

Automated, small sample-size adiabatic calorimeter

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An automated adiabatic calorimeter with an internal volume of 5 cm³, operable over the temperature range from 30 to 380 K is described. One of the main advantages of this calorimeter over others in use is the much abbreviated down time during sample changes, due to interchangeable sample vessels that fit into the heater/thermometer assembly. This calorimeter was tested by measuring the heat capacity of benzoic acid, and the results agreed with the literature values to within 0.5%.

INTRODUCTION

Calorimetry has been used for many years to measure the heat capacities of materials as a function of temperature. Accurate heat capacity data have been extremely useful to determine chemical thermodynamic quantities, to reveal phase transformations *definitively*,^{1,2} to determine the entropies associated with phase transformations, to determine whether a transition is of first or higher order.

Adiabatic calorimetry based on the heat-pulse method is considered to be the most accurate,³ and although it is not a new technique (see Ref. 4 for a review), recent technological advances have alleviated many of the problems associated with this technique. The collection and processing of the vast amount of data required to characterize a single material over the 10–300 K range have been simplified through the use of digital voltmeters, large core memory personal computers, and automatic shield controllers, leading to automated adiabatic calorimeters.^{5–13} Advances in electronics and materials science also have led to a significant reduction in sample size required to make accurate heat capacity measurements. The reduction in sample volume has progressed from 100 cm³ (Ref. 14) to 25 cm³ (Refs. 15 and 16) and even 10 cm³ (Ref. 6) for routine calorimetry. The past few years have seen the development of several adiabatic calorimeters requiring substantially smaller samples, of the order of a few cm³, down to about 0.5 cm³.^{17–21}

Our main purpose in developing a new automated small-sample adiabatic calorimeter was to increase the flexibility in our studies of solid-state polymorphism. (For typical studies see Refs. 1, 2, and 22.) In particular, we wished to be able to measure accurately the heat capacities of precious deuterated materials in order to pull together information from microscopic techniques, such as NMR and IR, in which deuterium plays an important role as a probe species. Deuteration (and other isotopic substitution) is not necessarily benign as far as the properties of the molecule in the lattice are concerned (see Ref. 23 for some examples in disordered solids) and for this reason it is not always possible to correlate results from thermodynamic measurements of natural-abundance isotopomeric molecules with microscopic measurements of isotopically enriched materials. In addition to deuterated materials, we have been faced frequently with the frustration of insufficient quantity of material to

meet our criteria of better than 1% accuracy in the heat capacity determination using a 25-cm³ calorimeter.

Our aim, therefore, was to design and construct an automated adiabatic calorimeter with a relatively small sample requirement (~5 cm³), preferably operable over the temperature range from room temperature down to a few ten's of Kelvin, i.e., the temperature range of most molecular solid–solid phase transformations. We also wished to keep the data-acquisition system as close as possible to that of our present system used for a 25-cm³ adiabatic calorimeter^{13,16}; this led us to use a calibrated miniaturized (12.1-mm-long) Pt resistance thermometer on the calorimeter vessel as our temperature probe, rather than thermocouples and a shield thermometer as Westrum and co-workers have used effectively.¹⁹ In addition, we wished to make the calorimeter amenable to loading solid samples of varying morphology, as well as liquid samples which would be solidified below room temperature; the design should also allow convenient loading of samples which are hygroscopic or air sensitive. Our final criterion for the design of this calorimeter, and the one in which our calorimeter appears to be most novel, is that we wished to be able to change the sample with minimum down time, and without disconnection of the heater or thermometer wires. This has been achieved by the use of interchangeable sample compartments which slip into the heater/thermometer assembly.

I. THE CALORIMETRIC SAMPLE CONTAINER AND HEATER/THERMOMETER ASSEMBLY

The basis of this calorimeter is a cylindrical sample vessel with an internal thermometer well, placed inside a heater/thermometer assembly. The apparatus is shown schematically in Fig 1.

The cylindrical sample container (18×18 mm) was constructed of thin-walled (0.3-mm) copper with a central thermometer well insert and a thicker copper flange. Six tapped holes (00-90 screws and tap from Spae–Naur) and a groove in the flange allowed an indium seal to be made with the lid. (0.5-mm-diam indium wire was purchased from Aldrich.) It was found that a copper washer was also needed above the lid in order to increase compression and guarantee a good hermetic indium seal. The use of the washer allowed the lid to be thinner than would otherwise have been re-

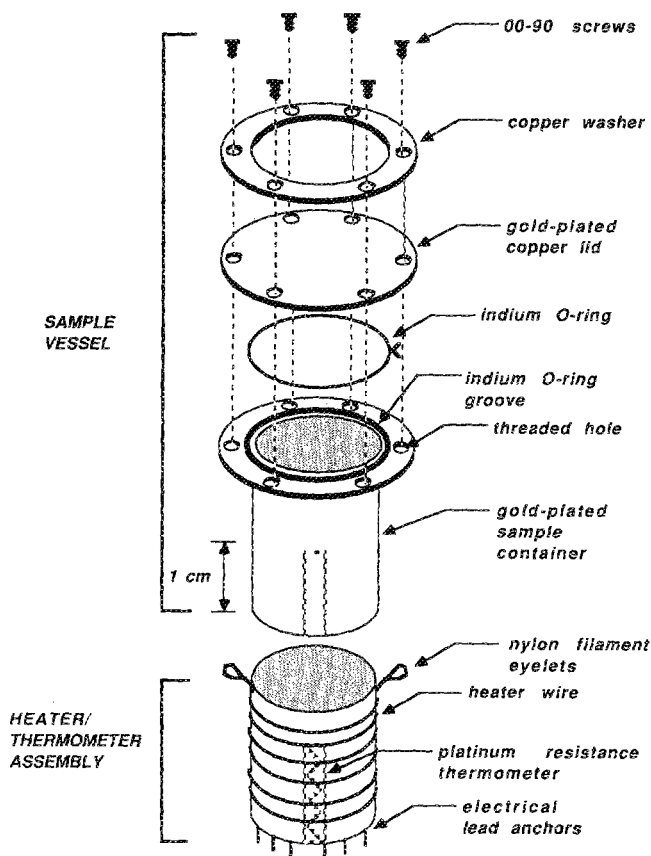


FIG. 1. The sample vessel and heater/thermometer assembly.

quired, thereby keeping the mass of the vessel to a minimum. The sample container and lid were gold plated so that salts which might oxidize copper could be investigated. The total volume of the sample container is $\sim 5 \text{ cm}^3$ and the mass was $\sim 11 \text{ g}$.

The heater/thermometer assembly was constructed of thin-walled copper (0.3 mm) with a central thermometer well. Small copper hooks were soldered to the walls of the assembly to allow it to be hung inside the adiabatic shield using nylon filament. Approximately 2.6 m of double silk-wound Karma wire (590- Ω resistance) was wound bifilarly around the heater/thermometer assembly and varnished into place using low-temperature varnish (GE 7031). A copper-Constantan junction which forms a thermocouple with the junction on the adiabatic shield was soldered onto the bottom of the heater assembly using indium metal.

Electrical lead anchoring posts were constructed out of 18 SWG copper wire and soldered into place on the bottom of the heater assembly. They were electrically insulated using low-temperature varnish (GE 7031) and 5-min epoxy. Silver tubes were press fastened and epoxied over the posts and all leads from the vessel were soldered into the tubes using thermal-free solder (Leeds and Northrup). All electrical leads were double-silk wound 38 SWG copper wire.

A platinum resistance thermometer purchased from and calibrated (4 to 380 K) by Lake Shore Cryotronics (Pt-103, 100 Ω at $T = 273 \text{ K}$) was varnished into the thermom-

eter well of the heater/thermometer assembly using GE 7031 low-temperature varnish.

The mass of the heater/thermometer assembly, including thermometer and leads was approximately 7.5 g, giving a total mass of the empty sample container, heater, and thermometer of $\sim 19 \text{ g}$.

II. THE SAMPLE LOADING PROCEDURE

The typical procedure for loading a sample in the calorimetric vessel is as follows. The preweighed sample container is filled and a length of indium wire of known mass is placed into its groove. The lid and copper washer are placed into position and the screws are very loosely started. The entire assembly is placed in a vacuum desiccator and dried under vacuum over P_2O_5 . The desiccator is opened in a glove box with a helium atmosphere and the screws of the indium seal are tightened. This allows the sample to be hermetically sealed with a small amount of helium gas trapped inside to enhance thermal equilibration. The assembly is reweighed to determine the mass of the sample.

The outside of the sample container is then lightly greased with Apiezon T grease (known mass, $\sim 10 \text{ mg}$) and then the sample container is placed in the heater/thermometer assembly. Apiezon T grease was selected over Apiezon M and N because the M and N melt at approximately 310 K²⁴ and they also have much larger low-temperature thermal anomalies,²⁵ and about twice the base-line specific heat of Apiezon T.²⁶ Apiezon T has an operating range up to $\sim 400 \text{ K}$.²⁴

Electrical leads are sufficiently long so that the entire sample vessel can be lifted away from the heater/thermometer assembly (which remains attached through its electrical leads to the adiabatic shield) without desoldering. This allows changing of samples by simply opening the lid to the shield, lifting out the assembly, slipping out the sample vessel, and replacing it with another sample vessel containing a new sample. The total time during which the vacuum is broken can be as low as 5 min.

Because there is no need to wait while the sample vessel is emptied, cleaned, and refilled, and also because the reduced exposure time of the enclosure can to the atmosphere allows the subsequent pumping down to proceed much faster (less than one day compared to two or three days), the total downtime between sample changes is decreased from approximately five days for a single sample vessel calorimeter to less than a day.

III. THE CALORIMETER

The cryostat, adiabatic shield and its controller, computer system and hardware, and the method of thermometer resistance measurement have been described previously.^{13,16} The measured resistance of the thermometer was converted to temperature using the method of cubic spline fit: a separate cubic polynomial is fit to neighboring points and each of these curves are pieced together so that they meet with no jaggedness (i.e., no kinks or sharp bends) or discontinuities.²⁷⁻²⁹ The temperature/resistance spline parameters were obtained from a cubic spline fit of the 110 points of the tem-

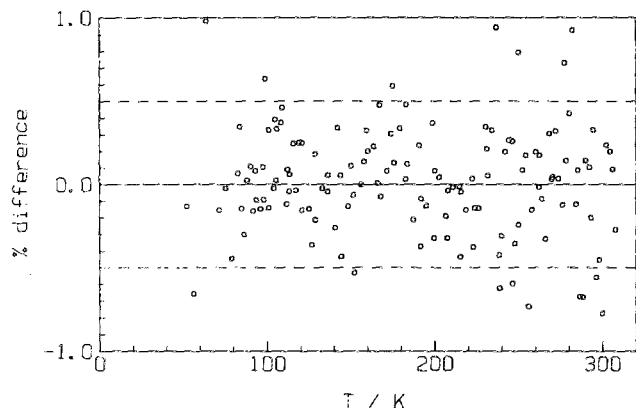


FIG. 2. The % difference between the measured heat capacity of benzoic acid and the literature values,³² as a function of temperature.

perature-resistance calibration data for the platinum resistance thermometer over the temperature range from 4 to 380 K.

Cubic spline fits were performed on the heat capacity of the empty vessel (generally within 0.2% of the smoothed empty vessel data), and on the literature data for Apiezon T grease²⁵ and indium metal^{30,31} so that their contributions could be accounted for in subsequent experiments. Corrections for the mass differences in Apiezon T and indium wire from one run to another amount to not greater than 0.04 % of the total heat capacity of the empty vessel over the entire temperature range.

It has been stated that a short time constant of thermal equilibrium within the sample vessel is the most important factor in design of an adiabatic calorimeter vessel.²¹ Throughout the range of the measurements thermal relaxation times following heating of the empty calorimeter were about 5 min, well within the desired range. However, it was found that the presence of grease between the sample vessel and the heater/thermometer assembly was essential in order to obtain these short relaxation times.

IV. BENZOIC ACID

As a test of the accuracy of the calorimeter, the heat capacity of 3.8817 g of Calorimetry Conference (NBS-49) benzoic acid was measured from 35 to 310 K using temperature increments of about 3–8 K. The measurements were limited at the low-temperature end by heat leaks from the vessel to the surroundings. The empty vessel contributed about 50% to the total heat capacity at the lowest temperatures, increased to about 70% by 90 K, and remained constant at about 70% to 310 K. (The contribution of the sample will be considerably increased in the denser materials which we intend to investigate.) A plot of the % difference between the experimental and literature values³² of the heat

capacity of benzoic acid is depicted in Fig 2. The results obtained with this calorimeter agree with literature to within 0.5%.

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