

## **MEASUREMENT OF THE THERMAL CAPACITY OF SOLIDS BY DSC**

*G. K. Demensky and O. A. Teplov*

BAYKOV INSTITUTE OF METALLURGY, ACADEMY OF SCIENCES  
OF THE U.S.S.R.

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The methods for determining the thermal capacity of solids using a SETARAM DSC-III calorimeter have been studied. Two methods can be employed: periodic heating and continuous heating. The method using periodic heating is characterized by an accuracy of 0.6%, while the method with continuous heating has an accuracy of 5%. Thermal capacity measurements on corundum, copper oxide and magnetite are reported.

The potentials of Calvet calorimetry are well known [1, 2]. The apparatus is usually a massive isothermal calorimeter with a high time constant, applied for studying high-temperature enthalpies, enthalpies of formation, adsorption, etc. Such instruments allow study of the temperature-dependence of the enthalpy of a material, and calculation of the mean thermal capacity for various temperature intervals. However, the method does not permit study of the phase transitions in detail. To measure true thermal capacity, the methods of choice are adiabatic calorimetry, triple thermal bridge, differential scanning calorimetry, etc. In the temperature range below 300 K, exclusively adiabatic calorimetry is suitable, allowing accuracies of 0.005%. During recent decades, differential scanning calorimetry (DSC) has become widespread; its temperature range covers 150 to 1100 K [2-6]. This paper deals with the methods of measuring the thermal capacity of solids with the SETARAM DSC-III calorimeter.

### **Methods of measurement**

Two methods can be used: (a) periodic heating, in which the temperature of the calorimeter rises during defined time intervals and measurements are taken in these intervals, the thermal capacity  $C_p$  subsequently being calculated; (b) continuous heating.

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### Measurement with periodic heating

The construction and potential of the SETARAM calorimeter are described in [6, 7]. The standard equipment comprises the calorimeter + an NR-9825 or Olivetti computer. The method for measuring thermal capacity in the continuous regime consists in recording the DSC heating curves with the empty crucible or with the crucible filled with the substance, computation of the curves and calculation of the thermal capacity values. Since the measurements are not carried out in "real time", it is necessary to record the heating curve of the empty crucible for each experiment.

Our apparatus contains an IN-110 mini-computer made by Intertechnique (France), allowing the collection and processing of analog signals in "real time". The capacity of the memory is 96 kByte; a rigid disc for storing 20 MByte is included. The computer can be programmed in BASIC, FORTRAN and ASSEMBLER. A large number of special functions for organizing data collection and processing are at disposal.

We assumed that the calorimeter normally operates with high time stability, and developed our method on this assumption. We first measured the thermal capacity of the calorimeter with the empty crucible. These data were approximated by a polynomial and used in this shape in all experiments. Since the curvature of the function thermal capacity *versus* temperature is slight in the temperature range 300

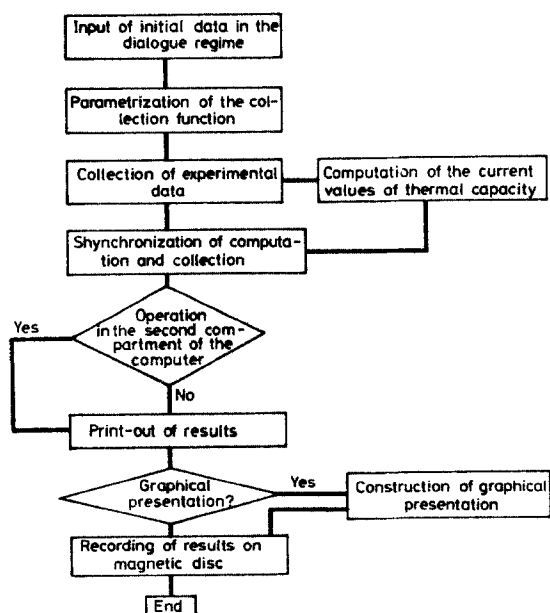


Fig. 1 Structure of the NSR program

to 1000 K, we chose a temperature increase of 5 deg as the standard step. We did not measure the temperature of the sample, but calculated it from the initial temperature of the programmer. The initial temperature was chosen so as to have a mean temperature that is a multiple of five. The structure of the NSR program for measuring thermal capacity is shown in Fig. 1. Signal collection is performed in the "ping-pong" regime: the signal is collected alternately in the two zones of the operative memory. While signal collection proceeds, e.g. in the second sub-group, the signal in the first sub-group is being processed and the result is presented on the display, where graphical presentation of the signal is also feasible.

The signal obtained from the calorimeter filled with the substance on heating through 5 deg is shown in Fig. 2. The processing of the signal consists in finding the

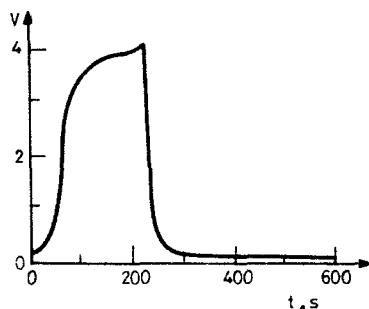


Fig. 2 Calorimeter signal corresponding to a temperature increase of 5 K

area under the curve between the initial and final levels. The points of the levels were the means of 10 points. The further calculation was carried out with the equation

$$C_p = \left( \frac{S}{K} - C_p^1 \right) \cdot M \cdot \frac{1}{D} \cdot \frac{1}{\Delta T}$$

where  $K$  is the calibration coefficient of sensitivity at the given temperature,  $D$  is the sample mass,  $M$  is the molecular mass,  $C_p^1$  is the thermal capacity of the empty crucible at the given temperature, and  $\Delta T$  is the temperature increase.

It should be noted that the heating time is strictly regulated by the apparatus and is equal to 200 s; it is followed by keeping the sample at constant temperature for 400 s, and the cycle is then repeated. The response time of the computer is 1 s. Thus, to measure the thermal capacity of a substance in the range 300 to 1000 K, 24 hours is required.

The calorimeter set includes a great number of crucibles: platinum, aluminium oxide, steel, etc. We chose cylindrical platinum crucibles, these being most resistant to chemical and thermal action. Four crucibles were adjusted to an equal mass of  $1.30530 \pm 0.0001$  g. The masses of the crucibles did not change during three years of

use. One of the crucibles was always applied as reference standard. In the preliminary measurement of the thermal capacity of the calorimeter with the empty crucible, it was found that a thermal imbalance of the cells (background) exists, varying with temperature. Its value was 20% of the thermal capacity of the substance at ambient temperature. This phenomenon is due to imperfections in the corundum tubes, in geometrical imperfections of installing sensors and heaters, and to differences in the computer sensors. We decided to reduce the imbalance of the cells to the minimum and thereby increase the useful signal. For this purpose we placed 0.0643 g corundum in the reference crucible. The background value at 300 K was then 1% of the thermal capacity of the substance. We measured the background in steps of 5 deg, approximated the data by a polynomial of the 4th order and included it in this form in the program. To utilize the range of the amplifier of the calorimeter (zero in the middle) to a greater extent, we shifted the zero position. This allowed an increase of the amplification coefficient of the signal and a reduction of the error of measurement of the area under the useful signal. In the discretization of the vertical over 4096 channels, the error in the determination of the area is around 0.02%. The construction of the instrument allows electrical calibration. For this purpose a corresponding block and calibrators are available in the set. Calibration was performed with 100 mW pulses lasting 200 s during continuous heating at a rate of 2 deg/min. The data were approximated by a polynomial of the 4th order. The random error was 0.1%.

### Results of measurements

To check the operation of the calorimeter regarding possible systematic errors, we measured the thermal capacity of a synthetic corundum sample (mass: 0.74703 g) in the interval 200 to 1050 K. From the approximation of the experimental values, we obtained the equation  $C_p = 149.8 - 0.1056 T - 20,541.1 T^{-1} \text{ J mol}^{-1} \text{ K}^{-1}$ . The standard deviation was  $\bar{S}_x = 0.04$ , and the statistical error at  $\alpha = 0.95$  was 0.1%. Figure 3 presents the

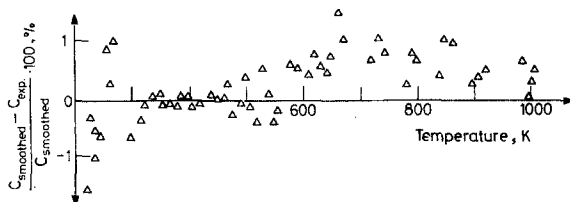


Fig. 3 Difference in per cents between the experimental and literature data vs. temperature for corundum

difference between the experimental values and those in the literature *versus* temperature. The literature data were taken from [8] in the form of two equations:  $C_p = 97.056 + 39.02 \cdot 10^{-3} T - 26.363 \cdot 10^5 T^{-2}$  for the interval 298 to 500 K, and  $C_p = 122.68 + 6.878 \cdot 10^{-3} T - 50.237 \cdot 10^5 T^{-2}$  for the interval 500 to 1200 K. It may be seen that the differences up to 600 K do not exceed 0.1% on average. Above 700 K, the difference has a systematic character and reaches 1%. The reason is not clear; however, a correction may be included in the program.

Using this method, we have measured the thermal capacities of  $\text{Co}_3\text{O}_4$  [9] and  $\text{Li} \dots \text{V}_2\text{O}_5$  [10]. The error in the measurements was 0.6%. In the range of liquid nitrogen temperatures the error is substantially higher. This is presumably due to the inhomogeneous flow of the cooling medium, and hence the inhomogeneous heating of the block.

#### *Thermal capacity of CuO*

The thermal capacity of copper oxide was measured by using the mixing method, as described in many papers. On the basis of such data, the equation  $C_p = 48.589 + 7.201 \cdot 10^{-3} T - 7.499 \cdot 10^5 T^{-2} \text{ J mol}^{-1} \text{ K}^{-1}$  is recommended in [11] for the interval 298.5 to 1700 K.

We measured the thermal capacity of CuO in steps of 5 deg in the interval 150 to 900 K. Conditions were identical to those for corundum: completely filled crucibles, and helium as gas. The experimental data found at low temperatures are listed in Table 1, demonstrating that data scattering in this range is very high, particularly in the vicinity of the lower temperature limit. In the range of medium temperatures up to 900 K, the data were approximated by the equation  $C_p = 49.923 + 0.64274 \cdot 10^{-2} T - 0.864967 \cdot 10^5 T^{-2}$ . Figure 4 presents the difference between the experimental  $C_p$  values and the smoothed curve for CuO. The standard deviation is  $S_x = 0.04$ ;  $n = 66$  and the statistical error at  $\alpha = 0.95$  is 0.2%.

Figure 5 shows the difference between the experimental and literature data *versus* temperature, indicating that the difference is systematic and amounts on average to

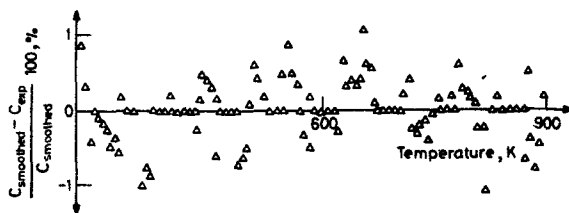


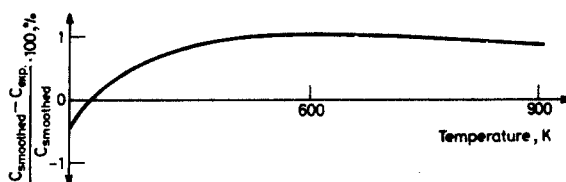
Fig. 4 Difference in per cents between the smoothed curve and the experimental points *vs.* temperature for CuO

**Table 1** Thermal capacity of CuO in the low-temperature range (Unit:  $\text{J K}^{-1} \text{mol}^{-1}$ )

$T, \text{K}$	$C_p$ [11]	$C_p$ exp.	$T, \text{K}$	$C_p$ exp.
160	27.76	25.25		
180	31.36	34.11	184	28.30
200	34.81	34.12	186	30.07
220	38.35	37.17	188	33.21
240	38.56	39.45	190	34.44
260	39.13	40.12	192	36.08
280	40.90	42.42	194	29.51
300	42.32	42.54		

$T, \text{K}$	$C_p$ exp.	$T, \text{K}$	$C_p$ exp.
155.50	174.66	165.50	33.87
156.50	22.64	166.50	39.03
157.50	22.73	167.50	35.92
158.50	19.74	168.50	36.00
159.50	24.00	169.50	31.16
160.50	26.99	170.50	35.56
161.50	21.79	171.50	36.78
162.50	24.11	172.50	34.80
163.50	29.81		
164.50	38.32		

**Fig. 5** Difference in per cents between the experimental and literature data vs. temperature for CuO

1%. Thermogravimetric analysis demonstrated that the substance used in the measurements had a non-stoichiometric composition, corresponding to the formula  $\text{CuO}_{0.92}$ . On recalculation of the experimental values to the molecular mass for this composition, they agree with the literature data within 0.5%.

#### *Measurement of thermal capacity in the region of phase transitions*

In the measurements of  $C_p$  in the region of the phase transition of  $\text{RbNO}_3$  (437 K), it was found that the period of keeping at constant temperature (400 s) after the heating period (200 s) is insufficient for the substance to reach equilibrium

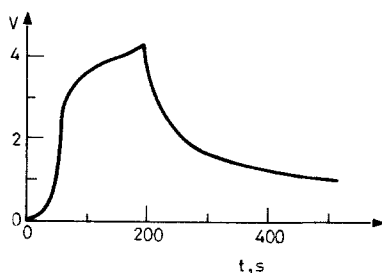


Fig. 6 Calorimeter signal in the phase transition range corresponding to a temperature increase of 5 K

(Fig. 6). Hence, the  $C_p$  value obtained in the forward slope of the phase transition is lower and in the reverse slope higher than the true value.

To eliminate this error, one must either pass to manual control of the heating cycle, or (if possible) program the heating of the calorimeter by means of the computer.

#### *Measurement of thermal capacity using a continuous linear heating regime*

This method has been applied with success in adiabatic calorimetry, in the Sykes method. However, the error of measurement frequently reached 3 to 5%.

#### *Method of measurement*

The programs NS and SONT for measuring  $C_p$  in the continuous heating regime are analogous with the NSR program. Data collection proceeds with a frequency of 4 Hz in the "ping-pong" regime. The collection zones 1 and 2 have 256 points each (Fig. 7). The calling frequency is 4 Hz, i.e. during 30 s 120 points are collected at a heating rate of 4 deg/min, corresponding to a temperature increase of 2 deg. Subsequently, data collection is passed to zone 2, and in zone 1 the area under the DSC curve is computed. The value is divided by the sensitivity at the given temperature, the background (stored in zone 4 of the operative memory) is subtracted, and the result, reduced to 1 mol of the substance, is transferred into

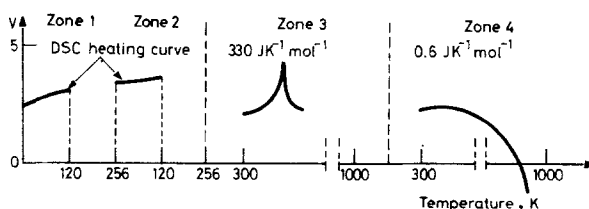


Fig. 7 Organization of the operative memory in data collection using the ping-pong regime

zone 3. The data can be presented in tabular or graphical form and also recorded on a magnetic disc. We used this program to measure the background, the thermal capacity of corundum at various heating rates and the thermal capacity of magnetite.

#### *Thermal capacity of the background*

We measured the thermal capacity of the empty calorimeter with an empty platinum crucible at heating rates of 2, 4 and 5 deg/min.

#### *Thermal capacity of corundum*

We measured the thermal capacity of corundum at heating rates of 2, 4 and 5 deg/min. The deviation of the experimental data from the literature data in 20 deg steps is shown in Fig. 8, demonstrating that the systematic error increases with increasing heating rate. In the initial period at around 50 K, when the steady state is being established, the results are unreliable and should either be corrected or discarded.

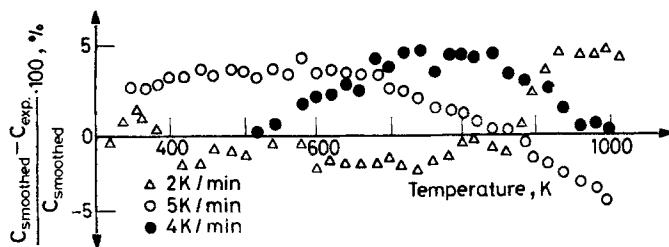


Fig. 8 Difference in per cents between the experimental and literature data vs. temperature for corundum at different heating rates.  $\times$  - 2 deg/min;  $\circ$  - 5 deg/min;  $\bullet$  - 4 deg/min

In all three cases the results turned out to be too high, by 2% on average at a heating rate of 2 deg/min, and up to 5% at 4 and 5 deg/min. These large differences prompted us to search for the reason leading to the errors.

#### *Role of the temperature controller*

A study of the  $C_p$  values obtained in successive measurement series, with shut-off heating in between, demonstrated that the values in the following series were higher than in the preceding series and higher than the true values; however, after some time they began to approach the true values. This led us to the thought that the integration time of the controller is high and that the controller will work off the irregularity of the shut-down heating, thereby changing the position, since overheating has a large effect on the temperature field of the calorimeter block. To



reduce this effect, we reduced the integration time (position 2) and derivation time (position 1) and increased the proportional component up to 80%.

### *Role of the program*

Originally, the  $C_p$  values were related to the computed temperatures on the basis of the initial programmed temperature. After preliminary measurements of the  $C_p$  values of corundum (shown in Fig. 8), we introduced some changes into the program. We calculated the temperature according to the equation in the operating manual of the calorimeter. The error in the temperature programming of the programmer is 0.01 deg; in this case the minimum error in  $C_p$  measurement for a temperature increase of 2 deg is 0.5%. In fact, by varying  $\Delta T$  in the computation by 0.01 deg, an error of 1% will arise:

$T = 20 \text{ K}, C_p = 195.79$ (magnetite, [12])						
$\Delta T$	2.055	2.045	2.040	2.035	2.025	1.955
$C_p \text{ exp}$	192.17	193.11	193.57	193.05	195.01	201.99

It follows from the above that, for accurate measurements of  $C_p$ , it is necessary to know the temperatures of the sample at the start and at the end of the measurement. However, what we measure is not the sample temperature, but the block temperature at some distance from the sample. By introducing certain empirically found corrections, we consider that we know the temperature of the sample. However, the thermal capacity of the sample itself will bring about a distortion of the temperature field, resulting in a distortion of the temperature of the sample. Hence, we will *a priori* always have an error, which will be the larger, the higher the heating rate; this was in fact found.

### *Thermal capacity of magnetite*

We measured the thermal capacity of magnetite single-crystals in the temperature interval 203 to 1030 K in steps of 2 deg, with a heating rate of 4 deg/min, in He atmosphere. The deviation of the results from the literature data ([12]) is shown in Fig. 9. Data collection and processing were performed with the improved program.

## **Discussion**

The measurement of thermal capacity using periodic heating certainly yields accurate results. Thus, the accuracy of 0.6% which we obtained for corundum

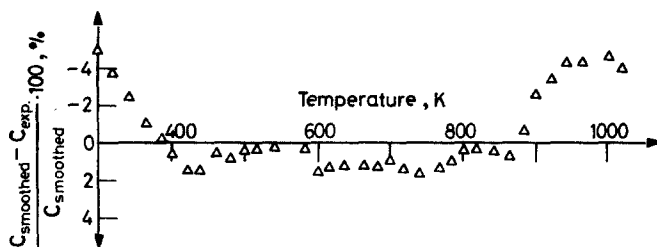


Fig. 9 Difference in per cents between the experimental and literature data vs. temperature for magnetite

agrees with the 0.5% error in [4]. For  $\text{Co}_3\text{O}_4$ , good agreement was also obtained with the low-temperature measurements performed by other authors. The error from the joint approach of these two groups of data amounted to only 0.3%. It should be noted that in our work the temperature step was 5 deg, while in [4] it was 20 deg. It would hardly make sense to increase this value, since thermal capacity has a defined curvature and one might risk passing to the range where mean thermal capacity values would be measured.

In the range of phase transitions, the steps should be even smaller. However, the main point in such measurements is to wait for equilibrium to be established in the substance. This is rather difficult with modern programmers; it becomes feasible when controlling computers are used. In addition, accurate temperature regulation will then also be feasible by changing the characteristic of the temperature controller depending on temperature.

Measurement in the continuous linear heating regime allows acceleration of the measurement. Thus, while it takes about 24 hours to measure  $C_p$  in the interval 300 to 1100 K in steps of  $\Delta T = 5$  deg in the period regime, the measurement in the continuous heating regime at 4 deg/min can be performed in about 4 hours. The accuracy will be reduced in the latter case; however, in very many cases it will be fully satisfactory. In addition, continuous heating will always be necessary when the transformation in the substance is retarded and establishment of the equilibrium may take hours or days (polymers) [13].

## References

- 1 E. Calvet and A. Prat, *Microcalorimetry (Russian translation)*, Inostrannaya Literatura, Moscow 1965.
- 2 N. D. Topor and Yu. L. Suponitsky, *Uspekhi khimii*, 53 ( . . . ) 1425.
- 3 U. Gaur, A. Mehta and B. Wunderlich, *J. Thermal Anal.*, 13 (1978) 71.
- 4 S. C. Mraw and D. F. Naas, *J. Chem. Thermodyn.*, 11 (1979) 567.
- 5 V. B. F. Mathot and M. F. J. Pijpers, *J. Thermal Anal.*, 28 (1983) 349.
- 6 J. Mercier, *J. Thermal Anal.*, 14 (1978) 161.
- 7 K. T. Marano, *Thermochim. Acta*, 26 (1978) 27.

- 8 G. T. Furukawa, T. B. Douglas, R. E. McCoskey and D. E. Ginnigs, *J. Res. NBS*, 57 (1956) 67.
- 9 G. K. Demensky, L. A. Petrov, O. A. Teplov, Yu. V. Tarasenko and N. M. Aristova, 9th All-Union Conference on Calorimetry and Chemical Thermodynamics (in Russian). Amplified abstracts of the papers. Tbilisi, 1982, p. 258.
- 10 S. E. Filippova, G. K. Demensky, I. A. Teplov and L. A. Reznitsky, *Izv. Akad. Nauk SSSR, Neorg. Materialy* No. 9 (1982) 1597.
- 11 Thermodynamic properties of substances (in Russian). Ed. V. P. Glushko, 1984.
- 12 F. Grønvold and A. Sven, *J. Chem. Thermodyn.*, 6 (1974) 859.
- 13 B. Wunderlich and G. Gaur, *Thermal Capacity of Linear Polymers* (Russian translation). Mir, Moscow 1972.

**Zusammenfassung** — Methoden zur Bestimmung der Wärmekapazität von Festkörpern wurden mittels des Kalorimeters SETARAM DSC-III untersucht. Zwei Methoden können angewandt werden, nämlich periodisches und kontinuierliches Aufheizen. Bei periodischem Heizen beträgt die Genauigkeit 0,6%, bei kontinuierlichem 5%. Über Messungen der Wärmekapazität von Korund, Kupferoxid und Magnetit wird berichtet.

**Резюме** — В работе изучены методики определения теплоёмкости твёрдых тел на калориметре ДСК-III «СЕТАРАМ». Возможны два метода работы-периодический нагрев и непрерывный. Метод периодического нагрева характеризуется точностью 0,6%, а непрерывного до 5%. Проведены измерения теплоёмкостей крунда, окиси меди и магнетита.