BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 41　593—600 (1968)

On the Glass Transition Phenomenon of Isopentane*[1]

Masayasu SUGISAKI, Keiichiro ADACHI, Hiroshi SUGA and Syûzô SEKI

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

(Received October 14, 1967)

Heat capacity measurement of isopentane was carried out for crystalline, liquid, glassy, and supercooled liquid states in the temperature region between 13 and 300°K. The glass transition phenomenon of isopentane was found around 65°K with drastic heat capacity change of 68.20 J/mol degK. This glass transition phenomenon is tentatively interpreted in terms of the Adam and Gibbs theory. The value of T_g/T_2, the ratio of glass transition temperature T_g, and the temperature of disappearance of the configurational entropy of the supercooled liquid T_2, for isopentane was found to be 1.30 which is concordant with the value cited by Adam and Gibbs. The residual entropy at absolute zero of the glassy isopentane was shown to be 14.06 J/mol degK. In addition the irreversible production of entropy during the glass transition intervals was found to be 0.08 J/mol degK. It is concluded that the neglect of the irreversible production of entropy leads no significant error in determing the residual entropy.

Recently, Turnbull and Cohen⁽¹⁾ have empirically found that the substance which satisfy the condition that the ratio T_b/T_m, of their normal boiling to their normal melting temperature is equal to or larger than 1.8 are easily supercooled. On the basis of this empirical rule they suggest that the substances which fulfill this condition may have much glass-forming tendency, if the liquid is cooled rapidly far below their melting point with no occurrence of crystallization.

There have been known many kinds of pure substances showing glass transition phenomenon. They may be classified into, (1) network glasses such as SiO_2 and other nonmetallic oxides, (2) inorganic and organic polymers, (3) hydrogen bonded substances, (4) low molecular weight materials, *etc.*⁽²⁾ In order to study the essential feature of the glassy state from theoretical as well as experimental points of view, it seems much desirable to investigate the simple low molecular weight substances. For such purpose we have undertaken to study the glassy state in relation to

---

[1] *1 This paper was read before the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, March, 1966.

1) D. Turnbull and M. H. Cohen, *J. Chem. Phys.*, **29**, 1049 (1958).

2) "Progress in Solid-State Chemistry," Vol. 3, ed. by H. Reiss, Pergamon Press Inc., New York (1967), p. 407.

its crystalline phase by use of the method of heat capacity measurement, and really found a characteristic heat capacity jump associated with the occurrence of the glass transition phenomenon.

Experimental

Apparatus. The adiabatic Nernst-type calorimeter[3] used in our laboratory was partly modified, so that rapid cooling may be easily carried out. For this purpose, liquid nitrogen or liquid hydrogen is able to be charged directly into the space between the outer and inner adiabatic shields as is shown in Fig. 1. Measurements of temperature were made with platinum resistance thermometer calibrated in terms of International Temperature Scale between 90 and 500°K and the provisional scale of the National Bureau of Standards between 11 and 90°K.[3]

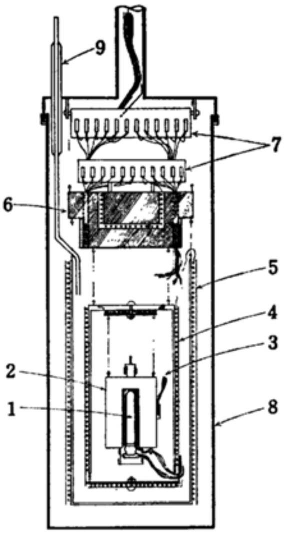

Fig. 1. Description of adiabatic calorimeter.
1) platinum resistance thermometer, 2) sample container, 3) thermo-couple, 4) inner shield, 5) outer shield, 6) copper block, 7) lead connector, 8) vacuum jacket, 9) transfer tube.

Sample. The commercial extra pure isopentane (Nakarai Chemicals, Ltd.) was purified by fractional distillation, and then distilled twice under high vacuum (10^{-6} mmHg). Impurities contained in each fraction were detected by gas chromatography technique and the purest fraction was employed for the heat capacity measurements. The amount of the impurities present in the sample was determined to be 0.014 mol percent by making use of thermo-analytical method as is described later.

Heat Capacity Measurements. Measurements of the heat capacities were made on a sample with single loading (0.2433 mol) which was sealed in a gold calorimeter cell, for the crystalline, liquid, glassy, and supercooled liquid states in the temperature region from 13 to 300°K. The reported values are based on a molecular weight 72.152 g and ice point is taken to be 273.15°K.

Our preliminary observation by differential thermal analysis clarified that cooling rate of 10°C/min was sufficient to supercool the liquid isopentane far below its melting point without any occurrence of crystallization. Consequently, liquid hydrogen was directly transferred into the space between outer and inner shields (see Fig. 1), in order to satisfy this cooling condition. From the results of the heat capacity measurements, it was found that the whole amount of the sample was completely superocooled down to 20°K without any occurrence of crystallization.

Furthermore, in order to determine the purity of the sample, detailed measurements of melting point and enthalpy analysis of melting, were also performed.

Experimental Results

Heat Capacity of Crystalline and Liquid States. The results of heat capacity measurements are listed in Table 1A for crystalline and liquid states, and are shown by hollow circles in Fig. 2. These values agree with those reported by Guthrie and Huffman[4] in 1943. They reported the nonexistence of the appearance of anomalous heat capacity of liquid state in the temperature region between 170—250°K which was first reported by Schumann and Aston (1942).[5] This fact coincides with our results.

The data of melting point in relation to mole fraction of the melt, and the heat of fusion, obtained from the results of heat capacity measurements, are shown in Table 2, and the relationship between melting point and inverse molten fraction is given in Fig. 3. The value obtained for the melting point of 100% pure isopentane is found to be 113.36±0.05°K.

From the melting curve, the amount of impurities in the sample was found to be 0.014 mol percent.

Heat Capacities of Glass and Supercooled Liquid. The results of the heat capacity measurements in the glassy and the supercooled liquid states of isopentane are shown in Table 1B, and shown by filled circles in Fig. 2. There appears a sharp rise of heat capacity at about 65°K which is characteristic to glass transition phenomenon of supercooled liquid. These results indicate that isopentane can be supercooled far below its melting point and can be transformed into a glassy state. It may be noted that the differences of the heat capacities between the crystalline and glassy states are smaller near 30°K in each side, similar to that of glycerol.[6]

The amount of heat capacity of the supercooled

---

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

[4] G. B. Guthrie, Jr., and H. M. Huffman, *J. Am. Chem. Soc.*, **65**, 1139 (1943).

[5] S. C. Schumann, J. G. Aston and Malcolm Sagenkahn, *ibid.*, **64**, 1039 (1942).

[6] G. E. Gibson and W. F. Giaque, *ibid.*, **45**, 93 (1923).

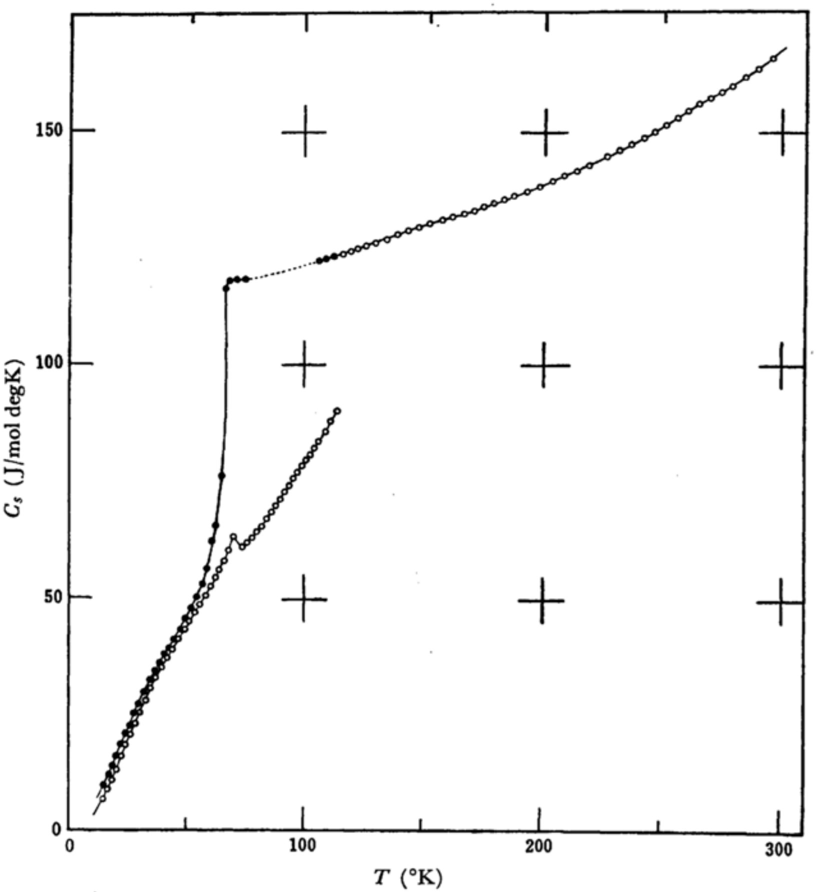

Fig. 2. Heat capacity curve of isopentane.

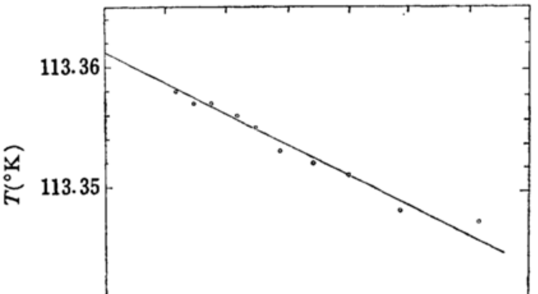

Fig. 3. Melting curve of isopentane.

liquid just above the glass transition point is nearly equal to the twice of that for the crystalline state. This fact is rather common feature at glass transition of almost all supercooled liquids.[7] When the supercooled liquid which had experienced glass transition, was heated up to above the glass transition temperature, the crystallization takes place at about 75°K. This crystallization phenomenon was observed experimentally with the start of gradual heat evolution effect. The heat capacity measurements, a little below the melting point were made with the supercooled liquid obtained by means of careful slow cooling. It was possible

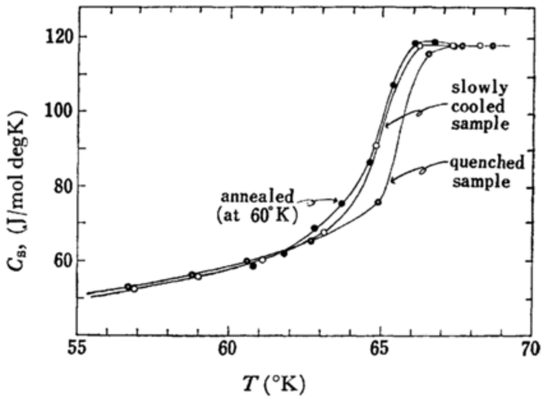

Fig. 4. Heat capacity of isopentane during the glass transition intervals.
●: annealed sample at 60°K, ○: slowly cooled one, ◎: quenched one

---

[7] R. O. Davies and G. O. Jones, *Proc. Roy. Soc.*, **A217**, 26 (1953).

for about 10°C below the melting point, and the temperature region where the heat capacity measurements were impossible is shown by dotted line in Fig. 2. Detailed measurements were also made in the glass transition intervals for various samples which had experienced the different thermal treatments. The results are shown in Fig. 4 and double circles represent the data for the quenched sample which was quenched to 25°K from room temperature during six minutes. The series of measurements for this quenched sample were made from 13°K to 68°K. After this series of measurements have finished at 68°K, the sample was slowly cooled down to 43°K during 4 hr.

The results with this slowly cooled sample are depicted by a series of circle in the Fig. 4.

Finally, this sample was again cooled down to 60°K from 68°K during 25 min and annealed for about 20 hr at this temperature. The filled circles are for this sample.

This series of measurements was continued to the temperature region above the glass transition

TABLE 1A. MOLAR HEAT CAPACITIES OF ISOPENTANE (CRYSTAL AND LIQUID) IN J/mol degK.

T (°K)	C_s	T (°K)	C_s	T (°K)	C_s	T (°K)	C_s
Series 1		72.61	62.931	140.72	127.89	208.79	140.08
		74.54	60.829	142.94	128.34	211.41	140.56
14.99	6.414	76.46	61.513	145.15	128.74	214.02	141.13
16.87	8.624	78.35	62.634	147.36	129.00	216.63	141.81
18.61	10.848	80.20	64.840	149.56	129.23	219.22	142.33
20.40	12.928	82.01	65.343	151.77	129.76	221.81	142.91
22.51	15.736	83.91	66.851			226.66	144.24
24.49	18.259	85.90	68.121	Series 5		229.22	144.74
26.40	20.447	87.86	69.683			231.76	145.56
28.34	22.632	89.78	71.167	155.44	130.38	234.30	146.13
30.31	25.200	91.67	72.520	157.62	130.64	236.83	146.74
32.67	27.777	93.53	73.888	159.79	130.80	239.47	147.22
35.12	30.402	95.37	75.232	161.96	131.21		
37.37	32.686	97.18	76.654	164.13	131.31	Series 7	
39.68	34.908	98.96	77.920	165.68	131.76		
42.07	36.936			168.44	132.24	234.70	145.95
44.42	38.989	Series 3		170.58	132.58	237.12	146.76
46.88	41.136			172.73	133.05	239.52	147.65
49.31	43.106	97.20	75.764	174.86	133.52	241.91	148.30
51.64	44.892	98.95	78.217	177.00	133.88	244.29	148.78
53.86	46.681	100.68	79.152	179.12	134.28	246.65	149.49
56.09	48.520	102.40	80.558	181.24	134.63	249.01	150.11
58.32	50.428	104.11	81.997	183.36	134.92	251.36	150.88
60.48	52.357	105.77	83.456	185.47	135.31	253.72	151.64
62.57	54.188	107.40	84.532			256.07	152.41
64.16	55.726	109.02	85.962	Series 6		258.39	153.12
66.15	57.753	110.61	88.151			260.69	153.83
68.12	60.251	112.13	96.408	165.68	131.76	262.99	154.60
70.10	63.005	113.36	123.38	168.23	132.24	265.28	154.96
72.04	62.502	114.83	124.83	171.13	132.68	267.57	155.65
74.00	60.598			173.88	133.13	269.84	156.59
75.95	61.336	Series 4		176.62	133.69	272.10	157.25
77.86	62.457			179.35	134.27	274.36	157.95
79.74	63.896	119.70	124.51	182.07	134.76	276.46	158.56
		121.53	124.63	184.78	135.25	278.85	159.13
Series 2		123.36	124.92	187.49	135.73	281.68	160.16
		125.19	125.05	190.18	136.21	284.50	161.05
60.18	51.999	127.23	125.52	192.87	136.76	287.30	161.92
62.43	54.179	129.50	125.62	195.54	137.28	290.08	162.98
64.60	56.669	131.76	125.99	198.21	137.83	292.85	164.17
66.69	58.302	134.01	126.42	200.87	138.36	295.61	165.15
68.72	60.140	136.25	127.02	203.52	138.99	298.34	166.17
70.69	63.533	138.49	127.66	206.16	139.38		

Table 1B. Molar heat capacities of isopentane (glass and supercooled liquid) in J/mol deg K

T (°K)	C_s	T (°K)	C_s
Glass		54.90	50.016
		56.92	52.436
Series 1		58.99	55.676
		61.08	60.210
15.60	9.398	63.09	67.832
17.34	11.707	64.82	90.959
19.06	13.834	66.20	117.61
20.61	15.779	67.30	117.66
22.59	18.289	68.24	117.68
24.47	20.546		
26.28	22.764	Series 3	
28.14	24.850		
30.05	26.976	60.79	57.671
32.34	29.462	61.75	60.944
34.73	31.882	62.77	65.565
36.93	34.042	63.70	72.107
38.99	35.852	64.98	82.561
41.03	37.612	65.37	96.907
43.08	39.302		
45.33	41.103	Supercooled liquid	
47.78	43.325		
50.33	45.659	66.02	116.34
52.54	47.773	66.69	117.47
54.67	50.115	67.35	117.62
56.72	52.939	68.31	117.79
58.79	56.253	69.59	117.78
60.61	61.971	70.85	117.60
62.71	65.400	72.12	118.07
64.92	75.800	73.39	117.78
66.54	116.04	74.67	118.13
67.66	117.79		
68.62	117.87	Series 4	
Series 2		105.96	122.38
		107.45	122.49
45.88	41.615	108.93	122.71
48.30	43.630	110.41	122.97
54.60	45.630	111.89	123.03
52.79	47.810		

temperature, until the heat evolution due to the crystallization was observed.

While the crystallization proceeds, the adiabatic condition of the calorimeter was watched to be satisfied. When the heat evolution effect has ceased at 106.2°K, the temperature of the crystalline phase was determined accurately. This procedure was necessary in order to determine the enthalpy of the glassy state on the basis of the enthalpy of the crystalline states as will be given in the next section.

Enthalpy Curves of the Glass and the Supercooled Liquid. The enthalpy curves of the glass and the supercooled liquid, calculated with the results of the heat capacity data are shown in Fig. 5.

Table 2. Heat of fusion of isopentane

T (°K) Melting point	$\int \Delta C_P \mathrm{d}T$ Heat input J/mol	$1/r$ Inverse of pre-melting fraction
113.341	601.9	8.73
113.347	820.7	6.19
113.348	1039.8	4.88
113.351	1258.7	4.03
113.352	1477.7	3.44
113.353	1759.3	2.89
113.355	2041.0	2.49
113.356	2322.5	2.19
113.357	2885.5	1.76
113.357	3448.1	1.47
113.358	4339.7	1.17

(Heat of fusion 5140±2 J/mol)

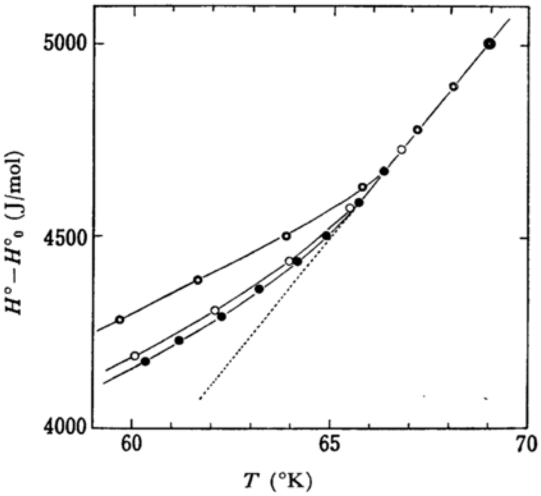

Fig. 5. Enthalpy curve of isopentane near the glass transition point.
●: annealed sample at 60°K, ○: slowly cooled sample, ◎: quenched sample

Each curve represents the various samples which had experienced different thermal treatments.

In the case of quenched sample, the enthalpy value of the supercooled liquid deviates from the equilibrium curve at about 66.5°K, and transforms into the glassy state. For slowly cooled sample, the curve deviates from the equilibrium value at the temperature 1°C lower than that for the quenched sample. The effect of annealing is really found in the enthalpy curve in such a way that the enthalpy curve of glass comes below the slowly cooled one. The triple circle near 69°K which is taken as the reference point for evaluation of absolute enthalpy of the glass was determined as the intersection of the curve for supercooled liquid and the isenthalpy straight line at 106.2°K of the enthalpy curve for crystalline state. The enthalpy curve of the crystalline state is easily

TABLE 3A. THERMODYNAMIC PROPERTIES OF ISOPENTANE (CRYSTALLINE AND LIQUID STATES) IN J/(mol degK)

T	C_P°	S°	$(H^\circ-H^\circ_0)/T$	$-(G^\circ-H^\circ_0)/T$
5	(0.255)	(0.085)	(0.063)	(0.021)
10	(2.030)	(0.655)	(0.499)	(0.155)
15	6.430	2.236	1.667	0.569
20	12.47	4.893	3.596	1.297
30	24.76	12.32	8.642	3.678
40	35.21	20.93	14.03	6.903
50	43.60	29.71	19.12	10.59
60	51.92	38.38	23.88	14.50
70	63.08	47.12	28.59	18.53
80	63.88	55.43	32.79	22.64
90	71.25	63.38	36.65	26.72
100	78.72	71.27	40.48	30.78
110	86.81	79.14	44.32	34.82
113.36		Fusion		
120	124.42	134.19	92.78	41.41
140	127.74	153.59	97.51	56.08
160	130.97	170.87	99.01	71.86
180	134.38	186.48	104.96	81.52
200	138.17	200.83	100.08	92.74
220	142.50	214.20	110.01	104.19
240	147.63	226.81	113.84	112.97
260	153.60	238.85	116.66	122.19
280	159.62	250.46	119.52	130.94
300	166.82	261.70	122.42	139.28

Values in parentheses are extrapolated by means of Debye function.

TABLE 3B. THERMODYNAMIC PROPERTIES OF ISOPENTANE (GLASSY AND SUPERCOOLED LIQUID STATES) IN J/(mol degK)

T	C_P°	$S^\circ-S^\circ_0(\mathrm{gl})$*	$(H^\circ-H^\circ_0(\mathrm{gl}))/T$	$-(G^\circ-H^\circ_0(\mathrm{gl}))/T$
5	(0.365)	(0.122)	(0.091)	(14.09)
10	(2.880)	(0.977)	(0.735)	(14.30)
15	8.660	2.951	2.373	14.64
20	15.03	6.315	4.733	15.65
30	26.95	14.73	10.21	18.58
40	36.75	23.88	15.67	22.27
50	45.13	32.97	20.72	26.31
60	58.77	42.16	25.70	30.52
70	117.28	55.45	38.60	30.91
80	118.63	71.21	48.52	36.75
90	119.98	85.26	56.38	42.94
100	121.33	97.72	62.81	48.97
110	122.67	108.68	68.19	54.55

$S^\circ_0(\mathrm{gl})=14.06$ J/(mol degK); $H^\circ_0(\mathrm{gl})-H^\circ_0(\mathrm{c})=2673$ J/mol.

The values between 70 and 110°K are evaluated by means of interpolation using equation $C_P=107.82+0.1351T$ (J/mol degK).

* (gl) indicates glassy state.

obtained by graphical integration of their heat capacity data.

Thermodynamic Properties of Isopentane. The values of heat capacity, entropy, and also the enthalpy and Gibbs energy functions of isopentane at selected temperature were listed for the liquid crystalline, glassy, and supercooled liquid states in Table 3.

Discussion

The heat capacities of isopentane have been measured by three investigators,[4,5,8] nevertheless, the occurrence of the glassy state of this compound

---

[8] G. S. Parks, H. M. Huffman and S. B. Thomas, *J. Am. Chem. Soc.*, **52**, 1032 (1930).

had not been known by any authors. As is described already, we have succeeded in obtaining the glassy state of the present material. The relation of the normal boiling to its normal melting points of isopentane is equal to 2.70. This fact is concordant with the Turnbull-Cohen empirical rule¹⁾ for obtaining glassy state by supercooling method; *i. e.*, the ratio should be equal to or larger than 1.8. The ratio $T_b/T_m=2.15$ for *n*-pentane suggests that this liquid might have also the tendency to be supercooled, whereas the crystallization has always occurred as far as our observation is concerned.

Now, in liquid isopentane two kinds of origin associated with the relaxation phenomenon may be considered, one is due to the degree of freedom of the internal rotation with respect to intramolecular C–C bond, and the other is due to the change of intermolecular configuration which is related to the shear and/or volume viscosity of liquid isopentane. Concerning the liquid state of isopentane, there is investigation with ultrasonic absorption technique by Young and Petrauskas.⁹⁾ Their results suggest that around 150°K the relaxation time with respect to the degree of freedom of internal rotation is longer than that for intermolecular configurational change. It is not clear, however, how is the relation between these two types of relaxation times for supercooled liquid near 65°K. We may safely conclude, anyhow, that ΔC_P, the increment of heat capacity at the glass transition point, is mainly associated with intermolecular configurational change, since the difference between the contributions due to the intramolecular rotation in the supercooled liquid and in the glass, may be too small to explain this ΔC_P.

Turning to the phenomenological interpretation of the glass transition phenomenon of supercooled liquid, there exist two kinds of opposite opinions. One is such that the glass transition occurs at temperature where a certain kind of thermodynamical quantity takes critical value; *i. e.*, the glass transition is like a second order phase transition.¹⁰⁾¹¹⁾ The other is such that the glass transition may be interpreted as the relaxation phenomenon due to the degree of freedom of molecular motions.¹²⁾

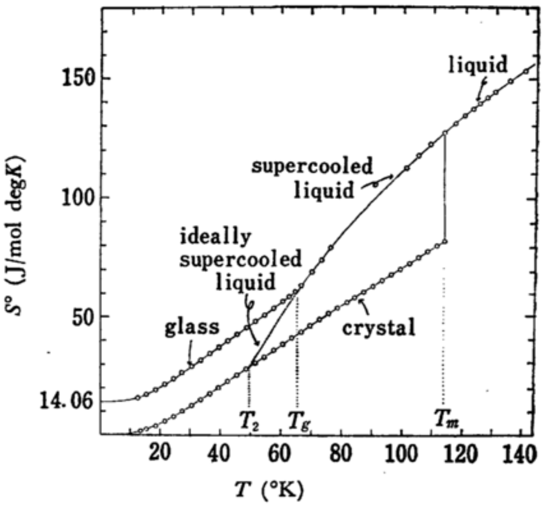

Fig. 6. Entropy diagram of isopentane.

According to Adam and Gibbs, the relaxation time of a system can be uniquely related to the configurational entropy of the system. This idea is based on the resolution of the well-known Kauzmann's paradox.¹³⁾ This theory shows explicitly the existence of temperature at which the configurational entropy of the system has critical value and it is called T_2, a glass transition temperature in the sense of thermodynamical equilibrium. According to their theory, the actual glass transition temperature T_g can be related to T_2 in the following equation;

$$S_{\mathrm{config}}(T_g) = \int_{T_2}^{T_g} \Delta C_P/T \, \mathrm{d}T, \text{ and}$$

$$S_{\mathrm{config}}(T_g) \equiv \Delta S_0 = (S_{\mathrm{glass}} - S_{\mathrm{cryst}})_{T=0}$$

From our results of the heat capacity measurements, ΔS_0 and ΔC_P are known, so the ratio T_g/T_2 can be calculated.

Figure 6 shows the entropy diagram of isopentane calculated from the data of the heat capacity measurements. From this entropy diagram, it is clear that T_2 (the temperature at which the configurational entropy disappears) situates at about 50°K. Consequently, the following relations are obtained,

$$T_g/T_2=65/50=1.30$$

and $$T_g-T_2=65-50=15 \text{ (°K)}$$

The relation, $T_g/T_2=1.30$, is corresponding to the average value of many substances cited by Bestul and Chang¹⁴⁾ and Adam and Gibbs.¹¹⁾

The consistency of the present results with Adam and Gibbs' theory seems to suggest that a certain kind of thermodynamical relation takes part in the glass transition phenomenon of the supercooled liquid.

Finally a few comments will be given concerning the irreversible phenomenon taking part in a glassy state.⁷⁾¹⁵⁾

---

9) J. M. Young and A. A. Petrauskas, *J. Chem. Phys.*, **25**, 943 (1956).

10) M. Goldstein, *ibid.*, **39**, 3369 (1963).

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

12) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

13) W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

14) A. B. Bestul and S. S. Chang, *J. Chem. Phys.*, **40**, 3731 (1964).

15) A. B. Bestul and S. S. Chang, *ibid.*, **43**, 4532 (1965).

Near below the glass transition temperature, we can observe usually an exothermic effect due to the stabilization phenomenon of the glassy state into a supercooled liquid.

This stabilization gives rise to an irreversible entropy production within the system. It is well known that a residual entropy of the glassy state generally involves the excess entropy due to these irreversible phenomenon. Davies and Jones(7) suggested the possibility that this entropy production can be estimated by considering the heat conduction between a system of configurational part and a system of lattice, each of which is in different temperatures. Consequently, the irreversible production of entropy can be expressed very simply by the following expression,

$$\Delta S_{\mathrm{irr.}} = \Delta C_P (1/\bar{T} - 1/T) \Delta T$$

where ΔC_P is the heat capacity of configurational part, T the temperature of a lattice, and $\bar{T}$ fictive temperature of a configurational system.

In order to estimate this quantity, the drift of temperature of the sample in the calorimeter was measured for long time during the glass transition intervals. This drift corresponds to the time derivative of T, or $\dot{T}$. Analysing the results of drift curve for quenched sample, $\Delta \bar{T}$ was found to be -0.0892°C with the assumption that configurational heat capacity is equal to that of the lattice.

Taking the following data $\bar{T}=65$°K, $T=60$°K, $\Delta C_P = 16.3$ cal/mol degK, we get $\Delta S_{irr} = 0.019$ cal/mol degK which is very small compared with the residual entropy at absolute zero, $\Delta S_0 = 3.36$ cal/mol degK.

We can safely conclude that the neglect of the irreversible production of entropy leads to no significant error on determing the residual entropy.

Summary

1) The results of the heat capacity measurements of isopentane were given for crystalline, liquid, glassy and supercooled liquid states in the temperature region between 13 and 300°K.

2) The glass transition phenomenon of isopentane was found near 65°K with the drastic change of heat capacity of 16.3 cal/mol degK.

3) The residual entropy of the glassy isopentane at absolute zero was found to be 3.36 cal/mol·degK.

4) The irreversible production of entropy during the glass transition intervals was estimated to be 0.019 cal/mol degK.