Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 283-289

A LOW-TEMPERATURE AUTOMATED ADIABATIC CALORIMETER
Heat capacities of high-purity graphite and polystyrene

*Zhi-Cheng Tan**, *Ji-Biao Zhang and Meng Shang-He*

Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

(ReceivedAugust 19, 1997; in revised form February 10, 1998)

Abstract

A computerized adiabatic calorimeter for heat capacity measurements in the temperature range 80–400 K has been constructed. The sample cell of the calorimeter, which is about 50 cm^3 in internal volume, is equipped with a platinum resistance thermometer and surrounded by an adiabatic shield and a guard shield. Two sets of 6-junction chromel-copel thermocouples are mounted between the cell and the shields to indicate the temperature differences between them. The adiabatic conditions of the cell are automatically controlled by two sets of temperature controller. The reliability of the calorimeter was verified through heat capacity measurements on the standard reference material α-Al_2O_3. The results agreed well with those of the National Bureau of Standards (NBS): within ±0.2% throughout the whole temperature region. The heat capacities of high-purity graphite and polystyrene were precisely measured in the interval 260–370 K by using the above-mentioned calorimeter. The results were tabulated and plotted and the thermal behavior of the two materials was discussed in detail. Polynomial expressions for calculation of the heat capacities of the two substances are presented.

Keywords: adiabatic calorimeter, α-Al_2O_3, graphite, heat capacity, polystyrene

Introduction

In accordance with the recent rapid progress in the field of materials science, needs for studies on the thermodynamic properties of a considerable variety of materials over a wide range of temperature have become more and more urgent. The heat capacity is not only a fundamental thermodynamic property, but also a characteristic datum closely related to the energetics and structure of materials.

* Author for correspondence: Fax: 86 411 4691570, e-mail: tzc@ms.dicp.ac.cn

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

It is of great significance to basic research in physics and chemistry, as well as to numerous technological problems in energy sources and materials. Among various thermodynamic experiments, measurement of the heat capacity is a unique method whereby fundamental thermodynamic quantities such as enthalpy, entropy and Gibbs free energy can be accurately and simultaneously derived. In addition, heat capacity calorimetric studies on phase transitions that often occur in the solid and/or liquid states provide definitive evidence of what happens in such phenomena. Because of the importance of heat capacity data in basic research and practical use, the construction of calorimeters for heat capacity measurements and relevant research is an active subject, not only in calorimetry, thermochemistry and thermophysics, but also in many other branches of science and technology. In this paper, we describe an automatic calorimeter equipped with a sample cell with an internal volume of 50 cm^3, which operates in the temperature range 80–400 K. The heat capacities of high-purity graphite (99.99%) and polystyrene (99.9%), which are very important construction materials for fabrication electronic beam power calorimeter, were precisely measured in the interval 260–370 K by using the above-mentioned calorimeter. The thermal behavior of the two materials is discussed in detail.

Apparatus

The equipment was based on the Nernst step heating method and the main concepts of previous adiabatic calorimeters were adopted [1]. The new calorimeter consists of a calorimeter cell, a thermometer-heater assembly, an adiabatic shield, a guard shield, two sets of differential thermocouples, and a vacuum can (Figs 1 and 2). The adiabatic calorimeter was described in detail earlier [2] and only the new features of the equipment are reported here.

The calorimeter cell is made of silver of 99.95% purity, 0.2 mm thick, gold-plated and polished. The main body is 33 mm in diameter and 60 mm high. The mass of the empty cell is about 50 g and its effective capacity is around 50 cm^3. In its center, a tapered entrant well is provided for insertion of the thermometer-heater assembly. Onto the outer wall of the well, eight L-shaped 0.15 mm thick radial silver vanes are brazed one by one with the use of silver alloys. A space exists between the outer edges of the vanes and the cylindrical inside wall, and four semi-circular vanes extend into the upper and the lower hemispherical spaces in the cell. A small amount of helium gas is introduced into the cell through a capillary copper tube fitted on the silver lid, to promote heat transfer. The cryostat includes an adiabatic shield, a guard shield, and a submarine-type vacuum can, which is immersed in a Dewar vessel filled with liquid nitrogen.

In order to obtain good adiabatic conditions between the calorimeter cell and its surroundings, two similar control circuits are used to control the temperature of the two shields. Each control circuit consists of a modified DWT-702 precise

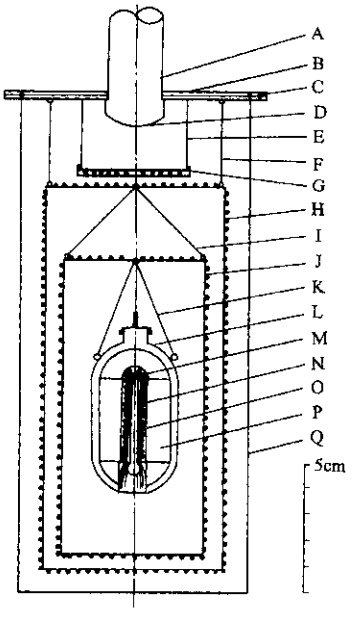

Fig. 1 Schematic diagram of the 80–400 K adiabatic calorimeter A: thin-walled German silver tube; B: flanged cover of vacuum can; C: o-ring fuse gasket; D: radiation trap; E: thermal anchor for leads; F, I, K: braided silk wires for hanging guard and adiabatic shields and sample container; H: guard shield with heater; J: adiabatic shield with heater; L: sample container; M: central reentrant well; N: heater of sample container; O: platinum resistance thermometer; P: L-shaped radial vanes; Q: stainless steel vacuum can

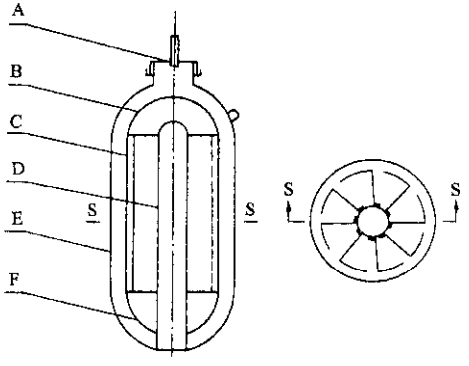

Fig. 2 Sample container A: lid with capillary copper tubing; B: upper vanes; C: side vanes; D: central reentrant well; E: outer wall of container; F: lower vanes

temperature regulator (made by No. 6 Automatic Instrument Manufacturing Co., Shanghai, China) and a thermopile. When these control circuits are operating,

the temperature difference between the calorimeter and its surroundings remains at 0.5 mK or smaller throughout the entire experimental process. The platinum-enclosed platinum resistance thermometer (No. 82021 4-lead, capsule-type, 25 Ω, 5 mm in diameter, 50 mm long) used in the adiabatic calorimeter cell was calibrated on the basis of ITS-90 by the Center of Low-temperature Metrology and Measurements, Academia Sinica.

The energy input to the sample cell is supplied by a d.c. voltage supply with a stability of about 5 ppm. A computer-based on-line measuring system has been designed which can automatically measure the current through the calorimeter heater, the voltage across it, and the duration of energy input, and it subsequently computers the energy introduced. The system is composed of a main computer, I/O data channels, an A/D converter, a sampling switch, an input interface and a clock signal. A Model 5000 Integrating Digital Multimeter (Sabtronics Instrument AG, Switzerland) is used as the A/D converter. The heating duration is measured by means of a digitally displayed electronic timer-controller with an accuracy of 10^{-3} s. The temperature of the platinum thermometer in the calorimeter cell is also measured automatically by the above-mentioned system.

Experimental

The operation of this apparatus is similar to that detailed in reference [3]. Especial care is taken to allow the calorimeter and the contents to reach thermal equilibrium after each energy input. In our experiments, the duration of energy input is 10 min, and thermal equilibration is attained within 10 to 15 min after the input, but it may take as long as several days if the sample in the calorimeter is undergoing a transition process. The temperature and electric energy are collected, printed and dealt with by an automatic control system [4]. The entire calorimetric measurements are fully automated. Under these conditions, the data-acquisition system is advantageous for the monitoring of the equilibration process. All the measurements are made at essentially the same heating rate (0.5 K min^{-1}), and the experimental temperature increment over the entire temperature range is about 5 K. We have tested the calorimetric apparatus by measuring the heat capacities of α-Al_2O_3 (99.993 mass% purity, prepared by No. 1 Reagent Manufactory, Shanghai, China) from 80 to 400 K. The heat capacities of high-purity graphite (99.99%) and polystyrene (99.9%) were also measured in the interval 260 –370 K by using the above-mentioned calorimeter.

Results and discussion

The experimental molar heat capacities of α-Al_2O_3 are listed in Table 1. In order to check the statistical error of this apparatus, a polynomial equation was fitted to our experimental data for α-Al_2O_3 from 80 to 400 K:

$$C_p=62.451016+47.129162X-17.575343X^2-0.0995764X^3+3.2193721X^4-$$
$$-1.8714473X^5+4.8207588X^6-1.2497155X^7-2.0049366X^8 \text{ (J K}^{-1}\text{ mol}^{-1}\text{)}$$

in which $X=(T-234.5)/154.5$

The overall precision of this apparatus may be gauged from the deviations of the experimental points from the polynomial. The percentage deviation of almost every point is within ±0.1%.

Table 1 Experimental heat capacity 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}
Series 1		Series 2		286.31	76.38
80.99	7.27	206.03	53.10	291.59	77.79
87.04	8.87	212.17	55.28	296.80	78.73
95.74	11.46	218.17	57.27	301.97	79.83
100.83	13.08	224.04	59.21	307.09	80.72
105.66	14.77	229.30	60.87	312.16	81.89
110.27	16.45	235.37	62.72	317.18	82.88
115.17	18.29	240.93	64.36	322.38	83.81
120.35	20.23	245.44	65.69	327.74	84.96
125.31	22.15	249.95	66.97	333.06	85.91
130.08	24.04	255.27	68.35	338.33	86.75
135.63	26.22	260.52	69.78	343.56	87.78
141.77	28.68	265.69	71.37	348.75	88.63
147.92	31.08	270.79	72.50	354.26	89.69
153.70	33.39	Series 3		360.08	90.55
159.28	35.63	219.50	57.76	365.99	91.53
164.67	37.79	224.53	59.37	372.00	92.39
169.91	39.67	229.96	61.32	377.95	93.31
175.01	41.80	234.71	62.53	383.87	94.16
180.31	43.89	239.46	64.07	389.75	94.92
185.83	45.92	244.94	65.47	Series 4	
191.21	47.93	250.34	67.00	294.89	78.46
196.46	49.82	255.65	68.50	299.87	79.38
201.59	51.60	260.89	69.92	305.01	80.73
206.61	53.40	266.06	71.27	310.10	81.41
212.14	55.33	271.16	72.76	315.14	82.50
218.15	57.37	276.20	73.88	320.14	83.43
		281.18	75.07		

Table 2 Experimental heat capacities of graphite and polystyrene

T/K	C_p/J K^{-1} g^{-1}	T/K	C_p/J K^{-1} g^{-1}	T/K	C_p/J K^{-1} g^{-1}	T/K	C_p/J K^{-1} g^{-1}
Graphite				Polystyrene			
276.56	0.6474	330.80	0.8015	276.40	1.128	332.23	1.375
281.72	0.6619	335.80	0.8148	281.66	1.151	337.14	1.392
286.80	0.6773	340.79	0.8292	286.87	1.175	342.47	1.425
291.78	0.6928	345.83	0.8406	292.04	1.202	347.26	1.452
296.69	0.7055	350.87	0.8558	297.18	1.222	352.02	1.482
301.53	0.7192	355.93	0.8695	302.28	1.243	356.70	1.555
306.30	0.7327	361.00	0.8845	307.34	1.266	361.20	1.689
311.00	0.7460	366.08	0.8960	312.37	1.288	365.48	1.791
315.94	0.7604	371.12	0.9090	317.37	1.311	369.67	1.825
320.94	0.7733	376.06	0.9221	322.35	1.333	373.83	1.837
325.87	0.7874			327.30	1.357		

The smoothed heat capacities were calculated by using the above-mentioned equation for α-Al_2O_3. The accuracy of this calorimeter may be assessed by comparing the results of this research with those of other investigators: our smoothed heat capacity values are coincident within ±0.2% with the commonly accepted values obtained by Ditmars and Douglas [5].

The heat capacities of high-purity graphite and polystyrene were also precisely measured in the temperature region 260–370 K. The results are reported in Table 2 and plotted in Fig. 3. The C_p–T curve of graphite in Fig. 3 indicates that

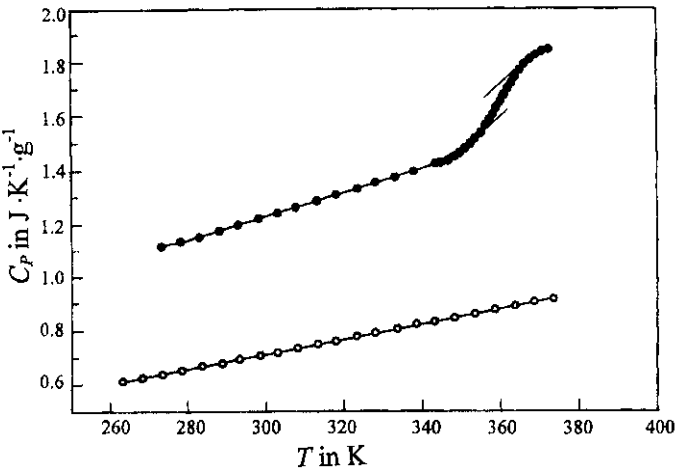

Fig. 3 Heat capacities of graphite and polystyrene; • – polystyrene o – graphite

there is no phase transition or thermal anomaly in our experimental temperature region, which means that the high-purity graphite is thermochemically stable in this temperature range. This result accords well with the structure of high-purity graphite. From the C_p–T curve of polystyrene, we can see that no phase transition was observed in the whole experimental temperature range, but a glass transition with a heat capacity jump of 0.222 J K^{-1} g^{-1} is found at approximately 360 K. From the experimental data, two polynomial equations are derived. For graphite, valid from 260 to 380 K:

$$C_p=0.784539+0.1374133X \quad (J\,K^{-1}\,g^{-1})$$

in which $X=(T-326.2727)/49.7603$.

For polystyrene, valid from 270 to 350 K:

$$C_p=1.274747+0.1468651X+0.02352279X^2-0.007293143X^3-0.06812298X^4+$$
$$0.00870865X^5+0.04628492X^6 \quad (J\,K^{-1}\,g^{-1})$$

in which $X=(T-309.43)/33.03$.

From 340 to 380 K, the equation is:

$$C_p=1.61388+0.364981X+0.0235977X^2-0.1628013X^3 \quad (J\,K^{-1}g^{-1})$$

in which $X=(T-358.15)/15.18$.

* * *

This work was supported financially by the National Natural Science Foundation of China with grant No. 29773048.

References

1 E. F. Jr. Westrum, G. T. Furukawa and J. P. McCullough, Experimental Thermodynamics, Vol. I (Eds. J. P. McCullough, D. W. Scott), Butterworths, London 1968, p. 133.
2 Zhi-Cheng Tan, Li-Xing Zhou et al., Scientia Sinica (Series B), 26 (1983) 1014.
3 M. A. White and M. J. M. Van Oort, Rev. Sci. Instrum., 58 (1987) 1239.
4 An-Xue Yin, Wen-Bing Wang, Zhi-Cheng Tan et al., Computers and Applied Chemistry (in Chinese), 17 (1990) 176.
5 D. A. Ditmars and T. B. Douglas, J. Res. Bur. Stand, 75A (1971) 401.