Metallic and Non-Metallic Materials," Proceedings of the First U. S. National Congress of Applied Mechanics, A. S. M. E., (1952) p. 453.

[26] A. J. Barlow, J. Lamb, A. J. Matheson, P. R. K. L. Padmini, and J. Richter, *Proc. Roy. Soc. A*, **298**, 467 (1967).

tion. This volume contraction will change the frequency distribution spectra and in turn affects the entropy of the phonon system[27] in a decreasing direction. Accordingly, T_2 thus obtained is an upper limit of the temperature at which the configurational entropy vanishes. On the other hand, the temperature at which the entropy curve of crystal (*a–b*) intersects curve *c–d* is considered as a lower limit.

For comparison, T_2 temperature along with the values of T_0 obtained from the viscosity data based on the Fulcher-Tammann-Hesse equation (Eq. (2).) are listed in Table 10 for two compounds. The second column shows the upper and the lower limits for T_2. Consistency between the values of T_2 obtained by the static method of calorimetry and T_0 by the dynamical method of viscosity measurements is fairly good. This agreement supports the Adam-Gibbs equation. Figure 8 depicts TS_c plotted against temperature for isopropylbenzene. Although estimation of S_c includes an unavoidable ambiguity due to the extrapolation of curve *a–g* (Fig. 7) up to about 160 K, a fairly well linear relationship was observed between them. For propan-1-ol[28] small deviation is seen in the plot of TS_c *vs.* T. For the supercooled liquid phases of *o*-terphenyl[2] and 2-methylpentane[38] as well as for the supercooled plastic crystalline phase of 2,3-dimethylbutane,[16] this relationship was found to hold also fairly well. In such a way, we can propose a rough method to interpret the relaxation time in terms of the configurational entropy by using the Adam-Gibbs equation for an equilibrium supercooled liquid phase and/or for a supercooled plastic crystalline phase.

TABLE 10. COMPARISON BETWEEN T_2 AND T_0

	Calorimetric T_2	Viscosity T_0
Isopropylbenzene	109.5—103.5K	93.8K
o-Terphenyl	207 —204K	200K

It may be added that the relation $TS_c \propto T-T_2$ has to lead the following thermodynamic functions:

$$C_{\text{conf}} \propto \frac{1}{T}\theta(T-T_0)$$

and

$$H_c \propto \ln\frac{T}{T_2}\theta(T-T_0) \ ,$$

where C_{conf} is configurational heat capacity and θ the step function.

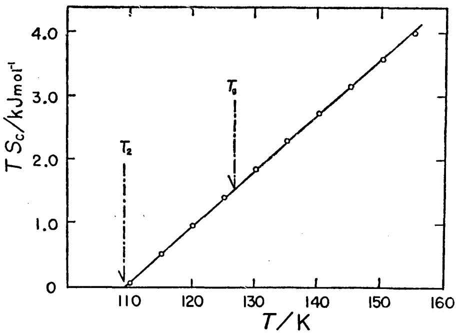

Fig. 8. Temperature dependence of the configurational entropy multiplied by temperature for isopropylbenzene.

Anomalous Behavior of the Heat Capacity in the Liquid State. Recently there have been suggested the possible existence of a phase change in a liquid state by several workers. In 1953 Moore *et al.*[6] found the discontinuities in the several physical properties such as heat capacity, vapor pressure, density, compressibility, and viscosity of liquid alkanes. For example, they found that the change of the heat capacity of *n*-heptane with temperature can be well represented by two straight lines with a more or less gradual transition from one to the other over a rather narrow temperature range. They attributed these discontinuities to the onset of specific molecular motions (*i.e.*, translation↔libration↔free rotation). Davies *et al.*[7] pointed out that the discontinuity in viscositity of liquid should correspond to a thermodynamic transition which is due to the restriction of the rotation of molecules (translation↔one axis rotation↔two axes rotation equivalent to free rotation). They referred to the analysis of the heat capacity data by Moore *et al.*, mentioned above, and they concluded that the transition should correspond to the third order in the sense of Ehrenfest.

As is well known, the viscosity, η, of liquids at temperatures fairly above their melting points is well described by the Arrhenius equation

$$\ln\eta = A+E/RT, \tag{5}$$

where A is a constant, R the gas constant, and E the activation energy for viscous flow. However, this equation is not usually applicable to liquids of high viscosity or to supercooled liquids. Fulcher[29] and Tammann & Hesse[30] found an empirical equation for these liquids

$$\ln\eta = A'+B'/(T-T_0) \ , \tag{2}$$

where A', B' and T_0 are constants. For some liquids it became apparent[31] that the viscosity could not be

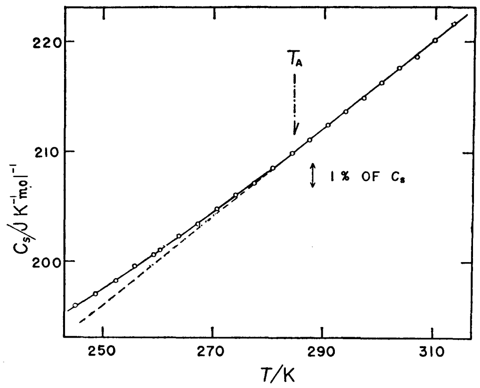

Fig. 9. Heat capacity of isopropylbenzene in the liquid state.

---

[27] C. M. Guttman, *J. Chem. Phys.*, **56**, 627 (1972).

[28] J. F. Counsell, E. B. Lees, and J. F. Martin, *J. Chem. Soc.*, *Sec. A*, No. 8, 1819 (1968).

[29] G. S. Fulcher, *J. Amer. Ceram. Soc.*, **8**, 339 (1925).

[30] G. Tammann and W. Hesse, *Z. Anorg. Allgem. Chem.*, **156**, 245 (1926).

[31] A. J. Barlow, J. Lamb, and A. J. Matheson, *Proc. Roy. Soc.*, *Ser. A*, **292**, 322 (1966).

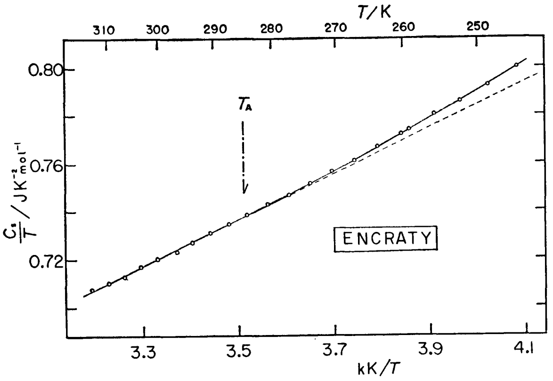

Fig. 10. Encraty *vs.* $1/T$ plot for isopropylbenzene in the liquid state.

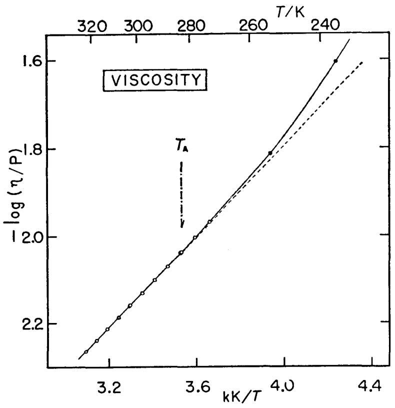

Fig. 11. Arrhenius plot of viscosity which can be compared with Fig. 10,
●: from Ref. 12. ○: from Ref. 19.

described by a single equation (Eq. (2)) over the whole temperature range except for the high temperature Arrhenius region. Thus, two sets of constants in Eq. (2) are required in two separate temperature regions. The temperature at which Arrhenius type temperature dependence changes into non-Arrhenius one is designated as Arrhenius temperature T_A. The temperature at which transformation of one type of non-Arrhenius behavior occurs into another type of non-Arrhenius behavior is designated as intersection temperature T_K. It is interesting to know how heat capacity behaves at T_A and T_K, and also to investigate the order of transitions if they exist.

The heat capacity data of isopropylbenzene over the temperature range in question are reproduced in Fig. 9 in an enlarged scale. Above *ca.* 285 K the heat capacity is well represented by a straight line, while below that it fails. The change of the heat capacity with temperature below T_A is not described by a straight line as was suggested by Moore *et al.* in the case of *n*-heptane. This is true of many compounds described later we examined for which the heat capacity data are available in the literature. The lowest temperature below which the heat capacity deviates from the straight line can not be determined within the temperature range of some 5 K because of the restriction of the precision in our heat capacity measurement. But it agrees with the Arrhenius temperature, T_A, of 283 K.$^{7)}$ The encraty, C_s/T, of isopropylbenzene is plotted against $1/T$ in Fig. 10, which will be compared with the plots of $\ln\eta$ *vs.* $1/T$ of the same substance given in Fig. 11. These figures show that above *ca.* 285 K both C_s/T and $\ln\eta$ vary linearly with $1/T$.

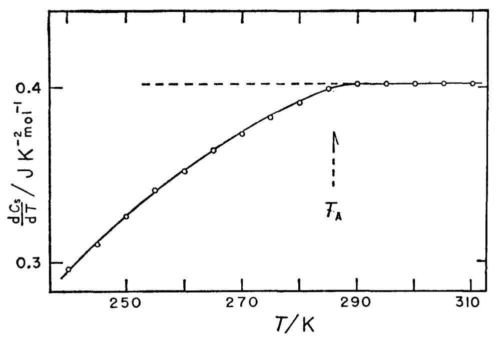

Fig. 12. Temperature derivative of heat capacity for isopropylbenzene in the liquid state.

At the third-order transition point the third derivative of the Gibbs free energy with respect to temperature $(\partial^3 G/\partial T^3)_p = -\partial(C_p/T)/\partial T$ is discontinuous, which should lead to a jump in dC_p/dT. dC_s/dT of isopropylbenzene determined from the smoothed curve of C_s is plotted in Fig. 12. By the way, in the case of isopropylbenzene $(C_p-C_s)/C_p$ at 313 K amounts to 0.63×10^{-4} which is within an experimental error, so we can regard C_s as C_p over the whole temperature range of our observation. No jump in dC_p/dT or d^2C_p/dT^2 is found, as is seen in Fig. 12. If dC_p/dT *vs.* T curve is concave upward up to T_A and then horizontal, the anomalous behavior of the heat capacity at T_A is compatible with the fourth-order transition because a jump appears in d^2C_p/dT^2 *vs.* T curve in this case. Actually, however, the dC_p/dT *vs.* T curve is convex upward, so this anomalous behavior is a transition, if any, of higher order than fourth. This fact is quite the same for *n*-butylbenzene,$^{32)}$ *n*-propylbenzene$^{32)}$ and ethylbenzene$^{33)}$, *etc.* In order to discuss the nature of the anomalous behavior of this kind, more detailed heat capacity measurements with higher precision and resolution would be required.

Liquids composed of spherical molecules such as neopentane$^{19,34)}$ and carbon tetrachloride$^{35-37)}$ show Arrhenius behavior of the viscosity and the linear temperature dependence of the heat capacity, C_s, over the whole temperature range investigated. These are just the behavior of isopropylbenzene and analogous compounds in the limiting higher temperature region above T_A. These facts suggest a similarity of

---

32) J. F. Messerly, S. S. Todd, and H. L. Finke, *J. Phys. Chem.*, **69**, 4304 (1965).

33) G. B. Guthrie, Jr., R. W. Spitzer, and H. M. Huffmann, *J. Amer. Chem. Soc.*, **66**, 2120 (1944); R. B. Scott and F. G. Brickwedde, *J. Res. Nat. Bur. Stand.*, **35**, 501 (1945).

34) J. G. Aston and G. H. Messerly, *J. Amer. Chem. Soc.*, **58**, 2354 (1936).

35) J. Timmermanns, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co. New York (1950).

36) D. Horrison and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, *Ser. A*, **230**, 230 (1957).

37) W. T. Richards and J. H. Wallance, Jr., *J. Amer. Chem. Soc.*, **54**, 2705 (1932).

38) D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 1704 (1946).

rotational modes in a period of successive translational jump for non-spherical molecules above T_A to those modes for spherical molecules.

In passing, we should call attention to the way of compilation of heat capacity data of liquids. Usually the temperature dependence of the heat capacity of liquid is expressed as a following equation over a whole temperature range.

$$C_p = a + bT + cT^2 + dT^3,$$

where a,b,c and d are constants. However, based on our results we propose to divide the temperature range of liquid at least into two parts for more appropriate method of the compilation, *i.e.*, above and below T_A.

Summary

(1) The heat capacities of isopropylbenzene were measured for the crystal from 14 to T_m (177.13 K), for the glassy state from 14 to T_g (around 126 K) and for the liquid from T_g to 313 K, on a sample with purity of 99.93%. The heat and entropy of fusion were found to be 7326 J mol^{-1} and 41.36 J K^{-1} mol^{-1}, respectively. Gibbs energy function, enthalpy function and entropy in the solid and liquid states were calculated at selected temperatures from 15 to 310 K.

(2) The calorimetric entropy in the ideal gas state at 298.15 K, 386.53 J K^{-1} mol^{-1}, was compared with the calculated one given by Taylor *et al.* It was concluded that the crystal follows the third law of thermodynamics. Based on this result, the residual entropy for the glassy state was determined to be 12.0± 0.5 J K^{-1} mol^{-1}.

(3) Aside from the primary glass transition phenomenon, a secondary relaxation was found in temperature drifts of the calorimetric cell in the temperature region centered at around 70 K and a step-like heat capacity anomaly was observed at around 75 K. This phenomenon was discussed with relation to the β-relaxation already observed by dielectric measurement.

(4) Temperature dependence of the configurational entropy of the supercooled liquid was investigated to see whether the Adam-Gibbs equation holds or not. And also, the agreement was found between the temperature at which catastrophe occurs in viscosity and the temperature at which the configurational entropy vanishes.

(5) A kind of heat capacity break was observed in the liquid state, which was discussed against the view that this behavior was compatible with the third-order thermodynamic transition. The temperature *ca.* 285 K at which anomalous behavior of heat capacity occurred was in agreement with that where a discontinuity in the temperature dependence of the viscosity was found.