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Calorimetric Study of the Glassy State. III.*[1] Novel Type Calorimeter for Study of Glassy State and Heat Capacity of Glassy Methanol*[2]

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An adiabatic Nernst-Type calorimeter with a cell for condensing a sample vapor as an amorphous state was constructed. By making use of this calorimeter, the heat capacities of the glassy, supercooled liquid, and crystalline states of methanol were measured from 20°K to 120°K. It was found that the state of methanol deposited on the chilled substrate at about 95°K from its vapor state shows a glass transition phenomenon at about 103°K accompanied with the sudden increase of heat capacity, ΔC_P, amounting to 26 J/(mol°K). The drastic crystallization with the exothermic effect coming to 1.54 kJ/mol was observed near 105°K. The residual entropy for the glassy methanol was found to be 7.07 J/(mol°K). Based on these results it seems very plausible to propose that any non-crystalline solid deposited on the chilled substrate from the vapor state will show the glass transition phenomenon.

Usually, a glassy state is considered as a non-crystalline solid which can be obtained by supercooling a liquid sample without any crystallization phenomenon. When the supercooled liquid goes further into a glassy state, a glass transition phenomenon is necessarily found out at a definite temperature characteristic of the sample.

Nowadays, we are able to obtain the non-crystalline solids by using other various kinds of method[1)] including the method of the supercooling of liquid. These methods are, *e. g.,* shock wave

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*[1] Our papers on isopentane (This Bulletin, **41**, 593 (1968)) and on cyclohexanol (*ibid.,* **41**, 1073 (1968)) may be denoted as 1st and 2nd papers of our series of investigation on the glassy state hereafter.

*[2] Read before The Third Japanese Calorimetry Conference held at Osaka in 1967. Part of this paper was reported as the short communication in this Bulletin (**40**, 2984 (1967)).

1) D. R. Secrist and J. D. Mackenzie, "Modern Aspect of the Vitreous State," Vol. 3, ed. by J. D. Mackenzie, Butterworths Scientific Publication, Ltd., London (1964), chapter 6.

treatment, neutron bombardment, vapor condensation, solution method (hydrolysis and anodization), and dehydration of hydrated crystal, *etc.* These non-crystalline solids prepared by these different methods have common features that they exhibit a crystallization phenomenon on heating.

Are they also plausible to be called as a glass? In order to reply this question, it seems to be most decisive to find out their glass transition phenomena, because the glass transition phenomenon is of characterisitc to the glassy state.

Up to the present time, there has been reported no successful and quantitative work which confirms the glass transition phenomena for such non-crystalline solids prepared by the above cited uncommon methods.

In order to find out the glass transition phenomenon of the non-crystalline state prepared by the vapor condensation method, we have constructed a novel type of calorimeter which involves the sample cell for condensing the sample vapor. By making use of this calorimeter, the heat capacities of the glassy, supercooled liquid, and crystalline states of methanol were measured successfully.

Experimental

Apparatus. The calorimeter consists of a filling tube made of monel and soft copper, a copper cell with a platinum resistance thermometer, inner and outer adiabatic shields, a copper block as thermal station, and a vacuum jacket and others. The filling tube, two adiabatic shields and the copper block are all wound closely with constantan heaters.

The total view of the constructed calorimeter and the sketch of the sample cell are given in Figs. 1 and 2. As is shown in Fig. 2, a part of the filling tube enters into the sample cell. During the procedure of sampling, this part of the filling tube is warmed by the heat conduction from the upper part of the filling tube which is wound closely with the constantan heater. The part of the filling tube inside the cell can be kept at about 15°C, when the temperature of the wall of the sample cell is adjusted to be about 80°K and the outer part of the filling tube is warmed around 30°C under high vacuum condition of about 10^{-6} mmHg inside the cell. In this case the heat conduction between the filling tube and the sample cell occurs spontaneously through the outer short stainless steel tubing put on the top of the cell. The amount of this heat conduction is estimated as 1.3 (J/s), when the above cited temperature difference is maintained. Therefore the effect of the thermal switch is necessitated whose power of the heat exchange is at least larger than 1.3 (J/s). For this purpose the conduction gas method by using helium gas is sufficiently adequate when the apparatus is operated above the boiling point of liquid nitrogen.

In order to carry out the heat capacity measurement under a good adiabatic condition, the adequate combination of monel and copper metals for the filling tube outside the cell is designed for preventing the heat leak through this tube.

Measurements of temperature are made with the platinum resistance thermometer calibrated in terms of International Temperature Scale between 90°K and 500°K and the provisional scale of the National Bureau of Standards between 11°K and 90°K. Measurement of heat capacity is made in quite a same fashion as that reported by Suga and Seki.2)

It is found that a heat capacity of the empty cell is about 8.5 (J/degK) at room temperature, and that the attainment of the thermal equilibrium after the finish of energy input takes about 25 min at all temperature region between 13 and 330°K, and that the values of heat capacity deviate from the smoothed curve within 0.1% in the temperature region between 13 and 330°K.

Next, the procedures for condensing the vapor of a sample into the calorimeter as an amorphous state will be described. Firstly the vacuum jacket is immersed into the liquid nitrogen, and helium gas at about one atmospheric pressure is then introduced as a conduction gas into the vacuum jacket, the filling tube and the copper block being simultaneously warmed up at the desired temperature with the constantan heaters wound around them. Their temperatures are registered by the seven chromel P-constantan thermocouples, one of which is attached on the copper block, all the

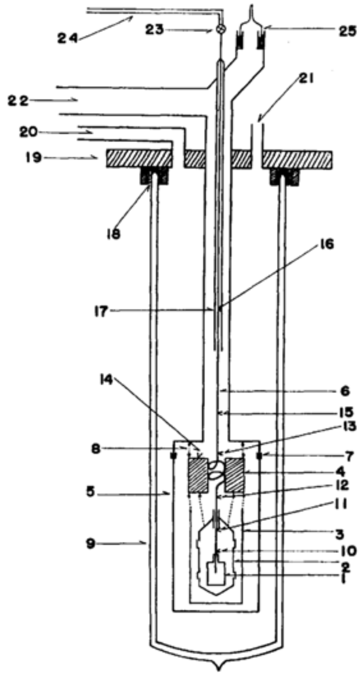

Fig. 1. Description of the type-2 calorimeter.

1) sample container, 2) inner shield, 3) outer shield, 4) copper block, 5) vacuum jacket, 6) filling tube, 7) wood alloy joint, 8) nylon thread, 9) glass dewar, 10)—16) thermocouples, 17) sheath of the filling tube, 18) picein joint, 19) brass plate for supporting the apparatus, 20) outlet tube, 21) tube for introducing liquid hydrogen or nitrogen, 22) to vacuum pumps, 23) needle valve for sampling, 24) glass tube for introducing the vapor of sample, 25) picein joint for taking out of lead wires.

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

TABLE 1. EXPERIMENTAL DATA OF METHANOL

Number of sample	Rate of condensation (g/hr)	Total amount of sample (g)	Heat of crystallization (kJ/mol)	ΔC_p at T_g (J/mol°K)	Amorphous part of sample (%)
1	0.101	1.214	1.54 ±0.05	26	100
2	0.366	1.645	0.57	10	37.4

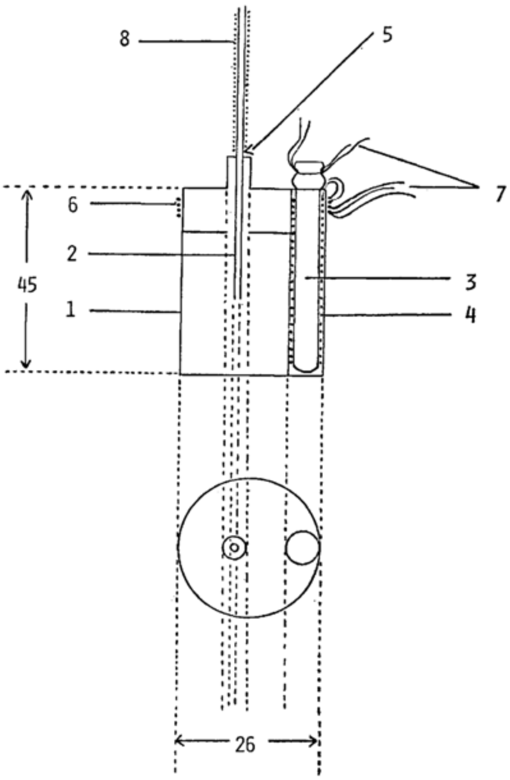

Fig. 2. Description of the sample container.

1) wall of the cell (made of copper), 2) filling tube, 3) platinum resistance thermometer, 4) constantan heater for energy-input, 5) thermocouple, 6) and 7) lead wires, 8) heater for sampling.

others being attached on the filling tube (see Fig. 1). The temperature of the sample cell is watched by recording the resistance of the platinum thermometer on the "Speedomax" recorder (Type G, Leeds & Northrup Co.). Under such an operation of the heaters, only the wall of the sample cell is chilled down to sufficiently low temperature, because the heat exchange between the filling tube and the sample cell is pressed down. The temperature difference between them can be easily regulated at any desired values up to about 200°C by changing the level height of liquid nitrogen or by changing the amount of electric current through the heater wound on the filling tube. When the temperature distribution of the calorimeter becomes to be steady, the vapor of the sample is slowly condensed into the calorimeter by opening the needle valve situated at the upper part of the calorimeter (see Fig. 1). The rate of condensation must be regulated to be very slow, since the surface of the amorphous sample produced in the cell may be warmed up above a crystallization temperature with the accumulation of the heat of condensation if the rate of condensation is pretty high. Usually the preparation of the vitreous sample needs about 10—20 hr and a total amount of condensed vitreous substance is of about 1—2 g. After the sampling is over, the heaters of the filling tube and of the copper block are switched off, and the total parts of the calorimeter are chilled down to 80°K, then helium gas (20 mmHg at 80°K) being introduced in the calorimeter cell in order to facilitate the attainment of the thermal equilibrium. Finally the conduction gas in the vacuum jacket is evacuated down to 10^{-6} mmHg for the realization of the adiabatic condition. With this adiabatic calorimeter measurements of the heat capacities can be carried out from 13°K to 330°K.

When the measurement is over, the calorimeter cell is heated up and the sample in the cell is gathered into the glass tube out of the calorimeter and its total amount is determined by measuring its weight.

Purification of Methanol. The commercial extra pure methanol (Wako Chemical Industries, Ltd.) was dried by magnesium metal (Lund and Bjerrum method). This product was distilled twice in high vacuum (10^{-6} mmHg) and the final product was degassed very carefully by repeating melting and freezing of the sample under high vacuum (10^{-6} mmHg). This final product was then introduced into the calorimeter in high vacuum (10^{-6} mmHg) as an amorphous state.

Preparation of Glassy Methanol. For this material, the outer jacket of the calorimeter was removed so that the temperature of the sample cell may be kept as low as possible. During the vitrification process, the temperature of the sample cell was kept between 94 and 97°K, and the filling tube around 220°K. Two kinds of rate of condensation were adopted as given in the second column of Table 1.

Heat Treatment adopted for the Heat Capacity Measurement. For the sample (1) heat capacities of glassy state were measured from 94°K to just above the glass transition temperature, and this sample was again chilled down slowly to 80°K as soon as the sample reached just above the glass transition temperature, and heat capacities were measured again from 80°K to 104°K. When the temperature of the sample reached about 105°K, a drastic crystallization took place and the temperature of the sample rises spontaneously due to the exothermic effect. For the sample (2) the measurements were made for the glassy state from 20°K to 104°K. After the crystallization, the crystalline sample was chilled down to 20°K and the measurements were made from 20 to 120°K.

Experimental Results

Results of Heat Capacity Measurement. *(a) Heat Capacity of the Crystalline State.* The numerical data for the sample (2) are given in

Table 2A, and are represented by hollow circles in Fig. 3. In this figure the smoothed curve above 120°K is drawn on the basis of Kelley's data.[3] It is found that our present data below 120°K agree with his data within the experimental error of 1.3% in the temperature region of liquid hydrogen, and 0.5% in the temperature region of liquid nitrogen.

TABLE 2A. HEAT CAPACITY OF METHANOL(CRYSTAL) IN J/(mol °K)

T (°K)	C_P	T(°K)	C_P	T (°K)	C_P
21.61	6.019	51.28	23.94	84.40	38.24
23.97	7.402	55.26	25.75	88.47	40.07
26.66	9.311	58.74	28.25	92.46	41.49
29.73	11.30	62.46	29.98	96.30	42.33
32.93	13.29	65.91	31.69	100.25	43.21
36.25	15.57	69.68	32.82	104.29	44.51
39.83	17.59	73.73	34.44	108.22	45.76
43.51	19.87	77.56	36.39	112.04	46.83
47.24	21.84	79.92	36.64		

TABLE 2B. HEAT CAPACITY OF METHANOL (GLASS AND SUPERCOOLED LIQUID) IN J/(mol °K)

T (°K)	C_P	T (°K)	C_P
sample (1)		60.19	29.06
series 1		63.38	30.54
96.30	44.30	66.65	31.97
97.96	45.96	70.05	33.31
99.58	49.77	series 3	
101.13	83.56	21.92	7.046
series 2		24.73	8.665
82.88	39.54	27.86	10.79
85.80	40.82	31.36	13.23
88.64	41.85	34.81	15.99
91.42	42.23	38.50	17.98
93.63	43.18	42.28	20.12
95.34	43.75	46.32	22.66
97.02	45.09	series 4	
98.74	47.21	72.26	34.56
100.39	57.28	76.22	35.96
101.97	76.84	80.86	37.71
102.96	71.62	85.50	39.54
103.87	68.92	89.27	41.04
105.16	67.70	92.02	41.80
sample (2)		93.79	42.45
series 1		95.54	43.09
23.64	8.074	97.25	43.97
26.64	10.03	98.94	44.88
30.03	12.33	100.58	48.64
series 2		102.14	58.56
49.39	24.21	103.54	53.43
51.85	25.42	104.82	54.04
54.38	26.40	106.22	53.61
57.14	27.58		

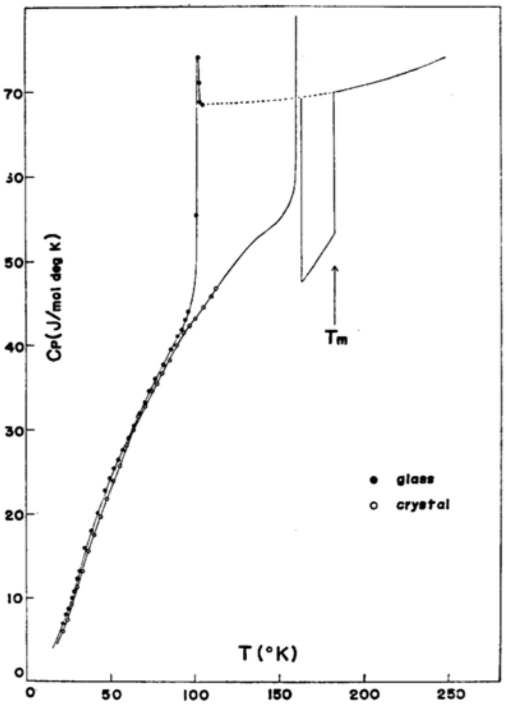

Fig. 3. Heat capacity curve of methanol.

The filled circles represent glassy and supercooled liquid states, and the hollow circles a crystalline state.

(b) *Heat Capacities of the Glassy and Supercooled Liquid States.* The results of the samples (1) and (2) are given in Table 2B and illustrated by the filled circles in Fig. 3. In this figure, the values for the sample (1) are plotted around the glass transition point and those for the sample (2) are plotted below 80°K (see Table 2A). As is seen in this figure it is found that the state of aggregation of methanol obtained by the present method of vapor condensation shows a glass transition phenomenon at about 103°K. On further heating, we found a drastic crystallization phenomenon at about 105°K just above this glass transition point. The dotted line represents the assumed heat capacity curve for the supercooled liquid which is obtained by an extrapolation of those of the normal liquid. The jump height of heat capacity (ΔC_P) at the glass transition point (T_g) and the total amount of exothermic effect accompanying the crystallization are given in Table 1. By comparing the heat of crystallization with the magnitude of ΔC_P at T_g for both samples, it is easily concluded that the sample (1) is in almost complete glassy state while the sample (2) is in partial glassy state. In Table 1 the amorphous part of the samples are also estimated by comparing the heat of crystallization with each other by assuming that the sample (1) is composed of 100 per cent amorphous material.

Thermodynamic Properties and Residual Entropy. The values of heat capacity, entropy, and also the enthalpy and Gibbs energy functions of methanol at selected temperatures are listed for the glassy and supercooled liquid states in Table 3.

TABLE 3. THERMODYNAMIC PROPERTIES OF METHANOL (GLASSY AND SUPERCOOLED LIQUID STATES) IN J/(mol°K)

T (°K)	$C°_P$	$S°-S°_0(gl)$*	$(H°-H°_0(gl))/T$	$-(G°-G°_0(gl))/T$
5	(0.310)	(0.082)	(0.070)	(0.012)
10	(1.700)	(0.619)	(0.447)	(0.172)
15	(4.350)	(1.796)	(1.297)	(0.499)
20	7.250	3.444	2.421	1.023
30	13.75	7.572	5.081	2.491
40	19.96	12.40	8.043	4.357
50	25.30	17.44	10.97	6.466
60	30.02	22.48	13.76	8.720
70	34.42	27.44	16.40	11.04
80	38.59	32.31	18.91	13.40
90	42.40	37.07	21.31	15.76
103	Glass transition point			
110	68.10	48.65	28.04	20.61
120	68.39	54.59	31.38	23.21
130	68.70	60.05	34.24	25.81
140	68.98	65.16	36.71	28.45
150	69.20	69.90	38.87	31.03
160	69.41	74.39	39.78	34.61
175.22	70.00	80.70	43.27	37.43

$H°_0(gl)-H°_0(c)$** = 1538 J/mol.

The values in parentheses are extrapolated by means of the Debye function.

*: (gl) indicates glassy state.

**: (c) indicates crystalline state.

The residual entropy, $S°_0$, which amounts to 7.07J/(mol°K), was also determined by using the results of heat capacity measurement. We could not measure unfortunately the heat of capacity 100 per cent glassy sample of methanol below 80°K, so the heat capacities of the glassy methanol below 80°K were calculated on the assumption that the additivity of the heat capacities of crystalline and glassy states holds as follows,

$$C_P(obs) = \alpha C_P(gl) + (1-\alpha)C_P(cryst),$$

here $C_P(obs)$ is the actually measured heat capacity of the sample, $C_P(gl)$ the heat capacity of completely glassy sample, $C_P(cryst)$ that of the crystalline sample and α the mole fraction of the glassy part of the sample. In the case of sample (2) α was estimated as 0.374, so the heat capacity of the glassy state below 80°K was calculated by using the values of the sample (2).

In passing, the entropy of the crystalline state is based on the Kelley's data.[3]

Discussion

Design of the Calorimeter. In the past, there has been known no successful work on the precise measurement of heat capacities for an amorphous material deposited directly onto the wall of a calorimeter cell from its vapor state.[4] This fact is due to some difficulties for constructing the calorimeter which fulfills the following few rather severe requirements.

(a) The calorimeter must be equipped with the filling tube, through which vapor of a sample passes, kept at a sufficiently higher temperature above the melting point of the sample, and with the calorimeter cell into which the vapor of the sample is condensed as an amorphous state, kept at a sufficiently lower temperature far below a glass transition temperature of the amorphous sample. For instance, the temperature of the filling tube should be higher about 100—200°C than that of the calorimeter cell if the glass transition point of the sample used situates around 100°K. (b) In order to hold the above cited steady distribution of large temperature difference in the calorimeter, a thermal switch is required whose power of heat exchange is sufficiently large enough. (c) It seems very difficult to obtain a considerable amount of a condensed amorphous substance, so a good adiabatic conditioning of the calorimeter is needed in order to perform precise measurements.

In order to satisfy the condition (a), all previous workers[4] have adopted the method of construction that a sample cell is directly immersed into the liquid nitrogen. This method is, however, inadequate to satisfy the condition (c), because a contamination during the sampling obstructs a realization of an adiabatic conditioning by high vacuum. By taking into consideration the above cited three conditions we have constructed the calorimeter with following devices.

(a) In order to maintain the steady temperature difference between the sample cell and the filling tube, the heat conduction between them is sufficiently reduced by joining them through a thin stainless tube (3 mm in diameter, 0.15 mm in thickness and 10 mm in length). (b) For simplicity of the handling of the apparatus, a conduction gas method was chosen as the thermal switch. If we adopt a mechanical thermal switch which has a comparable efficiency of heat exchange with that of the conduction gas thermal switch, the apparatus becomes to be very complicated. This complication necessarily causes an increase of heat capacity of the sample cell itself, so the mechanical switch is inadequate for the precise measurement.

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3) K. K. Kelley, *J. Am. Chem. Soc.*, **58**, 1144 (1936).

4) J. A. Pryde and G. O. Jones, *Nature*, **170**, 685 (1952); H. J. de Nordwall and L. A. K. Staveley, *Trans. Faraday Soc.*, **52**, 1061 (1956); R. H. Beaumont, H. Chihara and J. A. Morrison, *J. Chem. Phys.*, **34**, 1456 (1961).

(c) In order to realize a good adiabatic condition, it seems preferable to design the calorimeter equipped with two adiabatic jackets; the structure satisfies the conditions that the convection current of the conduction gas is facilitated, and that a heat leak due to radiation is completely precluded.

Glass Transition Phenomenon of Methanol. Van Thiel and Pimentel[5] observed that methanol deposited on the chilled substrate between 4.2 and 120°K gives an infrared absorption spectrum resembling that of the normal liquid methanol, and that once this deposited state was heated up above 120°K, the spectrum disappeared and changes to that characteristic of the crystalline state. Based on the above observation, they have conjectured that this deposited state of methanol might be a glass. However, their conclusion seems too hasty, because a glass transition phenomenon, which necessarily accompanies the glassy state, has not been discovered yet. Therefore, our present finding of the glass transition phenomenon certifies for the first time that the methanol condensed onto the chilled substrate below 105°K exists as a glassy state. Moreover, it is to be noted that the vitreous methanol of the sample (1) is composed of about 100 per cent amorphous material judging from the heat of crystallization as well as the jump height of heat capacity, ΔC_P, at T_g.

In general, it seems very difficult to obtain the completely vitreous state by the method of vapor condensation. In fact there has been no quantitative work of obtaining completely vitreous material by this method. In the case of our calorimetry, the temperatures of several parts of the apparatus can be regulated accurately and finely and also the rate of condensation can be controlled very precisely during the vitrification process, so that it is rather easy to obtain a completely vitreous material, when the suitable condition for the adjustment of temperature distribution is established. The fact that the sample (2) contains the appreciable crystalline part seems to be due to the warming up of the surface of the sample above the crystallization point by the high rate of condensation.

Judging from the results of our experiment on methanol it seems very plausible to propose that any non-crystalline solid deposited on the chilled substrate from the vapor state will show the glass transition phenomenon.

The authors would like to express their sincere thanks to the Toyo Rayon Co., Ltd. who defraid a part of the financial support for the present investigation.

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[5] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London (1960), p. 103.