OPTIMIZATION OF HEAT CAPACITY
MEASUREMENT USING DSC

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The methods of heat capacity data determination from DSC measurements were analysed and the negative effects increasing uncertainty of heat capacity were described. Optimization of stepwise method was done using molybdenum as a sample, and it leads to uncertainty of heat capacity up to 2 % in the temperature range from 288 to 823 K.

Introduction

The differential scanning calorimetry (DSC) is one of frequently used calorimetric methods to characterize almost any kind of material. DSC records heat flow (power) required to bring to zero the difference between temperatures of the sample and the reference material as a function of time or temperature. The construction of DSC can be done in two ways: heat flux DSC ("classical") has only a single heat source for sample and reference cell, whereas the power

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compensation instrument has individual heaters for sample cell and for reference cell. [1] The consequence of different construction of power compensation DSC is usually worse baseline stability, but on the other hand, higher sensitivity and possibility of faster temperature changes as compared to classical DSC. Generally, DSC can be used to check phase change effects (first and second order transitions) and their enthalpies, humidity and purity of materials can be determined, the kinetics of observed processes can be evaluated and also the specific heat capacity C_p (isobaric) can be measured. [2] All these properties can be determined in broad temperature range (depending on cooling accessory and construction of cell) and also with relatively low uncertainty when all negative effects are suppressed. Although the specification for the precision (repeatability) of C_p measurement is given as low as 0.1 % for power compensation instruments [1], the typical results have uncertainty about 7 %, but careful work can bring uncertainty of 3-5 % [3], 3 % [4,5] or even 1 %. [6] The explanation of the meaning of careful work, description of negative effect and optimization of heat capacity determination using power compensation DSC is described in this present work.

When the very precise measurement should be done using DSC, some general effects on equipment should be taken in account as well as some specific ones connected with selected calculation method etc. Calibration of DSC (calibration of temperature and enthalpy) is essential for any DSC equipment and it is described in every manual of any equipment. Rudtsch in his work [7] described in detail how calibration of temperature and heat flow rate can influence uncertainty of heat capacity measurement. Also Pak *et al*. [8] described influence of the baseline and heating rate (or frequency for temperature-modulated DSC) corrections on heat capacity determination. In the case of very precise experiment, attention should be paid also to the sample preparation. Sample is not given directly to DSC cell but is put into special crucible and this crucible is placed into the cell. The empty crucible is usually used as reference. The heat produced by the sample is detected by temperature sensor through the bottom of sample crucible and bottom of the DSC cell. The flatness of crucible bottom and DSC cell is the matter of DSC producer but the sample mass, shape and character (different particle sizes) can influence a lot the DSC results obtained. Thus, the best thermal contact can be obtained when the sample is spread in thin layer on the bottom of the crucible and the bottom is fully covered by the sample.

Among the effects which can negatively influence DSC measurement belong group of effects which can be called "surrounding" which is not usually mentioned in literature. Surrounding is everything what is present in the room where the DSC equipment is situated and these effects caused instability of baseline. The main aspect is that the temperature and humidity in the room should be stable as much as possible. Humidity is important when the DSC is connected to cooling device going to temperatures below 0 /C where the area around DSC cell can be covered with snow when the sample is changed. Also the number of people

working in the room and their kind of work can significantly influence baseline even if the DSC has its own special table resistant to vibrations. The best surrounding for DSC is closed room with constant temperature, humidity and without any person.

Another group of effects on DSC measurement are those connected with the selected method of C_p calculation. The specific heat capacity can be determined using DSC by two methods. Both these methods are based on comparison between baseline, standard material and sample DSC curves measured under the same conditions but the temperature program and evaluation of obtained curves is different. In both methods, the temperature profile starts and ends by an isotherm. These isotherms are necessary to arrange all three curves for evaluation – isotherm should overlap in all three curves. Standard is well defined material with known specific heat capacity in broad temperature range, and usually sapphire is used.
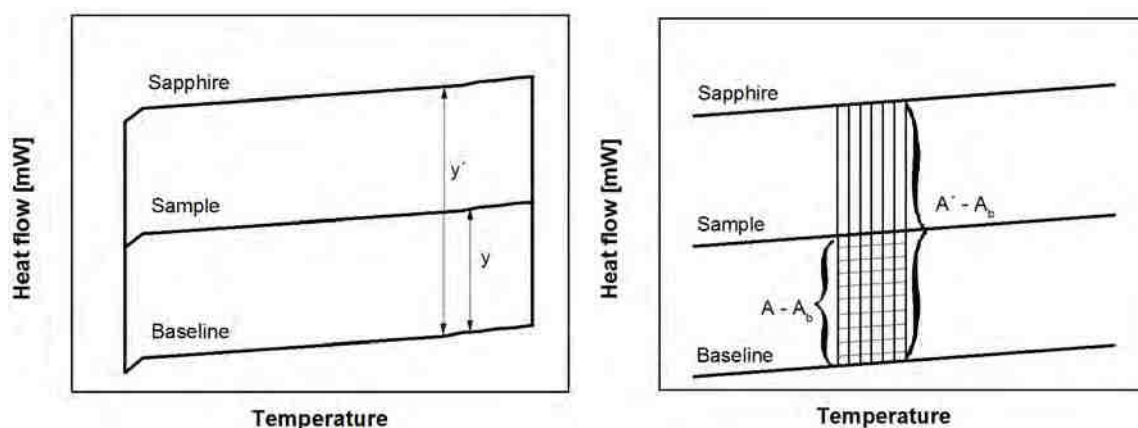

Fig. 1   The heat capacity determination by continuous (on the left) and stepwise method (on the right)

Continuous method for heat capacity determination means linear heating in broad temperature range. The heat capacity of the sample can be calculated according to the equation

$$\frac{C_p}{C_p'} = \frac{y}{y'}\frac{m'}{m}$$

(1)

where y is the difference between baseline and sample DSC signal at selected temperature, m is sample mass. Values with comma represent the same property for sapphire. This is apparent from Fig. 1 (left one). The continuous method can provide good results only when there are no negative effects during DSC experiments, and especially the baseline should be very stable. In other words, when the surrounding conditions of DSC equipment are stable then the continuous method can be successfully applied.

The second method is stepwise method which is most often used for heat

capacity determination and is described in detail in norm ASTM E1269-11 [9]. This method is based on comparison of areas under DSC curves obtained for standard and the sample according to the equation

$$C_p = C_p' \frac{m'(A - A_b)}{m(A' - A_b)}$$ (2)

where A is the area under the relevant curve in selected temperature range (and determined C_p is for the temperature in the middle of selected range), subscript b stands for baseline, comma in superscript is used for sapphire and the values without comma are for the sample. The illustration of this method is given in Fig. 1 (right). The stepwise method is more time consuming compared to the continuous one but usually it is more precise.

Experimental

The differential scanning calorimeter DSC Pyris (Perkin Elmer) with intracooler 2P was used to test the continuous and stepwise method for C_p determination. The melting temperature of several pure metals (Hg, Ga, In, Sn, Pb and Zn) was used to calibrate temperature. The enthalpy was calibrated using enthalpy of fusion of indium. The metals necessary for calibration were weighed into aluminium pans which were also used for other experiments. The amount of calibration metals was 10 mg, the heating rate 10 K min^{-1} and the protecting atmosphere of dry nitrogen with the flow rate 20 cm^3 min^{-1} was used.

Sapphire (standard reference material 720, NIST) was used as standard and pure molybdenum (reference material 781D2, NIST) was measured as a sample to easily check the uncertainty in temperature range of 263-823 K. Both sapphire and molybdenum were in the form of thin disc fully covering the bottom of the aluminium pan, and the masses were 27.84 mg sapphire and 78.56 mg molybdenum, respectively.

The continuous method was done in the temperature range of 263-823 K with the heating rate of 10 K min^{-1} and two minutes of isotherm at the beginning and at the end of experiment.

The optimization of stepwise method was done by checking the uncertainty of C_p for molybdenum during experiments with different width of temperature range, different length of isotherm at the beginning of experiment and also different heating rates. The other surrounding effects mentioned in introduction part were kept as low as possible.

Results and Discussion

For testing the uncertainty of heat capacity determined using our power compensation DSC Pyris 1 with intracooler 2P, both methods described in introduction part were performed. The continuous method was done in the range from 263 to 823 K and the calculated C_p values of molybdenum are given in Fig. 2 together with standard data [10]. As can be seen, the results for continuous method have huge uncertainty up to 30 % compared to standard data. Thus, this method is not successful in obtaining C_p data with low uncertainty.
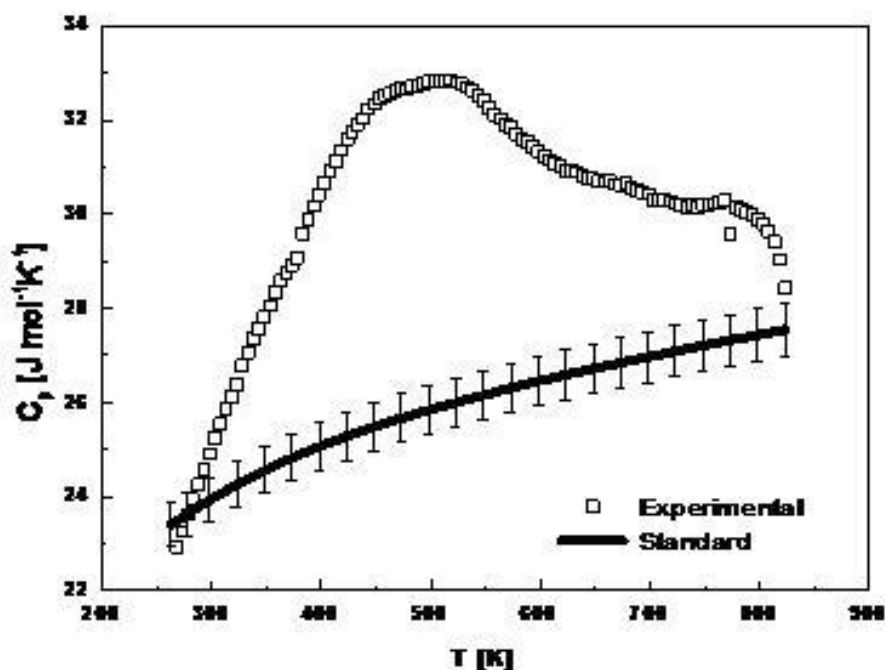

Fig. 2 Temperature dependence of heat capacity of molybdenum determined by continuous method and standard values with depicted 2 % of uncertainty

The only possible method to obtain C_p data with low uncertainty is application of stepwise method. At the beginning of testing this method, the results with ca. 5 % uncertainty were measured. Thus, the stepwise method was optimized to reduce the uncertainty to its possible minimum. In fact, what can be optimized is the length of the isotherm at the beginning and at the end of measurement, length of the "step" (i.e., temperature range of heating part), and the heating rate under the assumption that the sample and standard are prepared as perfectly as possible. Concerning calculation of the areas below DSC curves, the temperature interval of 2 K in the middle of measured "step" was chosen for all tested conditions.

Firstly, the length of the step was changed to be 2, 4, 6, 8 and 10 K. The obtained DSC curves for sapphire and molybdenum are illustrated in Fig. 3 for lower temperatures (298-308 K) and in Fig. 4 for higher temperatures (418-428
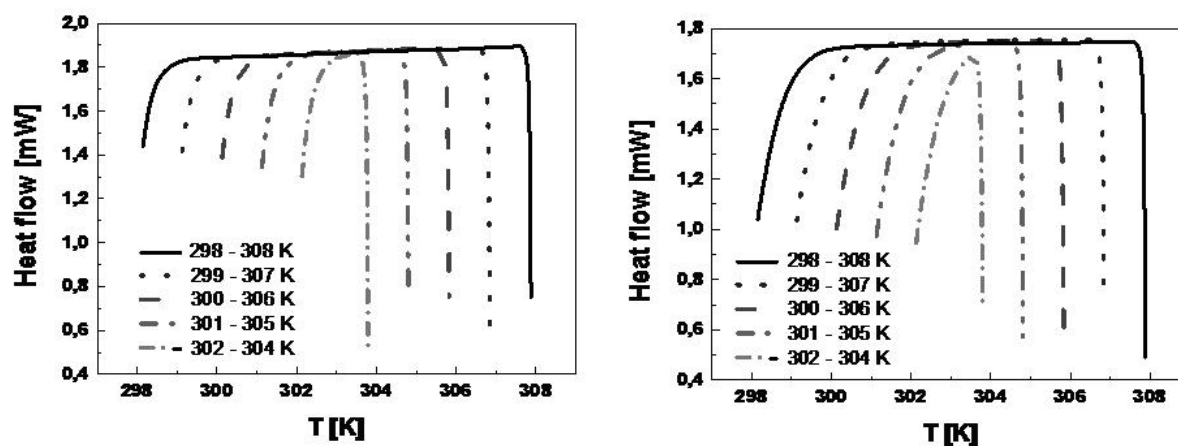
Fig. 3 Heat flow dependence on temperature for different length of the step in the temperature range of 298-308 K for sapphire (left) and molybdenum (right)

K). As can be seen in lower temperature range, the length of the step of 2 and 4 K is not applicable because there is no straight line during the step necessary for meaningful integration of the area below the curve. The higher length of the step (6 and 8 K) gave better results but still the uncertainty of determined C_p was about 3 %. Thus, the length of the step of 10 K was chosen as optimum for lower temperatures.

The increase in the temperature to 418 K and higher brings changes in observed behaviour for different length of the step (see Fig. 4). The linear part of DSC signal is longer at higher temperature as compared to lower temperature. Thus, the length of the step of 8 K is sufficient to obtain low uncertainty of C_p data for higher temperature. This is valid for sapphire as well as for molybdenum; although in all cases the linear part of the step is for molybdenum much shorter as compared to sapphire as is clearly seen in Figs 3 and 4. This shortness of linear part is caused by much longer leading edge for molybdenum as is illustrated in Fig. 5. At lower temperatures the length of leading edge was 2.5 K for molybdenum and 1.7 K for sapphire, whereas at higher temperatures it was only about half of these values (see Fig. 5). Concerning this, the optimal length of the step is 10 K for lower temperatures up to 418 K and 8 K for temperature 418 K and higher.

Secondly, the time of isotherm at the beginning and at the end of measurement was tested and its influence on uncertainty of C_p was analysed. The tested time of isotherms was chosen as 1, 2, 5 and 10 minute and the results show that except for 1 minute isotherm there was no difference between longer times at the beginning of experiment, and there was no difference between any tested time at the end of experiment. Taking total experimental time into consideration, the optimum isotherms were 2 minutes at the beginning and 1 minute at the end of each DSC scan.

The last optimization process was determination of the most suitable heating

rate to minimize the uncertainty of C_p. In broad temperature range and with the optimal length of step and isotherms (described in the part above) the heating rate of 0.5, 2, 5 and 10 K min^{-1} were tested, and the best results were achieved when 5 K min^{-1} rate was applied. The usage of lower heating rates brought higher uncertainty of C_p because the level of noise of DSC signal was too high. On the other side, higher heating rate caused that leading edge of the DSC curves was too long and there was almost no linear part of DSC signal.
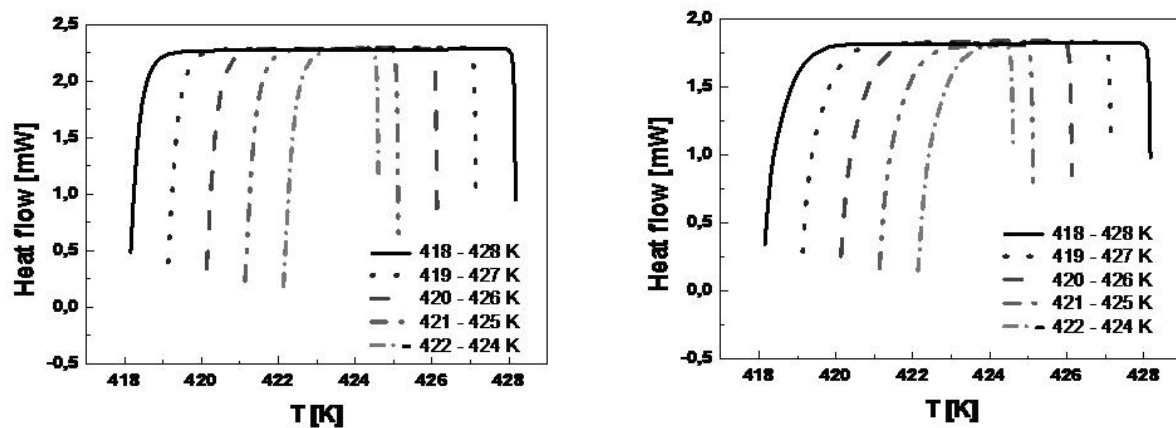

Fig. 4 Heat flow dependence on temperature for different length of the step in the temperature range of 418-428 K for sapphire (left) and molybdenum (right)
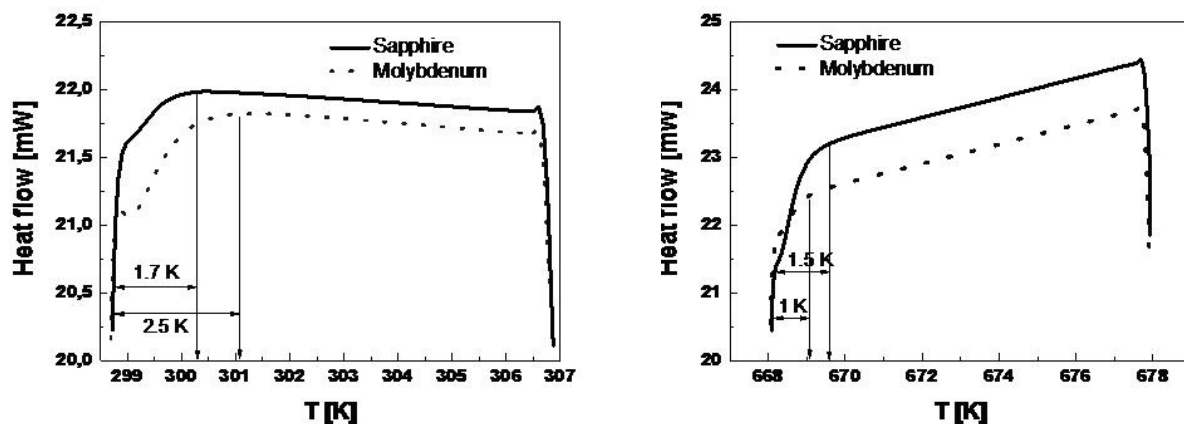

Fig. 5 Heat flow dependence on temperature for 10 K step in the temperature range of 298-308 K (left) and 668-678 K (right) for sapphire and molybdenum. The length of leading edge is depicted

The optimum thermal program of stepwise method is: 2 minutes of isotherm, heating step of 10 K (for temperatures up to 418 K) or 8 K (for temperature of 418 K and higher) made by the rate of 5 K min^{-1} and 1 minute isotherm at the end. When this temperature program is applied to baseline, then to sapphire and subsequently to the sample (Mo), the obtained heat capacity value has uncertainty up to 2 % at temperatures higher than 288 K and uncertainty up to 2.5 % at the temperatures below 288 K. The obtained values of C_p for molybdenum are summarised in Fig. 6 where the corresponding values of

uncertainty are depicted (five experiments were evaluated at each temperature).

The experimental data of C_p of molybdenum were numerically fitted and the best results were obtained using polynomial function

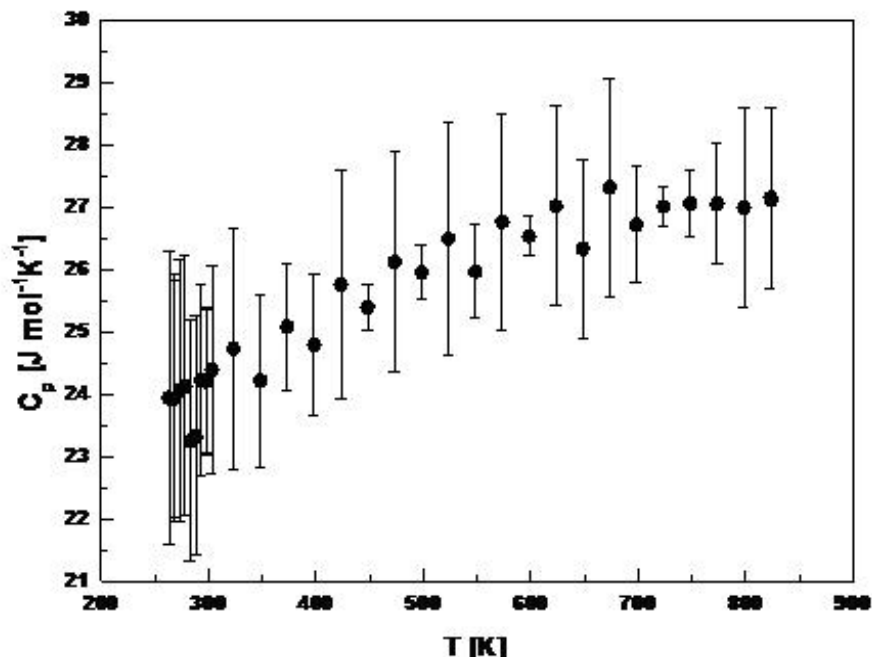$$C_p \, (\text{J mol}^{-1} \, \text{K}^{-1}) = A + BT + CT^2 \tag{3}$$

Fig. 6 Temperature dependence of heat capacity of molybdenum with illustration of standard deviation of all experimental data obtained at each temperature

where the values of parameters are given in Table I together with coefficient of determination. The illustration of this polynomial fit of experimental data is given in Fig. 7. There is also fit using standard C_p data of molybdenum [10] according to equations

$$C_p = 16.079 + 4.2065 \times 10^2 T - 6.4322 \times 10^5 T^2 + 3.8567 \times 10^8 T^3 \tag{4}$$

$$C_p = 20.102 + 1.7927 \times 10^2 T - 1.6046 \times 10^5 T^2 + 6.384 \times 10^8 T^3 \tag{5}$$

where Eq. (4) is valid for temperature range of 273-500 K and Eq. (5) for temperature range of 500-1000 K. As seen from Fig. 7, the experimental data of C_p can be described by these equations.

The C_p dependence on temperature fitted by polynomial function can be integrated in selected temperature range to calculate other thermodynamic properties such as enthalpy change ΔH, entropy change ΔS and change of Gibbs energy ΔG according to the equations

$$\Delta H = H_{T_1} - H_{T_{298}} = \int_{T_{298}}^{T_1} \frac{C_{p(s)}}{T} dT \tag{6}$$

$$\Delta S = S_{T_1} - S_{T_{298}} = \int_{T_{298}}^{T_1} \frac{C_{p(s)}}{T} dT \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Table I   Parameters of polynomial function describing temperature dependence of the heat capacity of molybdenum in the temperature range of 263-823 K

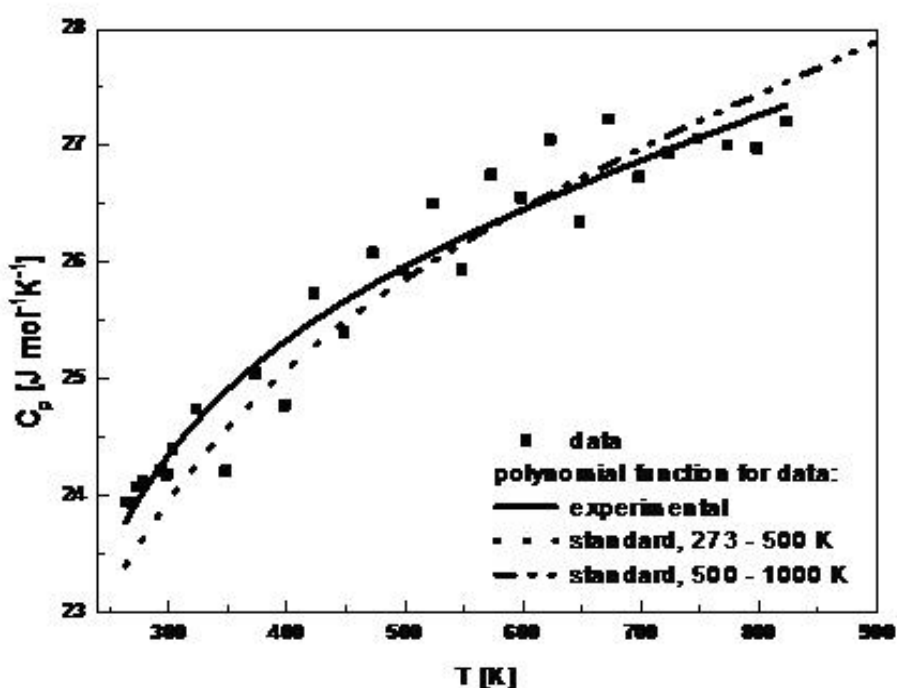| Parameters	Values of parameters in Eq. (3)
A	24.9 ± 0.6
B	$3.2 \times 10^{-3} \pm 0.8 \times 10^{-3}$
C	$-137 \times 10^3 \pm 32 \times 10^3$
R^2	0.9439

Fig. 7 Polynomial function of standard data [10] according to Eqs. (4) and (5) (dot and dash lines) and experimental data fitted by polynomial function according Eq. (3) (full line)
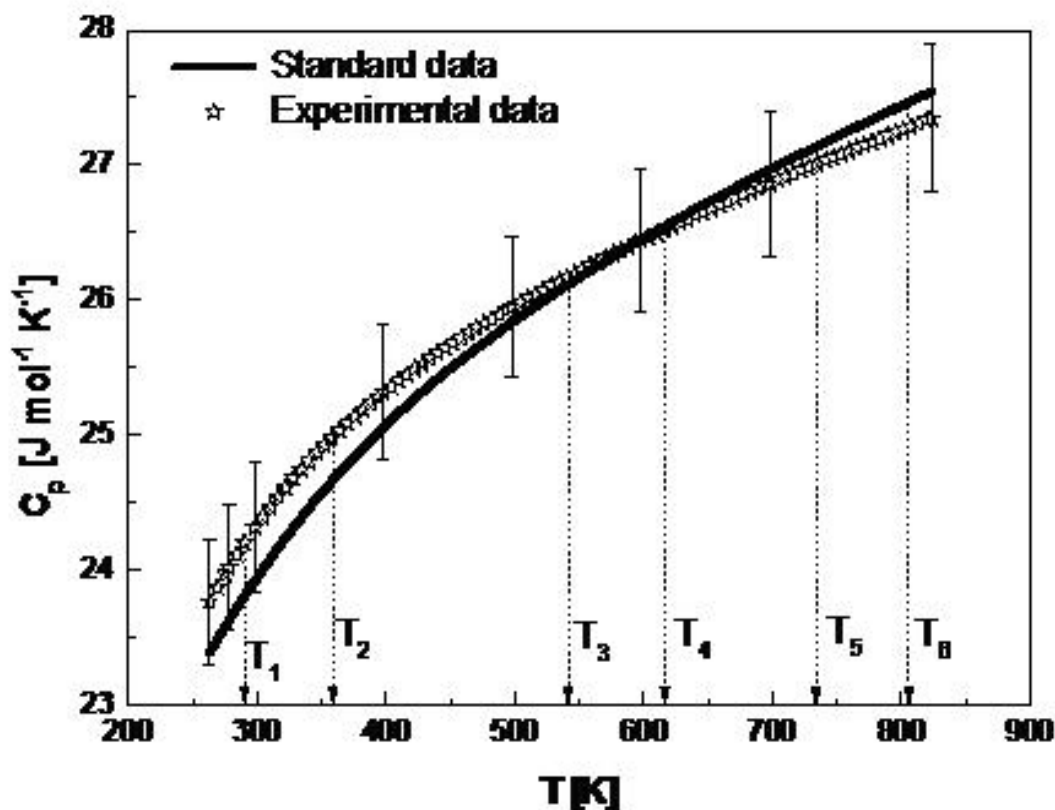
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Fig. 8 Polynomial functions of C_p of molybdenum for standard (line) and experimental (points) data with corresponding uncertainty. Temperatures selected for calculation of thermodynamic functions are depicted

Table II Thermodynamic properties: enthalpy change [J mol^{-1}], entropy change [J mol^{-1} K^{-1}], change of Gibbs energy [kJ mol^{-1}] calculated using polynomial function describing experimental data (Eq. (3)) and using polynomial functions describing standard data (Eqs (4) and (5)) and the difference (percentage of value determined for standard data) between corresponding thermodynamic property

T K	Experiment			Standard			Difference		
	ΔH_{ex}	ΔS_{ex}	ΔG_{ex}	ΔH_{st}	ΔS_{st}	ΔG_{st}	$\dfrac{\Delta H_{ex} - \Delta H_{st}}{\Delta H_{st}}$ $\%$	$\dfrac{\Delta S_{ex} - \Delta S_{st}}{\Delta S_{st}}$ $\%$	$\dfrac{\Delta G_{ex} - \Delta G_{st}}{\Delta G_{st}}$ $\%$
290	648	82	−23	403	46	−13	61	78	79
358	2323	113	−38	2052	74	−24	13	54	57
541	7015	140	−69	6733	116	−56	4	21	23
616	8991	146	−81	8708	122	−66	3	21	23
733	12123	154	−101	11850	129	−82	2	20	22
805	14077	158	−113	13815	132	−93	2	19	22

When the C_p value determined with some uncertainty is involved in consequent calculations, then the uncertainty of obtained quantity is even higher. This can be clearly seen in Table II where are the values of thermodynamic properties calculated for selected temperatures (illustrated in Fig 8) using polynomial function corresponding to the best fit of experimental data (Eq. (3) and parameters from Table I) and properties calculated using polynomial functions describing standard data (Eqs. (4) and (5)). In the last columns of Table II there are the differences between obtained values of thermodynamic properties expressed as percentage of values determined for standard data. As seen, these uncertainties are much higher than was the original uncertainty of C_p data.

Conclusion

The aim of this work was to describe the optimization of method for heat capacity determination using DSC Pyris 1 with intracooler 2P. During several experiments in broad temperature range, some negative effect on DSC measurement were detected. Sapphire was used as standard material and molybdenum as a sample because its heat capacity is well known in broad temperature range. Thus the uncertainty of obtained results can be evaluated. The molar heat capacities of molybdenum in the temperature range from 263 to 823 K were determined by stepwise method with uncertainty up to 2 % for temperatures higher than 288 K and uncertainty up to 2.5 % at temperatures below 288 K. Experimental data were fitted using polynomial function that was afterwards used to calculate other thermodynamic properties. These results were compared with the values calculated using polynomial function describing standard data and shows that uncertainty of determined thermodynamic properties is mostly much higher than was uncertainty of heat capacity data.

Acknowledgement

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