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A FULLY AUTOMATED ADIABATIC CALORIMETER FOR HEAT CAPACITY MEASUREMENT BETWEEN 80 AND 400 K

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A fully automated adiabatic calorimeter controlled on line by a computer used for heat capacity measurements in the temperature range from 80 to 400 K was constructed. The hardware of the calorimetric system consisted of a Data Acquisition/Switch Unit, 34970A Agilent, a 7½ Digit Nano Volt /Micro Ohm Meter, 34420A Agilent, and a P4 computer. The software was developed according to modern controlling theory. The adiabatic calorimeter consisted mainly of a sample cell equipped with a miniature platinum resistance thermometer and an electric heater, two (inner and outer) adiabatic shields, two sets of six junction differential thermocouple piles and a high vacuum can. A Lake Shore 340 Temperature Controller and the two sets of differential thermocouples were used to control the adiabatic conditions between the cell and its surroundings. The reliability of the calorimeter was verified by measuring the heat capacities of synthetic sapphire (α-Al_2O_3), Standard Reference Material 720. The deviation of the data obtained by this calorimeter from those published by NIST was within ±0.1% in the temperature range from 80 to 400 K.

Keywords: *adiabatic calorimeter, α-Al_2O_3, calorimetric automation, heat capacity, low temperature, temperature controller*

Introduction

Heat capacity is one of the fundamental thermodynamic data of materials and is very important to many physical and chemical theoretical researches and engineering technology design concerned with materials. Adiabatic calorimetry is the most reliable technique to obtain heat capacity and other thermodynamic data of substances; hence much work has been done to measure heat capacities with adiabatic calorimetric instruments all over the world [1–9]. Research on adiabatic calorimetry has been conducted in our Thermochemistry Laboratory since 1960s and several adiabatic calorimetric apparatuses have been constructed over the temperature ranges of 4.2–90 K [10–12], 80–400 K [13–21], 70–580 K [18–19], 300–600 K [20] and 400–1700 K [21], respectively. Traditional adiabatic calorimetric experiments have the disadvantages of complicated experimental procedures and large amounts of experimental data to be treated for obtaining high precision heat capacity values. Therefore, we reconstructed the most frequently used adiabatic calorimeter workable in the temperature range of 80–400 K and greatly simplified the experimental operation procedures by using modern computerized technology and controlling theory on the basis of our previous automated adiabatic calorimetric apparatuses. This new calorimetric instrument has the advantages of compact data acquisition and process system, advanced intellectual level and powerful processing ability of the software, better stability of measurement, higher reliability of data acquisition.

Apparatus

The new calorimetric system included a calorimetric cryostat, a data collection system, an adiabatic condition control system and a high vacuum pump system. The calorimetric cryostat consists of a sample cell, an inner and outer adiabatic shields and a high vacuum can. The data collection system consisted of a multi-channel data acquisition/switch unit (Agilent 34970A) for electric energy collection, a 7½ Digit Nano Volt/Micro Ohm Meter (Agilent 34420A) for acquisition of the temperature of the sample cell and a P4 computer equipped with a matched module and interface card GPIB (IEEE 488). The adiabatic condition control system consisted of a high precision temperature controller (Lake Shore, Model 340) and two sets of six-junction chromel–copel (Ni–55%, Cu–45%) thermocouple piles that were installed between the sample cell and the inner adiabatic shield and between the inner and outer adiabatic shield, respectively. The high vacuum pump system consisted of a combined rotational mechanical pump and oil diffusion pump (Edwards, Model NXK 333000). The block diagram of the adiabatic calorimetric system is shown in Fig. 1.

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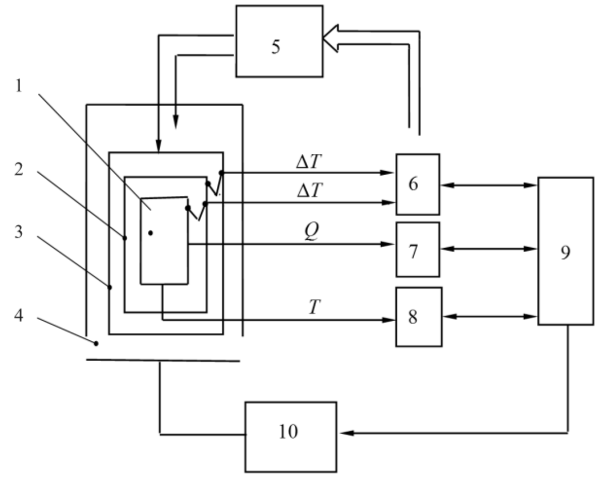

Fig. 1 Block diagram of the adiabatic calorimetric system 1 – sample cell, 2 – inner adiabatic shield, 3 – outer adiabatic shield, 4 – vacuum can, 5 – silicon controlled regulator, 6 – temperature controller (Lake Shore 340), 7 – Data Acquisition/Switch Unit (Agilent 34970A), 8 – 7½ Digit Nano Volt/Micro Ohm Meter (Agilent 34420A), 9 – computer, 10 – combined rotational mechanical pump and oil diffusion pump (Edwards, Model-NXK333000)

Sample cell

The sample cell was made of 0.3 mm thick gold-plated copper, 20 mm long, 20 mm in diameter with inner volume of about 6 cm^3. Three sheaths were fixed at the bottom of the cell for inserting the platinum thermometer and thermocouples. Electric heating wires (insulated Karma wire of 0.12 mm in diameter, R=120 Ω) were coiled on the outer wall of cell (Fig. 2a). A small amount of silicone thermally conductive sealant (type HT916, produced by Shanghai Huitian New Chemical Material Company, Limited) was used to seal the lid to the main body of the cell. On the lid there was a section of copper capillary for pumping out the air in the cell and introducing the helium gas to promote thermal equilibrium. The capillary was pinched off and the resultant fracture was soldered by solder to ensure the sealing of the cell.

Adiabatic calorimetric cryostat

The adiabatic calorimetric cryostat was shown in Fig. 2b. Two sets of six-junction chromel–copel thermocouple piles were installed between the sample cell and the inner shield, and between the inner and the outer shield to detect the temperature differences between them. The junctions of the thermocouple piles were inserted in the sheath fixed on the corresponding surfaces whose temperatures are to be detected. The detected signal of thermal electromotive force (emf) of the temperature differences were inputted into the 340 temperature controller which controls the current through the heating wires on the inner and outer adiabatic shields, respectively, to make the temperature of the inner and outer shields follow closely that of the sample cell, thus to minimize the temperature difference between the sample cell and the shields and to maintain good adiabatic condition.

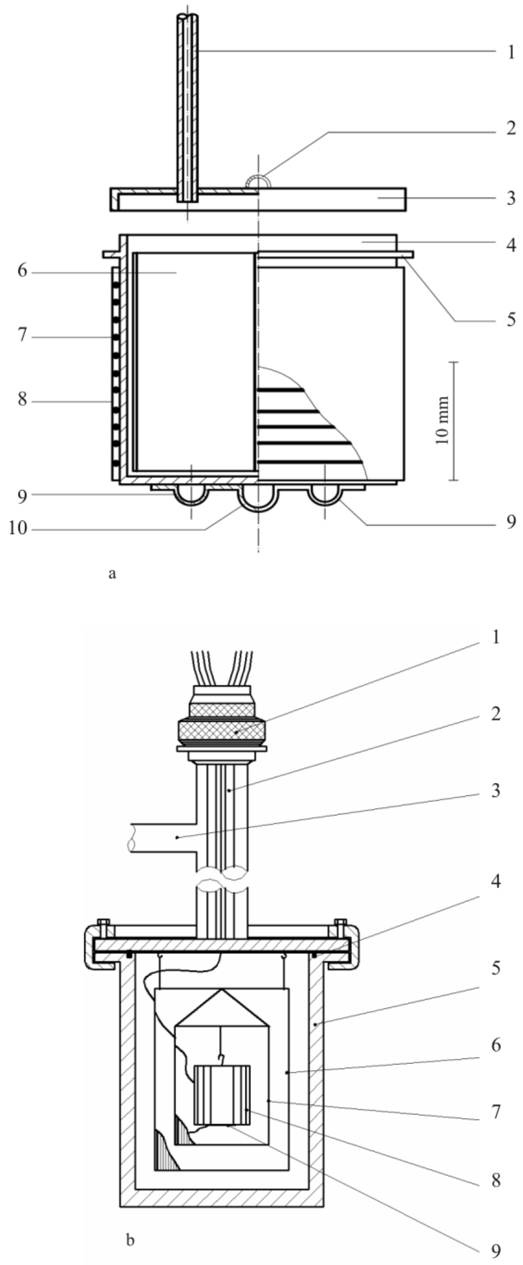

Fig. 2 Cross-sectional diagram of a – sample cell: 1 – copper capillary, 2 – lid ring, 3 – gold-plated copper lid, 4 – main body of the sample cell, 5 – sealing flange, 6 – gold-plated copper vane, 7 – Karma heating wire, 8 – aluminum foil, 9 – sheath for thermocouple, 10 – sheath for platinum thermometer. b – adiabatic calorimetric cryostat: 1 – sealing junction unit, 2 – vacuum tube, 3 – to high vacuum system, 4 – fuse gasket, 5 – vacuum can, 6 – outer adiabatic shield, 7 – inner adiabatic shield, 8 – sample cell, 9 – miniature platinum resistance thermometer

The sample cell and the adiabatic shields were placed in the high vacuum to eliminate the heat loss of the cell caused by convection heat transfer. During the heat capacity measurements the vacuum can was evacuated to 10^{-3}~10^{-4} Pa by means of the combined rotational and diffusion pump system.

A precision miniature platinum resistance thermometer (produced by Shanghai Institute of Industrial Automatic Meters, 16 mm long, 1.6 mm in diameter) measured the temperature of the sample cell. The resistance of the thermometer was measured by the 7½ Digit Nano Volt/Micro Ohm Meter (Agilent 34420A) with four-terminal resistance measurement circuit, and then inputted into the computer for processing after A/D conversion. Then the corresponding temperature was calculated according to the relationship between the resistance and temperature of the thermometer, which was calibrated in terms of ITS-90 by Station of Low-Temperature Metrology and Measurements, Chinese Academy of Sciences, R_0=100.1384 Ω.

Computer

The data acquisition system uses a P4 computer with Windows Operation System (OS), which has fast computing power and parallel processing function. The computer exchanges collected and controlled data information through GPIB (IEEE 488) card with PCI interface. The interface card (Agilent 82350A) was applied for data exchange because this card has a transmitting speed of 750 KB s^{-1}, which guarantees the information exchanging speed during the experimental process of adiabatic control, collection and control of electrical heating and collection of the temperatures of the sample. The software has an interactive execution to run functions at design time, and guarantees the practicality of the system.

Data collection unit

The A/D conversion of all the collected data was completed by the Data Acquisition/Switch Unit Agilent 34970A [22] and 7½ Digit Nano Volt/Micro Ohm Meter, Agilent 34420A [23]. The Agilent 34970A has a high precision of data conversion and stability, and has a resolution of 100 nV at 100 mV measuring range, which varies within ±0.0090% in a year. Over the measuring range of our experiments, the resolution of the resistance measurement is 0.1 mΩ with the variation of ±0.0140%, thus guaranteeing the high precision of data collection. The Agilent 34420A NanoVolt/Micro-Ohm Meter is a high-sensitivity multimeter optimized for performing low-level measurements. It combines low-noise voltage measurements with resistance and temperature functions, setting a new standard in low-level flexibility and performance. It has 7½ digits resolution and 100 pV/100 nΩ sensitivity (equivalent to the temperature resolution of $2.5\cdot10^{-5}$ K for the platinum thermometer with R_0=100 Ω).

Software

The software of the system mainly consisted of three modules (Fig. 3): data collection and control module, adiabatic environment control module and the module for the setting and revision of the experimental conditions and the data displaying.

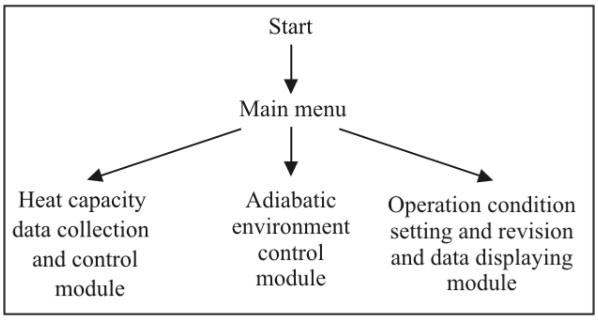

Fig. 3 Block diagram of the software for calorimetric measurements programmed by computer

Data collection and control module

The heat capacity measurement adopts the intermittent direct heating method, i.e. loading a certain amount (m) of sample in the sample cell of the calorimeter, inputting an appropriate amount of electric energy (Q) to induce a temperature rise of the cell (ΔT). Then measuring precisely Q and ΔT, the heat capacity of the sample cell (C_p) can be determined according to the following formula:

$$C_p = \frac{Q}{m\Delta T} \tag{1}$$

in which

$$Q = IV\tau (J) \tag{2}$$

where I, V and τ are current, voltage and duration of heating, respectively.

According to this principle, the heat capacity measurement can be conducted as follows. First the temperature of the sample cell is kept stable under strict adiabatic conditions, which procedure is called as temperature equilibrium period. During this period the temperature inside the sample cell is kept in good equilibrium due to excellent thermal conductivity of He gas filled in the cell and two radial copper vanes fixed in the cell. When the temperature of the sample cell reaches equilibrium, the computer controls 34970 A to input appropriate amount of current I and voltage V to heat the sample cell to induce a temperature rise of ΔT. The 34970A picks up the data of I, V and inputs them into the computer with an interval (e.g. 30 s) during the heating process. The computer controls the heating duration and calculates Q on the basis of the collected data of I, V and τ. Following the heating period the temperature T of sample cell is measured in the next temperature equilibrium period. The temperature increment of the sample cell, ΔT, caused by the energy input is calculated on the basis of the difference in temperatures between the neighbouring two equilibrium periods. The heat capacity values, C_p, can be obtained from formula (1). Through continuous circulations of above procedures the heat capacity data from low temperature to high temperature are obtained. In order to ensure enough precision of heat capacity measurements, some problems concerned must be considered and solved, such as the determination of the arrival of the equilibrium temperature during the thermal equilibrium period, the precise measurement of the equilibrium temperature of the sample cell and the temperature correction resulted from the heat exchange between the sample cell and its environment under non-ideal adiabatic conditions.

Following the heating period, the temperature of the sample cell will continue to vary because of the uneven distribution of the temperature of the sample cell caused by the continuous transferring of the introduced heat energy and the heat exchange between the sample cell and its environment owing to the non-ideal adiabatic conditions. After some time, however, the temperature variation of the sample cell due to the transferring of the introduced heat energy will decrease, while the heat exchange between the sample cell and its environment still exists. Under the condition that the temperatures of the inner and outer shields keep stable, the heat exchange between the sample cell and its environment will become stable and thus there is a linear relationship between the temperature of sample cell and the time of experimental measurement. According to this principle, the computer fits several collected temperature points of the sample cell *vs.* time to get the lines l_i or l_{i+1} (Fig. 4), whose slope is the variance ratio of the temperature as a function of time. The temperature of the calorimetric system can be regarded as reaching equilibrium if the variance ratio become small enough, e.g. 0.001 K min^{-1}.

On the other hand, except for the temperature variation, the deviation of the data collection also influences the slope of the line. The effect can be evaluated from the correlation coefficient of the fitted line. The more the correlation coefficient is close to 1 and the more the temperature points are focused around the line, the smaller the random error of the data collection. The present system takes the average of the absolute values of the differences between the measured values and the fitted values as the estimation criterion. When the average value is less than some value, e.g., 0.001 K, the random error of the data collection is neglected.

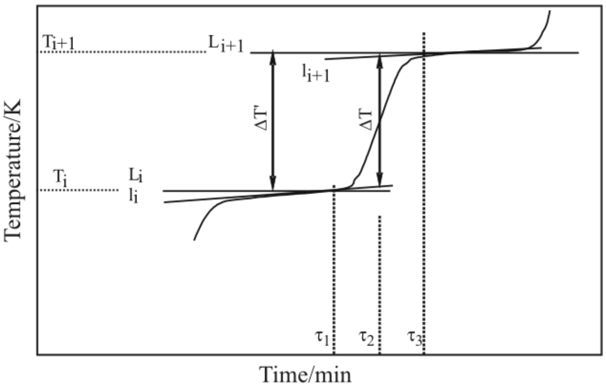

Fig. 4 The principle diagram of the temperature correction

The collected temperature data are processed automatically by the computer to determine the arrival of temperature equilibrium; when the above two criteria are satisfied the computer determines that the temperature of the calorimeter has reached equilibrium. Otherwise the temperature measurement time will be prolonged and another temperature point will be collected and the last ten temperature points will be processed with the same method as mentioned above until the two criteria are satisfied.

The precision of the temperature measurement of sample cell correlates with the random error of the temperature data collection except for the precision of the collecting equipments. To avoid this kind of error, the system collects several (e.g. 10) temperature points after the temperature of sample cell reaches equilibrium, ranks them according to the magnitude of the collected values, discards the maximum and minimum values among them and corrected the error by the figure filter technique as follows:

$$\overline{T} = \frac{1}{K}\sum_{i=1}^{n-2} T_i \tag{3}$$

in which $\overline{T}$ is the corrected temperature value, $K=n-2$, T_i is the collected temperature value, n is the times of the temperature data collection after the temperature equilibrium. The corrected temperatures are shown on L_i and L_{i+1} (Fig. 4).

The temperature rise during the heating period is the result of combination of the heating of the sample cell by the introduced energy and the heat exchange between the sample cell and its environment caused by the non-ideal adiabatic condition; the latter will lead to some error in the measurement results. In order to correct this error, lines l_i and l_{i+1} are extrapolated to intersect with the vertical line of the time axis at the middle point between the beginning and the ending heating time [Fig. 4, $\tau_2=(\tau_1+\tau_3)/2$]. The distance between the two crossing points is the corrected temperature rise, ΔT, which is just the temperature rise caused by the heat energy introduced during the heating period. This correction is performed through extending lines l_i and l_{i+1}, which are obtained when determining the arrival of the equilibrium temperature.

Taking ΔT into formula (1) produces C_p, which is the heat capacity value at the temperature of $(T_i+T_{i+1})/2$ (Fig. 4). The processing procedures are shown in Fig. 5.

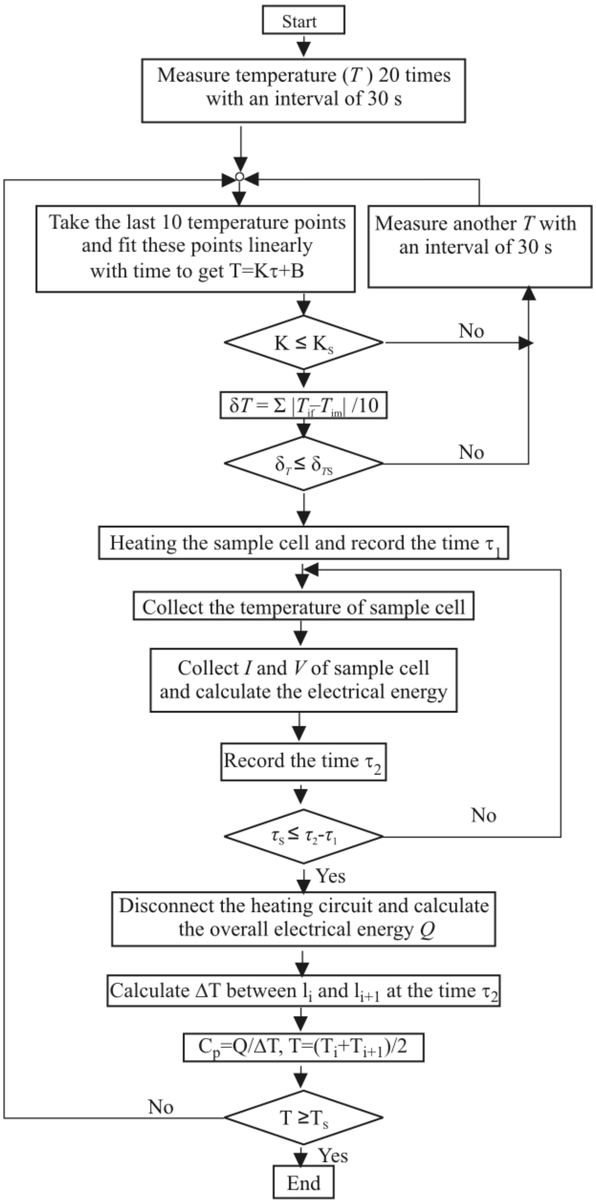

Fig. 5 Block diagram of acquisition and processing for heat capacity data controlled by computer

Adiabatic control module

The premise of good adiabatic conditions is to keep the temperatures of the inner and outer adiabatic shields tracing closely that of the sample cell. In order to realizing the premise, the heating current introduced into the sample cell is gradually smoothly increased in the initial period, kept a constant value in the middle period and decreased in the final period. If the temperatures of the inner and outer adiabatic shields are kept increasing synchronous with that of the sample cell, the temperature of sample cell will decrease after the heating period and the speed of the temperature decrease varies with the species, mass, heat conductivity of the samples and the temperature range of the measurement because of the uneven distribution of the interior temperature of the cell during the heating period. As a result the temperature of the inner shield will become higher than that of the sample cell; the results of heat capacity measurement are influenced. This system adopts the method of the intellectual control for the temperatures of the inner and outer adiabatic shields, that is, reducing properly the heating current of the inner adiabatic shield during the latter heating period according to the thermal properties of the sample and the actual condition of the measurement in corresponding temperature range and controlling the temperature of the inner shield slightly lower than that of the sample cell to avoid the over-regulation of temperature of the inner adiabatic shield, especially for the sample with small heat conductivity or with phase transition.

The module of setting and revision of operation conditions and data displaying

This system refreshes the screen every time when it collects the data, displaying in real time the various parameters and states, such as, the electric energy introduced into the sample cell, the temperature of the sample cell, the adiabatic control condition and the environment temperature. The measuring conditions can be set on the screen before the measurement and revised on the screen during the measurement. At the same time some information can be displayed on time, such as, the heat capacity of the sample varies with the temperature and the phase transition occurs, so as to understand the change of thermal properties of the sample on time. The parameters and states mentioned above can be displayed on the screen at the same time and can be processed because the software of the system is developed under multi-file application program and multi-channel module.

Calibration and discussion of results

The reliability of the newly constructed calorimetric system is verified by measuring the molar heat capacities of synthetic sapphire (α-Al_2O_3), Standard Reference Material 720. The results are listed in Table 1. In order to compare the values with those recommended by NIST [24], we calculated the molar heat capacities of α-Al_2O_3 in the temperature range of 80–400 K with an interval of 10 K using the non-linear insert method based on the measured molar heat capacity data. The results are shown in Table 2 and Fig. 6, from which it can be seen that the deviations of our values from the recommended values are within ±0.1%, which proves that the performance of the newly constructed calorimetric apparatus has been improved compared with the previous calorimeters [12, 15, 16].

Compared with the previous calorimetric system, the newly improved system has the advantages of significantly compacted and simplified device,

Table 1 Experimental molar heat capacities of α-Al_2O_3 (M=101.96 g mol^{-1})

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
78.636	6.377	159.716	35.898	280.221	74.988
79.621	6.725	163.370	37.371	283.636	76.003
80.914	7.105	166.940	38.836	286.970	76.623
82.612	7.649	170.434	40.202	289.848	77.225
84.261	8.043	173.857	41.462	292.652	78.015
85.868	8.526	177.215	42.745	295.379	78.494
87.435	9.002	180.512	43.985	298.106	79.019
88.968	9.467	183.752	45.191	301.288	79.646
90.466	9.920	186.939	46.442	304.545	80.502
91.933	10.366	190.075	47.587	307.229	80.953
93.370	10.812	193.163	48.720	309.918	81.498
94.780	11.264	196.591	49.964	312.585	82.032
96.163	11.722	200.349	51.294	315.238	82.527
97.522	12.178	204.043	52.561	317.878	83.033
98.858	12.627	207.679	53.872	320.502	83.476
100.171	13.065	211.258	55.055	323.493	84.108
101.464	13.501	214.781	56.284	326.855	84.726
102.736	13.952	221.677	58.482	330.201	85.325
103.990	14.438	225.053	59.618	333.529	86.152
106.588	15.363	228.384	60.716	336.818	86.670
110.464	16.756	231.671	61.722	340.706	87.329
114.184	18.093	234.923	62.690	345.119	88.148
119.983	20.085	238.140	63.684	349.510	88.825
120.933	20.668	241.288	64.568	353.864	89.563
123.067	21.594	244.470	65.503	358.182	90.249
126.341	22.851	247.582	66.492	362.435	90.734
129.520	24.083	250.679	67.275	366.655	91.608
132.614	25.297	253.746	68.197	370.843	92.381
135.628	26.489	256.786	69.051	374.999	93.160
138.569	27.649	259.773	69.865	378.887	93.546
141.441	28.771	262.804	70.671	383.002	94.013
144.251	29.854	265.768	71.443	387.425	94.611
147.308	31.010	268.706	72.194	391.816	95.131
149.304	32.036	271.620	72.936	396.207	95.735
152.497	33.269	274.509	73.667	400.363	96.183
155.971	34.693	277.377	74.360		

Table 2 Comparison of experimental molar heat capacities of α-Al_2O_3 with the recommended values by NIST

T/ K	$C_{p\,(Fit)}$/ J K^{-1} mol^{-1}	$C_{p\,(NIST)}$/ J K^{-1} mol^{-1}	δ*/ %	T/ K	$C_{p\,(Fit)}$/ J K^{-1} mol^{-1}	$C_{p\,(NIST)}$/ J K^{-1} mol^{-1}	δ*/ %
80	6.901	6.90	0.01	250	67.08	67.06	0.03
90	9.678	9.67	0.08	260	69.82	69.80	0.03
100	12.85	12.84	0.08	270	72.42	72.41	0.01
110	16.34	16.34	0.00	280	74.87	74.88	–0.01
120	20.07	20.07	0.00	290	77.20	77.23	–0.04
130	23.95	23.95	0.00	300	79.41	79.45	–0.05
140	27.93	27.93	0.00	310	81.51	81.56	–0.06
150	31.95	31.94	0.03	320	83.49	83.55	–0.07
160	35.95	35.94	0.03	330	85.37	85.44	–0.08
170	39.90	39.89	0.03	340	87.16	87.23	–0.08
180	43.75	43.74	0.02	350	88.84	88.92	–0.09
190	47.50	47.50	0.00	360	90.45	90.52	–0.08
200	51.12	51.12	0.00	370	91.97	92.04	–0.08
210	54.61	54.61	0.00	380	93.41	93.48	–0.07
220	57.95	57.95	0.00	390	94.91	94.84	0.07
230	61.14	61.14	0.00	400	96.18	96.14	0.04
240	64.18	64.17	0.02				

*δ=100 ($C_{p\,(Fit)}$–$C_{p\,(NIST)}$)/$C_{p\,(NIST)}$; δ is the deviation of the fit value of the experimental molar heat capacities from the recommended values by NIST

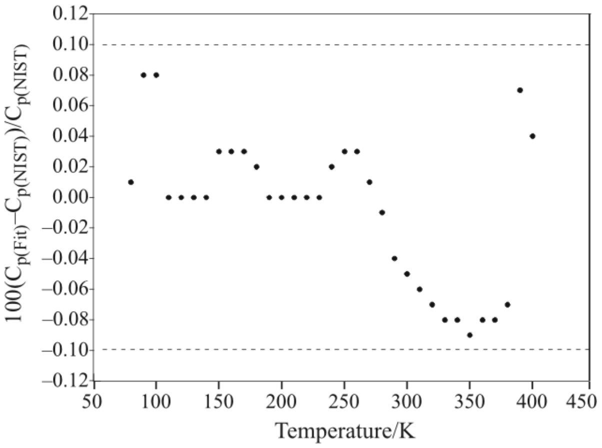

Fig. 6 Plot of deviations 100($C_{p\,(Fit)}$–$C_{p\,(NIST)}$)/$C_{p(NIST)}$ of our results for the molar heat capacities of α-Al_2O_3 from the recommended values by NIST, where $C_{p\,(Fit)}$ denotes the fit value of our experimental molar heat capacities, $C_{p\,(NIST)}$ denotes the recommended values by NIST

highly stability and precision, higher intellectual level and greater power of the software. Through the operation and testing for one and a half year it is verified that the calorimetric system is easy to operate and has stable performance and great power of automatic control and data processing. All the controlling and measuring procedures can be accomplished through the computer after the sample is loaded in the calorimeter. The calorimetric apparatus has already been able to be manufactured commercially.

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