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RECENT DEVELOPMENTS IN EXPERIMENTAL METHODS FOR HEAT-CAPACITY MEASUREMENTS

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Abstract—Recent significant advances in the experimental methods of heat-capacity measurement are surveyed in this review. Among them, laser-flash calorimetry and the high-resolution heat-capacity calorimeter, both of which have been developed in Japan, are discussed in some detail. The former is applied for measuring the heat capacity of small samples in the range 80–800°K with an imprecision of ±0.5% or less, and up to 1100°K with but slightly more imprecision. The latter enables to determine the heat capacity in the vicinity of phase transition with a temperature resolution within 3 μK, and an imprecision of ±0.05% or less in the heat capacity. Some of the recent results obtained by these techniques are also presented.

1. INTRODUCTION

In recent years several significant advances have been seen in calorimetric techniques, particularly in heat-capacity measurements, some of which made use of novel concepts and techniques. Before proceeding to the specified topics, it is worth while to survey briefly the general trend of the development of experimental methods.

The conventional adiabatic calorimetry has been well developed and the heat capacity of materials is determined with the sufficient precision and accuracy over the range of 0.3–600°K, and with somewhat more difficulty up to 1500°K. The endeavors to develop new experimental methods, which have been reported recently, extend the potential of calorimetric measurement in many respects. The main objects in these studies may be summarized as follows:

(1) To obtain reliable heat-capacity data with better precision and accuracy over a wider temperature range, particularly above 600°K.

(2) Measurement of heat capacity under extraordinary conditions, such as at very low or very high temperatures, under high pressures etc.

(3) High resolution measurement of heat capacity in the vicinity of phase transitions.

(4) Measurements on samples of small mass (less than 1 g).

Among the experimental methods adopted in these studies, a.c. calorimetry and pulse-heating methods have aroused interests, while refinements of conventional d.c. calorimetry showed some successful results.

The a.c. calorimetry, developed by Sullivan and Seidel[1] has shown its usefulness in the study of critical phenomena as this method affords very high resolution in the heat capacity. With this method magnetic and electric transitions of nickel, chromium, strontium titanate and sodium nitrite were studied in several laboratories[2–5] with success. As this method seems to have already established a good reputation, the great promise of this method in studying the effect of magnetic fields[2] and of high pressures[6] on the heat capacity is only noted here in passing.

The method of high-speed measurement of heat capacity of metallic materials at very high temperatures, developed by Cezairliyan *et al.*[7], is one of the most successful developments of the pulse-heating method. This method is based on rapid self-heating of the specimen by the passage of electrical current through it to very high temperatures in less than one second. The heat capacity of the specimen can be determined over a temperature range from 1500–3600°K with an experimental error of ±2% at 2000°K and of ±3% at 2800°K. Although it can be applied only to metallic and machinable samples, fairly good precision of the measurement at such high temperatures should be emphasized. Pulse heating by d.c. current of 10^{-4} sec duration on thin wires of metallic samples was also employed for heat-capacity measurements under very high pressures up to 10 GPa.[8,9] A method of pulse heating employing an electron beam as the heat source was also reported.[10]

Laser-flash calorimetry[11] is also classified as a pulse-heating method, with a flash of a ruby laser as the heat source. However, this method differs from other methods of pulse heating in being capable of measuring samples of both metallic and ceramic (insulating) materials. The temperature range of applicability is not necessarily limited to high temperatures, and satisfactory results have been obtained at temperatures from 80–1100°K[12], as described later. Laser energy was used[13] as the heat source also in the cryogenic region, from 2–20°K. One of the advantages of these methods is that the mass of the samples required for the measurement is small. Recently, Bachmann *et al.*[14] reported a new calorimeter for very small samples (1 ~ 500 mg) in the range 1 ~ 35°K, using the thermal relaxation technique.

A new calorimeter for measuring the heat capacity of small samples by ordinary adiabatic measurement was developed in USSR.[15,16] They used a calorimeter having a capacity of 0.3 cm^3. The heat capacity of benzoic acid was measured with an experimental error of ±0.2 ~ 0.3% from 12–300°K. Another important advance in ordinary adiabatic calorimetry is the development of the high resolution calorimeter by Seki and his group,[17] which will be described later.

In this presentation the author would like to explain in more detail both laser-flash calorimetry and the high resolution heat-capacity calorimeter, which have been developed in Japan and which have aroused wide interest.

2. LASER-FLASH CALORIMETRY

The use of laser-flash technique for the determination of heat capacity has aroused interest, because this technique can be applied to measurements over such a wide temperature range, i.e. from 80–1100°K. Thus far precise measurements of heat capacity including enthalpies of transition have been made by adiabatic

calorimetry at temperatures below 600°K, and by drop calorimetry at higher temperatures. Laser-flash calorimetry bridges with sufficient precision the ranges covered with these normal techniques by the use of only one apparatus. This method also has an advantage that it requires much smaller quantities of sample (0.03 ~ 5 g) than other methods.

The flash method for measuring the thermal properties including heat capacity as well as thermal diffusivity was first proposed by Parker *et al.*[18] in 1961. Since then, the flash method has become known as a convenient method for measuring thermal diffusivity at high temperatures. It was recognized earlier that one of the advantages of this method was to give heat capacity and thermal diffusivity data simultaneously. In fact, several papers[19,20] have been published which gave the heat capacity data as a means to obtaining thermal conductivity values.

However, the advantages of this method in heat-capacity measurement have been offset in many of the past studies by the unreliability of the resulting values as compared with those obtained by other methods. The discrepancy of the data obtained by the laser-flash method may be associated with a number of problems encountered with the method. The main difficulties were in making adjustment of the differences in the reflectivity of the surfaces of the samples and in obtaining accurate measurement of the energy of the laser flash.

We have endeavored[11,12,21,22] for several years to solve these problems, and now we believe that this technique is quite effective for measuring the heat capacity of materials over a wide temperature range. The details of this technique will be given below.

Apparatus for laser-flash calorimetry and the use of an absorbing disk

The apparatus of laser-flash calorimetry for the heat capacity measurement is shown in Figs. 1 and 2. Samples to be measured are in the form of a small disk pellet, 8 ~ 12 mm in diameter and 0.5 ~ 5 mm thick. Powdered samples are encapsulated in an aluminium container of the same size as above. The mass of the sample necessary for the measurement is 0.03 ~ 5 g. On the front surface of the sample, a thin plate of "absorbing disk" is attached.

The absorbing disk is made of a 50 mg disk of Glassy Carbon about 12 mm in diameter and 0.2 mm thick. It is attached to the sample surface with a very small amount (~1 mg) of silver paste or silicone grease, and plays the role of absorbing the impinged laser energy.

The use of the absorbing disk has several advantages:

(1) The differences in absorption efficiency of laser energy which are caused by the variant emissivity (reflectivity) of different samples can be avoided by the use of the absorbing disk. This makes it possible to determine the absolute heat capacity of the sample.

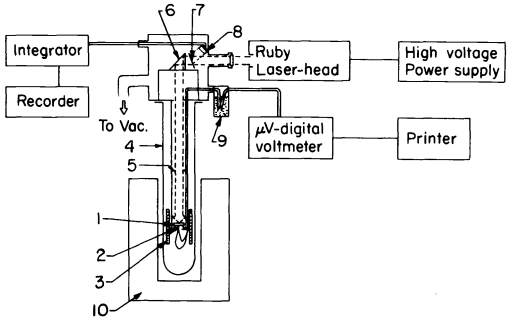

Fig. 1. Schematic diagram of apparatus of laser-flash calorimeter[11]: (1) sample, (2) thermocouple, (3) internal heater, (4) quartz container, (5) adjusting slit, (6) prism, (7) reflecting glass, (8) Si-photoelectric cell, (9) ice bath, (10) outer heater or liq. N_2 bath.

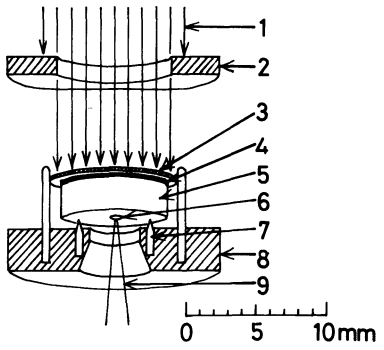

Fig. 2. Sketch of sample and its holding assembly;[23] (1) laser beam, (2) slit, (3) absorbing disk, (4) grease, (5) sample, (6) quartz pin, (7) sample holder, (8) silver paste, (9) thermocouple wire.

(2) It has been pointed out that for the samples with phase transitions, the heat capacity determination by laser flash method is difficult in the temperature region of the transitions, because the front surface of the sample is heated up markedly at the moment of the laser irradiation, from a temperature below transition to one above transition. Then, it is cooled down very quickly, again through transition from high to low temperature, by heat-transfer to inside the sample. By the use of the absorbing disk, this intense increase of temperature occurs only at the surface of glassy carbon, thus the sudden up-and-down temperature cycle through the transition can be avoided. Furthermore, because of the improvement of the precision in the measurement of temperature, the increment of temperature by a laser pulse can be chosen as small as 0.5°K or less in the transition region. The improved method has been proved experimentally to be capable of determining the heat-capacity anomaly fairly precisely. Examples will be shown later on the magnetic transitions of uranium monophosphide at 121°K.[12]

The most important components of the measurement of heat capacity are the precise measurements of the sample temperature and its increment, and of the energy applied to the sample.

In this method, the temperature rise of the sample is detected with a copper-constantan or a chromel-constantan thermocouple, attached to the back surface of the sample with silver paste. The electromotive force of the thermocouple is measured by a high-precision digital micro-voltmeter with a precision of $\pm 0.1\,\mu$V, and is recorded by a digital printer twice a second.

The maximum temperature rise of the sample, ΔT_m, is determined from the graphical plotting of the e.m.f., as shown in Fig. 3. In the measurement of ΔT_m, it is essential that the heat loss from the sample be minimized. In order to minimize the heat loss through conduction along the thermocouple, wires of 0.05 mm in diameter were used. The sample was held in a holder made of quartz, designed to minimize the contact with the sample, as shown in Fig. 2. The experimental error in the measurement of ΔT_m is estimated to be within ±0.2% for the pellets. For a sample of powder form, encapsulated in an aluminium container, a longer time duration is required to determine ΔT_m by extrapolation, as the thermal conduction within the sample powder is rather poor. In this case, a plot of log ΔT vs time elapsed gives better extrapolation.

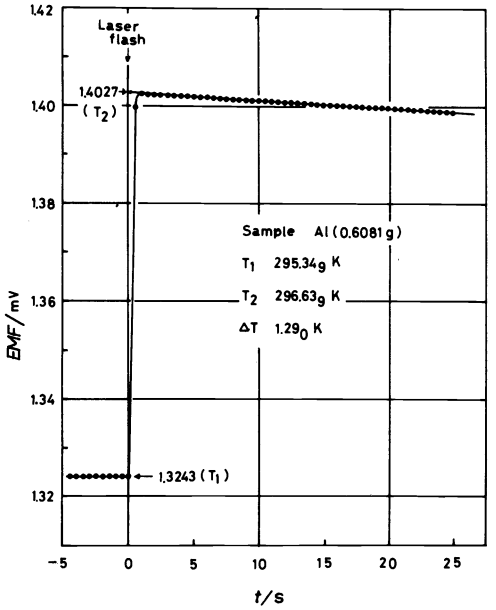

Fig. 3. Determination of maximum temperature rise[24] for 0.6081 g aluminium sample.

In order to determine the energy of the laser flash in each run of the measurement, a certain portion (several per cent) of the flashed laser beam is reflected by a glass plate on a Si-photoelectric cell. The amount of energy absorbed by the Si-photoelectric cell is indicated by an electronic digital integrator. The output of the integrator is assumed to be in linear relation to the energy absorbed by the absorbing disk. This was confirmed experimentally and is shown in Fig. 4. The imprecision of the energy determination is estimated to be ±0.2% or less.

The molar heat capacity of the sample, C_p (cal mol^{-1} K^{-1}) is given by

$$C_p = \frac{1}{m}\left(\frac{E}{\Delta T_m} - C\right), \qquad (1)$$

where E is the total energy of the laser flash absorbed by the absorbing disk and the sample (cal), m the quantity of the sample (mol), and C the heat capacity of the absorbing disk (cal K^{-1}). The heat capacities of silver paste or silicone grease, of the thermocouple, and of the aluminium container if it is used, should be included in the term C. The term C represents less than 5% of the total for pelleted samples, whereas it may be up to 40% for encapsulated samples.

The over-all imprecision in the determination of the heat capacity of a pellet sample by this method is within ±0.5% from 80–800°K. At higher temperatures, because of the enhancement of heat exchange by radiation, the imprecision increases and becomes ±2% at 1100°K. When an aluminium container is used, the precision becomes poorer, but the estimated experimental error is less than ±2% at room temperature.

Measurement procedures and some experimental results

The experimental procedure for the determination of the heat capacity of a sample is divided into two steps. The first is to determine the absolute heat capacity of the sample at room temperature, for which a sample of pure Al_2O_3 is used as the standard material. The results on uranium monophosphide[12] are shown in Fig. 5 for an example. As seen, the imprecision of this determination is believed to be ±0.3%.

The second step is to measure the heat capacity of the sample at higher or lower temperatures using as a standard the heat capacity of the sample at room temperature as determined above. For this measurement, sometimes, colloidal graphite was spread on the front surface of the sample instead of using an absorbing disk. The observed heat capacity values[23] from 80–800°K of the standard alumina showed good agreement with the NBS standard data. The deviations of the observed heat capacity are shown in Fig. 6 for low temperatures and Fig. 7 for high temperatures.[23] These results show that the heat capacity is now determined with an accuracy of ±0.5% from 110–800°K. Below 110°K, a small systematic deviation was occurred.

The heat capacity of high-purity aluminium was determined[24] from 80–850°K by this method, and is shown in Fig. 8. The mass of the sample was about 0.6 g. This figure shows that although the previous results of the

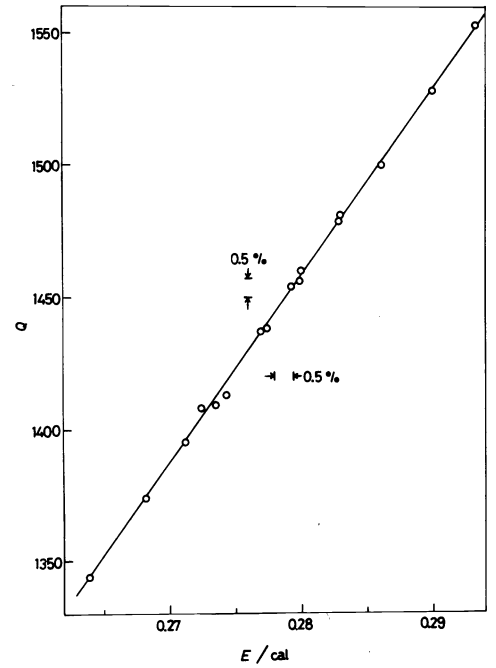

Fig. 4. Determination of energy absorbed by absorbing disk-sample assembly[23]. Q indicates output of the integrator.

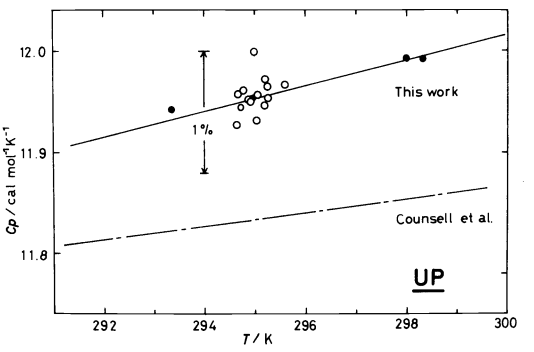

Fig. 5. Heat capacity of uranium monophosphide at room temperature. 3.5501 g UP sample.

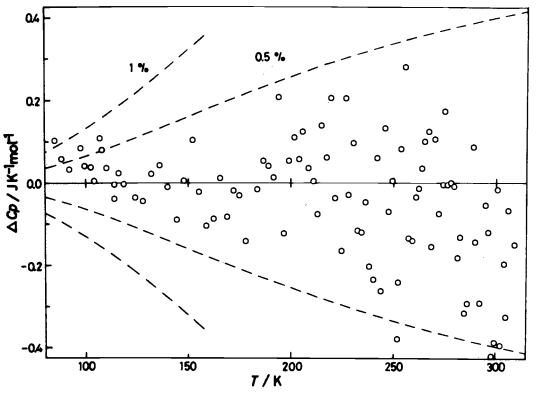

Fig. 6. Deviation of observed heat capacity of alumina from the reference data (I).[23] Low temperature.

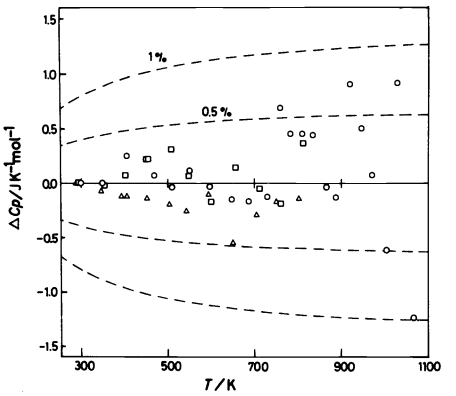

Fig. 7. Deviation of observed heat capacity of alumina from the reference data (II).[23] High temperatures.

high-temperature heat capacity have some divergence, the data by laser calorimetry have almost constant precision over the temperature range investigated.

Figure 9 represents the heat capacity of uranium monophosphide[12] including that obtained near the transition point, 121°K. The data obtained by the laser calorimetry at lower temperatures agreed very well with that obtained by adiabatic calorimetry,[34] and even better resolution of the heat capacity in the vicinity of the transition was obtained. This proves that utilization of an absorbing disk is very effective for the measurements on samples with a heat-capacity anomaly.

The heat capacities of Apiezon-N and Apiezon-T greases were also measured by using a small aluminum container. The weights of the samples used for the measurements are about 0.03 g.[23] Further refinements of this technique in the measurements of the samples of this sort can be expected, as well as in the measurements below 80°K.

3. HIGH-RESOLUTION HEAT-CAPACITY CALORIMETER

In study of critical phenomena, the experimental measurement of the thermodynamic quantities with high resolution both in the independent variable (particularly, the

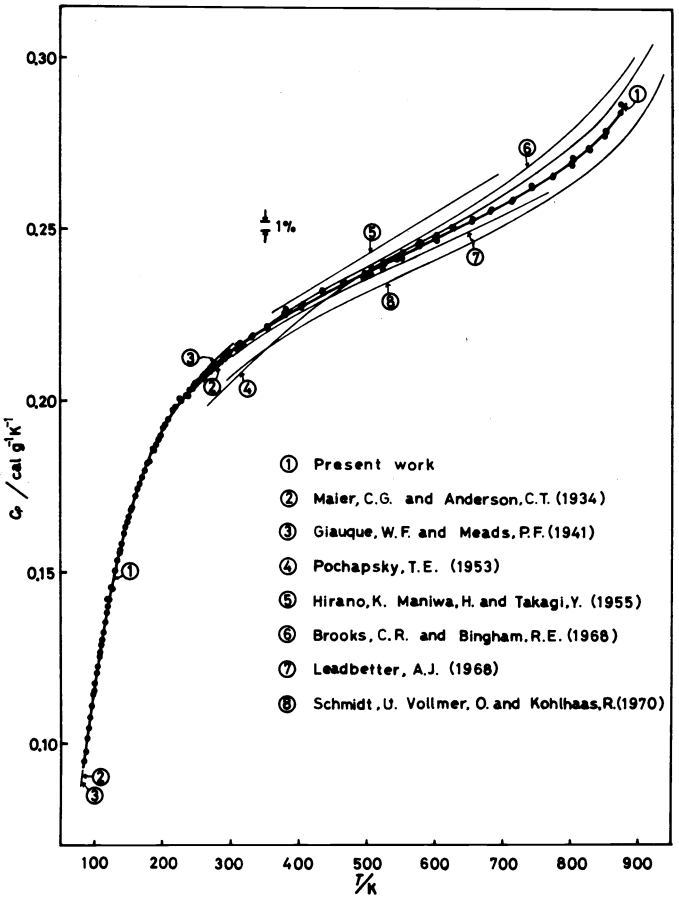

Fig. 8. Heat capacity of high purity aluminium.[24] 0.6081 g sample of 99.999% pure Al.

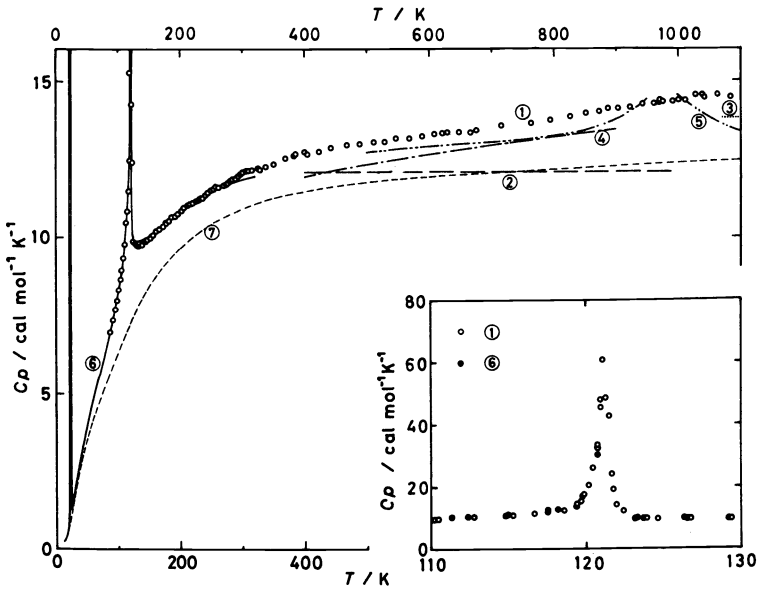

Fig. 9. Heat capacity of uranium monophosphide.[12]

temperature) and in the quantity measured is desirable. Two types of calorimeters are used for high-resolution measurement; both operate on different principles. One is the discontinuous heating method (the d.c. method) and the other the stationary state method (the a.c. method).

Recently, Seki and his group[17,25,26] have constructed an adiabatic-type high-resolution calorimeter which works in the temperature range between 12 and 300°K. As this apparatus has shown to be very useful for measuring heat capacity in critical phase transitions, some details of the apparatus are described here.

Construction of apparatus

The calorimeter consists of four major parts, viz. the cryostat, the adiabatic-control circuit, the temperature-measuring circuits and the energy supply and its measuring circuit (Fig. 10). A special feature of the apparatus is that it is equipped with two thermometers, a platinum resistance thermometer and a thermistor thermometer. The former provides an absolute temperature, while the latter enables precise measurement of small temperature increments in the calorimeter. The platinum resistance thermometer is also used for calibrating the thermistor. This feature endows the apparatus with a unique capability of measuring heat capacity with high accuracy and precision.

The calorimeter cell for single crystal samples is shown schematically in Fig. 11. This is a chromium-plated copper cylinder, about 30 mm in diameter and 60 mm long with the wall 0.3 mm thick. The cell has a copper bobbin 0.2 mm thick, the outer diameter of which is slightly smaller than the inner diameter of the cell. The samples are loaded in this bobbin, and the calorimeter heater is wound bifilarly on the bobbin and cemented in place with GE No. 7031 adhesive.

A demountable lid on the top of the cell allows loading it with a large-snugly-fitting single crystal. The cell is kept

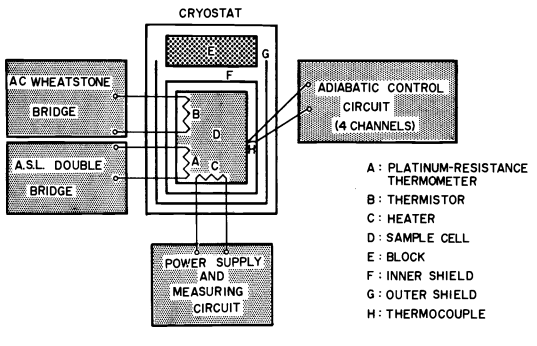

Fig. 10. Block diagram of the system of high-resolution calorimeter.[17]

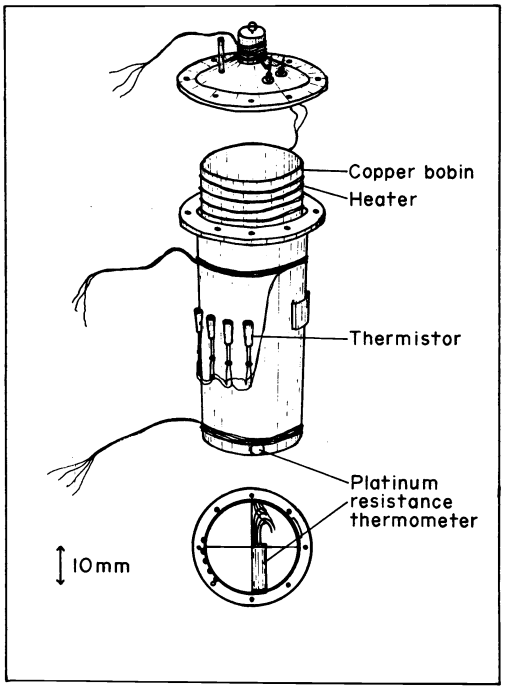

Fig. 11. Sketch of the calorimeter cell.[17]

vacuum-tight by the use of Apiezon-N grease or an indium o-ring. The two types of thermometers, a miniature, Minco platinum-resistance thermometer (13 mm long and 3 mm in diameter) and a bank of five glass-bead thermistors, are attached to the outside of the cell. Nominal resistance of the resistance thermometer is 100 Ω at 0°C, and that of the thermistor is 4 kΩ at 0°C and 0.13 kΩ at 100°C.

The cell is maintained adiabatic by the use of an adiabatic (inner) shield, a guard (outer) shield and a tempering block which are operated in a usual way. Temperatures of the bottom cone and other part of the inner shield are controlled separately. The temperature differences between the cell and the side and between the cell and the bottom of the adiabatic shield are sensed by thermocouples (chromel P-constantan) connected in series. The thermocouples are attached at five locations on the inside and outside of the cylinder and at three locations on the bottom cone of the inner shield.

The electromotive force of each series of the thermocouples is measured and amplified with d.c. microvoltmeter (Keithley model 149), the output of which is fed into a proportional-integrating circuit (Fig. 13) as an error signal, and drives the shield heater. The temperature differences between the block and the inner shield and between the outer and the inner shields are also controlled by other two channels of the regulating circuit.

In this way, the temperature difference between the inner shield and the calorimeter cell is controlled to less than 0.5 mK during both equilibration and heating periods, which sometime lasted for 24 hr.

Temperature of the sample is determined by the Minco platinum-resistance thermometer and a precision a.c. double bridge. The Minco thermometer was calibrated against a standard Leeds & Northrup Pt-thermometer. The deviation of the thermometer calibration from IPTS-68 is typically 4 mK and varies smoothly with temperature. The temperature determined is believed to be accurate to 0.01°K.

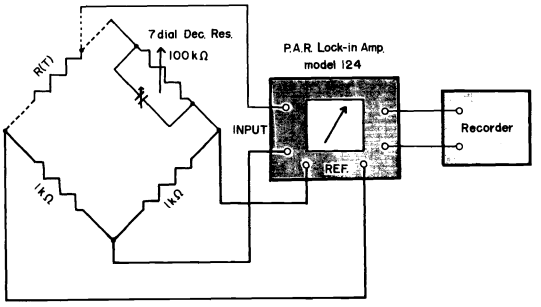

Fig. 12. A.c. Wheatstone bridge for the thermistor thermometer.[17]

Figure 12 shows the a.c. Wheatstone bridge for the thermistors used in the high resolution measurements. A lock-in amplifier is employed as a high-sensitivity detector. The balancing of the resistive and the reactive components can be performed easily. The variable air-capacitor connected in parallel with a decade resistor is used in balancing the reactive component. This system gives the temperature resolution to within 3 μK. The thermistor is calibrated against the Minco platinum thermometer (IPTS-68) at each measurement. For determining the relationship between the temperature scale and the resistance of the thermistor, the equation

$$T = \sum_{i=1}^{n} A_i (\ln R)^i \qquad (n = 2, 3 \text{ or } 4) \qquad (2)$$

was assumed and the expansion coefficients were determined by the least squares fit. The deviations of the observed values from this equation were found to be less than one mK, which was precise enough to determine absolute temperatures by means of this method.

Procedure and experimental results

The measurements and calculations of the gross heat capacity are carried out as follows. After the initial

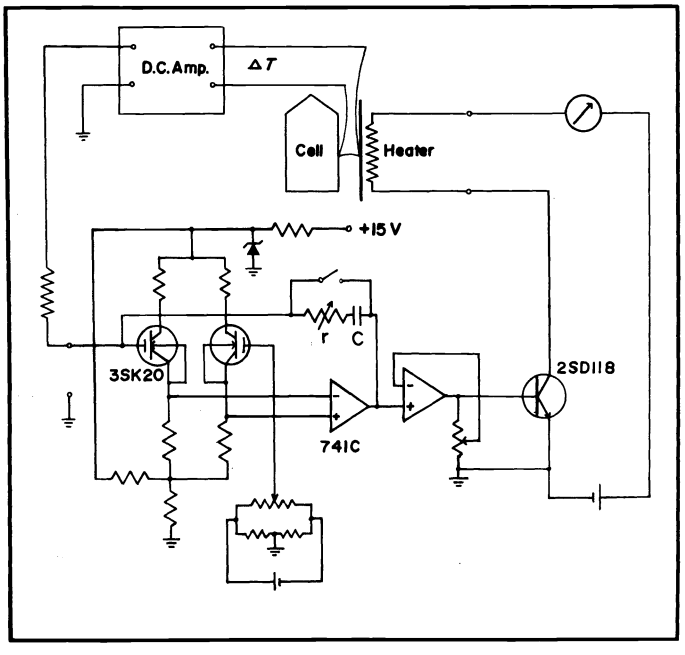

Fig. 13. Electric proportioning-integrating circuit for adiabatic control.[17]

temperature, T_i (i.e. the steady state temperature before heating) is measured, electrical energy, Q, is introduced into the calorimeter. When the equilibrium state is confirmed after switching the heater current off, the final temperature, T_f, is determined. The steady-state temperatures T_i and T_f are determined by following the temperature drifts as a function of time. The gross heat capacity is determined by the equation: $Q/(T_f - T_i)$ at the mean temperature $(T_i + T_f)/2$, where Q is the applied electrical energy.

For high-resolution measurements, the adiabatic regulation was strictly adjusted in order to eliminate the temperature drift for even a long time. The precise determination of the heat capacity when employing the small temperature increment is more liable to be affected by the heat leak. The thermistor was calibrated over a range of about 30°K including the temperature interval of the high-resolution measurement. The heat capacity is given by the equation,

$$C = Q/\left(\frac{\mathrm{d}T}{\mathrm{d}R}\right)_{T=T_{av}} \Delta R,$$

where

$$T_{av} = \{T(R_f) + T(R_i)\}/2$$

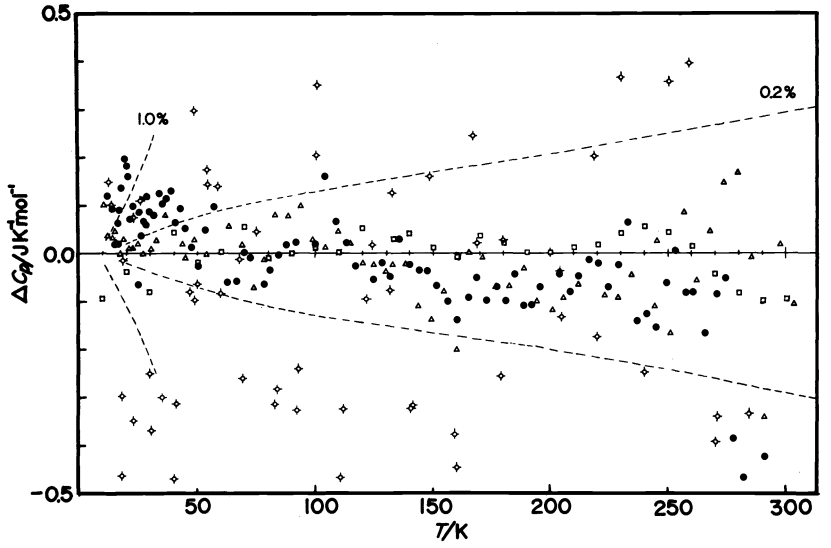

Fig. 14. Deviation plot of the measured values for the heat capacity of benzoic acid:[17] ●; this work, □, △, ◇; other investigators.

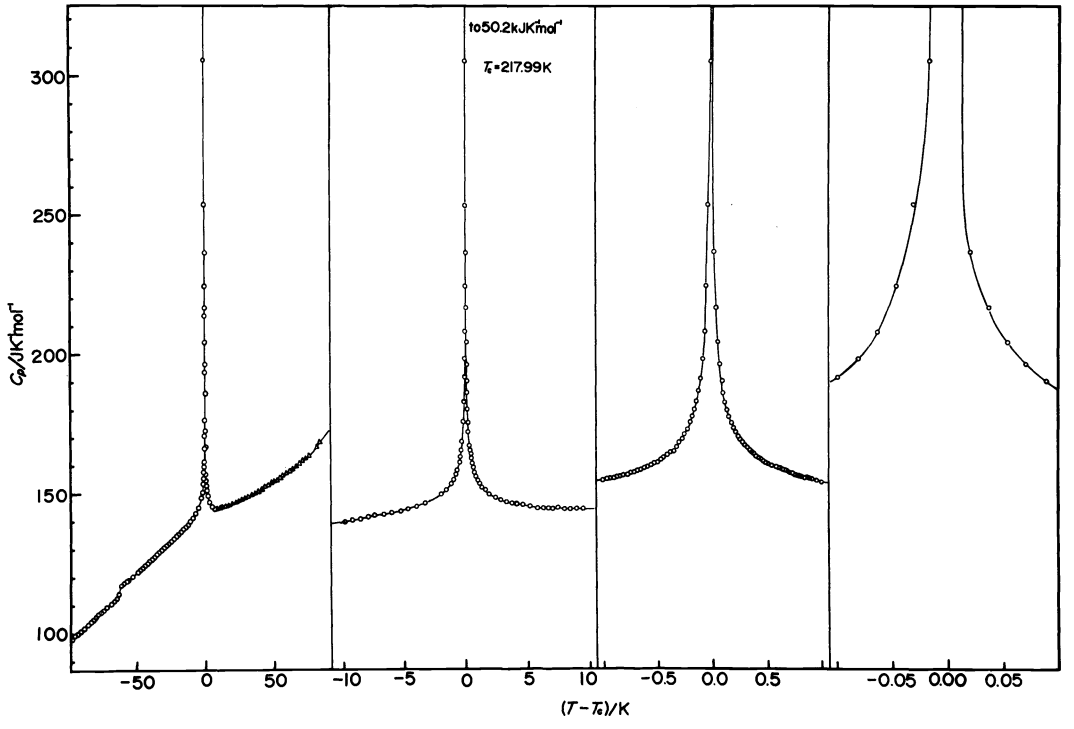

Fig. 15. Heat capacity of $SnCl_2\,2H_2O$ single crystals in the vicinity of the transition temperature.[25]

and

$$\Delta R = |R_f - R_i|.$$

R indicates the resistance of the thermistor.

In order to ascertain the over-all accuracy of the whole apparatus, the heat capacity measurement was performed on the calorimetric standard benzoic acid prepared by the US National Bureau of Standards. The weight of the sample was 12.6106 g. Figure 14 shows the deviation plots of the individual data points from the smoothed heat capacity of benzoic acid recommended by the US Calorimetry Conference.[27] The data by Furukawa *et al.*[28] and Cole *et al.*[29] are also plotted. The results are quite satisfying, and the inaccuracy and the imprecision of the measurement was confirmed to be less than ±0.1% and ±0.05%, respectively between 50 and 275°K.

The heat capacity of hydrated tin chloride ($SnCl_2 \cdot 2H_2O$) single crystal was reported by Matsuo *et al.*[25] with the use of this apparatus in the close vicinity of the phase transition temperature, $T_c = 217 \cdot 994 \pm 0.01$°K. Figure 15 shows the heat capacity curve obtained with the typical temperature increment of 10–30 mK. The highly symmetrical shape of the anomaly is to be noted. Its anomalous part, ΔC, could be expressed as $\Delta C = A_{\pm}|(T - T_c)/T_c|^{-\alpha_{\pm}}$. A quasi-isothermal absorption of the enthalpy was observed at the peak temperature, and it corresponded to 3.3% of the total transition entropy.

Tatsumi *et al.*[26] measured the heat capacity of Rochelle Salt ($NaKC_4H_4O_6 \cdot 4H_2O$) between 230 and 310°K with the high-resolution calorimeter. The heat capacity curves obtained in the vicinity of two Curie points are presented in Fig. 16 together with the results of other investigators.[30–33] The results of these precise measurements show definite evidence of local C_p maxima both for the lower and upper Curie points. This is for the first time that a local maximum in C_p at the lower Curie point has been detected; it amounts to only 0.2% of the total heat capacity. The results presented above clearly show the usefulness of the sophisticated, high-level precision (±0.05% or less) calorimeter.

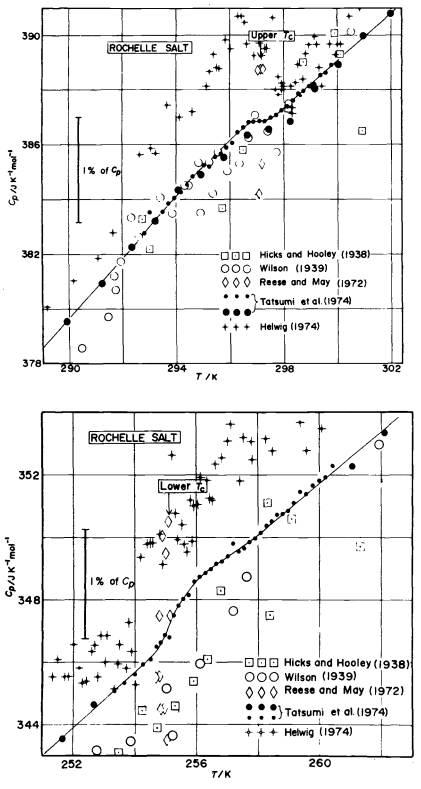

Fig. 16. Heat capacity of Rochelle salt in the vicinity of the transition temperatures.[26]

4. CONCLUDING REMARKS

In the previous sections, a summary of the recent techniques in the heat-capacity measurement has been presented. Although there are obviously many important contributions which should be discussed here in more detail, the emphasis in this presentation has been placed on the studies which has been developed in Japan and therefore are most familiar to the author. Further refinements and improvements of these novel techniques as well as conventional methods are still necessary for many measurements, as for instance, in the precise measurement of the powdered or granular samples of small mass at temperatures above 1000°K.

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