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AN ADIABATIC LOW-TEMPERATURE CALORIMETER FOR HEAT CAPACITY MEASUREMENT OF SMALL SAMPLES

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Abstract

A small sample adiabatic calorimeter for measuring heat capacities in the temperature range 60–350 K using the Nernst method has been constructed. The sample cell of the calorimeter is 6 cm^3 in the internal volume, equipped with a miniature platinum thermometer and surrounded by two adiabatic shields. Two sets of 6-junction chromel–copel thermocouples were mounted between the cell and the shields to indicate the temperature differences between them. The adiabatic conditions of the cell were automatically controlled by two sets of temperature controller. A mechanical pump was used to pump out the vapour of liquid nitrogen in the cryostat to solidify N_2 (1), and 60 K or even lower temperature was obtained. The performance of this apparatus was evaluated by heat capacity measurements on α-alumina. The deviations of experimental results from a smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.5% compared with the recommended reference data in the wole temperature range.

Keywords: adiabatic calorimetry, α-alumina, heat capacity, low temperature, small sample

Introduction

Adiabatic calorimetry at low temperature is the classical method for heat capacity measurement, from which many other thermodynamic properties such as enthalpy, entropy and Gibbs free energy, which are of importance to both theoretical and practical purposes, can be calculated. High accuracy of heat capacity measurements [1, 2] results from precise adiabatic control and rather large quantity of the sample used. In the adiabatic calorimeter of traditional type, the sample cell has the large internal volume of 30–100 cm^3 [3–6] to contain an ample amount of specimen in order to reduce the effect of undetectable heat leak on experimental results to a negligible level. The requirement of large amount of sample has made the traditional calorimeter unfit to investigate some new

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substances which are difficult to provide enough sample but valuable to be studied. These include substances of biological origin, compounds prepared by steps of low-yield reactions and optical or other isomers difficult to be separated. Nowadays, due to the progress in electronics and material science, the development of adiabatic calorimeter [7–15] enables the reduction of the sample amount required and attains the high accuracy. In this paper, we describe a small sample adiabatic calorimeter with a sample cell of internal volume of 6 cm^3 which is workable in the temperature range 60–350 K. The heat capacities of the standard reference material α-Al_2O_3 were measured to demonstrate the accuracy of this calorimeter.

Apparatus

Sample cell

A cross sectional view of the sample cell is shown in Fig. 1. The cylindrical main body was made of thin-walled (0.3 mm thick) gold-plated copper, 20 mm long, 20 mm in diameter. On the top of the outer surface of the cell, there is a flange (1.0 mm wide and 0.5 mm thick), where the sealant would stick. At the bottom of the cell, an Ω-shaped sheath (0.10 mm thick and 18 mm long) was silver-soldered to insert a miniature platinum-resistance thermometer. A heater (Karma wire of 0.12 mm in diameter, 105 Ω) was wound bifilarly on the surface of the cell and fixed by use of cycloweld, and was covered with a piece of aluminium-plated dacron film. The heating wire was wound evenly and covered almost the whole surface of the cell, so that the Joule heat generated in the wire spread evenly over the whole cell. In this way, local over-heating and its undesirable consequence (heat leakage and long equilibrium time) were decreased to a minimum. Four L-shaped 0.10 mm thick radial gold-plated copper vanes were placed in the cell to shorten the thermal equilibrium time. Thermal equilibrium in the cell filled with powder sample is usually reached in 2 minutes after the end of the heating period. The lid of the cell was made of gold-plated silver (21 mm in diameter, 0.30 mm thick, 1.0 mm high). Small amount of cycloweld was used to seal the lid to the main body of the sample cell. No leakage was found when the sealed cell was kept in 1×10^{-3} Pa vacuum in the temperature range of 60–350 K. At the centre of the lid, there is a ~5 cm long copper capillary for introducing the helium gas and hanging the sample cell. After the lid was sealed to the main body with cycloweld and 0.1 MPa helium exchanging gas was introduced, the capillary was pinched off and the resultant fracture was soldered with a little amount of solder to ensure the sealing of the cell. Finally, the capillary was curved to form a hook by which the sample cell was hung from the top of inner adiabatic shield by a length of nylon thread.

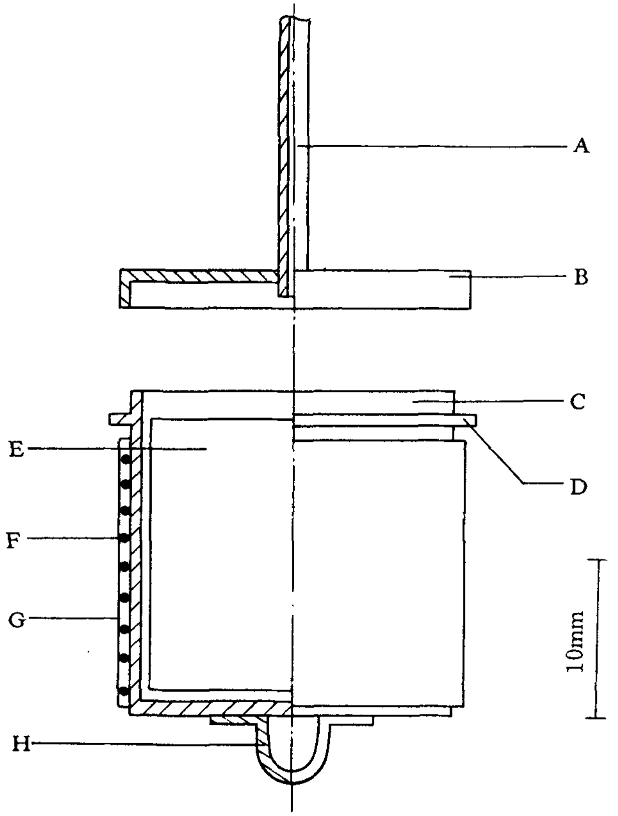

Fig. 1 Cross-sectional view of the calorimeter sample cell. A-copper capillary; B-gold-plated silver lid; C-main body of the sample cell; D-sealing flange; E-gold-plated copper vane; F-heating wire; G-aluminium-plated dacron film; H-sheath for platinum resistance thermometer

Thermometer

A miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm long, 1.6 mm in diameter and a nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The thermometer was placed in the copper sheath at the bottom of the sample cell, and a little amount of high vacuum silica grease (Dow Corning Co., USA) was used to ensure thermal contact between the thermometer and the sample cell.

Four leads of constantan wire (0.10 mm in diameter, 120 cm long) were used for connections to the thermometer. All eight lead wires connected with the sample cell were wound for two circles first along the inner surface and then on the outer surface of the inner shield, so as to lessen the heat leak to and from the sample cell through the electrical wires.

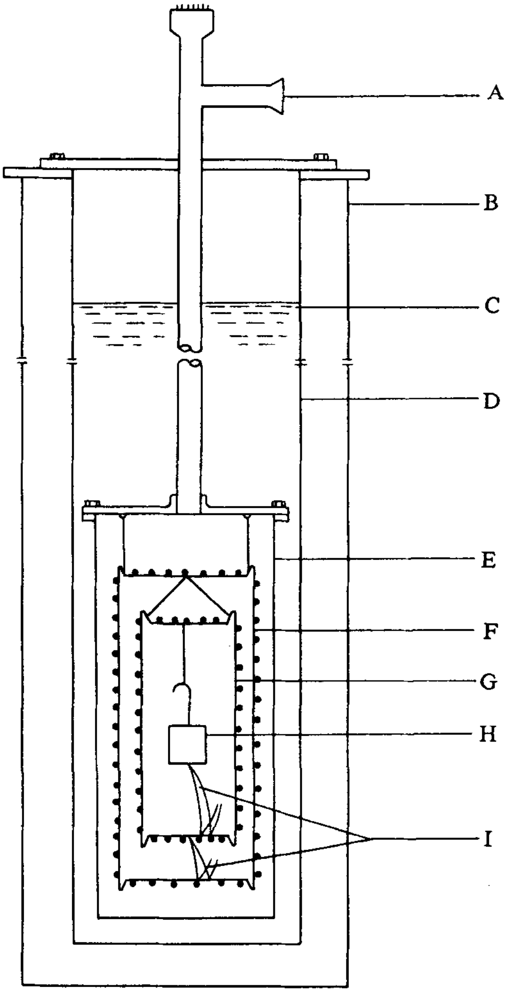

Fig. 2 Cross-sectional view of the adiabatic calorimetric cryostat. A-to high vacuum pump; B-steel frame of the Dewar vessel; C-coolant; D-Dewar vessel; E-vacuum can; F-outer adiabatic shield; G-inner adiabatic shield; H-sample cell; I-differential thermocouples

Cryostat

Figure 2 shows the cross section of the cryostat. The sample cell is surrounded by an inner adiabatic shield, which was made of chromium-plated copper, 0.5 mm thick, 45 mm in diameter and 110 mm long. The inner adiabatic shield consists of three parts: the upper lid, the lower bottom and the cylindrical main body. Manganin heating wires were wound evenly on all these three parts so that the sample cell is in an environment with little temperature gradient. The inner shield was hung from the top of the outer shield by three pieces of nylon thread. The construction of the outer adiabatic shield is similar to that of the inner one, except that the dimension of the outer shield is a little larger (65 mm in diameter, 150 mm long). The outer shield was hung from the top of the vacuum can, so that both two shields and the sample cell can be easily dismounted when changing the sample. To seal the chromium-plated brass vacuum can, we used an O-ring gasket made up of lead–tin alloy wire of 3.0 mm in diameter. During measurements, the space in the vacuum can was evacuated to about 1×10^{-3} Pa by an oil diffusion pump system. Pumping out the nitrogen vapour from the Dewar vessel by a mechanical pump, the remaining liquid nitrogen solidified, and the temperature was lowered to about 60 K or even lower.

Differential thermocouples

Two sets of chromel–copel (Ni-55%, Cu-45%) thermocouples were mounted between the sample cell and inner shield, and between inner shield and outer shield, respectively. Each set of thermocouples consists of 6 thermocouples so that the thermal EMF is 390 $\mu V\cdot K^{-1}$ at 300 K. Junctions of the thermocouples were fixed in place by dacron – base adhesive tape which is commercially available, and were insulated from the cell or the shields by some tiny pieces of insulating paper. On the side of sample cell, six junctions were divided into two groups, three junctions were fixed on the lid while the rest on the bottom of the sample cell. On the side of adiabatic shields, six junctions were fixed evenly across the surface. This reduced local over-heating on both sample cell and shields.

Adiabatic control

The temperature of the inner adiabatic shield was controlled to be the same as that of the sample cell by means of an autoadiabatic controlle (Model ACD-79, made by the National Institute of Metrology). A temperature controller (Model DWT-702, produced by No. 6 Plant of Automatic Meter of Shanghai) was used to control the temperature of the outer adiabatic shield a bit lower than that of the inner one. Both controllers operate in the proportional–integral–derivative mode. The principle of the automatic adiabatic shield control circuitry was described in detail previously [16, 17]. When the adiabatic circuits were operating, the temperature difference between the sample cell and the inner shield was kept to be 0.5 mK or smaller during the entire experimental process, except that about 30 s after the initial and the end of the energy input, a gradual difference about 5 mK occurred. The temperature drift of the sample cell could be controlled within 5×10^{-6} K·s^{-1} under this shield control condition.

Energy and temperature measurements

The energy introduced into the sample cell was supplied by a d. c. voltage supplier with a stability of 5 ppm, and was determined from the potential drops across the sample heater and a standard resistor (100 Ω) which was connected in series with the heater, and from the duration of the energy input. The heating period lasted 600 s, and was controlled by a digital electronic timer with a resolution of 10^{-4} s. The potential drops were measured by use of an integration digital multimeter (model 6030, Sabtronics, Switzerland). The working current of the platinum resistance thermometer was provided by a set of dry batteries with high stability. The potential drops across the thermometer and a 100 Ω standard resistor which was connected in series with the thermometer were measured by the same multimeter. The temperature of the sample was then calculated from the resistance of the thermometer.

Experimental

Sample

In order to assess the precision and accuracy of this apparatus, we measured the heat capacities of the standard reference material, α-alumina.

The α-alumina is spectroscopically pure reagent of 99.993 wt% purity (produced by No. 1 Reagent Factory of Shanghai). The spectroscopic analysis showed that the impurities contained in the sample were (wt%): Fe – 0.001, Mg – 0.002, Si – 0.003 and Ca – 0.001. In prior to heat capacity measurements, the sample was heated at 1900°C for 2 h. After the treatment, the X-ray diffraction analysis showed that the whole sample was in the α-phase. The mass of the sample loaded in the cell was 8.7353 g (=0.085673 mol). All measurements were carried out at the same heating rate (~0.3 deg·min^{-1}) so that the temperature increment over the whole temperature range was about 3 K.

Procedures

The heat capacites of the sample were measured as a function of temperature by the standard discrete heating method. In the intermittent mode, the sequence of heat capacity measurement is composed of two alternate periods: one is called the drift period during which the temperature of the sample is observed as a function of time; the other is the energy input period during which a definite amount of electrical energy is supplied to the sample. After the end of the

Table 1 Experimental molar heat capacity of α-Al_2O_3 {M(Al_2O_3) = 101.9613 g·mol^{-1}}

T/ K	$C_{p,m}$/ J·K^{-1}·mol^{-1}	T/ K	$C_{p,m}$/ J·K^{-1}·mol^{-1}	T/ K	$C_{p,m}$/ J·K^{-1}·mol^{-1}	T/ K	$C_{p,m}$/ J·K^{-1}·mol^{-1}
72.636	5.108	136.793	26.595	210.952	54.742	286.507	76.540
75.327	5.692	139.797	27.792	214.185	55.795	289.790	77.345
78.042	6.353	143.879	29.544	217.418	56.808	293.091	78.106
80.797	7.020	146.933	30.786	220.652	57.772	296.415	78.637
83.597	7.787	150.012	32.048	223.888	58.837	299.776	79.173
86.435	8.585	153.089	33.232	227.127	59.999	303.171	80.098
89.304	9.453	156.342	34.589	230.474	60.976	306.550	80.647
92.152	10.352	159.703	35.936	233.668	61.946	309.913	81.153
94.988	11.221	162.989	37.248	237.609	63.365	311.774	82.009
97.840	12.171	166.203	38.556	240.820	64.329	315.062	82.268
100.692	13.109	169.734	39.986	244.039	65.234	318.338	82.826
103.573	14.151	172.807	41.197	247.272	66.099	321.596	83.558
106.494	15.225	175.894	42.403	250.518	66.998	324.831	84.621
109.434	16.249	178.999	43.516	253.776	67.947	328.044	85.174
112.348	17.289	182.123	44.546	257.050	68.824	331.340	85.913
115.135	18.352	185.230	45.662	260.291	69.870	334.719	86.439
118.034	19.411	188.324	46.841	263.506	70.694	338.078	87.100
120.951	20.505	191.444	48.068	266.737	71.501	341.423	87.790
123.860	21.594	194.592	49.120	269.987	72.296	344.751	88.458
126.769	22.739	198.112	50.422	273.259	72.997	348.052	88.819
129.709	23.857	201.318	51.605	276.551	73.842	351.345	89.173
132.714	25.006	204.518	52.495	279.864	74.742		
133.772	25.441	207.716	53.600	283.198	75.746		

energy input, the sample temperature was measured until thermal equilibrium was reached. The heat input–equilibration cycle was repeated until the sample temperature had reached to above 350 K. A separate series of measurements on the empty cell were performed before the measurements on α-Al_2O_3.

Results and discussion

The experimental molar heat capacities of α-Al_2O_3 are listed in Table 1 in the sequence of temperature increment. The overall precision may be evaluated from the deviations of the experimental points from a polynomial. The whole temperature range (70–350 K) studied was divided into five regions and an independent sixth-degree polynomial was applied to each region. The deviations of experimental results from the polynomials are illustrated in a plot (Fig. 3). Except for some points, the deviations of almost all points lie within ±0.002 $C_{p,m}$.

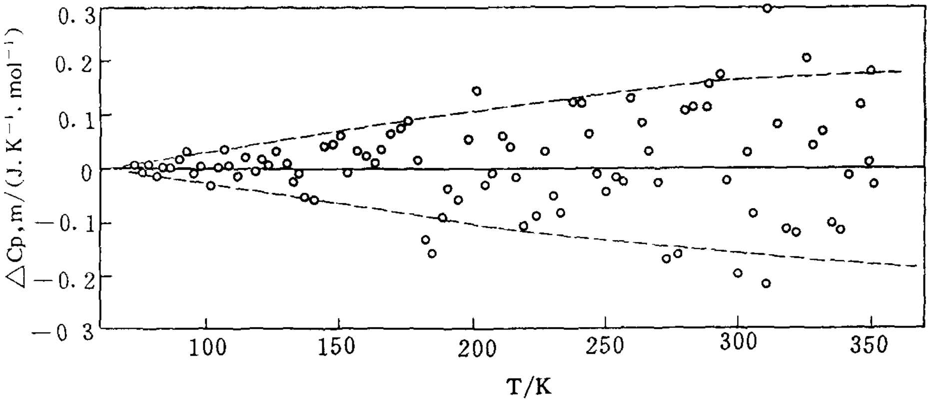

Fig. 3 Deviations of the measured molar heat capacity of α-Al_2O_3 from the smoothed curves. – – –, ±0.002 $C_{p,m}$

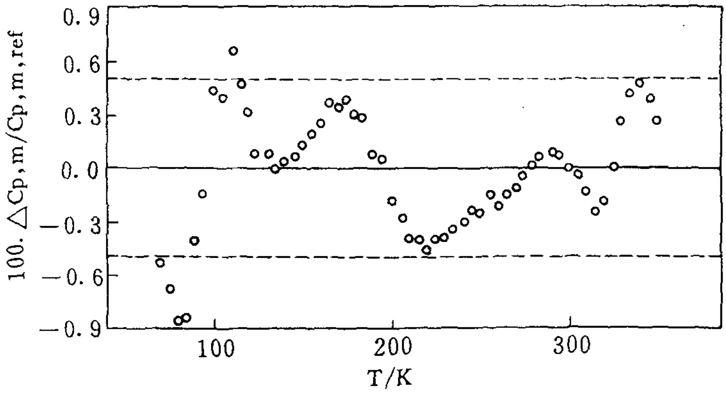

Fig. 4 Plot of deviations $100\Delta C_{p,m}/C_{p,m}$, Ref. of the measured values for the molar heat capacity of α-Al_2O_3, where $C_{p,m}$,Ref. is the molar heat capacity given by Ditmars *et al.* [18]

We have estimated the accuracy of the calorimeter by comparing our results with the recommended values for the heat capacity of α-Al_2O_3 reported by Ditmars *et al.* [18]. For the changes in temperature resulting from the conversion from IPTS-68 to ITS-90 are very small, while the experimental error of the measurements is relatively large, the recommended values are used directly. Except for some points below 110 K, all the results from five polynomials agree well with the recommended values, and the deviations of our results from the recommended values are less than ±0.005 $C_{p,m}$, as shown in Fig. 4.

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References

1 E. F. Westrum, Jr., G. T. Furukawa and J. P. McCullough, Experimental Thermodynamics, vol. 1, Calorimetry of Non-reacting systems, ed. J. P. McCullough and D. W. Scott, Butterworths, London 1968, p. 133.
2 E. Gmelin, Thermochim. Acta, 29 (1979) 1.
3 M. Tatsumi, T. Matsuo, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 48 (1975) 3060.
4 K. Moriya, T. Matsuo and H. Suga, J. Chem. Thermodyn., 14 (1982) 1143.
5 Zhang Zhi-ying, Scientia Sinica (Ser. B), 29 (1986) 1239.
6 Tan Zhi-cheng, Yin An-xue, Chen Shu-xia, Zhou Li-xing, Li Fu-xue, Cai Min-zhong, Zhang Shu-zheng, Pan Ru-wen, Li Shi-ran and Xia Yong-jian, Thermochim. Acta, 123 (1988) 105.
7 T Shinoda, H. Chihara and S. Seki, J. Phys. Soc. Jpn., 19 (1964) 1637.
8 E. Gmelin and P. Rodhammer, J. Phys. E: Sci. Instrum., 14 (1981) 223.
9 M. Ueda, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 43 (1982) 1165.
10 Y. Ogata, K. Kobayashi, T. Matsuo and H. Suga, J. Phys. E: Sci. Instrum., 17 (1984) 1054.
11 K. Chhor, J. F. Bocquet and C. Pommier, J. Chem. Thermodyn., 17 (1985) 379.
12 T. Matsuo and H. Suga, Thermochim. Acta, 88 (1985) 149.
13 M. J. M. van Oort and M. A. White, Rev. Sci. Instrum., 58 (1987) 1239.
14 M. Kano, J. Pyhs. E: Sci. Instrum., 22 (1989) 907.
15 M. Sorai, K. Kaji and Y. Kaneko, J. Chem. Thermodyn., 24 (1992) 167.
16 Tan Zhi-cheng, Zhou Li-xing, Chen Shu-xia, Yin An-xue, Sun Yi, Ye Jin-chun and Wang Xiu-kun, Scientia Sinica (Ser. B), 26 (1983) 1014.
17 Tan Zhi-cheng, Yin An-xue, Chen Shu-xia and Zhou Li-xing, Science in China (Ser. B), 34 (1991) 560.
18 D. A. Ditmars, S. Ishihara, S. S. Chang, G. Bernstein and E. D. West, J. Res. Natl. Bur. Stands., 87 (1982) 159.

Zusammenfassung — Es wurde ein adiabatisches Kleinproben-Kalorimeter zur Messung von Wärmekapazitäten im Temperaturbereich 60–350 K auf der Grundlage der Nernst'schen Metho-de konstruiert. Die Probenzelle des Kalorimeters besitzt ein Innenvolumen von 7 cm^3 und ist mit einem Miniatur-Platinthermometer ausgerüstet und von zwei adiabatischen Hüllen umgeben. Zur Anzeige der Temperaturdifferenz zwischen Probenzelle und den Hüllen wurden zwei Sätze Thermoelemente montiert. Die adiabatischen Bedingungen der Zelle werden durch zwei Sätze Temperaturkontrolleinheiten automatisch überwacht. Zum Abpumpen des Dampfes des flüssigen Stickstoffes aus dem Kryostat zur Verfestigung von N_2 (1) wird eine mechanische Pumpe eingesetzt und Temperaturen von 60 K oder darunter erhalten. Die Leistung dieses Gerätes wurde anhand von Wärmekapazitätsmessungen an α-Aluminiumoxid bewertet. Die Abweichung der experimentellen Ergebnisse von einer geglätteten Kurve liegt innerhalb von 0.2%, während die Ungenauigkeit gegenüber empfohlenen Bezugsdaten im gesamten Temperaturbereich innerhalb 0.5% liegt.