

SOME NEW ASPECTS OF ADIABATIC CALORIMETRY AT LOW TEMPERATURES *

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SUMMARY

Aspects of low temperature adiabatic calorimetry which we have developed in the past several years are reviewed with emphasis laid on the role which the matured experimental method can play in physical chemistry of condensed phases. Two types of adiabatic calorimeters are described, both of which work between 13 and 373 K on small amounts of samples and are fully computer-controlled. Some recent results of measurement on ammonium hydrogen oxalate hemihydrate, the thiourea carbon tetrabromide inclusion compound, schizophyllan solutions and swelling of vermiculite are presented to illustrate the versatility of the adiabatic calorimetry. Measurement of time dependent properties is also discussed.

INTRODUCTION

Low temperature calorimetry has a long history of development starting around the beginning of this century. At that time low temperature research was motivated by such fundamental issues as experimental verification of quantum theory and the third law of thermodynamics (ref. 1). The Einstein theory of the heat capacity of solids predicted strong decrease of the heat capacity at low temperatures while Nernst proposed his heat theorem stating that the entropy of a crystalline substance vanishes at zero Kelvin. These very general prediction could be tested by calorimetric experiments at low temperatures.

The earliest low temperature calorimeter was described by Eucken (ref. 2) who determined the low temperature heat capacities of HgCl , AgCl and PbCl_2 down to 100 K using, in the present terminology, an isoperibol calorimeter (a calorimeter in which the sample is surrounded by an isothermal enclosure). The basic principle of the experiment - determination of the heat capacity as the ratio of the Joule energy supplied to the sample to the temperature rise caused by the heating - is known today as the Nernst method because it was first proposed by him as described by Eucken (ref. 2).

The first adiabatic calorimeter (as opposed to the isoperibol) was described by Lange (ref. 3). In his calorimeter the sample was surrounded by a

temperature-controlled copper shield. Both adiabatic and isoperibol calorimeters were elaborated later in a number of thermodynamics laboratories in the world, especially in the US, and used to determine chemical thermodynamic properties of substances of basic and applicative importance. The high level of the standard of the chemical thermodynamic works attained before 1967 can be seen in the monograph, *Experimental Thermodynamics*, edited by IUPAC (ref. 4).

VERSATILITY OF ADIABATIC CALORIMETERS

One of the advantages of an adiabatic calorimeter is the wide temperature interval in which it works with an accuracy relatively independent of the temperature. This has been recognized by Gmelin who pointed out the importance of the temperature region below 120 K where a large number of interesting phenomena of physical and chemical importance occur and where general purpose calorimeters of the DSC type are not available commercially (ref. 5).

Versatility of an adiabatic calorimeter derives from its capability to measure the heat capacity of substances in a variety of physical states ranging from single crystals and powders to liquids and condensed gases. Measurement on various samples can be done without seriously straining the design of the apparatus or causing any extra complication in the experimental procedure (with the exception of the condensed gas calorimeter for which a special design is needed). Thus, once a properly designed calorimeter has been constructed, it can be used to study a great variety of substances.

Simplicity of the principle of the adiabatic calorimetry lies at the basis of the versatility of the method. It is assumed (and the calorimeter is to be so constructed that the assumption is correct) that all the electric energy introduced is used to heat the sample and sample cell. If any small part of the energy is lost to the surrounding or if extra energy is introduced from the surrounding by heat conduction, they should be corrected for as accurately as possible. The three quantities, the temperature T , energy input ΔE and the temperature rise ΔT caused by the energy input are all well-defined and accurately measurable quantities from which one obtains the heat capacity $C = \Delta E / \Delta T$ at the temperature T . It is important that the thermal conductance through the sample and between the sample and the cell is not involved in the theory of the adiabatic calorimetry.

What we actually measure in the adiabatic calorimetry is the energy (or enthalpy) rather than the heat capacity, as is obvious from the above discussion. The heating may or may not cause a temperature rise. If it does, we determine the heat capacity. If it does not, we are measuring an isothermal increase of the enthalpy, i.e., a latent heat of a phase transition

such as heat of fusion and heat of transition of a first order phase change. Thus one can measure the latent heat of a phase transition using the same adiabatic calorimeter that one uses for the heat capacity measurement. Insensitivity of the adiabatic method to the change of the thermal conductivity of the sample is an essential factor contributing to this. As one often experiences, some crystals shatter at a first order phase transition. This inevitably changes its bulk thermal conductivity. A similar change occurs at melting of a substance in a more remarkable proportion. Accuracy and precision of the heat capacity measurement made by a properly designed adiabatic calorimeter is not affected by such changes in the physical state of the sample.

SMALL-SAMPLE CALORIMETERS

In former times when determination of standard thermodynamic functions of various substances was the primary purpose of the low temperature calorimetry, one could expect that an ample amount of the sample was available for the experiment. Accordingly, sample cells of the internal volume as large as 145 cm³ were used to achieved the highest possible accuracy (ref. 6). If one wants to measure the thermal properties of a substance for some particular physico-chemically interesting properties it possesses, the amount of the sample available is often much smaller than this. Evidently, calorimeters that work on a small amount of sample greatly expand the scope of the calorimetric method of investigation to substances which are difficult to obtain in large quantities. These include highly purified organic and inorganic compounds prepared by a number of low-yield reaction steps, optical and other isomers which are separated with great difficulty and substance of biological origin. Studies of solid solutions also benefits from development of small sample calorimeters because homogeneous solid solutions are very difficult to prepare in large quantities. For these purpose we have constructed two types of low temperature adiabatic calorimeters.

Figure 1 shows the cryostat of one of them. The temperature range of this calorimeter is 13 - 373 K. The sample cell K is surrounded by two concentric adiabatic shields H and I. The temperature of the inner shield I is regulated against the surface temperature of the cell using a null-detection thermocouple that bridges the cell and the middle cylindrical part of the shield. The top and bottom faces of the inner shield are thermostatted against the cylindrical side. Similar temperature controllers regulate the temperature of the thermal anchor G and the outer shield H against the top of the inner shield. These are kept at temperatures 0 to 1 K below that of the inner shield.

The temperature of the sample is measured with a platinum or rhodium-iron

alloy resistance thermometer attached to the top of the sample cell as shown in

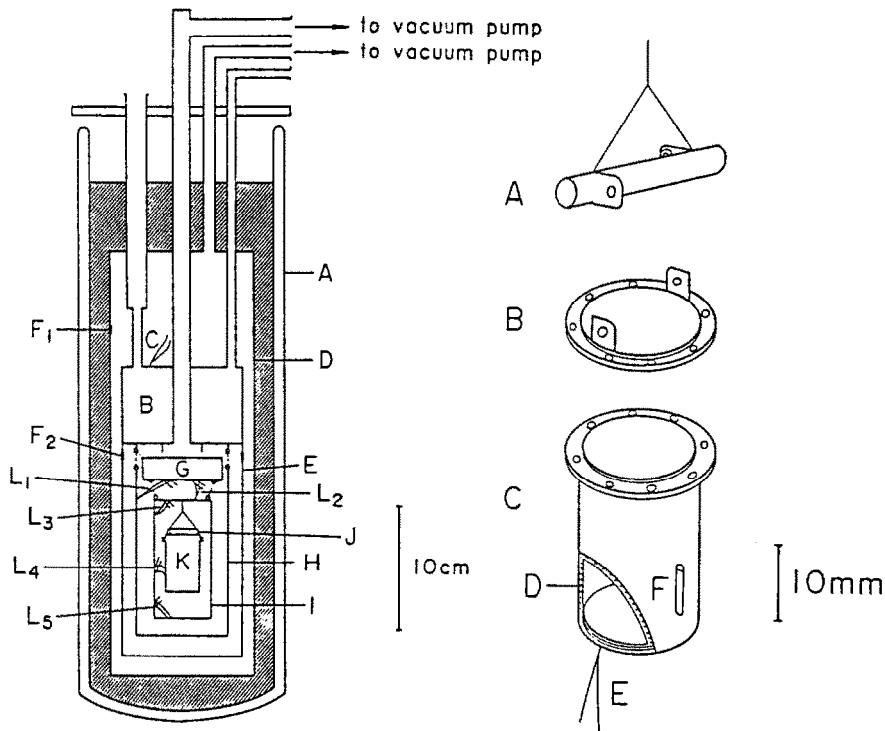


Fig. 1(left). Cross section of the cryostat for the small-sample calorimeter. See the text for the legends.

Fig. 2(right). The sample cell and thermometer unit. A: thermometer unit, B: cover, C: the main part of the cell, D: heating wire, E: heater leads, F: copper tube (to accept the thermocouple junction).

Fig. 2. The design was changed from the previous one (ref. 7) with respect to the amount of the copper used in the construction. The mass of the new cell is approximately $2/3$ of the previous one. The internal volume is 4.6 cm^3 . Thermal connection between the thermometer unit and the cell is secured by two pairs of the screws (not shown in the figure). Because of the small heat capacity of the unit, this simple thermal tie is efficient enough for rapid thermal equilibrium between the cell and the thermometer. An important consideration in the design of the cell is how to ensure rapid thermal equilibrium in the cell. This can be done by increasing the effective thermal conductance in the cell and by decreasing the thermal gradient caused by the Joule heating as much as possible. For the former purpose, thermal conduction

fins soldered to the inner surface of the cell are effective. Thermal conduction through sealed-in helium gas is also essential. For the latter, it is important to distribute the heating wire on a large part of the surface of the cell. This avoids local heating of the cell. With these considerations paid to the design and construction of the cell, the temperature of the cell loaded with a powder sample reached within ± 1 mK of the equilibrium value typically in less than 60 s after the heating. An interesting and effective way of avoiding overheating of the inner shield is to reduce the power of the sample heater for a fraction ($\approx 1/10$) of the total heating interval at its end. During this time the inner part of the sample which has been lagging in the temperature rise catches up with the other part of the sample (and the cell). The temperature gradient in the cell is much reduced by the time when the sample heater is finally turned off. If one chooses the reduced power and the time interval for the reduction properly, which is easily done after a little experience, the surface temperature of the cell is close to the final equilibrium value already at the end of the heating, resulting in a much reduced transient deviation (overshooting) of the inner shield temperature from that of the cell. Actual use of this contrivance has become feasible with the computer control of the whole calorimetric experiment.

PRACTICAL THERMOMETRY

There are two possibilities for the thermometry in the adiabatic calorimetry as to the measurement of the resistance of the thermometer; the AC and DC methods. AC bridges for thermometric resistance measurement are available commercially. They are free from short and long term drift other than that due to the drift of the standard resistor, have very high resolution ($\approx \pm 30$ μ K under normal condition) and are totally free from the effect of thermal EMF in the thermometric circuit. They are susceptible to external noises, but induction and other sources of the noise can be reduced to an acceptable level by a moderate care paid in wiring the electric circuits in the cryostat. AC bridges have removed all the difficulty and laboriousness that used to characterize the temperature measurement in the adiabatic calorimetry in the former time. In the DC thermometry, one uses a digital voltmeter to measure the resistance of the thermometer. Digital voltmeters of 10 nV resolution are available commercially. However, it has not been demonstrated that the 10 nV resolution (corresponding to 0.1 mK under normal conditions) can be fully utilized in actual calorimetric experiments, because of stray EMF, fluctuation of the current source, zero drift of the digital voltmeter itself and other sources of error. The DC thermometry is nevertheless an attractive possibility when the ultimate high accuracy is not required.

THE SMALL-SAMPLE CALORIMETER OF TEMPERATURE TRANSFER TYPE

If one wants to reduce the amount of the sample to 1 cm^3 or less and still retain the versatility of the adiabatic calorimeter, the heat capacity of the sample cell becomes impractically large compared with that of the sample. The thermometer contributes a substantial part of the cell heat capacity because of the heat capacity of itself and the metallic material of the thermometer unit. This can be avoided by using thermocouples as the working thermometer. However, measurement of the absolute temperature with thermocouples is susceptible to various sources of error. Most of the difficulties are connected with the absolute measurement of the EMF of the thermocouple and with the stray EMF that is inevitably generated in the thermometric circuit. These difficulties are greatly reduced if one uses the thermocouple for relative

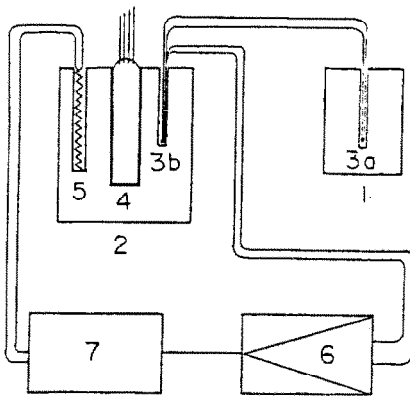


Fig. 3. Schematic diagram of the temperature transfer system. See the text for the legends

measurement, while measuring the absolute temperature by the well-established resistance thermometry (ref. 8). In this scheme the thermocouple is used as the thermal null-detector between the cell and a metallic block whose temperature is measured using a resistance thermometer. Figure 3 shows a block diagram of the temperature transfer thermometric system (ref. 9). In the figure the thermocouple junctions 3a and 3b detect temperature difference between the sample cell 1 and the thermometric block 2. The thermocouple EMF is amplified by the nanovolt amplifier 6 and power amplifier 7 and fed back to the heater 5 in the thermometric block 2. The platinum (or rhodium-iron) thermometer 4 measures the absolute temperature of the block which is at the same temperature as the sample when the null detector 6 is stationary at zero deviation. In the actual use of the temperature transfer system in the calorimeter, the transfer precision attained so far is $\pm 0.05 \text{ mK}$ at 300 K. The precision decreases at low temperatures to $\pm 0.2 \text{ mK}$ at 20 K, because of the decreased sensitivity of the thermocouple.

AUTOMATIC MEASUREMENT

Actual procedure of the heat capacity measurement is repetition of the temperature measurement and heating. This time-consuming and laborious procedure has been greatly changed by introduction of microcomputers which enable all the measurement to be performed automatically. Most of the operation which have been done manually can be performed equally well or better by electronic devices and the sequence of operations can be better systematized by a computer. Figure 4 shows the block diagram of the automatic version of the small-sample calorimeter of the temperature transfer type (ref. 7,9). The sample A and thermometric block B are surrounded by the shield C1 and C2. The

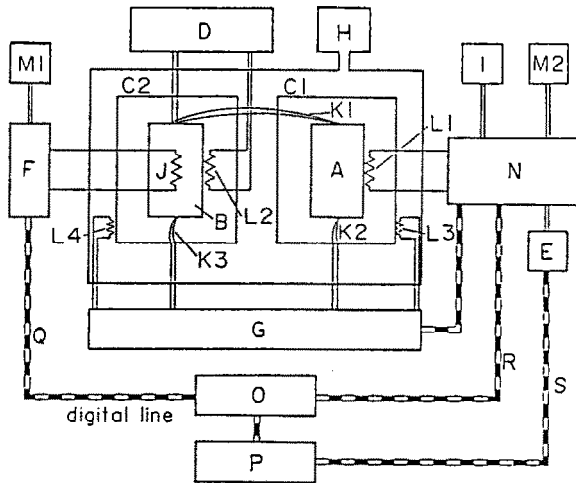


Fig. 4. Block diagram of an automatic small-sample calorimeter. See the text for the legends.

temperature transfer circuit D receives the difference signal from the thermocouples K1 and controls the temperature of B by regulating the current through L2. I is a constant current source for the sample heater L1, its power being measured by the digital voltmeter E whose input circuit is connected to L1 and a standard resistor M2 through the selector relay N. The thermometric bridge F measures the resistance of the thermometer J relative to another standard resistor M1. G is an adiabatic temperature controllers for the shields where the thermocouples K2 and K3 provide the input signals and the heaters L3 and L4 accept the fed-back powers. A microcomputer P controls the entire system through the interface O and digital lines Q, R and S. The procedure of the measurement has been programmed in the BASIC as a series of instructions written in about 6000 lines. Once started with input of the parameter values specifying the condition of the measurement, the computer runs all the measurement unattended by the experimenter.

The automation of the calorimeter has reduced the experimental time by a

factor of four or more and the experimenters labor immeasurably. It has also increased the precision of the measurement because of the digital averaging of the random errors in the thermometry and energy measurement.

MEASUREMENT OF THE TIME-DEPENDENT PROPERTIES

Heat capacity of a non-metallic condensed substance has, roughly speaking vibrational and configurational parts. The former is always present (the lattice and molecular vibrational heat capacities). Thermal equilibrium of the vibrational degrees of freedom is attained instantaneously on the calorimetric time scale. The temperature we measure in a calorimetric experiment is the vibrational temperature. In substances disordered with respect to position and orientation of the molecules, such as liquids and disordered solids, the energy carried by these degrees of freedom also changes as the temperature changes.

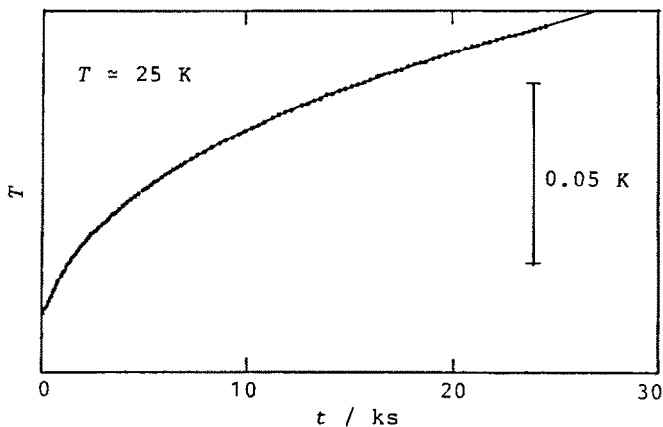


Fig. 5. Spontaneous temperature rise of a solid solution $(\text{KCN})_{0.7}(\text{KBr})_{0.3}$ (ref. 11).

However, since the rate of the configurational change depends on the temperature typically as described by the Arrhenius equation, it can be slow even in the calorimetric time scale at low temperatures. If such a substance is quenched from the high temperature, it retains the configurational enthalpy that is higher than the equilibrium value corresponding to the actual (vibrational) temperature. The excess enthalpy is liberated gradually and, if the sample is isolated adiabatically, its temperature (i.e. vibrational temperature) increases as the excess configurational enthalpy is transformed into vibrational energy. This is a sensitive way of detecting configurational relaxation in disordered systems (ref. 10). Figure 5 shows the temperature, as a function of the time, of a solid solution $(\text{KCN})_{0.7}(\text{KBr})_{0.3}$ quenched from 70 K to 25 K in an adiabatic calorimeter (ref. 11). It approaches the equilibrium gradually. However, the curve cannot be characterized by a single exponential function. Detailed study of such behavior, typical of a glass transition,

requires precise measurement of the temperature for a long time. The temperature rise (in this case ≈ 0.06 K) is small in most of the subtle glass transitions in glassy crystals (ref. 10), which means that the measurement has to be made with a highest possible precision in order to be usefully analyzed for the parameters characterizing the relaxation.

Spontaneous heating has also been observed in substances that undergo metastable to stable phase transitions. A particularly interesting case is that of the Martensitic transition in $(\text{CH}_3\text{NH}_3)_2[\text{TeCl}_6]$ (ref. 12). Stabilization to the low temperature phase took place step-by-step when observed under the adiabatic condition as shown in Fig. 6 where the temperature of the sample, adiabatically isolated in the calorimeter, is plotted against the time. The series of steps indicated by horizontal bars in the figure probably represent a Martensitic transformation taking place in one crystallite after another.

Measurement on such time dependent phenomena is an obvious departure from the traditional field of calorimetry which is, by definition, measurement of

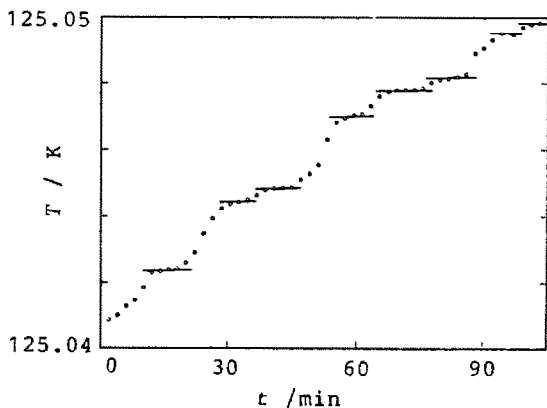


Fig. 6. Spontaneous temperature rise of $(\text{CH}_3\text{NH}_3)_2[\text{TeCl}_6]$ undergoing a Martensitic phase transformation (ref. 12).

the energy difference between two equilibrium states. In the time dependent measurements, one is interested in the path by which the two equilibrium states are connected, thus broadening the scope of the calorimetric experiment.

SOME RECENT RESULTS

A few examples are given below from recent measurements performed in our laboratory illustrating various aspects of the adiabatic calorimetry discussed above.

Figure 7 shows the heat capacity of ammonium hydrogen oxalate hemihydrate and its deuterate analog (ref. 13). The broad lambda anomalies are due to ferroelastic phase transitions. The anomalous heat capacity is separated from the normal contribution usually by interpolation of the data points

representing the heat capacities well above and well below the transition temperature into the transition region. This procedure is always encumbered by the presence of a certain degree of arbitrariness involved in the choice of the interpolation function and the data points used for the optimization of the interpolation function. In order to reduce the arbitrariness, we expressed the vibrational heat capacity by the Debye and Einstein heat capacity functions, and determined the parameters involved by the least squares fitting. The

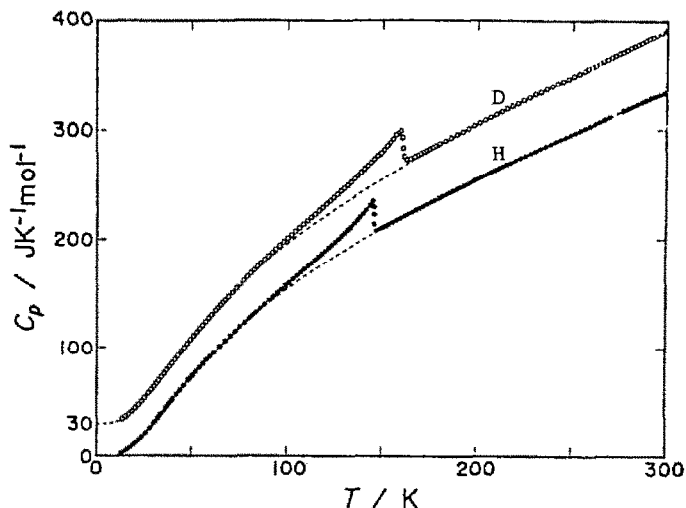


Fig. 7. Heat capacities of ammonium hydrogen oxalate hemihydrate and its deuterate analogue (ref. 13).

broken lines in the figure represent the normal heat capacities thus determined. This procedure can be successful only when the experimental data are available for a large interval of temperature. The next example is also related to an anomalous heat capacity of the lambda type. The thiourea inclusion compound $(\text{Thiourea})_3 \text{CBr}_4$ undergoes a phase transition at 202 K (ref. 14). As shown in Fig. 8, the anomalous heat capacity has a strong peak at the transition temperature. In contrast to the lambda peaks of ammonium hydrogen oxalate hydrate for which the anomalous heat capacity ends with a finite discontinuity, the heat capacity of the thiourea compound increased apparently without limit as the transition temperature was approached. In such cases smaller and smaller temperature steps are required in order for the finite temperature step to be a good approximation to the infinitesimal temperature increment. The temperature resolution of $\pm 30 \mu\text{K}$ attained by the AC thermometric bridge allows C_p determination in temperature steps as small as 30 mK to be made without substantial loss of precision. It is important in such measurement to ensure rapid thermal equilibration in the cell, otherwise long extrapolation of the temperature vs. time curve needed for the temperature determination introduces a large relative error in the temperature increment.

Also non-linearity of the thermometric bridge becomes relevant here, even if it

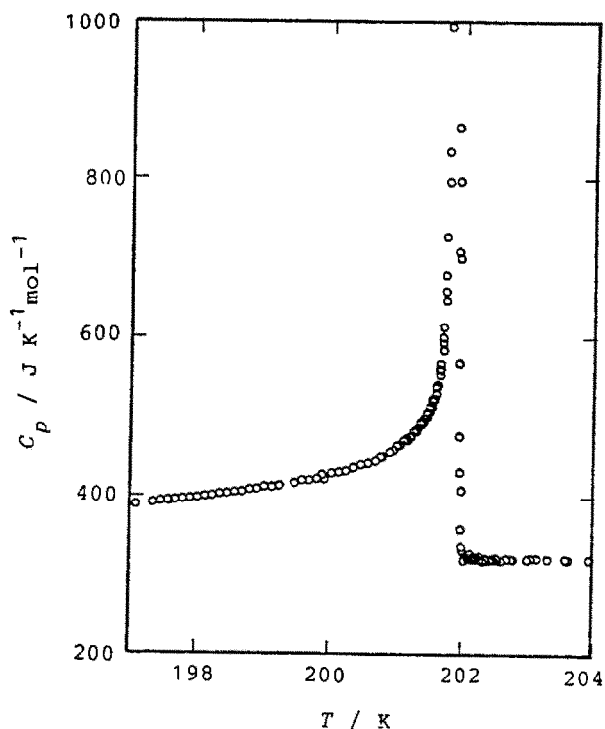


Fig. 8. Heat capacity of a thiourea inclusion compound $(\text{thiourea})_3\text{CBr}_4$ around the lambda transition (ref.14).

may be safely ignored in the ordinary C_p measurement where the temperature increments are 1 K or more. It should be added that extremely high temperature-resolution has been attained by AC calorimetry (ref. 15,16).

The final two examples are related to heat capacity anomalies in aqueous solutions. Figure 9 shows the heat capacity of an aqueous solution of schizophyllan, a polymeric carbohydrate produced by a fungus *Schizophyllum Commune*. The peaks are caused by order-disorder changes in the hydrogen-bonded network formed by hydroxyl groups of the schizophyllan molecule and solvent water (ref. 17). The anomalous heat capacity could be reproduced by a statistical theory of rod-like polymers (ref. 18). The small sample calorimeter was crucial for this measurement because the amount of the schizophyllan sample was limited. In most of the measurements ca. 300 mg of schizophyllan of a uniform molecular weight was used.

It has been known by X-ray and neutron diffraction that the mineral vermiculite swells in aqueous solutions by absorbing water between the sheets of aluminosilicate layers. The swollen (i.e. osmotic) vermiculite collapses to the original (i.e. crystalline) form as the temperature increases. Figure 10 shows the heat capacity of an aqueous vermiculite undergoing the osmotic-to-

crystalline phase change (ref. 19). The peak at 285 K was reproducible and indicates that the swelling is a thermodynamic phase transition characterized by a sharp transition temperature, rather than coagulation or sedimentation which some other colloidal solutions are known to undergo irreversibly. The clay mineral swells by more than ten times by volume under suitable conditions. Therefore, the amount of the sample had to be limited to $\approx 1/10$ of the internal

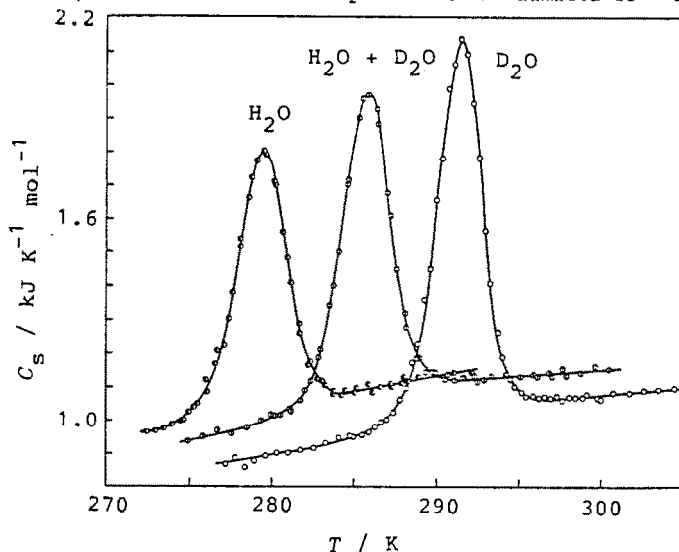


Fig. 9. Heat capacities of aqueous and deuterio-aqueous solutions of schizosyllan (ref. 17,18).

volume of the cell, the remaining 9/10 being occupied by the solvent water. In this experiment, the water and mineral moved in the cell relative to each other over a macroscopic distance as the transition proceeded. Therefore the equilibrium was reached very slowly and use of an adiabatic calorimeter was essential for the determination of the thermal anomaly.

CONCLUSION

It has been a generally accepted view that the low temperature calorimetry is a laborious and time-consuming experiment that keeps the experimenter under constant stress for long time. This has been totally changed since the introduction of microcomputers. Once the calorimeter has been set up and the run started, the experimenter has only to check the print out from time to time and adjust some of the experimental parameters if he or she finds it appropriate to do so. Analysis of the data thus obtained can also be made very efficiently on microcomputers. Easy access to a large computing capacity made available by powerful microcomputers enables us to try in the data analysis

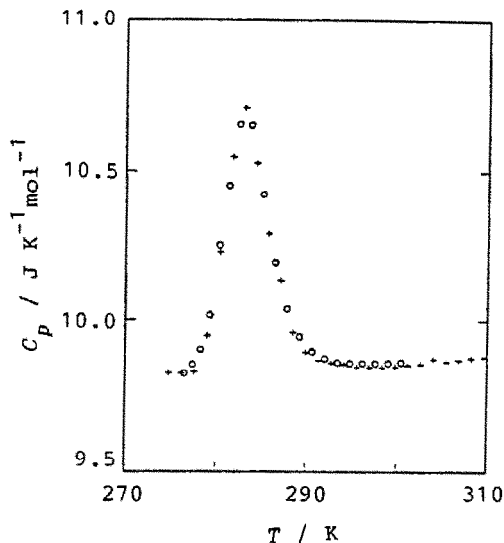


Fig. 10. Heat capacity of aqueous vermiculite undergoing the swelling transition (ref. 19).

various numerical techniques which previously required prohibitively lengthy computation.

The large amount of the samples required, for which adiabatic low temperature calorimetry is often remembered, has also been changed. It has been reduced to 1 cm³, a reduction by a factor of 10 to 100 from a previously customary sample amount. However, there is still much to be done in this direction because even 1 cm³ of the sample would be impractically large for a number of synthetically, physicochemically and biochemically interesting substances.

Unlike most of the other calorimetric apparatus low temperature adiabatic calorimeters are not available commercially. Experimenters who want to start low temperature calorimetry have to learn by themselves thermometry, low temperature technique, vacuum technique, electronics and AC and DC weak-signal processing. The author believes that vast applicability of adiabatic calorimetry, of which only a part was discussed in this article, justifies the investment.

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