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ADIABATIC MICROCALORIMETERS FOR HEAT CAPACITY MEASUREMENT AT LOW TEMPERATURE*

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ABSTRACT

Technical problems in the design and construction of small sample adiabatic calorimeters are pointed out and solutions to them discussed. Two calorimeters constructed on the design principle are described with illustrative examples of data obtained with them. Hard and soft wares for fully automatic operation of the two calorimeters are described in some detail.

INTRODUCTION. ADIABATIC CALORIMETRY

Low temperature calorimetry has long been one of the standard methods of investigation in chemical thermodynamics (1). It determines values of thermodynamic functions of substances at the standard state from which we can calculate the equilibrium constant of reactions involving the substances. The absolute entropy determined by the low temperature calorimetry has been a uniquely important experimental quantity in the verification of the third law of thermodynamics. In the recent years, the calorimetry is finding more and more applications in the study of phase transitions and critical phenomena. The AC calorimetry is particularly suitable for the study of the critical phenomena because its high resolution in temperature makes it possible to approach the critical point closely (2). High absolute accuracy of the adiabatic calorimetry is most useful in determination of the temperature, enthalpy and entropy of phase transition, even though a specially designed adiabatic calorimeter proved to be powerful in the field of the critical phenomena as well (3). An adiabatic calorimeter measures the enthalpy of transition with the same accuracy for a first order transition as for a phase transition of a higher order.

More recently, it has been found that relaxational effects (glass transition) in glasses and disordered solids can be studied by adiabatic calorimetry. Because of the high temperature stability of the adiabatic calorimeters, a relaxation time as long as 10^5 s can be determined (4). The use of the calorimeter for such a dynamic study may be called the calorimetric spectroscopy in analogy with the dielectric and mechanical spectroscopies.

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SMALL SAMPLE CALORIMETERS

In the former times it was a standard practice of the adiabatic calorimetry to use samples as much as 30 - 50 g (1). Because of the large amount of samples, any small residual heat leakage to and from the sample cell was relatively unimportant. However, it has been realized that the large amount of the substances required for the heat capacity measurement limited the application of the calorimetric method to the more common substances and often excluded interesting substances available only in a small quantity (5). It is therefore desirable to construct adiabatic low temperature calorimeters that work on small samples. In the past several years, we made effort to this end in two ways. One is to decrease the sample size of a low temperature calorimeter of the ordinary design. It has now become possible to work on a 5 g sample. The other is a twin calorimeter of the temperature transfer type (6). In this calorimeter, the design of the cell is simplified because only a thermocouple is attached to the cell instead of a platinum resistance thermometer. A 0.6 cm^3 cell has been found practical in this calorimetric system as will be described below.

MINIATURIZATION OF A LOW TEMPERATURE CALORIMETER OF TRADITIONAL DESIGN

Our previous experience showed that a short time constant of thermal equilibrium within the sample cell was the most important factor to be considered in

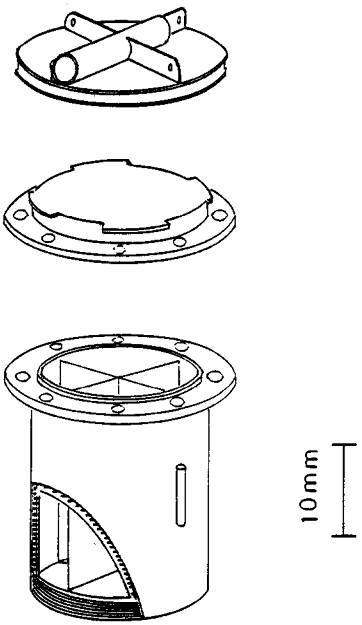


Fig. 1. Thermometric unit(upper) and small size sample cell (lower).

the design of a sample cell. If the equilibrium in the cell is reached rapidly only a short extrapolation of the temperature drift curve is needed in the calculation of the heat capacity and inaccuracy introduced by the extrapolation is accordingly small. This is particularly significant when one measures the heat capacity in small steps of the temperature. The short time constant also decreases the overall time spent in the experiment.

The cell shown in Fig. 1 was designed with this consideration in mind. The heater ($\sim 700\ \Omega$) was wound on the outer surface of the cell. It is covered with an outer shell. The lid is hermetically sealed with an Indium O-ring and eight pairs of screws. A pair of crossed vanes soldered to the inner wall shortens the thermal path from the heater to the sample. Because the heating wire covers a large part of the cell, the joule heat is generated evenly over the surface of the cell. Local heating and its undesirable consequences (long equilibrium time and heat leakage) are thus avoided. Thermal equilibrium in the cell is reached usually in two min. for powder and liquid samples. The thermometer was fixed in the thermometer unit. The cell and the thermometer unit is connected together by a bayonet fitting. When replacing the sample, one detaches the cell from the unit at the bayonet fitting and leave the latter in the cryostat. By this device, one is relieved of the care which otherwise one has to exercise to spare the thermometer any mechanical shock likely to be inflicted on it during replacement of the sample. The detachable thermometer unit is also convenient if one wants to use several types of cells to suit various materials available in various quantities. One has only to design the cells with the same bayonet fitting that match the same thermometer unit.

It is important to keep undetected heat leak to and from the cell at the lowest possible level. We do this by tight temperature control of the adiabatic shields. The high gain negative feed-back loop designed to control the shield temperature consists of a well-insulated differential thermocouple, low-drift DC amplifier, power amplifier and well-insulated heating wire. Electrical and thermal time lag in the feed-back loop should be as small as possible. This avoids oscillation of the feed-back control. It is often effective as a remedy against electrical interference and spurious EMF in the thermocouple circuit to incorporate an electro-optical coupler in the amplifier.

The electrical wires leading to the cell are an unwanted but unavoidable thermal path through which the heat leaks. Alloy wires were used for the connection of the thermometer. They are 20 times less conducting thermally than a copper wire of the same dimension.

By the use of this calorimeter, we measured the heat capacity of various substances which undergo phase and glass transitions. Those studied most recently include $(CD_3ND_3)_2[SnCl_6]$ (Sample mass 5g) (7) and schizophyllan liquid crystal, a polysaccharide of biological origin (1g of Schizophyllan in 4g of

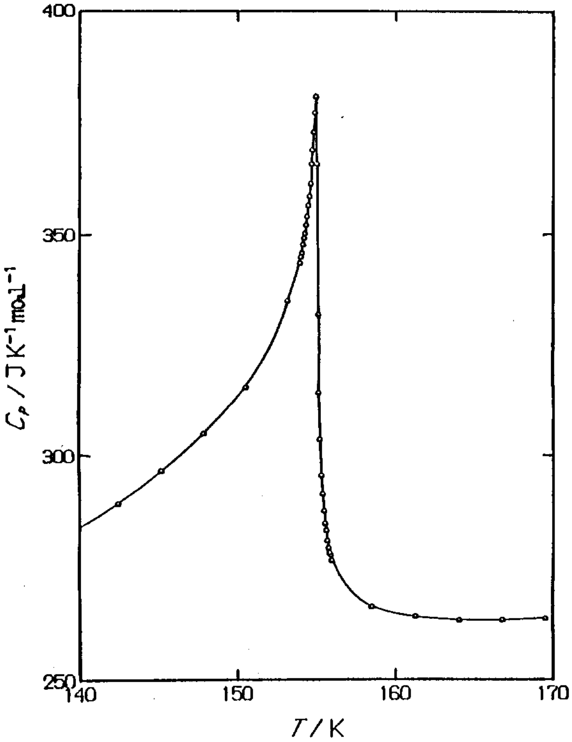


Fig. 2 Heat capacity of $(CD_3ND_3)_2SnCl_6$ crystal around the critical temperature

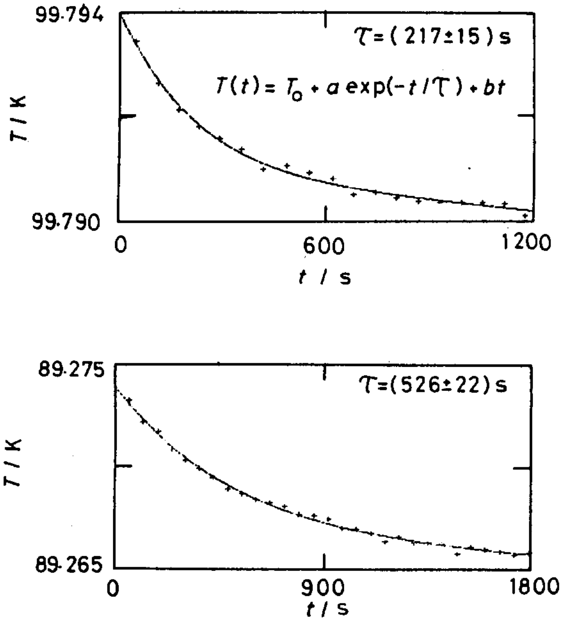


Fig. 3 Relaxational behavior of ice doped with NH_4F observed around 90 K.

water) (8). Anomalous heat capacity of the former is plotted in Fig. 2. In the measurement, temperature steps as small as 70 mK were found to be practical at 155 K. For the schizophyllan sample, a small heat capacity anomaly whose integrated enthalpy change amounted only to ∿0.6 J was reproducibly determined to ±0.1 %.

As an example of the relaxational effect studied with the present calorimeter, we show the temperature drift curves recorded at the relaxational anomaly around 90 K of ice doped with NH_4F (Fig. 3) (9). This system was studied in a series of the calorimetric study of the phase transition in doped ice I_h. No phase transition was found in agreement with Westrum's result (10). Ammonium fluoride is soluble in ice I_h but turned out to be ineffective as an initiator of the phase transition (11). However a relaxational anomaly occurred at a lower temperature than in pure ice (12,13). The good thermal integrity of the cell and the sample has made it possible to identify the relaxational effect of a rather short (in thermal time scale) time constant.

A SMALL SAMPLE CALORIMETER OF THE TEMPERATURE-TRANSFER TYPE

If one wants to reduce the sample size still further, one finds that even the miniature platinum resistance thermometer occupies an inconveniently large space in the cell. We modified the calorimeter to a twin type to avoid this (6). The modified calorimeter works on the adiabatic principle but the method of thermometry is changed. The temperature of the cell is now measured relative to that of a thermometric copper block with a thermocouple. The temperature

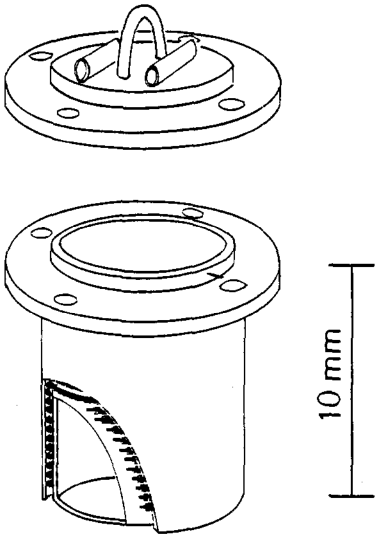


Fig. 4 Miniaturized sample cell with 0.6 cm^3 internal volume.

of the block is so controlled that it follows the temperature of the cell as closely as possible. In the present apparatus we can control the temperature to ± 5 nV in terms of the thermocouple output signal corresponding to ± 0.1 mK at room temperature. The temperature of the cell thus transferred to the thermometric block is measured with the standard thermometry. Construction of the cell has been simplified because a thermocouple junction has replaced the Pt resistance thermometer (Fig. 4). The two pieces of the copper tubing on the top of the cell accept thermocouple junctions for the temperature transfer and adiabatic control. The heater was wound around the cylindrical part of the cell and covered with a copper sheath. Two cells of this type were made: one of the internal volume of 0.6 cm^3 and the other 1.2 cm^3. We measured the heat capacity of the standard benzoic acid on a 0.3159 g sample. The result shown in Fig. 5 agreed satisfactorily with the accepted value in most of the temperature region. The amount of the substance used in this measurement was 1/20 - 1/100 of those in the previous measurements.

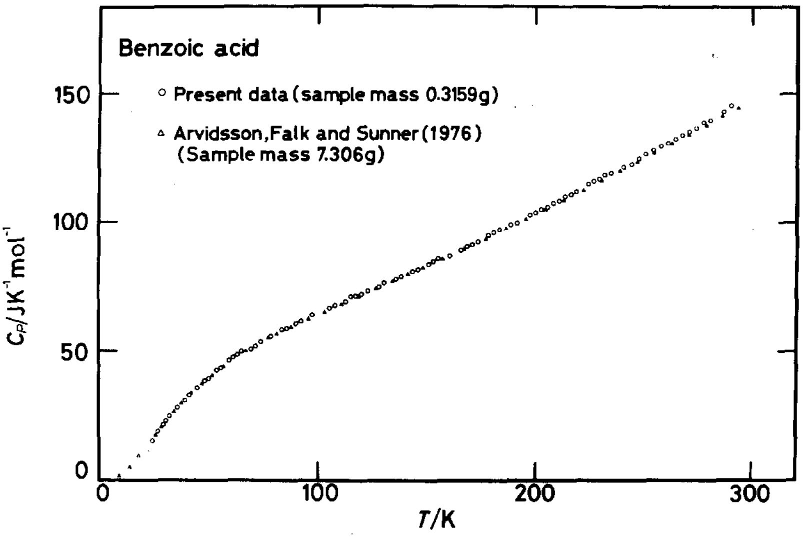


Fig. 5 Molar heat capacity of the standard benzoic acid crystal.

Satisfactory performance of the calorimeter on a substance which undergoes a strong first order phase transition was shown by a measurement on ammonium hexafluorovanadate(14). This compound underwent a phase transition at 280.44 ± 0.05 K. The sample, 0.2675 g in the mass, was prepared by solid state reaction in Bordeaux, France. As shown in Fig. 6, the data obtained on $(NH4)_3[VF_6]$ are of the same quality as those on the analogous $(NH_4)_3[FeF_6]$ plotted in the same figure. The latter was obtained with an ordinary large scale adiabatic calori-

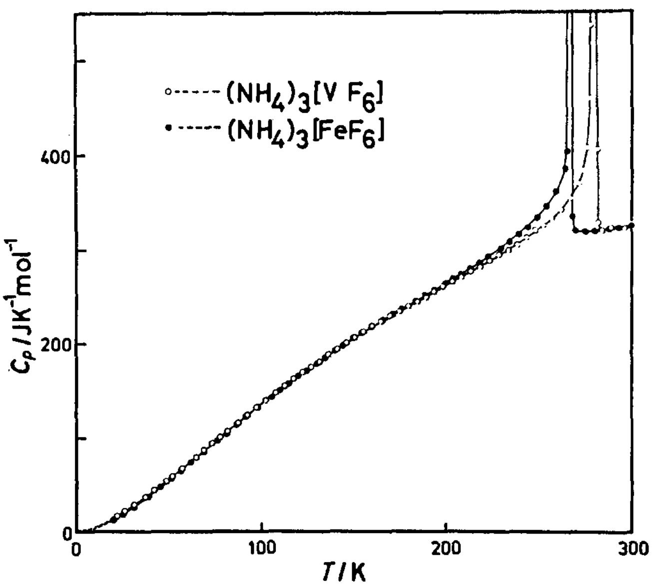


Fig. 6 Heat capacities of $(NH_4)_3[VF_6]$ and $(NH_4)_3[FeF_6]$ crystals measured by a miniaturized and an ordinary adiabatic calorimeters.

meter (15) with the sample mass of 32.4949 g.

AUTOMATION OF THE ADIABATIC CALORIMETER

Heat capacity measurement from 13 to above 300 K is a laborious and time consuming work. It takes long time because a large number of data are needed to cover the temperature range. It is laborious because each measurement consists of recording a long series of multi-digit numbers read on a manually balanced thermometric bridge. However, automatic resistance bridges have been available for some time and personal computers of sufficient capability have recently become inexpensive. Operation of the calorimeter is a sequence of repetitive steps of temperature measurement and heating. This can be automated most conveniently by the use of a dedicated computer.

The two types of the calorimeters described above have been fully automated. Once the sample is mounted in the cryostat, the cryostat evacuated and the adiabatic control suitably adjusted, the computer runs the cycles of measurement, printing out the molar heat capacity at the end of each cycle. A simplified flow chart of the operation is shown in Fig. 7. In the flow chart, the branch point A is passed downward when it is reached for the first time in the run. On the second and later passages, the program branches to the right to calculate and print out the results. Decision whether to stop the measurement or to continue on to the next cycle is made at the branch point B.

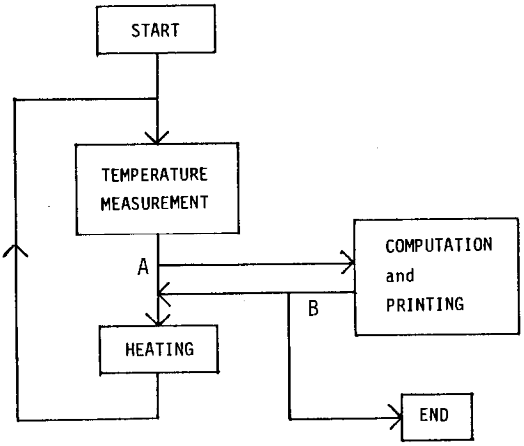


Fig. 7 Schematic flow chart of the operation for the automatic heat capacity measurement.

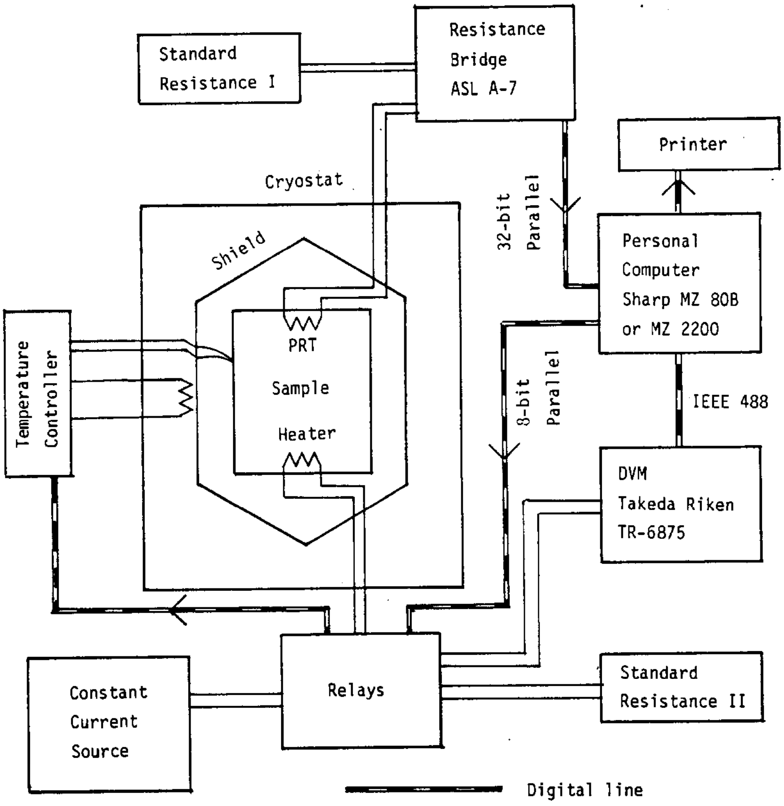
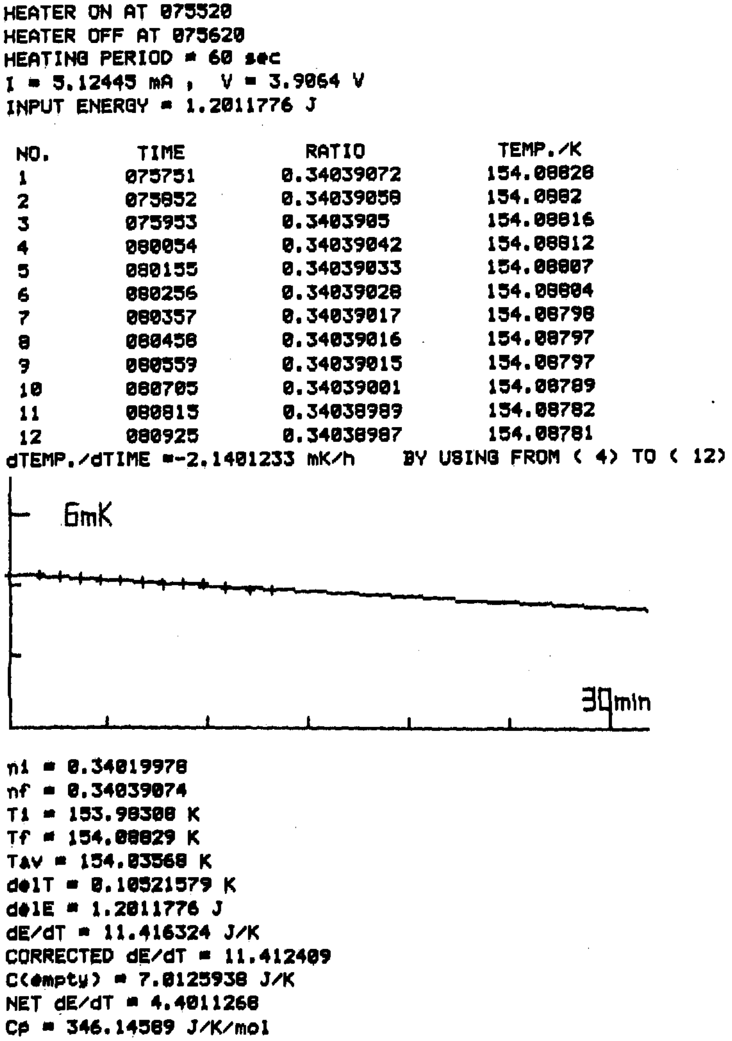


Fig. 8 Block diagram of the on-line automated calorimetric system.



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HEATER ON AT 075520
HEATER OFF AT 075620
HEATING PERIOD = 60 sec
I = 5.12445 mA ,  V = 3.9064 V
INPUT ENERGY = 1.2011776 J

 NO.        TIME          RATIO           TEMP./K
 1          075751        0.34039072      154.08828
 2          075852        0.34039058      154.0882
 3          075953        0.3403905       154.08816
 4          080054        0.34039042      154.08812
 5          080155        0.34039033      154.08807
 6          080256        0.34039028      154.08804
 7          080357        0.34039017      154.08798
 8          080458        0.34039016      154.08797
 9          080559        0.34039015      154.08797
 10         080705        0.34039001      154.08789
 11         080815        0.34038989      154.08782
 12         080925        0.34038987      154.08781
dTEMP./dTIME =-2.1401233 mK/h    BY USING FROM ( 4) TO ( 12)
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ni = 0.34019978
nf = 0.34039074
Ti = 153.98308 K
Tf = 154.08829 K
Tav = 154.03568 K
delT = 0.10521579 K
delE = 1.2011776 J
dE/dT = 11.416324 J/K
CORRECTED dE/dT = 11.412409
C(empty) = 7.0125938 J/K
NET dE/dT = 4.4011268
Cp = 346.14589 J/K/mol
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Fig. 9 Reproduction of a typical experimental result.

A block diagram of the automated calorimeter is shown in Fig. 8. A personal computer (Sharp MZ 80B or MZ2200) accepts the 32-bit temperature data from the resistance bridge (ASL Model A7) which measures the resistance of the Pt thermometer against the standard resistance I, and calculate the temperature using a stored set of calibration constants of the thermometer. The computer actuates the relays to start heating the sample and to select the voltage (either across the calorimeter heater or the standard resistance II) to be measured by the digital voltmeter (Takeda Riken TR 6875). The DVM gives the data back to the computer through the IEEE 488 line. The adiabatic shields are controlled in the same way as in the manual operation, with a small modification that the computer tells the controllers to change their basic output power according to whether the calorimeter is being heated or approaching thermal equilibrium.

The program written in BASIC has a large degree of freedom to decide the experimental condition given as ten numerical parameters. Some of the more important are the length of the heating and rating periods, frequency of the temperature measurement and the number of the data to be taken into the least square fitting for the determination of the final and initial temperatures by extrapolation. The reading of the thermometric bridge is taken at two-second interval and 10 to 100 readings are averaged to one temperature datum, thus reducing the random noise by a factor of upto ten. The gross heat capacity thus determined is reduced to the molar quantity by using the stored empty cell data and keyed-in mole factor, with small correction made for the heat capacity of the conduction He gas. Typical experimental result is reproduced in Fig. 9.

The automated calorimeters work routinely. Most of the heat capacity data described above were obtained with the automated system.

CONCLUSION

Low temperature calorimetry has been developed for long time and is matured now. The question raised by Westrum, "Quo vadis, low temperature calorimetry?" (16) may have a number of answers. Among them will be those discussed here; microcalorimetry, automation and calorimetric spectroscopy. Needless to say, it is better to have a calorimeter which can produce the same quality of data with less amount of sample. Thus the miniaturization of calorimeter is one of the eternal subjects imposed to scientists engaging in the field of experimental chemical thermodynamics.

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