Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 387–397

EXPERIMENTAL EVALUATION OF PROCEDURES FOR HEAT CAPACITY MEASUREMENT BY DIFFERENTIAL SCANNING CALORIMETRY

*K. L. Ramakumar**, *M. K. Saxena and S. B. Deb*

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

(Received October 3, 2000; in revised form May 4, 2001)

Abstract

Experimental evaluation of the procedures adopted for heat capacity measurements employing differential scanning calorimetry (DSC) has been carried out by taking nickel and sapphire as test samples. Among the various methodologies reported in literature, the absolute dual step method was chosen for this purpose due to its simplicity and minimum number of measurements required. By proper temperature and heat flux calibration employing indium as reference, it was possible to obtain the calibration factor independent of temperature. This was ascertained by analysing other pure metals namely Sn, Zn, Cd, and Pb and determining their melting temperatures and heats of melting. Various operator- and sample-dependent parameters such as heating rate, sample mass, the structure of the sample, reproducibility and repeatability in the measurements were investigated. Heat capacities of both nickel and sapphire have been determined using the above method. Further, the heat capacity of nickel has also been determined using the widely employed three-step method taking sapphire as the heat flux calibration standard. Both methods yielded the comparable heat capacity values for nickel. Based on the parameters investigated and their influence, it could be concluded that reasonably precise and accurate heat capacity measurements are possible with DSC. One advantage of this method is the elimination of a separate calibration run using a reference material of known heat capacity.

Keywords: DSC, dual step method, heat capacity, nickel, sapphire, temperature and heat flux calibration

Introduction

Differential scanning calorimetry (DSC) is known as a potential method for measuring thermal and thermodynamic properties of materials. This is a technique in which the heat flow rate to the sample is monitored *vs*. time or temperature while the temperature of the sample is programmed in a specified environment. The differential signal measurement and the dynamic mode of operation are the two important char-

---

* Author for correspondence: E-mail: klram@magnum.barc.ernet.in

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

acteristic features of DSC. Due to this, disturbances such as temperature variations in the environment of the measuring system, thermal contact betwen the sample, sample pan and the heating block etc. affect the two measuring systems in the same way and are compensated when the difference between the signals is formed. As the measured signal is proportional to heat flow rate, time dependences of a transition can also be observed. Experimental data obtained by DSC allow heat capacity, heat of transition, kinetic data, purity and glass transition measurements using only mg sample amounts. Time required for the measurement of heat capacity (C_p) over a wide temperature range is also shorter as compared with the conventional calorimetric measurements. However, unlike in the conventional techniques such as drop calorimetry which is static in operation for achieving thermal equilibrium between the sample and the environment, this very dynamic nature of the instrument operation, in which the rate of change of temperature is continuously monitored and correlated to the heat flow rate, makes the technique of DSC suspect with regard to the sample attaining complete thermal equilibrium with the heating environment for a meaningful C_p measurement. Attempts have been made in literature to circumvent this limitation of DSC by resorting to elaborate calibration procedures to obtain true heat flow rate from the measured quantity. Several variants of the experimental procedures are in vogue for heat capacity measurements by DSC. We can mention (i) the classical three-step procedure, which is widely used, (ii) the absolute dual-step method, (iii) the modified classical method, and (iv) the discontinuous procedure. The important features of each of these methods have been described in literature [1]. In addition, a number of other parameters; operator-dependent, sample-dependent as well as instrument-dependent, influence the overall performance features of DSC. In the present work, an experimental procedure based on a modified dual-step method has been used to evaluate the applicability of DSC for heat capacity measurements and achievable overall uncertainty in the heat capacity measurements. This procedure has been chosen in preference to other procedures mentioned above as it is the simpliest and most convenient to use, takes less time to complete the measurements, and with the proper optimization of the experimental parameters, it may result in comparable, if not better, precision. Some of these parameters such as heating rate, structure of the sample, mass of the sample, and reproducibility in the measurements by taking different sample aliquots were also investigated to ascertain the effect of these factors on heat capacity measurements employing DSC. High purity nickel and sapphire (Al_2O_3) were taken as test samples. The heat capacity values of nickel determined by the dual-step method directly and also by employing sapphire as the heat flux calibrant were compared to evaluate the applicability of the dual-step method for C_p measurements by DSC.

Procedure employed for heat capacity measurement

The knowledge of the heat capacity of a material as a function of temperature is the basis for the determination of any thermodynamic quantities. The use of normal, not hermetically sealed DSC crucibles always gives the heat capacity C_p at a constant pressure. The change of pressure in the sealed crucibles is generally small and the measured heat capacity is nearly the same as that at normal pressure.

In the present work, a hybrid of the absolute dual step method and a modified discontinuous procedure has been employed. One important assumption, however, was necessary to be made; the calibration factor $K_\phi\,(T)$ has been assumed to be constant with time (and temperature). Then careful calibration of the heat flow rate within the temperature interval needs only to be carried out once. The specific heat capacity of the sample C_s(J g^{-1} K^{-1}) can then be calculated using the following equation

$$C_s = \frac{K_\Phi\,(T)(\Phi_s - \Phi_b)}{\beta m_s}$$

where (ϕ_s–ϕ_b) is the blank corrected net heat flow rate in watts into the sample, β is the heating rate ($\Delta T/\Delta t$), and m_s is the mass (g) of the sample. The calibration factor $K_\phi(T)$ consists of both temperature as well as caloric calibration and is determined separately using high purity indium as calibrant. The software provided along with the instrument takes this $K_\phi(T)$ and the mass of the sample as inputs and from the heat flow (in W)–time plot, the area is calculated to tabulate directly the heat flow in J g^{-1} at different temperatures of interest.

The steps involved in the procedure used are: (i) determination of the heat flow rate of the zero line (blank) using empty Al crucibles of equal mass in the sample and reference sides. This zero line reflects the asymmetry of the instrument, and (ii) Al_2O_3 of known mass in Al crucible is placed in the sample side and the experiment is repeated under identical conditions (given in Experimental) as are used in the blank experiment. From the heat flow-temperature plot, the quantity of heat flow into the sample at different temperatures (in the present work we have selected a temperature range of 323–773 K in steps of 50 K) for a 1 K interval is calculated and is corrected from the blank value obtained in a similar way. This gives C_p directly in J g^{-1} K^{-1}. A number of operator-, sample-, and instrument-dependent parameters should be carefully optimised to realise high precision in heat capacity measurements.

Experimental

A heat flux heat exchanging calorimeter has been used. It has a disk-type measuring system with solid sample support. The main heat flow from the furnace to the samples passes symmetrically through a constant disk. Further details of the instrument were given elsewhere [2]. The samples enclosed in high purity aluminium pans are positioned on this symmetrical disk. Separate temperature sensors (chromal–alumel thermocouples) measure the temperature of sample and reference. Temperature as well as the heat flux calibration was carried out using high purity indium standard.

Materials

High purity indium (≈25 mg) and nickel (≈10 mg). Two types of Al_2O_3 samples were used. One was a sapphire standard (≈60 mg) in disk form of about 0.5 mm thick. The other sample was high purity Al_2O_3 powder. The analysis by atomic emission spectrometry indicated the purity of the compound to be better than 99.99%. The powder was heated to 900°C for one h, cooled in a desiccator before use.

High purity metals, Pb and Zn (in the form of fine granules), and Sn, Cd (in the form of thin discs) were used to ascertain the temperature independent nature of the calibration factor.

Brief procedure

In all the experiments, the supporting material used was Al pans of equal mass. The sample was put in Al pans and sealed with Al lids by crimping. For reference, a blank Al pan crimped with Al lid was taken. After placing the sample and reference at their respective designated places in the DSC cell, heating protocol was started which includes (i) heating to 323 K, (ii) isothermal at 323 K for 30 min, (iii) heating to 773 K at a preselected uniform rate (2, 5 or 10 K min^{-1}) and (iv) isothermal at 773 K for 30 min. Minimum four independent experiments were performed for each sample. A separate blank experiment was also carried out without the sample. In all the cases the same heating protocol was maintained. All the experiments were carried out in flowing-Ar atmosphere. Data processing for base line correction was carried out using the software provided along with the instrument. Heat capacity values were calculated as described in the previous section.

The heat capacity of nickel was also determined employing the three-step method. In this case, sapphire was used as heat flux calibrant. This was done primarily to compare the two methods for the determination of C_p values. The calculation methodology is described elsewhere [3–5].

Results and discussion

One of the most important requirements of thermal measurements by DSC is the temperature as well as heat flux calibration of the system. Generally, static methods which ensure thermal equilibrium are applied to realise proper temperature calibration. In DSC, these can be achieved only approximately. As the point of temperature measurement is not the point where the sample is located, a systematic error will always occur in the scanning operation, which depend upon instrument and experimental parameters. In addition, owing to the design of the DSC measuring system, the heat flow rate into the sample cannot be measured directly; the measurement always yields only a heat flow rate at a certain distance from the sample, outside the sample crucible. Due to the finite thermal conductivity of the material between this point of measurement and the sample, the measurement signal is always an approximate representation of the real value. Generally, linear approximations are resorted to while calculating the calibration factors to correlate the measured quantity with the real value. Owing to the dynamic mode of operation of DSC, and the manner of measurement of temperature, it is suspected that (i) the temperature and caloric calibrations carried out at a finite temperature may not be valid at other temperatures, (ii) calibration factors are different for heats of transitions and heat capacities. It should be mentioned that all the initial experiments were carried out at 5 K min^{-1} heating rate as a tradeoff between releasing thermal equilibrium and faster analysis time. The temperature and caloric calibration (peak area of heat of transition (s→l) has been carried out using high purity indium (melting temperature 429.6 K, and heat of transition (s→l) 28.64 J g^{-1}). The calibration factor has been determined using the above values. A typical DSC curve for indium is given in Fig. 1. The fact that the calibration factor is reasonably constant has been verified by determining the melting temperatures and heats of transitions (s→l) of Sn, Pb, Zn, and Cd.

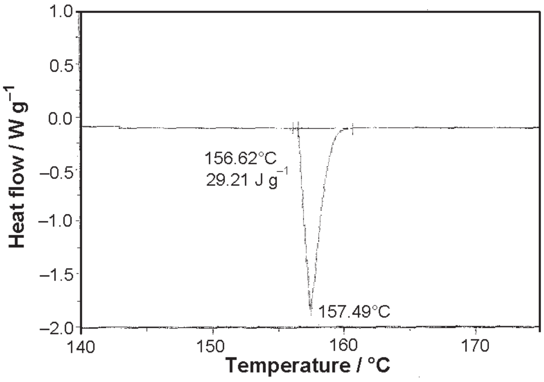

Fig. 1 Typical DSC curve of indium. Temperature and heat flux calibration

Table 1 gives the melting temperatures and heats of melting obtained for Sn, Pb, Zn, and Cd using the calibration factor obtained with indium. Excellent agreement between the expected [6] and determined values for melting temperatures as well as heats of melting indicate that under experimental conditions, it is justified in assuming the constancy of the calibration factor K_ϕ (T) with respect to temperature and heat flow into the sample. The heat capacity of high purity nickel was also determined using the same calibration factor.

Table 1 Validation of calibration factor $K_\phi(T)$ determined from indium at other temperature

Material	Melting temperature/K		Heat of melting/J g^{-1}	
	determined	reported [6]	determined	reported [6]
Lead	600.7	600.5	22.99	23.04
Tin	505.5	504.9	59.2	59.59
Cadmium	594.4	594.1	52.1	54.33
Zinc	696.1	692.5	111.2	112

The results shown in Table 2 indicate that within the experimental uncertainties the same calibration factor could be used both for transition as well as heat capacity measurements. Results obtained by Höhne and Gloggler [7] on power compensation DSC also indicated only a 1% difference between the calibration factors determined using heats of fusion and specific heats. The calibration factor was found to be independent of temperature. Sarge and Cammenga [8], however, observed variations even among the calibration values determined in replicate using sapphire as calibrant. These authors used a heat flux DSC and carried out experiments at 10 K min^{-1} heating rate.

Table 2 C_p of nickel determined employing absolute dual step (using indium as calibrant) as well as the classical three-step method (using sapphire as calibrant)

Temperature/K	C_p with indium as calibrant	C_p with sapphire as calibrant	Literature value [10]
		J g^{-1} K^{-1}	
373	0.478±0.05	0.475	0.467
423	0.499±0.05	0.496	
473	0.522±0.04	0.519	0.515
523	0.551±0.03	0.547	
573	0.584±0.08	0.580	0.569
623	0.625±0.06	0.628	0.628
673	0.537±0.05	0.540	0.544
723	0.548±0.04	0.551	

During the course of our initial experiments, significant variations in the calibration factor were observed. The reason for the same could be traced to the fluctuating base line mainly because of operator-dependent parameters such as the positioning of the sample in the DSC cell, impurities in Ar gas, and mechanical disturbances during measurements. It was also required to carry out the cleaning of DSC cell by oxygen purging at 773 K periodically. It may also be desirable to carry out base line measurements before and after the sample to confirm the reproducible behaviour of the instrument.

In order to evaluate the method used, the C_p of nickel was also determined employing the three-step method with sapphire as the heat flux calibrant. This method is

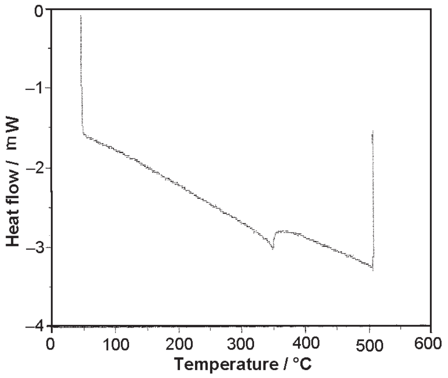

Fig. 2 DSC curve for nickel

similar to the ASTM procedure [9]. Instead of using the calibration factor for every temperature of interest, we have used the average value as described previously. A typical DSC curve for Ni is shown in Fig. 2. The results are also given in Table 2. It should be mentioned that the two calibration factors (obtained from indium and sapphire) are within 3% of each other. The good agreement in C_p values obtained by using both methodologies and also the literature data [10] confirm it.

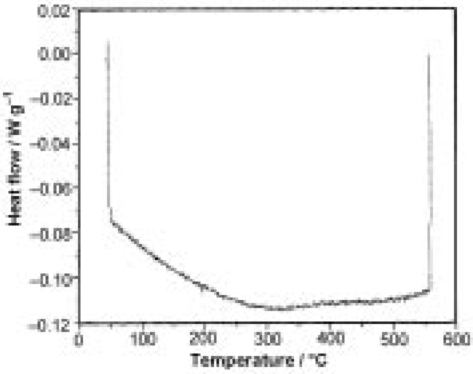

Fig. 3 DSC curve for sapphire

Subsequent experiments were carried out with sapphire to evaluate various parameters. It should be mentioned that the foil and disk samples could be comfortably sealed in Al pans. For Al_2O_3 powder sample, maximum care was taken to ensure that proper thermal contact was established between the powder sample and the supporting Al pan. The sample material was uniformly spread in the entire region of the Al pan before sealing by crimping. Figure 3 gives a typical DSC curve obtained for sapphire. The blank experiment was carried out every day to confirm the reproducibility in the measurements. As the Al pans used for sealing were of equal mass, the heat flux measured could be considered independent of the mass of the supporting material.

Effect of heating rate

The DSC curves were obtained for both the blank and the Al_2O_3 sample at three different heating rates; (i) 2, (ii) 5, and (iii) 10 K min^{-1}. The variation of heat flux measured as a function of temperature at these different heating rates is given in Fig. 4. Adequate care was taken to ensure reproducible geometry during the positioning of the Al pans in the DSC cell. A greater heat flow into the sample at lower heating rate of 2 K min^{-1} at all temperatures is observed. This could be due to the reduced thermal lag because of attainment of thermal equilibrium and minimisation of the systematic errors during temperature and heat flow measurements as mentioned in the previous section. Heat flow into the sample is also high at higher temperatures as compared to lower temperatures for a given heating rate. However, we have observed that the shape of DSC curve got affected to a larger extent at lower heating rates than at

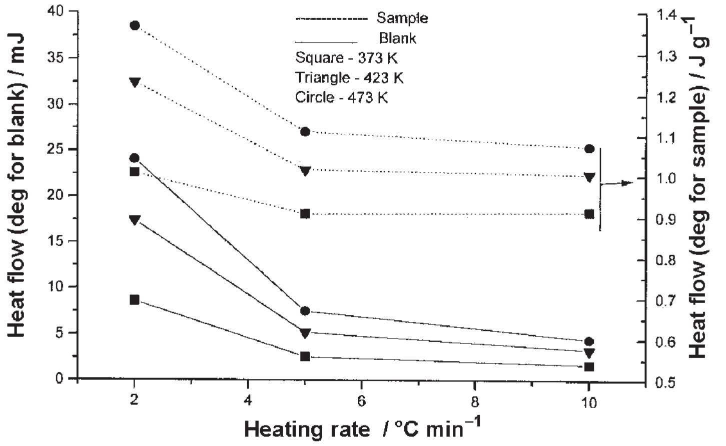

Fig. 4 Effect of heating rate on the heat flow

higher heating rates due to environmental factors such as the mechanical disturbances, positioning of the sample at the designated place in the DSC cell. At relatively higher rates of heating rate (5 and 10 K min^{-1}), the difference between the heat flow at different temperatures is low and become almost independent of heating rate. Thus extraneous parameters may have less influence on the heat flow at these ramps than at lower heating ramps. Even though it is advisable to maintain same heating rates for blank as well as for the sample, current experiments indicated that except for the heating rate of 2 K min^{-1}, the blank correction became independent at other heating rates studied. At lower heating rates, the same heating rate should be applied for both the blank and the sample.

Effect of structure of sample

Two extreme cases were investigated. In one case, Al_2O_3 sample was put in thin disk form, which ensured a proper thermal contact with the measuring system. In the other case, Al_2O_3 powder was taken, uniformly spread to cover the entire area inside the Al pan, which was then crimped. The DSC curves taken for both cases showed a more or less similar behaviour in the temperature range studied. However, replicate analyses of powder samples showed relatively larger spread in the results compared to the disk sample. It should be mentioned that even though proper care was taken to ensure uniform spreading of the powder, it was not possible to realise close packing of the sample. The trapped air between the solid particles could result in variable heat flow into the sample resulting in larger uncertainties in the C_p measurements. No measurement were made to investigate the effect of particle size on C_p measurements.

Table 3 C_p values (J g^{-1} K^{-1}) for disk and powdered samples of Al_2O_3 measured at heating rate =5 K min^{-1} and reported values [11]

Temperature/ K	Disk sample (61.49 mg)			Powdered sample					Reported values [11]
	Run-1	Run-2	Mean	I (31 mg)	II (61 mg)	III (41 mg)	IV (44 mg)	Mean	
373	0.89	0.87	0.88±0.01	0.87	0.85	0.83	0.84	0.85±0.01	0.91
423	0.97	0.94	0.96±0.01	1.00	0.94	0.92	0.92	0.94±0.03	0.97
473	1.01	1.00	1.00±0.01	1.09	0.99	1.01	0.98	1.02±0.04	1.02
523	1.04	1.04	1.04±0.01	1.11	1.03	1.06	1.02	1.06±0.04	1.06
573	1.07	1.09	1.08±0.01	1.15	1.07	1.09	1.07	1.09±0.03	1.09
623	1.07	1.09	1.08±0.01	1.18	1.09	1.11	1.10	1.12±0.04	1.12
673	1.12	1.11	1.11±0.01	1.19	1.12	1.13	1.12	1.14±0.03	1.14
723	1.16	1.16	1.16±0.01	1.22	1.16	1.14	1.17	1.17±0.03	1.16
773	1.22	1.21	1.21±0.01	1.22	1.19	1.14	1.21	1.19±0.03	1.17

Reproducibility

So as to evaluate the operator-dependent parameters such as the effect of positioning of the sample in the DSC cell and sample-dependent parameter such as the sample size, further experiments were carried out by repeating the analysis on the same sample and also by taking different sample amounts. The effect of sample amount was studied only in the case of powder sample. Table 3 gives the results of this experiment. It is seen that under the conditions of analysis heat capacity measurements for disk as well as powder sample of different amounts are comparable with the experimental uncertainties. Accuracy in C_p measurements is about 10% with respect to reported values [11]. In both cases heat capacity could be measured with a maximum accuracy of about 10%. Figure 5 shows the results on C_p of sapphire determined in the present work using the modified dual-step method. Literature data are also shown for comparison.

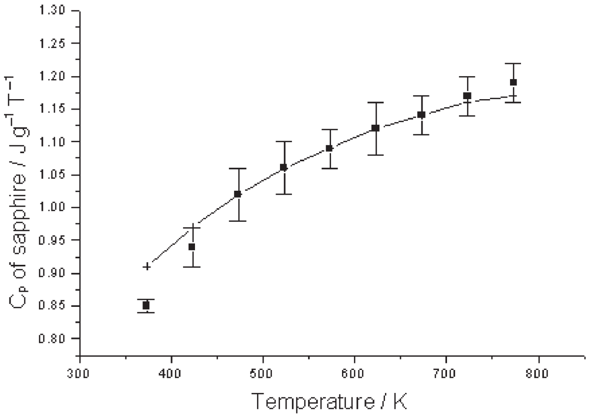

Fig. 5 C_p of sapphire as a function of temperature. Line – literature data [11]; symbol – experimental data

Conclusions

(i) With the modified dual step method it is also possible to obtain the heat capacity values within 5% precision and accuracy.

(ii) Relatively higher heating rates of 5 and 10 K min^{-1} did not as much influence the heat capacity measurements as the heating rate of 2 K min^{-1}. In the latter case, for proper blank correction the same heating rate should be used for both blank and sample.

(iii) Both the disk as well as the powder sample gave consistent and reproducible results. However, the disk sample gives relatively narrower spread in results compared to the powder sample, presumably because of proper thermal contact. With proper precautions, it could be possible to get reproducible and accurate results even in the case of powder samples.

(iv) The operator-dependent and sample-dependent parameters such as repeatability and the reproducibility in heat capacity measurements could be controlled in order to give results within acceptable limits.

(v) It was necessary to carry out a blank run at least once every day to confirm the proper functioning of the instrument.

References

1 G. W. H. Höhne, W. Hemminger and H.-J. Flammersheim, Differential Scanning Calorimetry, Springer–Verlag, Berlin 1996.

2 M. K. Saxena, K. L. Ramakumar and V. Venugopal, Preprints Vol., DAE Symp. Nucl. Radiochem., (NUCAR-99), BARC, Mumbai, January 9–22, 1999, Paper No. RA-38, p. 393.

3 M. K. Saxena, K. L. Ramakumar, S. B. Deb and V. Venugopal, Proc. 12th. Nat. Symp. Thermal Analysis, DDU Gorakhpur University, Gorakhpur, India, March 26–27, 2000, Paper No. PHY-4, p. 33.

4 K. L. Ramakumar, M. K. Saxena and S. B. Deb, ibid, Paper No. PHY-27, p. 33.

5 M. K. Saxena, K. L. Ramakumar, S. B. Deb and V. Venugopal, Abstract book of Conf. Power from Thorium: Status, Strategies and Directions, (INSAC2000), BARC, Mumbai, June 1–2, 2000 Paper No. INSAC2000/49 p. 143.

6 CRC Hand Book of Chemistry and Physics, D. R. Lide (Editor-in-Chief), 80th Ed., CRC Press, New York 1999.

7 G. W. H. Höhne and E. Gloggler, Thermochim. Acta, 151 (1989) 295.

8 S. M. Sarge and H. K. Cammenga, Thermochim. Acta, 94 (1985) 17.

9 D-3947 80, Annual Book of ASTM standards, Part 25, ASTM, Philadelphia, Pa (1980).

10 K. Raznjevic (Ed.), Hand Book of Thermodynamic Tables and Charts, McGraw–Hill, New York 1975.

11 D. A. Ditmars, S. Ishishara, S. S. Chang and G. Bernstein, J. Res. Nat. Bur. Stands., 87 (1982) 159.