An automated high precision calorimeter for the temperature range 200K–400K. Part 1: Design and performance

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Abstract. A fully automated calorimeter has been designed and tested over the temperature range 200K–400K. The system may be used for measurements with an absolute accuracy of 0·2% of samples of approximate mass 50g and thermal capacity 15 JK^{-1}. The temperature of the sample is determined by a quartz crystal thermometer of resolution 100 μK which is not in direct thermal contact with the sample. The performance of the system is illustrated by results obtained on high purity copper, distilled water and $K_2PbCu(NO_2)_6$ which exhibits very sharp first order phase transitions at about 273·4K and 281·8K.

1. Introduction

Measurements of specific heat are generally limited to three temperature ranges, low—below 20K, intermediate—between 20K and 300K and high—above 373K (see, for example, McCullough and Scott 1968). Measurements in the intermediate range can be made with high accuracy but those in the high temperature range are characterized by rather poor absolute accuracy and low temperature resolution.

The calorimeter system described here was designed specifically for measurements, within the overlap range 200K to 400K, with an absolute accuracy of about 0·2%. A number of magnetic and other phase transitions lie within this temperature range and the thermodynamic parameters which characterize them are currently being systematically investigated using this system.

Two general methods are available for measuring specific and latent heats—a.c. methods as adopted, for example, by Garnier and Salamon (1971) in which the specimen temperature is modulated by a.c. heating. Other more conventional methods (Martin 1960) are based on the measurement of the change in temperature of the specimen caused by d.c. heating either continuously or in the form of heat pulses. The advantages of a.c. heating arise from the fact that the modulated temperature of the specimen may be measured to high accuracy and resolution using phase sensitive detection. Thus they may provide accurate relative measurements of specific heat and high temperature resolution, but the absolute accuracy of measurement of specific heat is relatively low.   By contrast, the more conventional techniques

are capable of producing highly accurate absolute measurements of specific heat but this is achieved at the expense of temperature resolution.

In the calorimeter system described here the specimen is heated by d.c. and some innovations in design have resulted in increased temperature resolution and improved relative accuracy, both of which are comparable with those characteristic of a.c. heating methods. For optimum performance large specimens of mass about 50g are required. A.c. heating methods typically require much smaller samples, which is obviously of great advantage for observations on some materials. We have adopted continuous rather than pulse heating as this greatly facilitates automation of data collection.

2. Design

The cryostat is sketched in figure 1. The sample A of mass about 50g is suspended by electrical leads within two thermal shields B1 and B2, surrounded by a vacuum chamber C which in operation is maintained at a pressure of 10^{-3} Atm^{-2}.
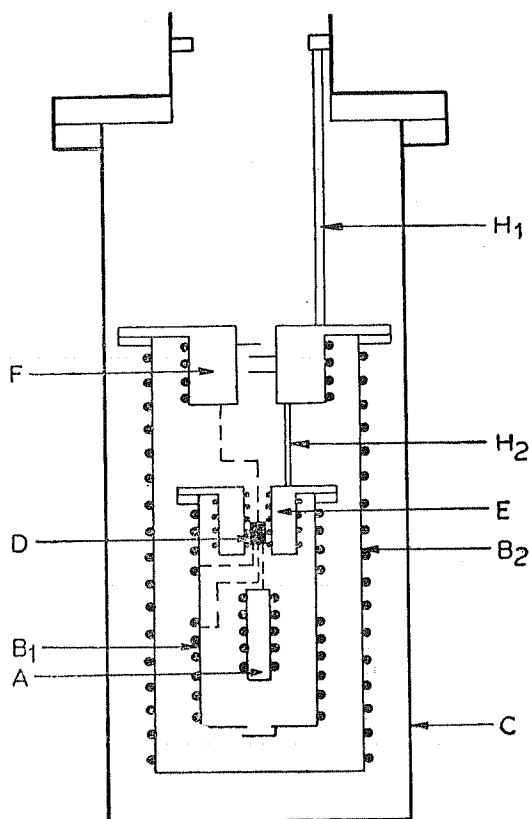

Figure 1. Schematic diagram of adiabatic calorimeter. H_1 and H_2 are stainless steel supports; F is the outer shield heat sink; E is the adiabatic shield heat sink; A is the specimen; C is the vacuum jacket; B_1 and B_2 are respectively the adiabatic and outer shields, and D is the quartz thermometer. Thermocouples are indicated by broken lines and heaters are indicated by series of points.

The sample heater is of 48 swg manganin wire wound on the sample and the current input leads are of 38 swg manganin wire. Potential leads are attached to the current leads at points midway between the sample and the adiabatic shield heat sink *E* (Martin 1972).

A quartz crystal thermometer D (Hewlett-Packard Type 2801A) is fitted in close thermal contact with the copper block E which functions as a heat sink and a temperature reference point. This thermometer is capable of resolving temperature differences of 100 μK and the reproducibility of absolute temperature measurements over the range 200K–400K is better than 0·05K. The quartz crystal thermometer was calibrated against a platinum resistance thermometer (Rosemount E109) which in turn was standardized at fixed reference temperatures (0°C and 100°C). The performance of quartz crystal thermometers has been discussed by Benson and Krause (1974). During the course of a measurement the difference in the temperatures of the sample A and the reference temperature block E is measured by a three-couple copper-constantan thermopile.

The adiabatic shield B1 is in close thermal contact with the temperature reference block E and is surrounded by a floating thermal shield B2 attached to a copper block F which acts as a heat sink. The two thermal shields are each supported by three stainless steel tubes which are indicated as H1 and H2 in figure 1. During a measurement run the system in its vacuum jacket is immersed in either a dry ice or an ice bath.

The instrumentation for measurement and control is shown schematically in figure 2. The specimen A, the temperature reference block E and the heat sink F already referred to are so indicated on figure 2. Power is supplied to the sample heater, of resistance about 600Ω, from a controlled power supply Z. The difference in the temperature of sample A and the temperature reference point E is measured by the three-couple copper constantan thermopile, referred to above, and the Keithley nanovoltmeter XI. The temperature difference signal is fed to the control unit Y1 so that the difference in temperatures of the sample and the reference point E is minimised to better than 1 mK. The temperature differences between the reference point E and two positions on the adiabatic shield are monitored by X_3 and X_4 and are controlled to better than 5 mK using two control units Y_3 and Y_4 for two separate heaters wound on the adiabatic shield. The difference in the temperatures of the floating shield and the reference temperature block is monitored by X_2 and controlled to be at an offset temperature of about 2K by the heater control unit Y_2. Power from Y_2 is fed via a potential divider to heaters on the heat sink F and on the floating shield B2. The offset temperature is chosen to give optimum operation of the inner three control units.

Data are collected at preset intervals by a data logging system and directed to a DEC computer and stored on file for later analysis. The output of the quartz crystal thermometer is in the form of a sine wave of frequency about 20 mHz. This is measured by a frequency counter which accumulates the data over a time interval of 10 s and the reference temperature is indicated to 100 μK. The temperature of the specimen is equal to the reference temperature corrected for the sample—reference temperature difference measured by the thermopile and integrated by *G* over the identical 10 s time intervals required for the determination of the output frequency of the quartz crystal thermometer. The potential difference across the sample heater and the current through it (as determined from the potential difference
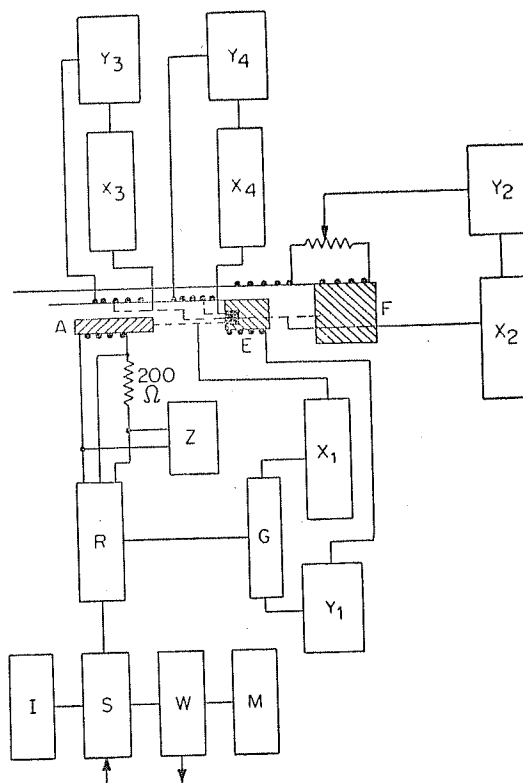
Figure 2. Block circuit diagram for control and measurement associated with calorimeter. X_1, X_3 and X_4 are Keithley 148 nanovoltmeters; X_2 is a Keithley 149 microvoltmeter; Y_1, Y_2, Y_3 and Y_4 are heater control units; Z is a 0–30V power supply; G is a 10 s integrator; R is a serial interface; S is a data logger; W is a video terminal; M is a magnetic tape recorder, and I is a digital voltmeter. A is the sample, E the adiabatic heat sink, F the outer heat sink.

across a 200·0 Ω series resistor at 20°C) are recorded at each of the data sampling points.

The principal feature of the system is the use of a quartz crystal thermometer to measure temperature and its placement on the adiabatic heat shield rather than on the sample. This removes the necessity for having bulky accessories attached to the sample and overcomes the need for a sample holder when measurements are made on solid samples. However, the data collection arrangements ensure that the specimen temperature may be determined accurately from the quartz crystal thermometer measurements. The sample with its bifilarly wound manganin heater of resistance $\sim 600\ \Omega$ is wrapped in thin aluminium foil which is held in position with fine insulated copper wire. The three junctions of the copper-constantan thermopile are insulated by a thin layer of G.E. varnish.

The temperature variations of the specific heats of the ancillary materials used in the preparation of the specimen have been determined to an accuracy better than 0·5% in separate control experiments. These data have been fitted by the method of least squares to a polynomial in temperature from which the specific heat values may be calculated to within 1% at any temperature in the range 200K–400K. For aluminium

foil our values agree closely with those given by Giauque and Meads (1941). Our values for the insulated copper wire used are approximately 10% higher than those for pure copper, the difference being due to the enamel coating. The masses of all the materials used in preparing a specimen for measurement amounting *in toto* to less than 1g may be determined to better than 1 mg.

A computer programme has been written which *inter alia* converts the quartz crystal thermometer readings to absolute temperatures, obtained in the calibration against a standardized platinum resistance thermometer, and corrects for the thermal capacity of the ancillaries attached to the specimen.

3. Performance

The overall accuracy which may be achieved is determined by the uncertainty of measurement of various contributory parameters. The measurements of time intervals are accurate to better than 0·1%; measurements of heater currents and potential differences are made with about 0·02% accuracy and it is estimated that the uncertainty in energy delivered to the specimen due to the heat generated in the leads to the heater is 0·1%. Half the masses of the heater leads and the thermopile wires are assumed to contribute to the thermal response of the sample. The uncertainty in the mass of the ancillary materials used in the preparation of the sample is about 25 mg. For a sample of mass 50 g the uncertainty in specific heat associated with the leads and ancillary materials amounts to 0·05%.

The available temperature resolution is 0·1 mK although, typically, temperature fluctuations lead to a scatter of temperature of $\pm$0·3 mK.

Uncertainty in determining heat leaks from the surroundings to the sample due to convective, conductive and radiative processes give rise to uncertainties in the determination of the energy input to the sample. Convection as a source of heat transfer is entirely negligible at the pressure maintained in the vacuum chamber. Heat transfer by conduction is confined to that along the leads between the sample and the temperature reference point E (of figure 1). The temperature difference between E and the sample is typically about $\pm$1 mK which corresponds to a conductive heat flow of magnitude 2 μW to be compared with a typical power input to the sample heater of 20 mW. Thus corrections due to conductive leak inputs are about 0·01% of the total energy supplied to the sample and are negligible.

Radiative heat leaks are minimized by gold plating the inner surface of the adiabatic shield and by wrapping the sample in aluminium foil. During a measurement run the temperature difference between the sample and the adiabatic shield is controlled within a maximum of 5 mK. Approximate calculations show that at 300K this temperature difference results in a radiative heat leak of about 10 μW (0·05% of sample heat input). However, at temperatures around 400K the radiative heat leak amounts to 0·12% of the sample heat input.

We estimate the accuracy of absolute measurement of specific heat as 0·2%. The relative accuracy of measurement and temperature resolution are interrelated. The best accuracy of 0·2% may be achieved for temperature intervals of about 150 mK, whereas for temperature intervals of 10 mK the accuracy of measurement of specific heat is reduced to about $\pm$ 3%.

Optimum performance of the system is achieved for specimen heating rates lying

between 1 Kh⁻¹ and 15 Kh⁻¹ for which the system operates automatically over the temperature range 200K to 400K.   At these heating rates the temperature differences through typical metal samples may be reduced to less than 0·5 mK.   In operation the calorimeter is cooled to the base temperature and approximately one hour is required for the controllers to lock on during which time some attention to the adjustment of the controls is required.

The present low temperature limit of operation is set by the quartz crystal thermometer which becomes highly nonlinear for temperatures ranging below 190K.   The upper temperature limit is set by breakdown in properties of the insulants and construction materials, e.g. solder, which are used.

4. Results

The performance and accuracy of measurement of the system were tested by making a series of measurements on a sample of mass 66·20 g of annealed polycrystalline copper of purity 99·9996%.

Measurements from 200K to 400K at heating rates of 3 Kh⁻¹ and 6 Kh⁻¹ gave results for the temperature variation of specific heat which were in mutual agreement to better than 0·2%.   Martin (1960) determined the specific heat of high purity copper at temperatures below 300K and our results agree with his in the range 200K–300K.   Previously published data and our results on the temperature variation of the specific heat of copper are plotted on figure 3.   Previous data for the range 300K to 370K were obtained using higher temperature methods for which the absolute accuracy is not high.   Extrapolation of high and low temperature curves of previously published data are not conformable.   Our measurements are conformable with the
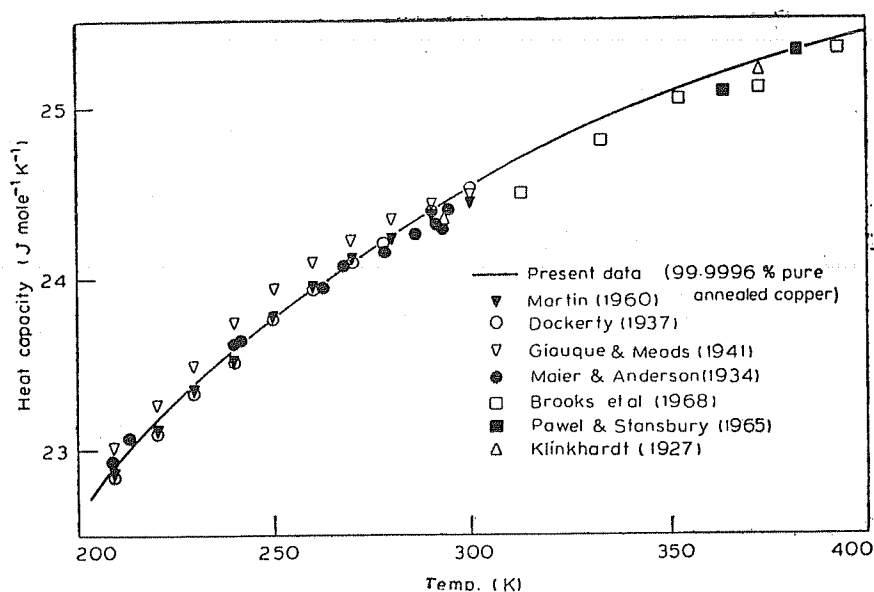

Figure 3. Temperature variation of specific heat of copper. Present measurements on 99·9996% copper and other available data.

lower temperature data and are consistent, within the experimental uncertainty, with previously reported high temperature data. The numerical values of the specific heat of high purity copper at 5K intervals from 205K to 390K are given in table 1.

The uncertainty in the measurement of specific heat decreases with increasing temperature due mainly to problems associated with radiation heat transfer. Data close to 400K are reproducible to 0·3% but around 250K the reproducibility is to 0·1%. Measurements on different samples of copper were in agreement to within 0·2%.

The results of measurements of the specific heat of water from 280K to 350K are plotted in figure 4. These data agreed with accepted values (Osborne *et al* 1939) to within 0·2%.

An important use of the system is to investigate phase transformations which often involve very rapid variations in specific heat. The performance of the calorimeter

Table 1. Absolute specific heat (*Cp*) of annealed high purity copper

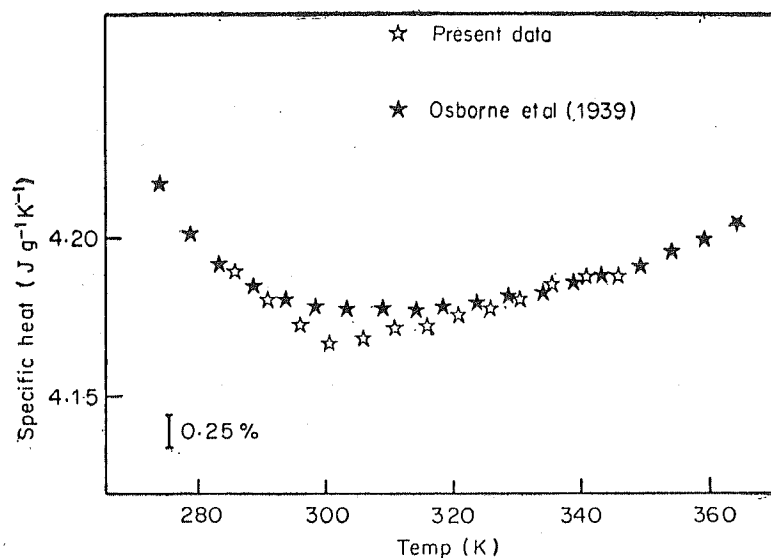| Tempe-rature K	Specific Heat J/mole/K	Tempe-rature K	Specific Heat J/mole/K	Tempe-rature K	Specific Heat J/mole/K	Tempe-rature K	Specific Heat J/mole/K
205	22·78	255	23·85	305	24·60	355	25·12
210	22·91	260	23·95	310	24·67	360	25·16
215	23·03	265	24·02	315	24·72	365	25·20
220	23·16	270	24·09	320	24·78	370	25·25
225	23·27	275	24·16	325	24·85	375	25·29
230	23·39	280	24·23	330	24·91	380	25·33
235	23·48	285	24·31	335	24·96	385	25·37
240	23·57	290	24·39	340	25·00	390	25·40
245	23·67	295	24·45	345	25·04		
250	23·76	300	24·53	350	25·08		

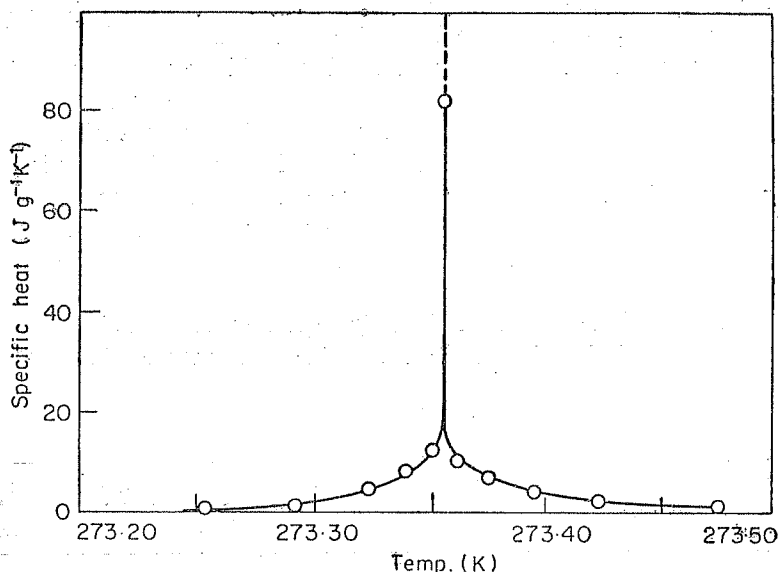**Figure 4.** Temperature variation of specific heat of water.

Figure 5. First order Jahn-Teller transition in $K_2PbCu(NO_2)_6$.

in measurements of this kind was tested using a sample of $K_2PbCu(NO_2)_6$ which exhibits Jahn-Teller transitions at about 273·4K and 281·8K. The temperature variation of the specific heat of this material has been reported by Harrowfield and Weber (1972). The mass of the sample was 13 g and 30 mW power was supplied to the sample continuously. Experimental results obtained at temperatures around the transition at 273·4K are plotted in figure 5. At temperatures away from the transition the specific heat was averaged over a temperature interval of 50 mK; nearer the transition temperature the averaging was performed over smaller temperature intervals. At the transition the sample temperature remained constant to within $\pm$ 5 mK during a time interval of approximately 120 s. The transition temperatures and the latent heats of transformation were determined as:

Transition at 273·36K $\pm$ 0·03K   Latent heat 0·95 Jg^{-1}

Transition at 281·8K $\pm$ 0·4K   Latent heat 0·97 Jg^{-1}

These are in reasonable agreement with the results obtained by Harrowfield and Weber (1972).

Further details of the individual electronic units of the calorimeter system will be published in due course.

5. Acknowledgement

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