Equilibrium and non-equilibrium transitions studied by adiabatic calorimetry[1]

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Abstract

The principle and recent technical development of adiabatic low temperature calorimetry are described with experimental results taken mostly from the authors' laboratory. Topics on the equilibrium and quasi-equilibrium heat capacities include the separation of the Schottky heat capacity from the experimental data on bromo-hydroxyphenalenone and non-Debye excess heat capacity of a glassy hydrocarbon. Relaxation of glassy crystals of rubidium cyanide and C_{60} and stabilization of a supercooled phase of methylammonium hexachlorotellurate are discussed. A unique adiabatic calorimeter of top-loading construction recently completed in the authors' laboratory is described along with an experimental result on a glassy liquid prepared at a cooling rate 100 times greater than was possible with a calorimeter of the conventional design. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Adiabatic calorimetry was started about 100 years ago as an experimental method to determine the heat capacity of solids at low temperature. It provided the key experiments for the quantum hypothesis and for the third law of thermodynamics. After these early developments, it grew into a very specialized experimental method of chemical thermodynamics in 1940s, 1950s and 1960s. A large number of important papers were written by Aston [1], Clusius [2], Eucken [3], Furukawa [4], Giauque [5], Huffman [6], Johnston [7], Lange [8], Martin [9], McCullough [4], Morrison [10], Nernst [11], Seki [12], Southard [13], Staveley [14], Stout [15], Strelkov [16], Suga [12], Westrum [4] and many others as quoted in [4]. A general overview with historical comments was given by Gmelin [17]. In 1970s, the number of scientists engaged in adiabatic heat capacity calorimetry decreased sharply. The same trend continued in 1980s. This occurred for various reasons including shift of scientific interest among different fields, lack of funding for thermodynamic research and fast development in spectroscopic and other experimental methods. However, the highly specialized design and construction of the adiabatic calorimeter may have been one of the reasons for the decreased activity in this field. Only a small fraction of science students coming to the laboratory had the hand-skill and patience needed to construct and operate an adiabatic calorimeter. A typical adiabatic calorimeter has 40–50 thin (0.075 mm) electric wires running a long way in the cryostat, insulated electri-

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cally from each other and from the cryostat while in good thermal contact with various components of the cryostat. Familiarity with cryogenic and vacuum techniques is also a necessity for adiabatic calorimetry along with practical knowledge of weak signal electric circuit. These are skills not readily available in the era of convenient commercial instruments. In 1970s, 1980s and 1990s commercial instruments for various spectroscopic and diffraction experiments developed with a pace that exceeds by far the development in adiabatic calorimetry.

In spite of these drawbacks, some laboratories have continued to be active in low temperature adiabatic calorimetry. The aim of the heat capacity measurement has changed considerably over the past decades. Previously, determination of the third law entropy was of paramount importance. Also determination of a whole set of thermodynamic functions could be the reason for an elaborate calorimetric experiment. Today calorimetry is used in combination with other experimental methods such as X-ray diffraction, vibrational spectroscopy, electric and magnetic measurements and microscopy. To be useful in such applications, the calorimetric method has to be easy to use by unskilled experimenters. Automatic measurement, which was already conceived in 1957 [18] and became practical when personal computers arrived at university laboratories 15 years ago, is a substantial step toward this direction, even though this does not eliminate the requirement for various manual skills described above.

Problems involving absolute values of the entropy can be answered only by calorimetric experiments. What is the entropy of a particular glassy substance? This is a fundamental question about the structure of amorphous substances. To answer the question on the experimental side one has to prepare the glassy sample in the calorimeter. This often requires a new type of calorimeter. Time-dependent properties, previously outside the scope of calorimetry, have now become important topics of the low temperature calorimetry [19–21]. The glass transition of amorphous materials is routinely examined by DSC and compared with dielectric relaxation experiments at higher frequencies. The adiabatic calorimetry has the time window at longer times than DSC and appropriate for slower relaxations with a time constant of hours and days.

In the present article we describe recent technical developments in the experimental method of adiabatic calorimetry and results obtained by applying them to time-dependent measurements.

2. Adiabatic heat capacity calorimetry

In an adiabatic calorimeter, the sample sealed in a vacuum tight container is placed in an evacuated and temperature controlled environment in a cryostat. The temperature control is such that the heat leak to or from the sample is kept as small as possible all through the experiment. One starts the experiment by measuring the sample temperature for some time (e.g., 600 s). Then the sample is heated with an accurately measured amount of Joule energy (which takes 30–1000 s depending on the temperature). The temperature is measured again after the heating. The heat capacity of the sample and the sample cell is given by the ratio of the Joule energy to the temperature increment resulting from the heating. This method is called adiabatic even though the sample is heated by electric heating. It is because the heat is produced in the sample and not transferred through the boundary between the sample and the environment.

3. Experimental apparatus

To achieve a good measurement based on the adiabatic principle, one needs thermometry, electric energy measurement and adiabatic control all done precisely and accurately. The temperature is usually measured with a platinum or rhodium–iron resistance thermometer of nominal resistance of 27 Ω at 273 K calibrated on the International Temperature Scale 90. The largest improvement in the current calorimeters over the former ones (of 20 years back) is the automatic resistance thermometry available now[2]. The AC resistance bridge is stable against instrument aging, tolerant to ambient condition changes and immune to stray thermal EMFs. The basic resolution is 1 in 3 million corresponding to a temperature resolution of 0.1 mK. By the averaging capability of an automatic

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[2]Manufactured by Automatic System Laboratory, and Tinsley, UK.

measurement the resolution could be 0.05 mK. The random error in the heat capacity arising from the resolution of the temperature measurement is typically 0.01%, assuming that we heat the sample by 1 K for one determination of the heat capacity. The Joule energy supplied to the sample is measured with a digital voltmeter to an accuracy that easily exceeds the accuracy of thermometry. This is because the determination of the heat capacity involves the temperature increment by which we lose two to three significant numbers of the raw temperature data while we retain the whole significant numbers of the energy measurement. The stable, reproducible and computer controlled thermometry with a self-balancing AC bridge is the most important feature of a modern adiabatic calorimeter.

The energy measurement consists of the voltage and current measurements and the measurement of the time interval of the heating. The quartz clock of a computer, with the time delay arising from the computer program being taken into account, is accurate for our purpose in which the time interval to be measured is 30–1000 s. Power supplies now commercially available are sufficiently stable as the current source for heating the sample. The sample is a material of any physical form, crystals, powder or liquid of a volume 1–5 cm^3, sealed in the cell.

The adiabatic control is the most intricate part of the experiment, but the principle is simple. Heat transfer between the sample cell and the environment takes place through radiation, conduction through electrical lead wires and residual gas. In principle these thermal paths are eliminated if the sample cell is surrounded by a shield held at the same temperature as the cell. In an actual calorimeter, the adiabatic shield is powered with a heater controlled by the signal from a differential thermocouple bridging the sample cell and the shield. With a typical zero stability of 0.1 μV of the amplifier in the temperature control, the shield can be kept within 3 mK of the temperature of the cell. However, because of its large surface area the temperature of the shield can be non-uniform. Also heat conduction through the leads adds to the temperature non-uniformity. The design (uniform distribution of the heating wire over the shield and the location of the thermocouple and the binding post of the leads to the thermometer and sample heater) of the shield is very important. The temperature uniformity is improved by

controlling the temperature of the shield in several (usually three) parts. Uniform distribution of the heating wire over the metallic part of the cell is also important. This ensures uniform generation of heat in the cell during the heating, effectively decreasing the equilibrating time within the cell. It is an important characteristic of a calorimeter when we measure a relaxational effect discussed below. In an apparatus designed and constructed with attention paid to these details, the residual heat leak can be such that the drift rate of the sample temperature is less than 10 mK/h at most of the temperature above 25 K. At lower temperatures, the sensitivity of the thermocouple decreases and the heat capacity of the sample and the cell also decreases. Both contribute to an increased temperature drift rate. At higher temperatures (above the room temperature), desorption of gas from the cryostat material can be a problem in the form of an additional thermal path between the cell and the shield. This can be avoided by degassing the cryostat prior to the heat capacity measurement. Actual temperature drift curves are shown in Fig. 1. These curves were recorded during the measurement of the heat capacity of rubidium cyanide [22]. If the sample
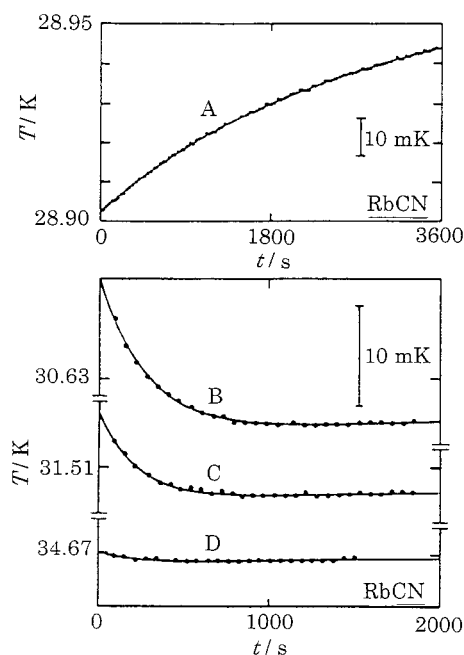

Fig. 1. Temperature drift curves recorded around the glass transition temperature of rubidium cyanide [22].

behaves in a normal manner, with no relaxational property involved, the temperature drift follows curve D of Fig. 1 converging rapidly to the final equilibrium value. Other drift curves are explained later.

4. The equilibrium heat capacity

The internal energy of a solid is carried by vibrational and configurational degrees of freedom. The heat capacity can be decomposed into the two components in the same way. The first is always present. The latter occurs in disordered solids. One is often interested in the configurational part and, to evaluate it, one subtracts from the experimental values the vibrational part estimated by various means. It frequently happens that such analysis is problematic because the vibrational heat capacity accounts for the most of the experimental value, with only a small part coming from the interesting degrees of freedom of the substance. Some years ago we wrote a computer program for evaluation of the vibrational heat capacity in the quasi-harmonic approximation. The program finds the Debye and Einstein temperatures that best reproduce the experimental heat capacity using, as auxiliary data, spectroscopically known normal mode frequencies of the substance under study. An innovation introduced in this analysis was to recognize that the characteristic temperatures derived by the fitting should be independent of the data set used in the fitting [23]. This requirement limits the range of the possible model heat capacity function. We used this procedure to evaluate the tunnel splitting energy of a proton in a hydrogen bonded crystal bromo-hydroxyphenalenone [24]. Fig. 2 shows the Schottky heat capacity due to the extra energy level derived from the experimental data. Because of its small magnitude, the extra heat capacity could be separated from the vibrational part only by the systematic procedure. In Fig. 3 we plot the optimum Debye and Einstein temperatures against the temperature of the upper end of the data set used to determine the characteristic temperatures (the temperature of the lower end was fixed at 13 K). We see that the characteristic temperatures thus determined are constant enough to be truly characteristic of the substance.

An amorphous substance at low temperature is not in thermal equilibrium by itself and changes gradually
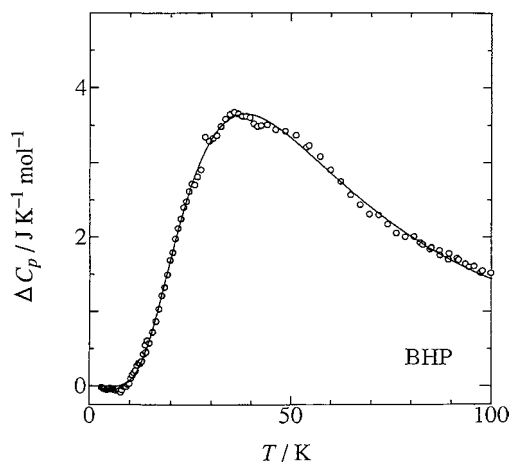

Fig. 2. Schottky heat capacity of a tunneling proton in bromo-hydroxyphenalenone [24].

when annealed near the glass transition temperature. However, it remains unchanged at low enough temperature practically indefinitely. For substances in such a state, we can define and measure their heat capacity as if they were in thermal equilibrium. The low temperature heat capacity of amorphous substances is of interest because the high absolute accuracy of the calorimetric data (admittedly with the lack of specificity about the molecular energy) complements nicely with the spectroscopic data. The latter is specific with respect to the molecular energy scale but devoid of information about the number of vibrational
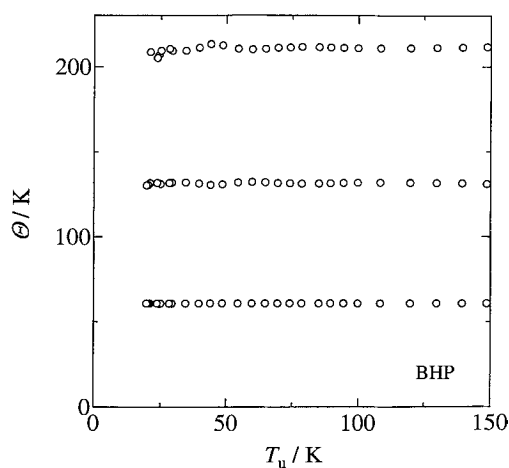

Fig. 3. Debye and Einstein temperatures of bromo-hydroxyphenalenone versus variation of the data set used in the fitting [24].
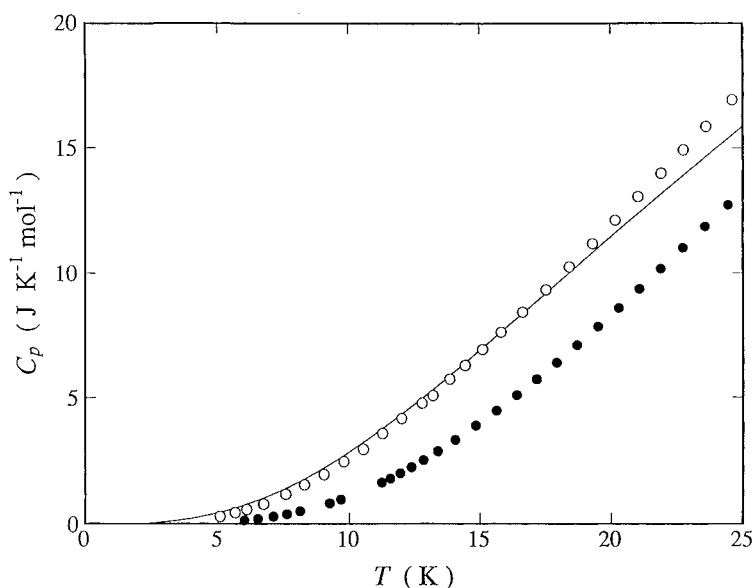
Fig. 4. Heat capacity of crystalline (filled circles) and amorphous 1-butene [25].

modes involved in spectroscopically observed transitions. The number of modes is a trivial problem for a crystal because of the periodicity of the structure. But it is essential for an amorphous substance. Fig. 4 shows that the heat capacities of amorphous and crystalline 1-butene [25]. The heat capacity of the amorphous phase greatly exceeds the normal Debye heat capacity of the crystalline phase. The excess part is attributed to local vibrations (the low energy excitations) of the disordered structural unit. For this substance the neutron scattering spectra gave the energy of the excess phonons while the heat capacity gave the absolute value of the excess density of state. By combining these two we described the dynamics of amorphous material in detail [26]. The equilibrium and quasi-equilibrium heat capacities thus give useful information not easily available in other quantities.

5. Time-dependent measurement by an adiabatic calorimeter

A time-dependent effect in the heat capacity measurement was first noticed by Giauque and Stout [27] when they studied ice in their calorimeter. They found slow thermal equilibrium around 90 K. The effect was later studied using a calorimeter equipped with a temperature controlled (as opposed to 'floating') adiabatic shield [28]. This allowed the authors to follow the sample temperature quantitatively for a longer time (more than 20 days) as it approached thermal equilibrium. The adiabatic calorimeter worked in this case as a time domain spectrometer with a time window of up to a month. The lower limit of the window is determined by the time constant of thermal equilibration in the sample cell. This is 30–120 s in our calorimeter, depending on the sample and the temperature. Fig. 1, curve D, reproduces a normal equilibration behavior of the sample cell.

If a slow relaxation takes place in the sample with the relaxation time longer than the characteristic time of the cell, it appears as a curved temperature–time relation as plotted in curves A–C in Fig. 1 [22]. We note here that the thermometer of the calorimeter measures the temperature of the vibrational degrees of freedom. These degrees of freedom reach thermal equilibrium within itself instantaneously. The configurational degrees of freedom can be much slower in equilibration and may lag behind the vibrational degrees. It is often assumed (but may not be strictly correct), that the configurational state can be described by a temperature (the fictive temperature). The slope of the curves (A–D) is determined by the sign of the deviation of the vibrational and configurational fictive
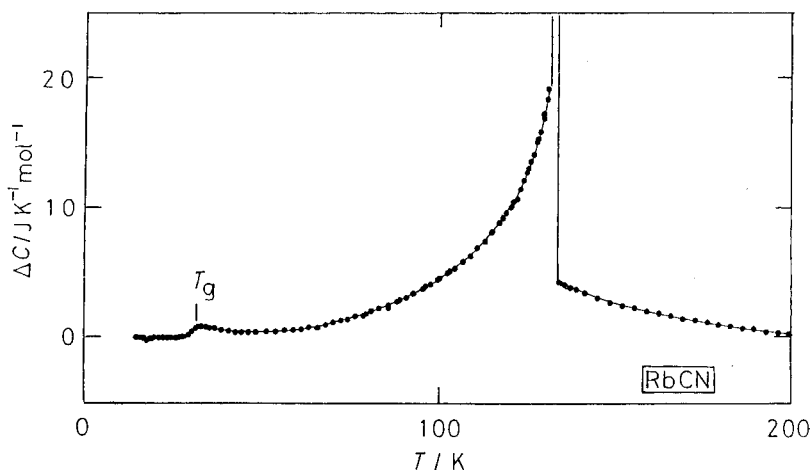
Fig. 5. Excess heat capacity due to the glass transition and phase transition in rubidium cyanide [22].

temperatures. (The heat leakage was negligible in this case.) If the vibrational temperature is lower than the configurational, then the temperature drift curve is positive. In the opposite case the drift will be negative. Curve A of Fig. 1 shows the first case and B and C the second. The theoretical curves reproducing the experimental points in Fig. 1 were calculated using a single exponential function for each of the temperatures. The relaxation time determined by the calorimetric method is close to those determined by dielectric measurement for RbCN.

In the same approximation, the temperature drift rate as a function of the temperature can be analyzed for the relaxation time determined at each temperature. This was first done for a proton order–disorder system, tin dichloride dihydrate [29]. The enthalpy versus temperature diagram first constructed and utilized in the analysis turned out to be useful for any relaxing systems and has been used in extremely nonlinear cases as well. The relation between the relaxation times from dielectric and calorimetric measurements has been discussed by Jeong [30] at the Seminar.

If one can detect a relaxational effect (i.e., a glass transition) by an adiabatic calorimeter, it means that the configurational degrees of freedom carries a part of internal energy. That this is by no means obvious will be understood if one recalls that the most basic mechanism of dielectric relaxation (the Debye dipoles reorienting independently) does not involve thermal or configurational energy. For RbCN, the experimental heat capacity definitely has an extra contribution above the glass transition temperature [22]. In this respect the glass transition is useful for determination of the vibrational base line of the heat capacity because we are sure that the heat capacity below the glass transition temperature comes solely from the vibrational degrees of freedom. Fig. 5 shows the excess heat capacity determined by the base line extrapolated from below the glass transition using the Debye and Einstein functions.
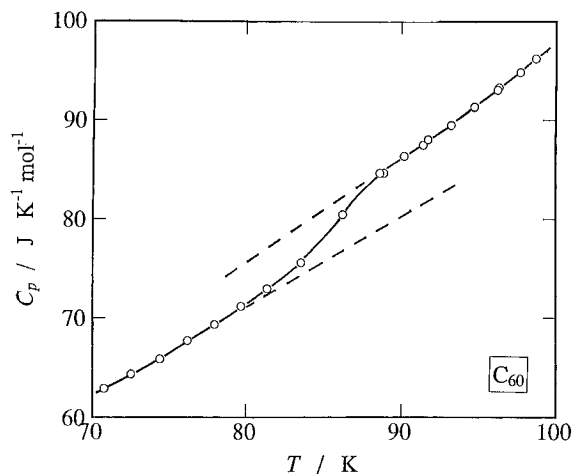

Fig. 6. Heat capacity anomaly of C_{60} at the glass transition [31].
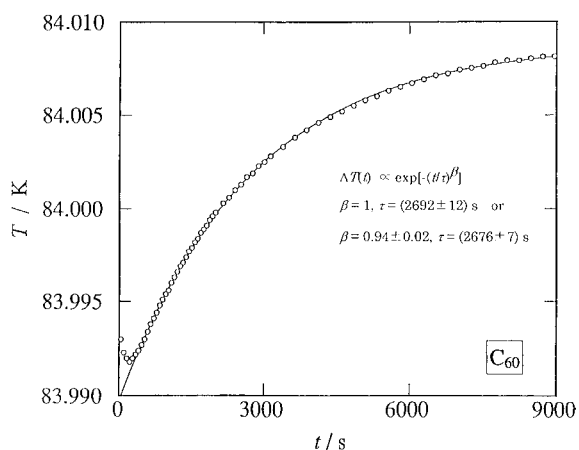
Fig. 7. Spontaneous heating of C_{60} compared with single τ and stretched exponential functions [31].

As a seemingly rigid crystal such as RbCN undergoes a phase transition and relaxational transition, so does the crystal formed by the most symmetric molecule, C_{60}, undergoes an order–disorder transition and a glass transition of a different nature. Figs. 6 and 7 show the heat capacity around the glass transition and spontaneous heating curve of C_{60} [31]. We notice that the single exponential curve is very closely followed by the exothermic curve. The configurations involved in this relaxation are the different orientations of the molecule relative to the crystal axis. This situation is different from that of RbCN where the mutual orientations of the CN ions is responsible for the configurational energy. At lower temperatures where the configurational degrees of freedom is frozen, the heat capacity is solely vibrational. We combined our data on C_{60} with those for lower temperatures from [32] and analyzed by the method described above and obtained (42.6±0.4) and (53.4±0.4) K for the Debye and Einstein temperatures each representing three degrees of freedom (Fig. 8). The experimental data are reproduced well, giving a certain degree of physical significance to these parameters.

In some crystals, a phase transition does not occur at the temperature where the two phases have the same free energy. The high temperature phase supercools to some extent and then suddenly stabilizes to the low temperature phase. Thermodynamics tells only that the phase of the higher Gibbs energy changes to the phase of the lower Gibbs energy. The actual process is complicated by nucleation, growth, interfacial energy and other factors. In methylammonium hexachlorotellurate [33], the stabilization proceeds in a particularly unusual way. We studied this substance in relation to orientational order–disorder changes along with analogous hexabromotellurate and hexaiodotellurate. But it turned out to be of interest from the kinetics of the transformation as well. When the substance (the hexachlorotellurate) in the ambient temperature phase was cooled to a temperature where it is metastable, it converted to the stable phase by small discrete steps. The process was followed by
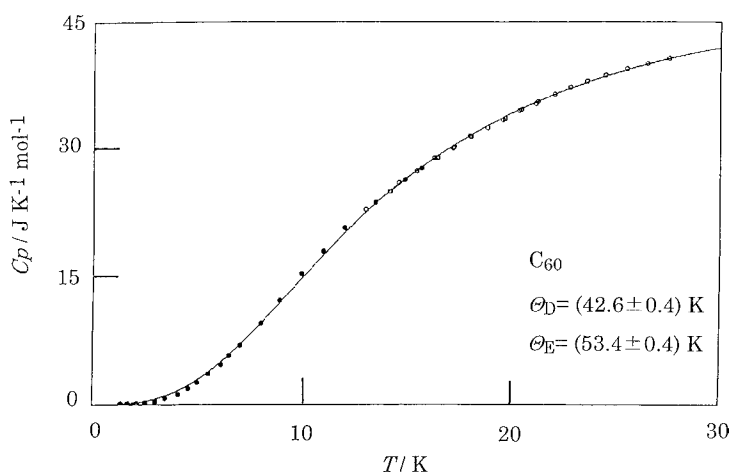

Fig. 8. Low temperature heat capacity of C_{60} compared with the best fit harmonic heat capacity functions. Data from [31,32].
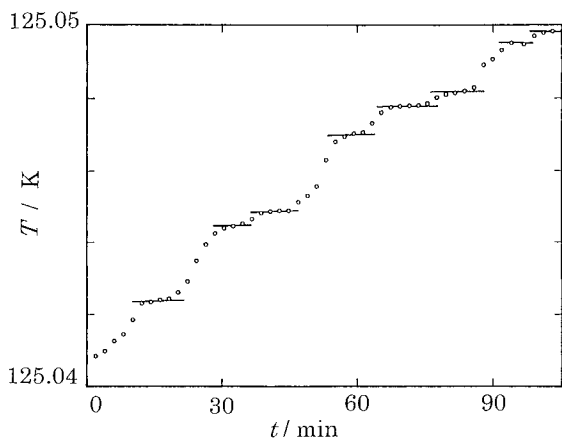
Fig. 9. Spontaneous heating of methylammonium hexachlorotel-lurate proceeding in steps of ca. 1 mK corresponding to 2.5 mg of the crystal [33].

measuring the temperature of the sample kept in thermal isolation. As Fig. 9 shows the temperature increased in steps of a size of about 1 mK. A 1 mK step of the temperature was equivalent to 2.5 mg of the crystal changing from the high temperature to the low temperature phase. The crystal transformed in discrete units of this size for an unknown reason. It was also found that when the heat evolution plotted in Fig. 9 finally ceased, the sample was not yet fully in the low temperature phase. By further (super)cooling, we could transform the remaining high temperature phase to the low temperature phase until, at a sufficiently low temperature, the whole sample transformed. Such martensitic behavior was also found in tetrapotassium hexacyanoferrate trihydrate [34]. The two crystals are common in having a layered structure. This structural feature may be involved in the peculiar kinetics of the transformation.

6. Relaxation in glassy liquids

The relaxation of a liquid toward equilibrium is commonly studied by dielectric spectroscopy and frequency dependent heat capacity. The relaxation time, single or distributed, describes the response of the sample adequately. However, the temperature dependence of the relaxation time does not follow a simple Arrhenius plot. This is because the liquid becomes more and more structured as the temperature

decreases. At low temperatures the relaxation time increase more than the Arrhenius equation predicts. One recognizes a possible connection between the non-Arrhenius behavior and the configurational entropy of the liquid. Roughly speaking, a more structured liquid means a smaller entropy and longer relaxation time. This idea has been expressed in the Adam–Gibbs theory of the relaxation time. Since the heat capacity gives the temperature dependence of the configurational entropy, the implied connection between the equilibrium (entropy) and kinetic (relaxation time) parameters can be tested by combining the calorimetric and relaxational data. Fig. 10 shows the plot of the logarithm of the dielectric relaxation time of 3-bromopentane against the Adam–Gibbs parameter consisting of the configurational entropy and the temperature [35]. We see a linear relation between these quantities over a wide temperature range, covering 12 decades of the relaxation time. The same data produces a heavily curved $\ln(\tau)$ versus $1/T$ relation in the Arrhenius plot. Formation of the local structure in this liquid is clearly reflected in the heat capacity curve given in Fig. 11 where one notices a very large heat capacity of the normal and supercooled liquids compared with that of the solid.

7. An adiabatic calorimeter designed for measurement on frozen unstable phase – top loading adiabatic calorimeter

When we study time-dependent properties, the substance we deal with have been decided more or less by chance. In rubidium cyanide, the rate of reorientation of the cyanide ion became comparable with the calorimetric experimental time at 30 K. In other substances discussed above the situation is the same. We detected a time-dependent effect by the temperature measurement when the relaxation time of the process came in the time window of the calorimeter. Once we found the occurrence of a time-dependent effect by the precise thermometry, we varied the experimental parameters (the cooling rate, annealing conditions) within a certain range to further characterize the kinetic process. This type of experiment has broadened the realm of adiabatic calorimetry from the traditional measurement of equilibrium thermal properties to include the kinetics of the equilibra-
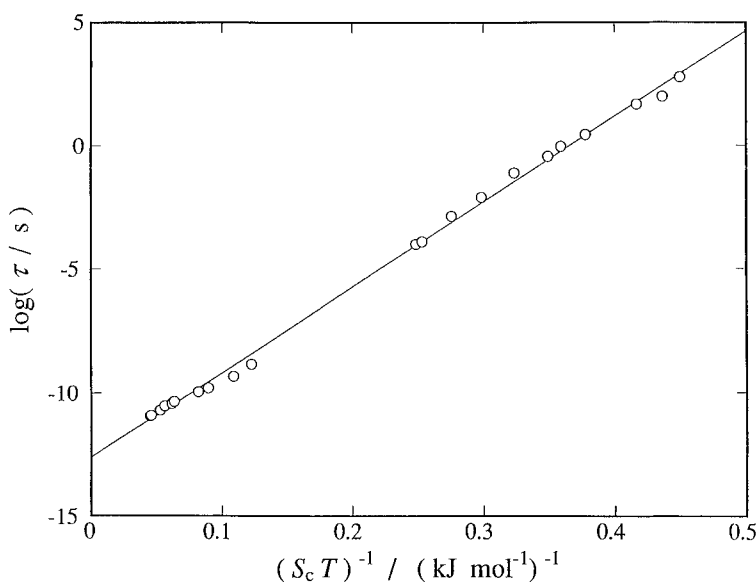
Fig. 10. Adam–Gibbs plot of the relaxation time of 3-bromopentane [35].

tion. However, it has been still limited with respect to the substance which we can be studied by this method. In order to further broaden the scope of calorimetric experiments, we constructed a top-loading adiabatic calorimeter. The limitation of a traditional adiabatic calorimeter with respect to the sample that can be studied comes from the fact that the sample is necessarily placed at the ambient temperature for several hours. In setting up an experiment, we put the sample in the cell, mount the cell in the cryostat and fix the

Fig. 11. The heat capacity of 3-bromopentane in liquid, crystal, supercooled liquid and glassy states [35].

adiabatic shield, with all the electric leads and thermocouple junctions to be soldered and fixed in place. Then we close the vacuum and evacuate it. If one is interested in studying the kinetic effects that take place above room temperature, the traditional adiabatic calorimeter is perfectly adequate. But kinetic effects below the room temperature can be studied only if the sample can be brought off-equilibrium by the mild cooling rate available in the ordinary adiabatic calorimeter.

We circumvented this difficulty by separating the calorimeter into a center stick and the cryostat [36]. As shown in Fig. 12 the center stick is a length of stainless steel tube. At the lower end of the stick is attached the sample cell. The cell can be filled and sealed with an indium gasket at liquid nitrogen temperature. It can also be filled at ambient temperature and then rapidly cooled by plunging into liquid nitrogen. The center stick, with the frozen unstable sample attached, is then inserted into the precooled cryostat. This takes less than 30 s. Throughout the set up of the experiment, the sample remains below 80 K. Thus, a glassy sample prepared, e.g., by pouring a liquid onto a copper slab cooled to 77 K can be set up in the calorimeter without suffering stabilization.

We studied the glass transition of a 1:1 mixture of propanediol and propanediamine with this calori-
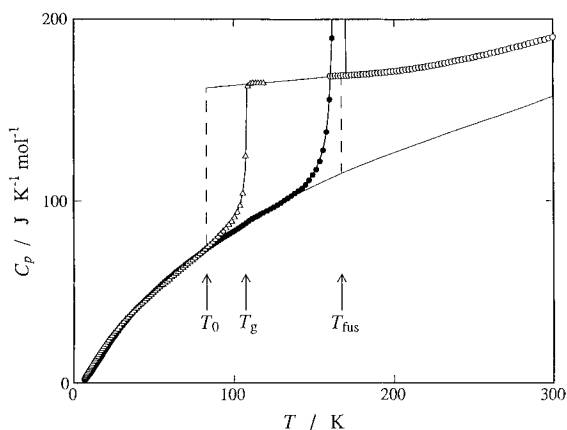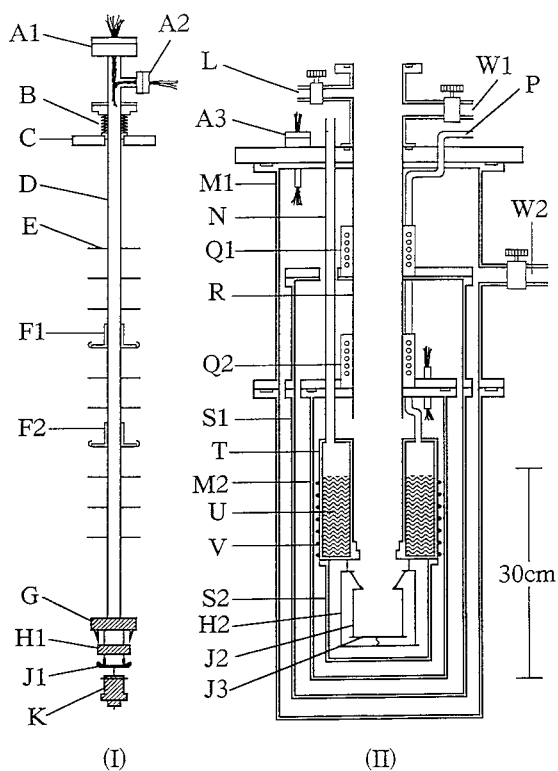
Fig. 12. A top-loading calorimeter [36]. A(1–3): Feed-through of the electric leads; B: bellows; C: vacuum flange; D: stainless steel tube; E: radiation buffle; F(1,2): thermal contacts; G: thermal contact to the helium tank; H(1,2): outer shield; J(1–3): parts of inner radiation shield; K: sample cell; L: helium curtain port; M(1,2): vacuum can; N: liquid helium inlet; P: helium exhaust outlet; Q(1,2): heat exchangers; R: Central channel; S(1,2): radiation enclosures; T: helium tank; U: liquid helium; V: heater; W(1,2): evacuation ports.

meter. The result summarized in the enthalpy–temperature diagram is shown in Fig. 13. It compares the glassy samples prepared at three cooling rates. The rapidly quenched glass could be prepared only in the present calorimeter. The others (normally quenched and slow quenched) were also prepared in the same calorimeter but they could well be prepared in a conventional calorimeter. We have just started doing experiments with the new apparatus. We found (1) the large excess enthalpy retained in RQG, and (2) the enthalpy relaxation starting more than 50 K below the glass transition temperature. These results are already different at this preliminary stage from what we know about the glassy state from our previous experiments using traditional calorimeters.
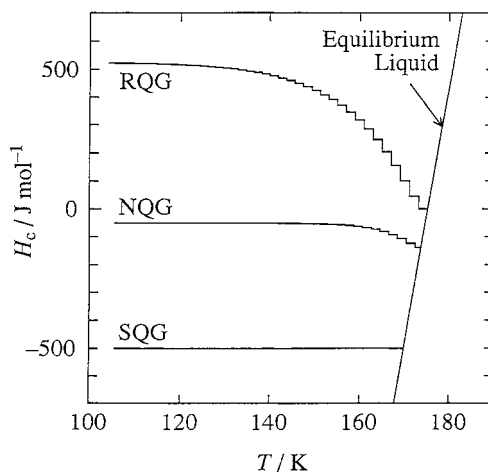

Fig. 13. Excess enthalpy of glassy mixture (1:1) of propanediol and propanediamine [36].

8. Conclusion

The adiabatic calorimeter has a unique capability of producing heat capacity data over a wide range of temperature from 5 to above 373 K with a relatively uniform accuracy and sensitivity. The configurational relaxation time of a substance changes vastly in this temperature interval. At the temperature where the relaxation time coincides with the time window of the calorimeter, we find a time-dependent effect in the calorimetric experiment. By analyzing the enthalpy relaxation effect, we can derive kinetic parameters that may be interpreted in terms of molecular quantities. A calorimeter in which we can prepare samples strongly deviating from thermal equilibrium has been constructed. The new apparatus broadens the area of calorimetric investigation to substances and phases in extreme states not attained with previous calorimeters. It is hoped that the several examples discussed above are persuasive that adiabatic calorimetry rewards those who have the patience and the trained hand-skill needed for its operation with the unique experimental results which it generates.

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