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Thermochimica Acta 347 (2000) 79–84

thermochimica acta

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Details of calibration of a scanning calorimeter of the triple heat bridge type

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Received 1 October 1999; accepted 2 October 1999

Abstract

It was shown that traditional procedure of measurement of heat capacity by the triple heat bridge method causes systematic error tied with a non-compensated asymmetry of a device. Two variants of calibration of triple heat bridge scanning calorimeters based on a ratio of signals from two cells are examined and compared to the conventional procedure of heat capacity measurements with DSC. Efficiency of calibration has been tested in experiments with rubidium nitrate and potassium chloride. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calibration; Scanning calorimeters; Triple heat bridge; Rubidium nitrate

1. Introduction

The triple heat bridge method is used to measure heat capacities of solid and liquid substances in the temperature range from 250 to 700 K. The principles of this method were proposed by Yagfarov [1] and improved by Kabo et al. [2]. The device is shown in Fig. 1. Temperature differences between the heater block and three cells appear during heating of the calorimeter by the heater (3) at a constant rate. These differences are proportional to individual heat flows and hence to heat capacities of cells. It is assumed that the major part of the heat flows is passed through the rods (7). Copper cells (4, 5, 6), constantan rods (7) and the copper heater block form three differential thermocouples, electromotive forces (e.m.f.) of which are proportional to the heat flows passed through the rods. Samples are loaded into the cells in hermetically sealed crucibles. The inner volume of the calorimeter is filled with argon at P=6.5 kPa. In the classical variant of the method, the measurement consists of a single run. One cell is empty, the second cell contains a reference sample with known heat capacity, and the third contains a crucible with a tested sample. Two e.m.f. values are measured (Fig. 2): U_{10} between the reference cell and the empty cell, and U_{20} between the test cell and the empty cell. The heat capacity of the tested sample C_x is calculated from its relation to the heat capacity of the reference sample C_s

$$\frac{C_x}{C_s}=\frac{U_{20}}{U_{10}} \tag{1}$$

The uncertainty of measurements has been found to be 2–3% [1,2], but our experience shows that it may significantly exceed this level in some experiments.

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PII: S0040-6031(99)00419-0

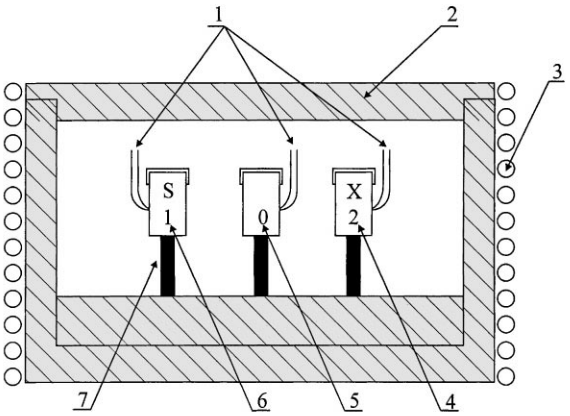

Fig. 1. Construction of a calorimeter of the triple heat bridge type. 1, thermocouples; 2, cover; 3, heater; 4, sample cell; 5, empty cell; 6, reference cell; 7, Constantan rod.

2. Experimental, results and discussion

To determine possible errors we have investigated individual heat flows of three empty cells illustrated in Fig. 3. The normal heating mode with the rate of

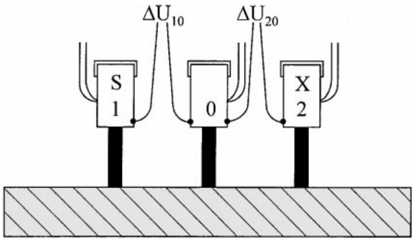

Fig. 2. Working principle of the calorimeter of the triple heat bridge type.

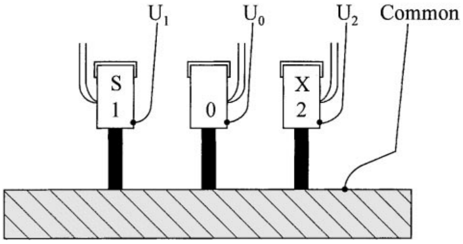

Fig. 3. Scheme of measurements of individual heat flows.

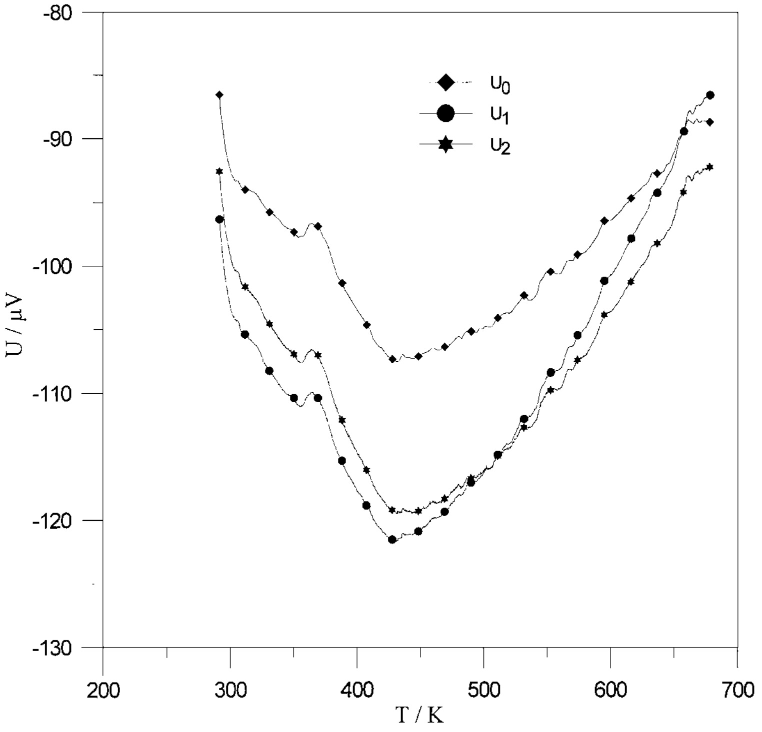

Fig. 4. Individual e.m.f. of three empty cells during linear heating.

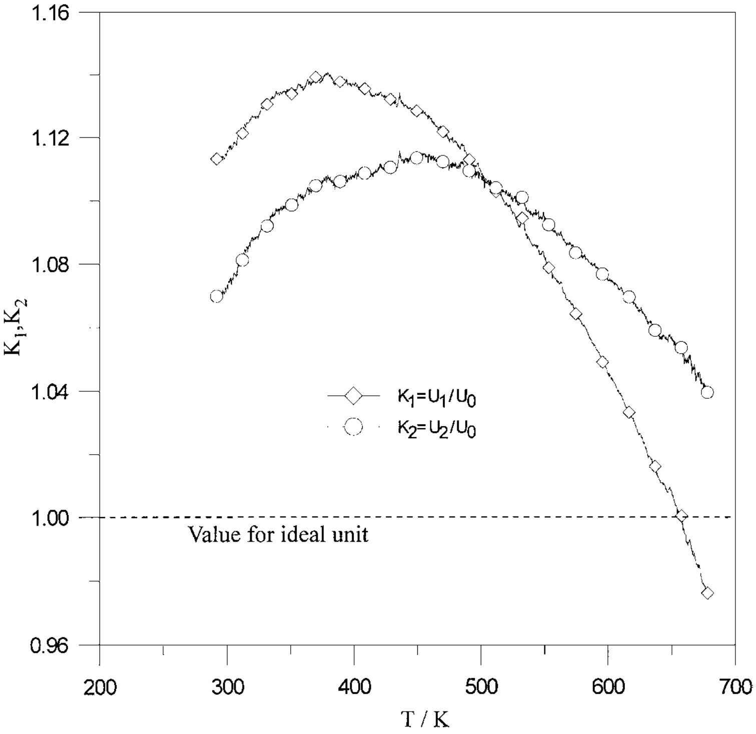

Fig. 5. Actual asymmetry of the calorimeter.

1 K s^{-1} was implemented with assistance of an electronic control unit. The registered e.m.f. (Fig. 4) and their ratios (Fig. 5) show significant differences. Hence, the assumption of symmetrical configuration is not supported, and Eq. (1) leads to systematic errors in measurements. There are two kinds of asymmetry we have to take into account, viz. asymmetry of sensitivities U/W (U is e.m.f., W is the heat flow) and differences in heat capacities of the empty cells. Small peaks in e.m.f. appeared in the range T=350–370 K (Fig. 4), that may be caused by deviation from the linear heating mode due to unstable AC power supply. It is important that no peaks are in the ratios of e.m.f. (Fig. 5). In the higher temperature range (T>450 K), the registered e.m.f. decreased, which may be indirect evidence of increased heat transfer through gas heat conductivity and radiation.

A correction to account for the asymmetry was applied using the equation:

$$C_x = C_s \frac{U_x - K_1(T) \cdot U_o}{U_s - K_2(T) \cdot U_o} \tag{2}$$

where $K_1(T)$ and $K_2(T)$ are functions determined in experiments with the empty cells (Fig. 5). The $K_1(T)=K_2(T)=1$ applies for the ideal symmetrical unit. The real deviation from unity in the actual cells is significant (up to 12%) and depends on heating mode and temperature. We have made test measurements for KCl, $RbNO_3$, and Cu, and showed that the uncertainty indeed does not exceed 2% if Eq. (2) is used. Measurements at heating and cooling modes with the rate of 1 K s^{-1} for $RbNO_3$ showed good agreement (Fig. 6). It should be noted that Eq. (2) provides the correction only for the different heat capacities of empty cells. Probable differences in sensitivities $k=U/W$ are not taken into account. Such differences may be caused by different thickness of the heat-conducting rods, by different heat transfer through radiation for the different cells, and by deviations in the composition of the material of the constantan rods. In addition, changes of sensitivity may occur during aging of the device, which is why additional calibration experiments are necessary with substances, for which heat capacities are well known.

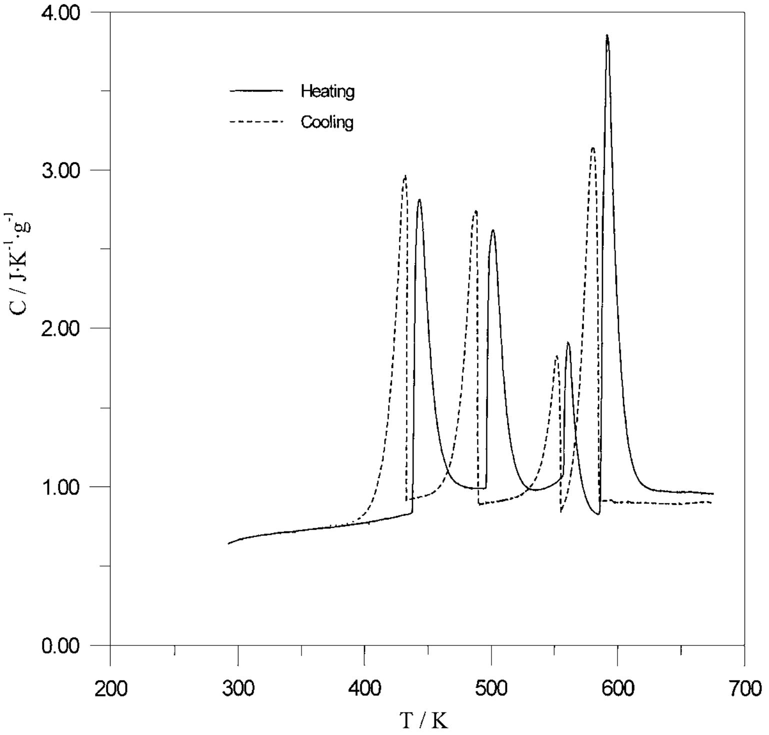

Fig. 6. Results of measurements for rubidium nitrate.

To diminish the influence of asymmetry and to simplify the process of measurements, we have investigated a new configuration with two cells (Fig. 7). One advantage of such a scheme in comparison to the former one (Fig. 3) is the fewer number of parts, the state and, hence, the instability of which influence the measurements. A copper cylinder was used as a constant reference sample in cell (1). In the constant heating mode, the heat capacity of the tested sample can be found by means of equation

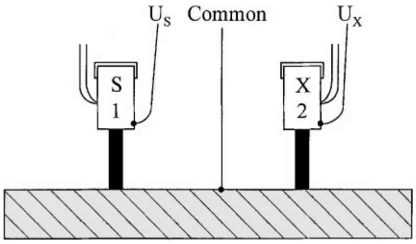

Fig. 7. Configuration of the calorimeter with two cells.

$$C_X = A(T)\frac{U_X}{U_S} - B(T) \tag{3}$$

This equation takes into account the different sensitivities of the cells. The temperature dependence of parameters $A(T)$ and $B(T)$ was found from the results of two calibration measurements for two samples of different masses of copper granules. The procedure of calibration consisted of the following steps.

(1) The cells were flushed with argon, cleaned with hydrogen at T=450 K to remove oxides, and degassed. The surfaces were stabilised by heating to 750 K, evacuating and cooling in cycles. Absence of gas emission in vacuum at high temperatures (700–750 K) and repeatability of signal from the cell with the reference sample in heating cycles with the constant rate should be achieved. This step is essential for preparation of the device. If the apparatus is used daily, its properties are stable, as our experience has shown. However in case of interruption in use for 10 days or more, the cleaning procedures should be repeated.

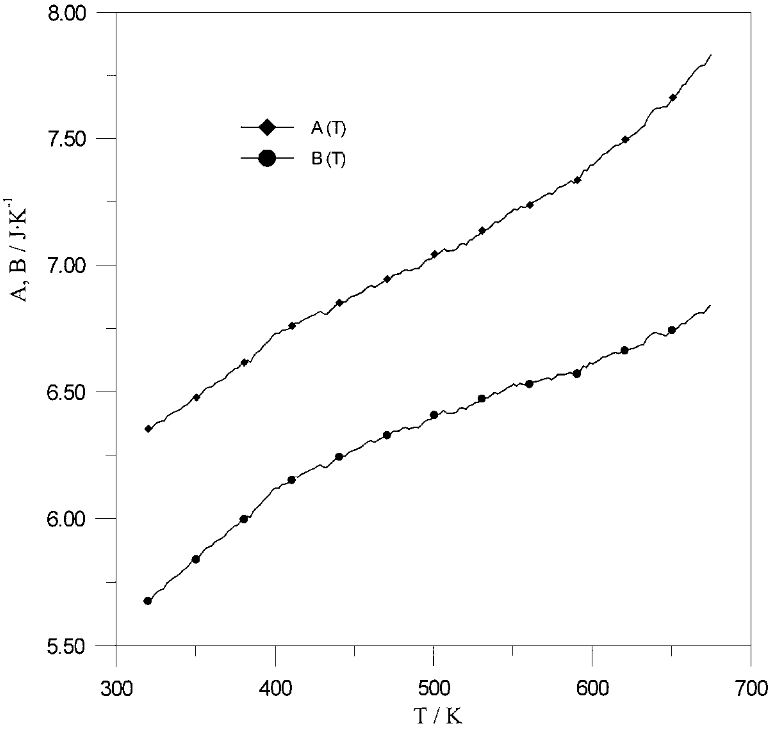

Fig. 8. Temperature dependence of the calibration parameters A and B (Eq. (3)).

(2) Calibration should first be done with a copper sample in cell (2) with a mass of 105–110% of the mass of the reference sample, and then repeated with a mass of 90–95% of the mass of the reference sample.

(3) Systems of two linear equations can be built at each temperature point of the calibration measurements in step (2). Parameters $A(T)$ and $B(T)$ result from the solution of these systems. Such a calculation is based on the supposition that temperatures of the cells are equal. In practice, our selection of masses of samples kept the temperature difference less than 0.5 K. A computer programme has been developed for automated evaluation of the calibration functions $A(T)$ and $B(T)$ from four tables $U(T)$ resulting from steps (2) and (3).

The temperature dependence of parameters A and B is shown in Fig. 8. Test measurements for KCl showed that simplification of the scheme has not resulted in decreased precision.

Let us compare the new procedures to the one used in the conventional DSC for heat capacity measurements [3]. In the conventional DSC, differences

Table 1
Assumptions accepted in different calibration procedures

Method of calibration	Triple heat bridge (Eq. (1))	THB (Eq. (2))	THB with two cells (Eq. (3))	DSC (Eq. (4))
Exact repeatability of heating mode				+
Symmetry of heat capacity of empty cells	+			
Symmetry of sensitivity U/W	+	+		
Linear relation of e.m.f. U to heat flow W	+	+	+	+
Small temperature differences	+	+	+	+

between the e.m.f. of two cells are measured in two calibration runs and in one run with a tested sample. The content of one cell remains constant. The heat capacity of the tested sample may be expressed as

$$C_x = A'(T) \cdot (U_X - U_S) - B'(T) \quad (4)$$

where $A'(T)$ and $B'(T)$ are functions derived from the calibration runs. This procedure resolves the problems of asymmetry if the heating mode is the same in three runs. Deviations from the standard heating mode introduce errors to the results even if symmetry of the device is ideal. Use of the ratio U_X/U_S in the new procedure according to Eq. (3) instead of the difference $U_X - U_S$ in the conventional DSC minimises the influence of deviations from the standard heating mode. As shown in Figs. 4 and 5, the e.m.f. ratios are more robust than the individual signals of the cells. Features of the different calibration methods are compared in Table 1.

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