CHAPTER 2  
EXPERIMENTAL TECHNIQUE FOR  
HEAT CAPACITY MEASUREMENT
2.1 A BRIEF NOTE ON THE METHOD OF MEASUREMENT OF HEAT CAPACITY OF SOLIDS

Generally used methods of measuring heat capacity are based on Eq. 1.1.1. The heat content of the sample is changed by a measured amount and the corresponding temperature change is determined. There are two basic methods employed to determine the specific heat of solids.

In one method the Joule heat flowing in a resistance wire attached intimately to the sample gives the change in enthalpy and the temperature change is determined by a temperature sensitive transducer attached to it.

In the other method, the sample is brought to equilibrium first with a high temperature reservoir (furnace) and subsequently with a thermally isolated system (calorimeter) at a lower temperature. The resulting loss in the sample enthalpy is ideally equal to that gained by the calorimeter. The change in the enthalpy of the calorimeter can be obtained from the change in the temperature of the calorimeter if its heat capacity is known (method of mixtures) or from the amount of material which has undergone a phase change (isothermal calorimeter) if the latent heat of phase transformation is known.
In all these methods, it is necessary to take into account the actual change of heat between the sample and calorimeter and their surroundings and allowance must be made for departure from ideal conditions.

In the present study, the former method given above is followed in setting up the experimental technique to determine the specific heat of solids at laboratory temperatures with ease and reliable accuracy. An adiabatic calorimeter is designed and fabricated for this purpose.

The block diagram of the set up is shown in Fig. 2.1.1. The set up consists of specially designed silver calorimeter (S.C) into which the sample is inserted. A manganine heater wire of SWG 26 is wound on the calorimeter. Iron-constantan unijunction thermocouple (TC) is inserted into the sample. The design details of the silver calorimeter assembly are presented in the following section. A constant current source namely, power supply (PS) No. SPS 8072 is used to pass a known constant current through the heater wire which is intimately wound on the calorimeter. 0-500 mA range milliammeter (A) shown in the figure indicates the current flowing through the circuit. The current flow can be adjusted using the rheostat (Rh).
Fig. 2.1.1 - Block diagram of the experimental setup to determine the heat capacity of solids.

PS Azeo Power Supply Model No. 8072
K Plug key
A Milliammeter
SC Silver Calorimeter
TC Thermocouple
OC Operational Amplifier Circuit
DPM Digital Panel Meter
T T Calorimeter heater leads, terminals.
The change in the temperature of the sample as a result of Joule heating of the sample is detected by the thermocouple. The output of the thermocouple is fed to the input of the operational amplifier circuit OC. The output of the operational amplifier is given to the digital panel meter (DPM) Model No. 200B (Zenith make).
A BRIEF DESCRIPTION OF THE ADIABATIC CALORIMETER

The calorimeter used in this study, shown schematically in Fig. 2.2.1, is an adiabatic calorimeter.

Number of designs of the apparatus have been described in the literature and those due to Southard and Brickwedde, Scott et al., and Johnson and Eckerr are only a few to note here. Though the general design of the present apparatus follows the concepts of Southard and Brickwedde, the details differ considerably.

It consists of a silver calorimeter (S.C). A cylindrical silver tube of length 2.2 cm and internal diameter 0.7 cm is coated on the outer envelope with araldite uniformly for electrical insulation. Manganine wire of SWG 26 is wound non-inductively on this tube to serve as electrical heater to supply heat to the calorimeter and hence to the sample. The resistance of the heater wire wound on the calorimeter is found to be 5.26 Ω. To ensure intimate and rigid contact of the heater wire to the silver tubing (calorimeter), a thin layer of araldite is coated uniformly over the heater wire windings. The heater wires (H,H), after passing through the porcelain tubes (PP) and the porcelain beads (PB), are attached to the two terminals (TT) which are fixed on the hylum cap (C). The porcelain tubes (PP) groove through an insulating circular plate of diameter 0.025 m and thickness 5 mm. The
Fig. 2.2.1 - Adiabatic calorimeter

SC  Silver calorimeter
S   Specimen, I insulating plate
HH  Heater leads, PP Porcelain tubes
TC  Thermocouple
F   Thermos flask
C   Hylum cap
PB  Porcelain beads
G   Glass tube containing thermocouple
TT  Calorimeter heater leads' terminals.
material of the insulating plate is teflan. This plate has a central hole. The glass tubing into which the thermocouple [TC] is assembled is fitted to the sample. The glass tube passes by a tight fit through the hole in the hylum cap and the central hole in the insulating plate [I] as shown in Fig. 2.2.1. With this type of arrangement the silver calorimeter stands vertically and rigidly. The calorimeter assembly is housed in a wide mouth thermosflask where the hylum cap tightly fits into the mouth of the thermosflask. The side wall of the hylum cap is soft padded with a thin teflan tape.

The sample with a central hole of 1 mm diameter and 3 mm depth drilled axially at one of its surfaces fits tightly into the calorimeter. In this hole of the sample goes the fine junction of the thermocouple. A drop of glycerin is put into the hole of the sample for proper thermal contact between the sample and the thermocouple junction.
2.3 A BRIEF ACCOUNT OF ELECTRONIC CIRCUITRY USED FOR MEASUREMENT OF HEAT CAPACITY OF SOLIDS

The thermo e.m.f. developed across the junction leads of the thermocouple inserted into the sample, when the sample is heated slowly, is to be detected with greater accuracy to determine the temperature change as a result of heat supplied to the calorimeter. The greater the accuracy, the more accurate would be the heat capacity measurement. To obtain this the thermo e.m.f. is amplified using an operational amplifier. The amplifier circuit is shown in Fig. 2.3.1. The operational amplifier used is 741. The base diagram of the OP amp is shown in Fig. 2.3.2.

The operational amplifier for its working, a dual power supply +12 V and -12 V is to be used. The circuit employed to obtain +12 V -12 V is shown in Fig. 2.3.3.

The off-set adjustment is to be made initially by connecting the Inverting input of the Op-AMP to ground. Once this is done, the circuit is ready for measurement of thermo e.m.f.
Fig. 2.3.1 - Amplifier circuit

\[ R_i = \text{Input resistance } 10 \text{ k} \]

\[ R_f = \text{Output resistance } 100 \text{ k} \]
Fig. 2.3.2 - Base diagram of Op Amp 741

1. Offset null
2. Inverting input
3. Non-inverting input
4. $V^-$
5. Offset null
6. Output
7. $V^+$
8. N.C.
Fig. 2.3.3 - Circuit diagram for dual power supply.
2.4 STANDARDIZATION OF THE HEAT CAPACITY MEASUREMENT TECHNIQUE

The standardization of the heat capacity measurement technique involves the determination of water equivalent of the calorimeter and its contents using a standard specimen whose heat capacity is known. Since thermocouple is the temperature sensing transducer, it is to be calibrated initially.

The thermocouple (iron-constantan) is taken out from the sample and placed in a water bath whose temperature can be varied and controlled at any desired temperature. After making the off-set adjustments, the thermocouple leads are connected to the input terminals of the operational amplifier circuit.

The temperature of the water bath is varied in steps of 2° C from 25° C to 45° C and the corresponding digital panel meter display readings are recorded. At any desired temperature, the temperature of the water bath could be controlled to an accuracy of ± 0.01° C. The thermostat model No. G.L 15.01 supplied by Toshniwal Brothers is used in the present study. The digital panel meter display readings, which are in millivolts versus temperature of the thermocouple are given in Table 2.4.1.
TABLE 2.4.1

Digital panel meter display reading versus temperature of iron-constantan unijunction thermocouple

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>DPM Display (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>-1.14</td>
</tr>
<tr>
<td>30</td>
<td>0.15</td>
</tr>
<tr>
<td>32</td>
<td>0.74</td>
</tr>
<tr>
<td>33</td>
<td>1.36</td>
</tr>
<tr>
<td>36</td>
<td>2.85</td>
</tr>
<tr>
<td>38</td>
<td>3.68</td>
</tr>
<tr>
<td>41</td>
<td>5.20</td>
</tr>
<tr>
<td>44</td>
<td>6.75</td>
</tr>
</tbody>
</table>
The variation of digital panel meter display reading with temperature is shown in Fig. 2.4.1. This curve is a straight line and gives the calibration curve for the thermocouple.

After calibration, the thermocouple is inserted into the hole drilled axially in specimen which is tightly fitted into the silver calorimeter. Spec. pure aluminium is chosen as a standard sample to determine the water equivalent of the calorimeter and its contents. The length and diameter of the sample are 2.15 cm and 0.7 cm respectively. The circuit connections are as shown in Fig. 2.1.1.

In the present study it is aimed to measure the heat capacities at 30°C. To compensate for radiation losses it is desirable to heat the sample from below 30°C to above 30°C by equal temperature intervals. These should be as small as possible so as to reduce the radiation losses inspite of compensation involved. In this study the sample is heated from 27.5°C ($T_1$) to 32.5°C ($T_2$) by Joule heating at constant current flowing through the circuit. From the calibration chart (Fig. 2.4.1) the DPM display readings $V_1$ and $V_2$ are noted corresponding to the temperatures 27.5° and 32.5°C respectively.
Fig. 2.4.1 - Calibration curve for the Iron-constantan unijunction thermocouple.
To start with, the sample is brought initially to a temperature of 25°C by keeping the calorimeter in contact with water free ice-piece. Now a current of 200 mA is passed through the heater wound around the calorimeter. As a result, the temperature of the specimen increases and hence the display reading. When the display reading reaches $V_1$, the electronic timer is started and it is stopped when the DPI-1 shows $V_2$. So, the time $'t'$ required for the temperature of the specimen to raise from 27.5 to 32.5°C is noted from the electronic timer.

The amount of heat supplied ($Q_1$) to the calorimeter and its contents and the sample is given by

$$Q_1 = I^2 R t$$  \hspace{1cm} 2.4.1$$

where $I$, $R$ and $t$ represent the current flow in 'A', resistance of the heater in $\Omega$ and time of passage of current through the heater to raise the temperature of the calorimeter from $T_1$ to $T_2$ in s respectively. The quantity of heat $Q_1$ is utilised in raising the temperature of the calorimeter.

The heat gained ($Q_2$) by the calorimeter and its contents and the specimen is given by

$$Q_2 = (\omega + mC) (T_2 - T_1)$$  \hspace{1cm} 2.4.2$$

where $'\omega'$ denotes the water equivalent of calorimeter and
its contents, 'm' represents the mass of the sample and 'C' denotes its specific heat.

If there are no radiation losses and other heat losses, which are true in the present set up, then \( Q_1 \) must be equal to \( Q_2 \). Hence

\[
I^2 R t = (\omega + mC)(T_2 - T_1)
\]

The mass of the aluminium sample used in the present study is \( 1.701 \times 10^{-3} \) Kg. The heat capacity of aluminium at \( 30^\circ C \) is \( 904 \) J Kg\(^{-1}\) K\(^{-1}\). Using the known values of \( m, C, (T_2 - T_1), I, R \), and \( t \), can be estimated using Eq. 2.4.3. Since most of the variables in Eq. 2.4.3 are kept constant it is only 't' that we measure. The reliability of the technique depends on how accurately we measure 't', the rate of heating (how much uniform and steady it is) and the stability of the constant current source. The experimental runs are made 10 times and the 't' values are noted. In all these runs 'I' is kept fixed at 200 m A. For each 't' value obtained \( \omega \) is calculated. The values of \( \omega \) obtained for the runs are given in Table 2.4.2. The standard deviation \( (\sigma) \) and the percentage of error \( (E) \) in \( \omega \) are estimated using the following relations

\[
\sigma = \left[ (1/N) \sum (x - \bar{x})^2 \right]^{1/2}
\]

\[
E = (\sigma/\bar{x}) \times 100
\]
TABLE 2.4.2

Values of water equivalent of calorimeter and its contents ($w$) for different trials

$I = 200 \text{ mA}$
$R = 5.26 \text{ \Omega}$

<table>
<thead>
<tr>
<th>Trial</th>
<th>Time ($t$)</th>
<th>$w$ ($\text{Js}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>169.0</td>
<td>5.57</td>
</tr>
<tr>
<td>2</td>
<td>171.8</td>
<td>5.69</td>
</tr>
<tr>
<td>3</td>
<td>171.4</td>
<td>5.68</td>
</tr>
<tr>
<td>4</td>
<td>171.7</td>
<td>5.69</td>
</tr>
<tr>
<td>5</td>
<td>169.5</td>
<td>5.59</td>
</tr>
<tr>
<td>6</td>
<td>170.5</td>
<td>5.64</td>
</tr>
<tr>
<td>7</td>
<td>170.8</td>
<td>5.65</td>
</tr>
<tr>
<td>8</td>
<td>171.3</td>
<td>5.67</td>
</tr>
<tr>
<td>9</td>
<td>169.3</td>
<td>5.59</td>
</tr>
<tr>
<td>10</td>
<td>169.8</td>
<td>5.61</td>
</tr>
</tbody>
</table>

**Average** $5.64 \text{ Js}^{-1}$
where $X$, $\bar{X}$ and $N$ denote respectively, any value of $\omega$, average value of $\omega$, and the number of observations. The standard deviation is 0.012.

The percentage of error is 0.22. The accuracy of the measurement of $\omega$ estimated using the relation

$$\Delta \omega = \omega \frac{\Delta \{ -mC + \left[ I^2 R(T_2 - T_1) \right] \}}{\{-mC + \left[ I^2 R(T_2 - T_1) \right] \}}$$

comes out to be 0.05 $Js^{-1}$. Therefore $\omega$ determined in this study is given by $5.64 \pm 0.05$ $Js^{-1}$. Thus within the limits of experimental errors, the accuracy in the heat capacity measurement of the present set up may be claimed to be about 1\%.
2.5 MEASUREMENT OF HEAT CAPACITIES OF STANDARD SAMPLES - COMPARISON WITH LITERATURE DATA

The performance and accuracy of the measurement of heat capacity using the experimental set up developed in the present work have been tested by making a series of measurements on samples of spec pure copper, iron (wrought) and brass (70% Cu + 30% Zn).

The test samples namely copper, iron and brass are machined to the same dimensions as that of aluminium sample used for determining w the water equivalent of calorimeter and its contents. These samples tightly fit into the calorimeter. Holes of 1 mm diameter and 3 mm depth are drilled axially at one end surface of the samples for insertion of the thermocouple junction. The masses of the samples have been determined using monopan balance.

The test sample is inserted into the calorimeter. A current of 200 mA is passed through the calorimeter heater. When the display reading of DPM is $V_1$, the digital stop watch is started and the time 't' taken for the thermo e.m.f. to build up to $V_2$ is noted. Using the water equivalent of the calorimeter and its contents, w, and employing Eq. 2.4.3, the heat capacity of the sample is calculated. The experiment is repeated for 10 times and
the average of the values is recorded. The heat capacity obtained for copper, iron and brass in the present study are given in Table 2.5.1 along with the literature data.

The agreement between the present values and the literature values of heat capacity data on test samples is excellent and this indicates the reliability and accuracy of heat capacity measurement technique developed by the author.
TABLE 2.5.1

Heat capacity for test samples - Comparison with literature data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat capacity at 30°C (J kg⁻¹ K⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>395 ± 4</td>
<td>390</td>
</tr>
<tr>
<td>Iron (Wrought)</td>
<td>463 ± 5</td>
<td>460</td>
</tr>
<tr>
<td>Brass</td>
<td>385 ± 4</td>
<td>387 (25°C)</td>
</tr>
</tbody>
</table>

Literature
REFERENCES


