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AN AUTOMATED ADIABATIC CALORIMETER FOR HEAT-CAPACITY MEASUREMENTS BETWEEN 20 AND 90 K *

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ABSTRACT

An adiabatic calorimeter and cryostat assembly with an automatic shield temperature control system has been constructed and tested by measurements on α-Al_2O_3. The heat capacity of α-Al_2O_3 has been measured and the results are compared with those of other investigators.

INTRODUCTION

Adiabatic calorimetry is generally believed to give the most accurate and precise heat capacity data at low temperatures. Numerical values of static equilibrium properties such as enthalpy, entropy and Gibbs energy function can be derived from C_p measurements. It is our main purpose in constructing the present adiabatic calorimeter to precisely measure low-temperature heat capacity and to study in detail related thermodynamic properties as well as other thermal behavior for new materials of importance in science and technologies. Since α-Al_2O_3 is a standard reference material for heat capacity measurements, we have measured the heat capacity of α-Al_2O_3 over the range 25–90 K so as to test the performance of the calorimetric apparatus set up by ourselves. In this paper we briefly describe the special features of the calorimeter system and report the results of heat capacity measurements on α-Al_2O_3 which is of high purity and prepared in our country.

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EXPERIMENTAL

Calorimeter and cryostat

The design of the calorimeter is similar in principle to those described previously by Furukawa and Reily [1] and Tan Zhicheng et al. [2]. Figure 1 shows a schematic drawing of the calorimeter and liquid helium cryostat assembly. The adiabatic calorimeter consists of seven major parts, viz. a sample vessel, a thermometer–heater assembly, an adiabatic shield, two rings and a thermal anchor for temperature control of electrical lead wires, a vacuum can and a stainless steel Dewar vessel.

The sample vessel is essentially all silver (99.95% purity) construction with outer surfaces gold-plated. It has a cylindrical body section and a hemispherical top and bottom. The main body is 33 mm in diameter, 60 mm high and has 0.3 mm thick walls. The mass and the effective capacity of the empty vessel are about 50 g and 50 ml respectively. In its center a tapered re-entrant well is provided for locating the thermometer and calorimeter heater assembly. Eight L-shaped 0.15 mm thick radial silver vanes are

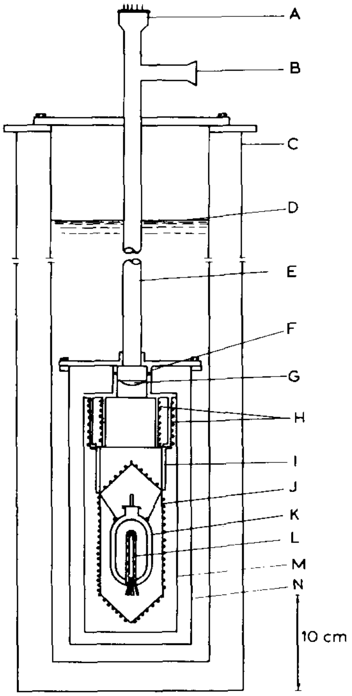

Fig. 1. Adiabatic calorimeter and cryostat. A, high-vacuum seal joints; B, to high vacuum pump; C, stainless steel Dewar vessel; D, liquid He; E, thin-wall stainless steel tube; F, thermal anchor for leads; G, radiation trap; H, temperature control rings for leads; I, teflon ring; J, adiabatic shield; K, sample vessel; L, thermometer–heater assembly; M, radiation shield; N, vacuum can.

brazed onto the outer wall of the well and an appropriate space is kept between the outer edges of the vanes and the inside wall of the vessel, so as to improve heat distribution within the container and to achieve more reproducible surface temperatures between the vessel plus sample and empty vessel measurements. The charging aperture of the sample vessel is closed by a 10 mm diameter silver disk which is soldered to the top and carries a copper tube (1 mm o.d. and 0.8 mm i.d.) used both for evacuating and introducing low pressure helium gas to promote thermal equilibration during measurements. The vessel is sealed by crimping, cutting and soldering of the copper tube. Neither leakage nor deformation occurred upon subjecting the vessel to 0.2 MPa internal pressure or 10^{-4} Pa evacuation.

The platinum resistance thermometer (No. 81018, 5 mm in diameter, 50 mm long) was made by the Instrument Manufactory of Yunnan, China, and calibrated at the National Institute of Metrology (NIM) in terms of IPTS-68: $R_0 = 24.5715\ \Omega$, $W_{100} = 1.39267$. The electrical heater which surrounds the thermometer is a copper tube wound with insulated Karma wire (0.15 mm diameter) and has a resistance of approximately 100 Ω at 273 K. The thermometer–heater assembly is centrally located in the re-entrant well of the sample vessel.

The adiabatic shield, which was machined to be as thin as possible to yield a short thermal response time, is essentially a thin gold-plated copper shell of 0.6 mm thickness consisting of three sections, a cylinder and two end cones (90°). Screws hold the two cones to the cylinder. A thin film of grease is used between the surfaces that are in contact. For the heater wire, an evenly spaced groove (0.4 mm wide × 0.2 mm deep) was machined helically on the cylinder and spirally on the cones. The distribution of the heater wire grooves was made very nearly the same over the entire shield surface to yield even heating. A pair of enameled manganese wires (0.16 mm diameter) was wound into the tightly fitting groove of the shield to serve as the shield heater, which on the cones and on the cylinder is connected in series and has a total resistance of approximately 920 Ω at room temperature.

Temperature control of the electrical lead wires is realized through the thermal anchor and two rings, i.e. the outer and the inner rings which are made of gold-plated copper and wound with manganese wire to serve as the heater. All electrical leads enter the calorimeter through the high-vacuum seal joints at the top of the cryostat and traversed the length of the high vacuum pump-out tube. The leads are then attached to the thermal anchor at which the electrical leads are brought to the temperature of the refrigerant in which the calorimeter is immersed, and then attached to the outer ring and the inner ring in sequence. At the two rings the temperature of the leads is raised close to that of the adiabatic shield. After the inner ring and before the sample vessel the leads are attached to the adiabatic shield, at which the leads can be maintained at the same temperature as that of the sample vessel.

Three sets of 10-junction chromal-to-copper differential thermocouples are mounted between the sample vessel and the adiabatic shield, between the adiabatic shield and the inner ring and between the inner ring and the outer ring to sense corresponding temperature differences.

The submarine-type vacuum can, which houses high vacuum (10^{-4} Pa) for the calorimeter vessel to minimize gaseous heat conduction, is a stainless steel cylinder of 115 mm inside diameter, 302 mm in height and with 2 mm thick walls. The cover of the cylinder is flange-coupled with the gasket made from 2 mm diameter high purity indium wire.

A Model DGS-200 stainless steel Dewar vessel, which is 300 mm in inside diameter, 1332 mm in height and 24 l in effective capacity, is used for the refrigerant compartment of the cryostat. During the experiment the Dewar vessel is first filled with liquid nitrogen. When the sample vessel is cooled to about 77 K, liquid helium is transfered into the Dewar vessel in place of the liquid nitrogen and then the sample can be cooled further, down to about 10 K. A superconductor lever device serves as the liquid helium level indicator, whose sensor is positioned at the bottom of a calibrated fine stainless steel tube, which is inserted into the Dewar vessel and can be moved vertically up and down to check the liquid helium level.

Temperature and energy measurements

The temperature of the calorimeter vessel is measured by the platinum thermometer. The resistance of the thermometer is determined by comparing the potential drop across the resistance thermometer with that of a 10 Ω standard resistor. The potential drops are measured by means of a d.c. comparator potentiometer with a resolution of 0.01 μV (Shanghai Electric Meter Manufacturing Co., type UJ-42). With the 25 Ω platinum thermometer the temperature resolution of the measurement system is about ±0.1 mK in the range 20–90 K. The overall accuracy of measurement of absolute temperature is estimated as ±5 mK and of measurement of temperature increments as ±1 mK.

The electrical energy introduced into the calorimeter vessel is supplied by a d.c. voltage supply with a stability of 1 ppm, and is determined from the potential drops across the sample heater and a standard resistor (100 Ω) connected in series with the heater and from the duration of energy input. The potentials are measured using a digital voltmeter with a resolution of 1 μV (Beijing, Radio Instrument Co., type DO-17). The heating time is controlled and measured by a JK-1 type digitally displayed electronic timer-controller (made in our thermochemistry laboratory), which is placed in the energy measurement circuit and has a measuring error of 1 ms. The data process for temperature and energy measurements is performed by a IBM-PC/XT computer.

Automatic adiabatic control system for the calorimetric vessel

The adiabatic condition of the calorimetric vessel is realized by a combination of a radiation shield, a high vacuum to minimize gaseous heat conduction, and temperature control of electrical leads to the sample vessel. Three similar feedback circuits are used to control the temperature of the adiabatic shield surrounding the sample vessel, and the temperatures of the outer and inner rings on which the electrical leads are wound. For each temperature control channel the signal from the differential thermocouples is amplified by a microvolt amplifer and the amplified signal is monitored by a recorder coupled to a controller which provides PID (proportional integral differential) control mode. The output of the controller in turn controls the output potential of a stabilized power supply to deliver corresponding current to the heater on the shield or rings. By using the control system the temperature differences between the calorimetric vessel and the adiabatic shield can be kept within ±5 mK during the heating period and ±1 mK during the equilibration period, whereas the observed temperature drift rates of the calorimeter vessel are usually maintained within about 0.1 mK min^{-1} during the drift period.

Procedures

The heat capacity of the sample is measured as a function of temperature by the standard discrete heating method. In this intermittent mode the sequence of heat capacity measurement is composed of two alternating 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.

The sample of α-Al_2O_3, under a pressure of about 4 kPa helium gas, was sealed into the vessel which was then installed in the cryostat. The cryostat was warmed to 300 K and evacuated for several hours before cooling. When evacuated to about 10^{-3} Pa, the vacuum can of the cryostat was filled with helium as exchanging gas and the refrigerant (first liquid nitrogen then liquid helium) was transferred into the Dewar vessel.

After the sample vessel was cooled to the lowest temperature required by the experiment, the vacuum can was evacuated to at least 10^{-4} Pa. The adiabatic shield controls were put into operation and the initial temperature was measured. Electrical energy was then introduced to raise the temperature of the sample by about 10% of the absolute temperature if below 50 K, or by about 5 K if above 50 K. After the energy input the sample temperature was measured until thermal equilibrium was reached. The heat input–equilibration cycle was repeated until a temperature of about 90 K had been reached, usually in a series of overlapping runs. A separate series of measurements on the empty vessel alone with a small pressure of helium gas was made.

Sample and treatment

The α-Al_2O_3 was a spectroscopically pure reagent of 99.993 wt.% purity (made by No. 1 Reagent Manufactory of Shanghai, China) The spectroscopic analysis showed that the sample contained the following impurities (in p.p.m. by weight): Fe, 1; Mg, 2; Si, 3; Ca, 1. The sample was pretreated at 1920–1970 K for 2 h to make sure that only α-phase was present and also to increase its density. The X-ray diffraction analysis showed that the whole sample was in the α-phase after the treatment. The size of most of its particles observed under the microscope was about 50 μm. Furthermore, results of thermogravimetric analysis performed in an air atmosphere showed that the sample underwent no variation in weight during heating and cooling, which proved that the sample does not absorb moisture or gaseous substances from the air.

RESULTS AND DISCUSSION

We have tested the calorimetric apparatus by measuring the heat capacity of α-Al_2O_3. The sample that was sealed into the calorimeter vessel weighed

TABLE 1

Experimental molar heat capacity of α-Al_2O_3

T	C_p	T	C_p	T	C_p
25.834	0.166	45.142	1.040	68.686	4.300
25.943	0.168	46.668	1.187	70.053	4.607
27.719	0.211	47.327	1.239	71.827	4.967
29.534	0.242	48.426	1.344	74.545	5.592
29.770	0.251	50.088	1.513	76.110	5.942
31.574	0.316	51.672	1.694	77.780	6.344
32.351	0.341	52.544	1.795	78.255	6.468
33.442	0.389	54.412	2.010	80.775	7.130
34.646	0.423	55.373	2.106	81.413	7.302
35.419	0.470	57.016	2.353	83.710	7.834
37.511	0.563	58.699	2.614	84.839	8.190
38.263	0.583	60.231	2.813	85.792	8.452
39.729	0.687	61.304	2.950	86.908	8.748
40.190	0.695	62.437	3.204	89.734	9.590
41.587	0.791	64.225	3.487	92.509	10.441
42.181	0.841	66.175	3.846		
44.291	0.983	67.991	4.154		

T measured in K; C_p measured in J mol^{-1} K^{-1}; $M(Al_2O_3) = 101.9613$.

35.5130 g (in vacuo). The heat capacity of the sample was obtained from measurements on the charged and empty vessel with correction for any differences in the heat capacity of the sample vessel when filled and when empty. The results were corrected also for curvature, the correction for all points being within 0.5–0.01% of the heat capacity values.

The experimental values of the molar heat capacity of α-Al_2O_3 are listed in Table 1 and fitted by the least squares method to a sixth-degree polynomial

$$C = \sum_{i=0}^{6} A_i X^i (\mathrm{J\ K^{-1}\ mol^{-1}})$$

in which $A_0 = 2.656727$, $A_1 = 4.995634$, $A_2 = 2.948665$, $A_3 = 0.103174$, $A_4 = -0.4095967$, $A_5 = 0.03465246$, $A_6 = 0.1049203$, and $X = (T - 59.171)/33.337$. This equation is valid from 25 to 90 K.

We have assessed the accuracy of the calorimetric apparatus by comparing our results with the commonly accepted data published by the National Bureau of Standards. The standard percentage deviation (percentage r.m.s. deviation) of the molar heat capacity values of α-Al_2O_3 obtained by this research from those reported by Ditmars et al. [3] is within ±0.75 to ±0.1% in the temperature range 25–90 K.

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