An On-line Automated Adiabatic Calorimeter in the 13—300 K. Heat Capacity of Cyclohexanol†

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A computerized adiabatic calorimeter system operating in the temperature range 13—300 K is described. A digital voltmeter is used for energy measurement and the duration of energy input is determined by a program unit operated by 1 Hz pulse. Temperatures of the calorimeter are measured by a 25 Ω platinum resistance thermometer and an automated ac double bridge. The measured resistance is converted into temperature (IPTS-68) by a calibration table stored in a mini-computer. Criterion for the realization of thermal equilibration is that a temperature drift calculated from the latest six data becomes smaller than a preset value, usually $7\times10^{-8}\ \Omega\ s^{-1}$. The system is able to measure the heat capacity of solid and liquid in an intermittent heating mode and gives the computed results during measurement. Some examples of the test runs on cyclohexanol crystal are shown and the results are compared with those obtained by manual measurements by use of dc Müller bridge. A relaxational heat capacity anomaly observed in glassy crystalline state of cyclohexanol is discussed in correlation with a secondary relaxation observed by previous dielectric measurement.

Adiabatic calorimeter with intermittent heating mode is believed to give the most accurate and precise heat capacity data at low temperatures.[1] Numerical values of the static equilibrium properties such as enthalpy, entropy and Gibbs energy function can be derived from the data. While, a series of systematic studies on glassy states of materials[2] have proved that the calorimetric technique under a good adiabatic condition provided valuable information on dynamical nature of molecular motion through the observation of relaxational behavior of enthalpy of the specimen. Thus, temperature changes due to enthalpy relaxation in cyclohexanol crystal[3] at around 150 K were followed to give calorimetric relaxation time, which was correlated with dielectric relaxation time.[4] Kinetic parameters derived from calorimetric measurement of 1,2-difluoro-1,1,2,2-tetrachloroethane crystal[5] were correlated with those obtained by NMR techniques. A relaxational process due to possible rearrangement of proton configuration in hexagonal ice[6] was persued for about a month.

The relaxation time obtained by this method ranges 5 minutes to one week (or of the order of 10^{-3} to 10^{-7} Hz in terms of frequency). Since it is almost impossible at the present stage to get such a long relaxation time by other techniques, the calorimetric method provides complementary knowledge on the dynamics of slow molecular motion in the condensed state. The prolonged observation of temperature of a system with extremely long relaxation time necessitates to build an automatic data acquisition system for calorimetry.

The development of modern electronic techniques makes possible to replace the laborious manual operations by an automatic measurement and control without loss of accuracy. There are many approaches[7-10] to the problem of automatic data acquisition in calorimetry according to the heating mode and to the method of temperature measurement. Here, a new approach of data acquisition system suitable for our purpose is reported. The system is able to give quick information of any thermal anomaly that may be encountered during measurement. The electronic system, the soft ware logic, and the method of processing the data are described. The operation of the system is illustrated by results on cyclohexanol crystal.

Automatic Heat Capacity Measurement System

An adiabatic calorimeter[11] with an immersion-type cryostat was used for the present purpose. A sample cell loaded with platinum resistance thermometer and heater is surrounded by two (inner and outer) adiabatic shields and by massive thermal station. Heat capacity of the cell is measured as a function of temperature by the standard discrete heating method. In this intermittent mode, the sequence of heat capacity measurement is composed of two successively alternating periods. One is called a drift period during which the temperature of the calorimeter cell is measured as a function of time. The other is the energy input period during which a definite amount of electrical energy is supplied to the calorimeter cell. The supplied energy is assessed on the basis of measurements of voltage and current across and through the cell heater as well as of time interval of the energy input.

Adiabatic condition of the calorimeter cell is realized by use of high vacuum and four-channels temperature controller. Each channel consists of a multi-junction thermocouple, dc amplifier and power amplifier. Controllers with proportional-integral-differential control mode are indispensable for the automatic control of the shield temperature in the discrete heating method. Small temperature difference was set between the inner and the outer shields, and the inner shield and the station, so as to produce the least temperature drift rate of the cell.

Figure 1 is a block diagram illustrating the system for automatic heat capacity measurement. This system may be divided into four major parts: (1) measuring circuits, (2) control system, (3) interface system, and (4) minicomputer.

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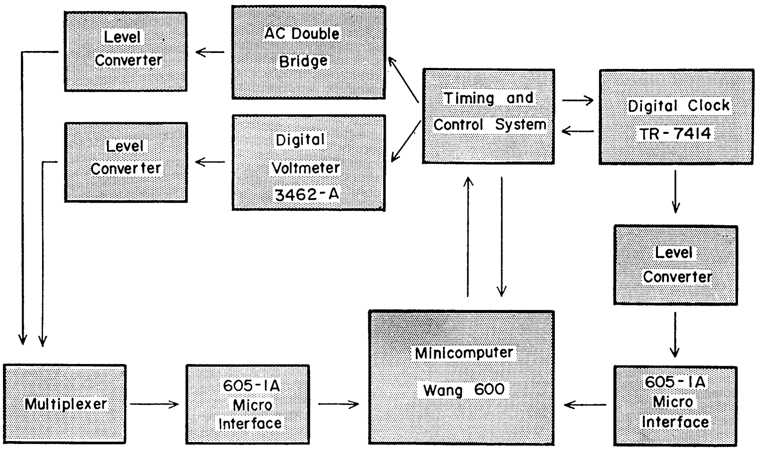

Fig. 1. Block diagram of the system for the automatic heat capacity measurement.

(1) Measuring Circuits. Resistance of the working platinum thermometer was measured by the Automatic System Laboratory A-7 precision ac double bridge. The bridge utilizes inductive voltage divider arranged as a Kelvin double bridge and is energized at 390 Hz. The bridge measures the ratio between two resistances R_t and R_s. Changes in resistance are automatically balanced and the ratio $R_t/(R_t+R_s)$ is displayed in seven digits. A capsule type platinum thermometer (Leeds and Northrup, 8164) was used in conjunction with one of four standard resistors (General Radio card-type 1440, 0.01, 0.1, 1, and 10 Ω). The four standard resistors were mounted inside a double-walled air thermostat.

The maximum temperature coefficient of the standard resistor was stated by manufacturer to be ±20 ppm/K, while the bridge has $\pm 4\times 10^{-7}$ inaccuracy. Thus, for the measurement of temperature with the accuracy better than 4×10^{-7}, the thermostat must be controlled within ±5 mK. The assembly shown in Fig. 2 consists of two parts; the boxes made of aluminum plate, A—C, and copper box, D. The spaces between A and B, and between B and C are packed with styrofoam insulation E and heater F. A and B are thermostatted independently at 36 °C and 33 °C, respectively, by use of the regulator circuit with thermistors as temperature sensors. The copper box housing the standard resistors G is wrapped by polyurethane H, and is positioned on wooden pedestral I. The thick copper wall plays a role as a buffer against fluctuation of temperature inside the aluminum box A.

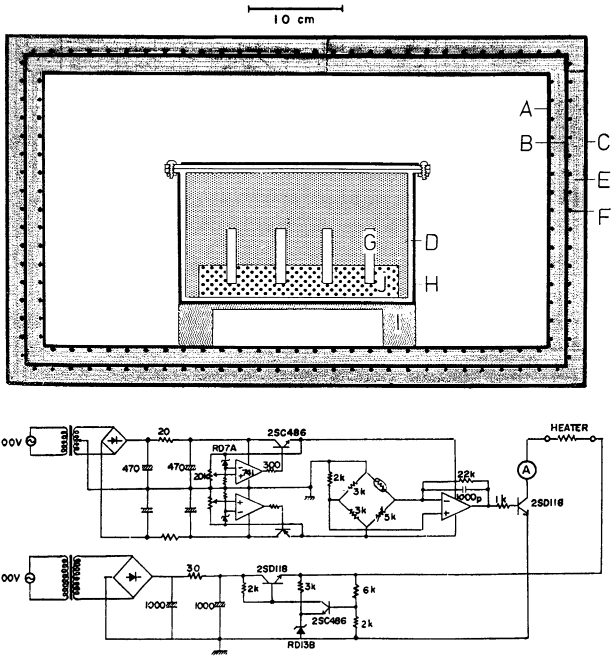

Fig. 2. Schematic drawing of an air thermostat for standard resistors and its regulator circuits.
A—C, Aluminum plates; D, copper box; E, styroform insulation; F, regulator heater; G, card-type standard resistor; H, polyurethane insulation; I, wooden pedestral; J, polyvinylchloride supporter.

The condition of the bridge balance has been given by Harris[12] in detail. Noise induced in the leads of the thermometer was liable to induce hunting in the bridge balance at the band width of 100 Hz. Since the bridge had the band widths of 100, 25, and 6.2 Hz as received from the manufacturer, it was modified so that any of setting with 30, 7.5, and 0.94 Hz could be adopted for avoiding the situation. For further improvement of the bridge balance, a normal counting logic system must be applied beside a short-cut logic system as pointed out by Martin *et al.*[8]

The electrical power supplied to the calorimeter cell was determined as follows. Values for the heater current are obtained by measuring the voltage across a 100 Ω standard resistor placed in series with the calorimeter heater. The voltages across the heater and the standard resistor are measured by means of a digital voltmeter (DVM, Hewlett-Packard 3462 A). The two DVM inputs are selected by a magnecraft mercury relay at an interval of 30 seconds during a heating period. The electrical energy dissipated in the calorimeter heater can be assessed by the equation, $E=60\sum_{i=1}^{N} V_i I_i$, where N is the total count during the heating or the heating time in unit of minute because the heating time is chosen to be multiple of one minute as will be described later.

In the drift period, the current from the power supply is circulated through a dummy resistance in place of the calorimeter heater in order to maintain a constant drain on the power supply. The resistance used as a calorimeter heater (*ca.* 100 Ω) and the dummy resistance are switched by use of a magnecraft type MCN-IN high-speed mercury-relay, which has exceedingly low stray emf and contact resistance. All timing operations are based on a digital clock (Takeda Riken TR 7414B). As received from the manufacturer the clock had no output of one-second clock pulse which is required for the system control. One-second clock pulse fed into the Timing and Control described below are therefore taken out from the digital IC mounted in the clock.

The instrument has a claimed accuracy of 0.01% which comes from the stability of quartz crystal oscillators in it.

(2) Timing and Control System. The Timing and Control System (TCS) controls all timing operations on the basis of 1 Hz pulse generated by the digital clock. This system serves as an assistant of the mini-computer which is a data-entry-only device (or, has no interrupt system). When an energy-input command is issued from the program of the mini-computer, TCS transforms it into the electrical command signal. At the instant the energy input command signal coincides with the one-second-clock pulse, TCS makes the timer start and allows the magnecraft mercury-relay for energy input to be turned on. From this instant the energy input period starts. In the present work, the heating time interval is selected to be multiple of 1 min or 1 h. In this period, select signals are generated every 30 s from the clock and serves to select either voltage or current reading by operating a magnecraft mercury-relay.

Since the DVM can not measure voltage within a claimed accuracy (0.0004%) immediately after a sudden change in an input voltage, trigger pulses for the DVM readings are generated twice by TCS in each V and I reading period, and the second reading at the mid-time of each period is adopted. In the drift period, TCS supplies trigger pulses for DVM readings every 10 s, which are available for adjustment of the variable dummy resistance. In a normal use, an energy input is performed automatically under a program control and the heating period is fixed to the preset time interval. However, if desired, the heater on-off operation can be made manually, which is helpful in such a case as enthalpy determination of phase transition.

(3) Interface System. The interface system consists of level converter, multiplexer and micro-interface Wang 605, which interfaces the peripheral devices to a mini-computer Wang 600. The digital output levels of these measuring instruments are not directly compatible with TTL/DTL levels of Wang 600. Therefore, a level converter assembly is required between the computer and the peripheral devices. There exists no necessity of sampling of data from the ac double bridge and from the DVM in the same period. A multiplexer selects the data from the bridge in the drift period and the data from DVM in the heating period.

(4) Mini-computer and Program. The mini-computer Wang 600 takes advantages of facilities of a cassette system offering a low-cost alternative to disk and card systems. The resistance values of a working thermometer are stored on a cassette tape at an interval of 0.1 K over the temperature range from 10 to 380 K.

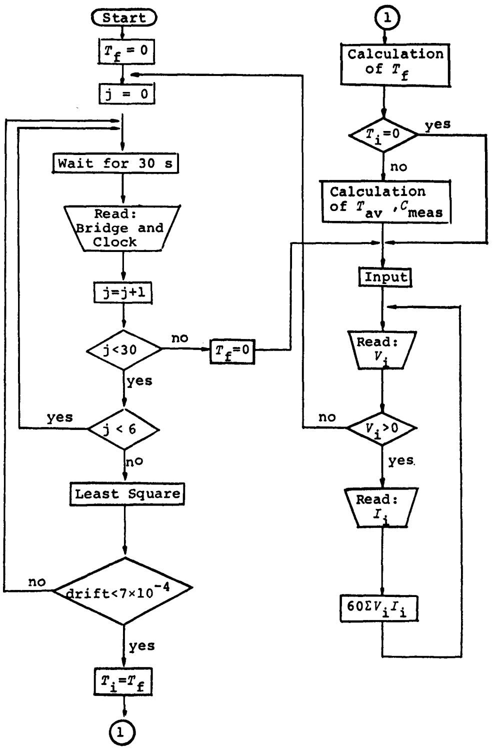

Fig. 3. Flow chart for the procedure of automatic operation of heat capacity measurement.

A flow chart for the procedure of automatic operation is drawn in Fig. 3. A typical sequence of program is as follows.

Step (1): In a drift period, the computer commands every 30 s the ac double bridge to transfer the measured resistance of a thermometer, data transfer being performed at the time when the bridge becomes at balance.

Step (2): Next the computer asks the clock to tell the time at which the measurement was made. The time is stored into a register and printed out along with the values of the measured resistance.

Step (3): The program examines whether the number of data points is smaller than six. If the answer is "yes," the program returns to step (1), after waiting for 30 s. If the answer is "no," the program proceeds to step (4).

Step (4): If the number of data points is smaller than 30, a temperature drift rate is determined from last six pairs of data by the least squares method. When a specimen accompanies with an enthalpy relaxation phenomenon, spontaneous temperature increase or decrease should be observed. In that case, 30 data points are accumulated and are used to analyse a kinetic characteristics of the relaxational process. Then, the program branches to step (7).

Step (5): A decision is made whether the drift rate is smaller than a preset value, usually 0.7 mK/ks. If not, the program judges that the thermal equilibrium in the calorimeter cell is not established yet, and the program returns to Step (1). If so, the last six values of resistance are averaged to give an equilibrium resistance. Then, the computer converts this resistance value to temperature on the basis of T *vs.* R conversion table stored in a data bank. The corresponding value is designated as a final temperature, T_f.

Step (6): The computer calculates T_{av} which is equal to the averaged value of initial, T_i, and final, T_f, temperatures, and C_{meas} $(=60\,\Omega\ V_iI_i/(T_f-T_i))$. When the heat capacity of the empty sample cell and the weight of a sample are already known, the molar heat capacity of the sample can be calculated.

Step (7): The energy input command is issued from the program to TCS.

Step (8): Reading commands for DVM readings are generated by TCS. The computer receives these values from DVM and calculates the energy dissipated in the cell per 1 min. As Wang 600 is a data-entry-only device, a check is made whether the sign of entered data is positive or not. TCS assigns positive sign to the data from DVM and negative sign to the data from the ac double bridge. The positive sign means that the calorimeter heater is in on-state, and the input energy per 1 min must be added to give a total input energy and step (8) is repeated. In a case of negative sign the program will return to step (1) and the next cycle commences.

Calibration of the Thermometer

A platinum thermometer of 25 Ω ice-point resistance employed as working thermometer was calibrated against the laboratory standard thermometer certified at the US National Bureau of Standards according to the IPTS-68. The two thermometers were mounted in a massive copper block and the respective resistances were measured simultaneously at any fixed temperature. Since the standard thermometer is calibrated by d.c. method and since the value of resistance read with a.c. method is slightly different from that with d.c. method, the resistance of the standard thermometer was measured by Müller bridge (Leeds and Northrup, G-3), while that of the working thermometer with a.c. double bridge at fixed frequency of 390 Hz. An apparent resistance value including effects of lead impedance, self-heating and thermometer inductance *etc.* was related with IPTS-68 scale realized by the standard thermometer.

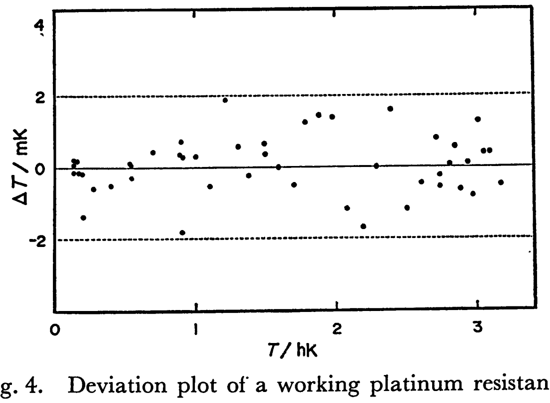

Fig. 4. Deviation plot of a working platinum resistance thermometer.

The resistance-temperature relation was established by measurements at eight fixed temperatures and by use of the interpolation formula according to the IPTS-68 in the temperature range from 13.81 to 320 K. The calibration table was given at an interval of 0.1 K and was stored in the casette tape. Figure 4 shows the deviations of the measured temperatures with use of the working thermometer from the IPTS-68 temperature scale.

Test Run for Cyclohexanol

The performance of the present automatic system was determined by measuring the heat capacity of cyclohexanol crystal. Table 1 reproduces a part of the experimental results taken with unattended operation for the low-temperature modification of cyclohexanol crystal. The bridge balance was taken at 0.94 Hz band width and the first data in an equilibration time was obtained usually about 4 min after an energy input. The notations A, B, E, C, D, G, H, and Y stand for resistance (in Ω), real time (in s), initial temperature (in K), heat capacity (in J K^{-1}), average temperature (in K), real time when an energy input was over, amount of input energy (in J) and the time duration of energy input (in s). A slight irregular variation of the bridge readings with time is not due to actual change of temperature but due to noise appearing in the thermometry circuits. This was confirmed by measuring the resistance of the thermometer with d.c. bridge. Difficulties of complete elimination of noise in the bridge circuitry lead us to take the method of averaging the latest six data points in determining an equilibrium temperature.

Figure 5 gives a graphical plot of the heat capacity data obtained for cyclohexanol crystal around liquid nitrogen temperature. In the figure, the filled circles represent the data obtained by the present automatic system with a.c. thermometry, while the open circles by the manual method with d.c. thermometry. Both of them coincide each other within 0.1% error. The accuracy of the calorimeter with d.c. thermometric technique has already been determined[11)] by the use of standard benzoic acid crystal recommended by the US Calorimetry Conference.[13)]

β-Relaxation Phenomenon of Cyclohexanol

A secondary (β) relaxation was observed[4)] in the glassy crystalline state of cyclohexanol by dielectric measurement. The dielectric loss peak associated with the β relaxation was much smaller than that of primary (α-relaxation responsible for glass transition around 150 K. A plot of logarithm of the frequency of maximum dielectric loss against reciprocal temperature gave a linear line for the β relaxation, in contrast to the nonlinear behavior for the α relaxation. Since the glass

TABLE 1. REPRODUCTION OF A PART OF THE EXPERIMENTAL HEAT CAPACITY DATA

5.709694	A	6.149571	A
4.079	B	7.211	B
5.709691	A	6.149571	A
4.112	B	7.244	B
5.709649	A	6.149571	A
4.174	B	7.277	B
5.709674	A	6.149571	A
4.207	B	7.309	B
5.709679	A	6.149571	A
4.241	B	7.343	B
5.709679	A	6.149571	A
4.284	B	7.376	B
85.554173	E	89.522641	E
22.5004	C	23.3444	C
84.533582	D	88.539411	D
11127.0	G	20300.0	G
45.918231	H	45.886583	H
1200	Y	1200	Y
5.931621	A	6.363621	A
5.700	B	8.812	B
5.931621	A	6.363628	A
5.733	B	8.845	B
5.931621	A	6.353628	A
5.766	B	8.878	B
5.931621	A	6.363621	A
5.799	B	8.911	B
5.931621	A	6.363624	A
5.832	B	8.944	B
5.931621	A	6.363624	A
5.865	B	8.977	B
87.556242	E	91.454699	E
22.9353	C	23.7501	C
86.555207	D	90.488670	D
13748.0	G	22951.0	G
45.904483	H	45.861427	H
1200	Y	1200	Y

transition temperature of cyclohexanol observed calorimetrically corresponded to the temperature at which the dielectric relaxation time of α relaxation becomes of the order of 10^3 s, we extrapolated simply the Arrhenius plot to the same time scale. The temperature at which the mode for the β relaxation is expected to be frozen in was about 75 K.

We have pointed out[4] already that the heat capacity of the glassy crystalline cyclohexanol started to deviate from that of low-temperature modification at around 70 K and the anomalous increase may be associated with the onset of motion responsible for the β relaxation. A close examination of the previous heat capacity data of cyclohexanol in that temperature region does not disclose any anomalous behavior in temperature drift. This may be due to rather large heat leakage arizing from incomplete adiabatic condition at that time. Since the techniques in realizing adiabatic condition have been much improved, we attempted to reinvestigate the thermal behavior of glassy crystalline cyclohexanol.

The glassy crystalline cyclohexanol was prepared by cooling the high-temperature modification with an average rate of -3 K min^{-1} in the temperature interval between 270 K and 90 K and the heat capacity measurements were initiated. Table 2 lists the heat capacity data relevant to the temperatures in problem. Series I is for the specimen cooled rapidly from 90 K to 20 K with the rate of -1 K min^{-1}, while series II is for annealed specimen at 64 K for about 40 h. These data are plotted in Fig. 6 in the form of excess heat capacities over that of low-temperature modification so as to exaggerate an anomalous behavior that may be encountered. Also shown below in the figure is the rate of temperature drift. Thermal equilibrium was attained usually during 4 or 5 min after turning off the calorimeter heating. At temperature around 60 K, a marked exothermic temperature drift was observed for quenched specimen. The drift changed into an endo-

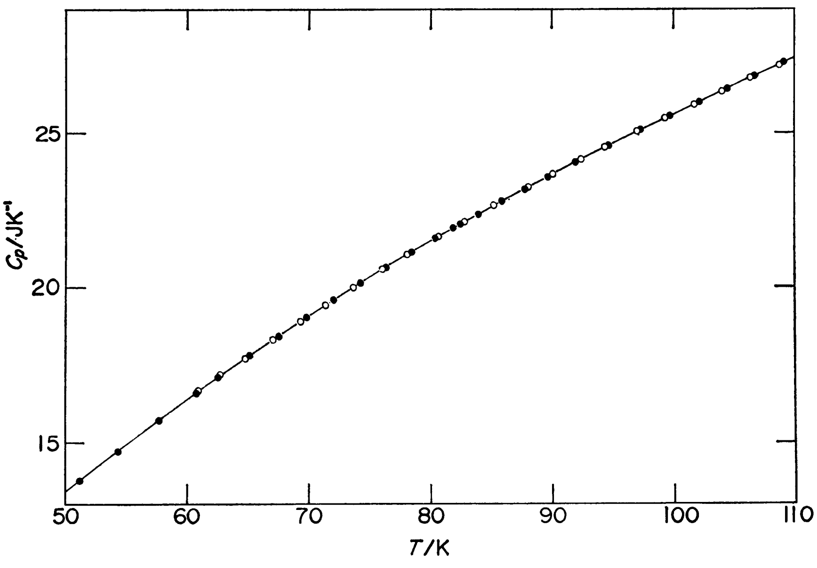

Fig. 5. Heat capacity curve of cyclohexanol crystal.
○: Measurement with d.c. thermometry, ●: measurement with a.c. thermometry.

Table 2. Heat capacities of cyclohexanol in glassy crystalline state

The samepl weight is 24.746 g. Series I is for the specimen cooled from 90 K to 20 K with the rate of -1 K min^{-1}. Series II is for the specimen annealed at 64 K for 40 h.

$\frac{T}{\text{K}}$	$\frac{C_s(\text{gl})}{\text{J K}^{-1}}$	$\frac{C_s(\text{c})}{\text{J K}^{-1}}$	$\frac{\Delta C_s}{\text{J K}^{-1}\,\text{mol}^{-1}}$
	Series I quenched specimen		
57.07	16.140	15.570	2.307
60.65	17.165	16.593	2.315
63.71	18.020	17.428	2.396
66.30	18.718	18.128	2.388
68.81	19.377	18.782	2.408
71.22	19.995	19.382	2.481
73.57	20.581	19.962	2.505
75.84	21.151	20.516	2.570
78.06	21.693	21.028	2.692
80.22	22.204	21.524	2.752
82.59	22.756	22.051	2.853
85.16	23.346	22.633	2.886
87.77	23.942	23.190	3.044
90.46	24.531	23.740	3.201
	Series II annealed specimen		
58.27	16.497	15.921	2.331
60.86	17.237	16.652	2.368
63.34	17.933	17.335	2.420
65.74	18.594	17.978	2.493
68.05	19.210	18.582	2.542
71.62	20.121	19.487	2.566
75.19	20.990	20.361	2.546
77.47	21.545	20.888	2.659
79.70	22.082	21.408	2.728
81.88	22.589	21.892	2.812
84.01	23.083	22.374	2.870
86.27	23.597	22.872	2.934

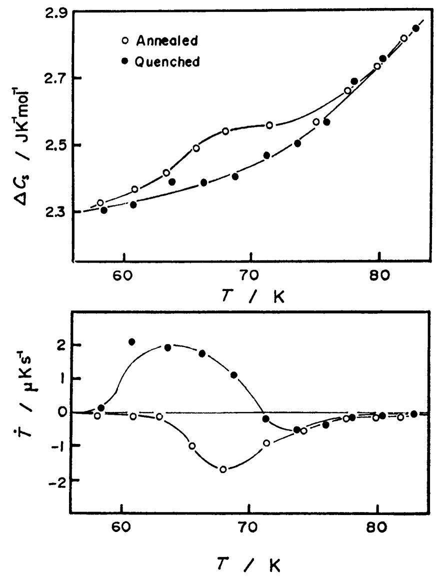

Fig. 6. Heat capacity curves of glassy crystalline cyclohexanol (above) and temperature drift rate (below). See Table 2 caption.
●: Series I (quenched specimen),
○: Series II (annealed specimen).

thermic one around 70 K on further heating and returned to normal behavior around 80 K. In this temperature interval, no energy-input command signal was issued during equilibration period and 30 data points were accumulated for each drift period. In the calculation of heat capacity, effect of the temperature drifts was treated as if they were arizen from thermal leakage.

While for the annealed specimen, a humped heat-capacity anomaly was observed and the corresponding temperature drift was endothermic in the relevant temperature interval. These thermal behavior are characteristic of a freezing phenomenon and it seems to be natural to ascribe these anomalies to the β relaxation.

Many explanations can be offered to account for the presence of secondary relaxation. We have discussed previously[4] the origin of the β relaxation of cyclohexanol crystal in terms of intramolecular motion of OH groups between two hydrogen-bonded states, in an analogous way with those traditionally invoked for polymer and molecular glasses.[14] Systematic studies[15] of a number of molecular glasses which lack either a side chain or any other internal degree of freedom have revealed a remarkable similarity in the dielectric relaxation of these glasses to those of polymers, and a surprizing uniform pattern of behavior. The conclusion drawn from the study was that the molecular mobility seen as β relaxation is intrinsic nature of the glassy state. Although a few models were proposed for the structure of amorphous solid that is consistent with the general occurrence of β relaxation phenomenon, there seems no experimental method that favors one of them. An accurate statistical mechanical approach to the description of thermodynamic and kinetic features of the frozen-in disordered system is highly desirable.

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